TEXTILE AUXILIARIES AND CHEMICALS

WITH PROCESSES & FORMULATIONS

EIRI

We Create Industrialists

TEXTILES AUXILIARIES AND CHEMICALS

WITH PROCESSES & FORMULATIONS

Written By :

EIRI Consultants and Engineers

ISBN : 978-81-86732-93-9

ENGINEERS INDIA RESEARCH INSTITUTE
4449, Nai Sarak, Main Road, Delhi-110 006 (India)
E-Mail : eiribooks@yahoo.com

Preface

At present, Textile Auxiliaries and Chemicals have got tremendous demand in India as well as in overseas countries. Considering to this, EIRI have recently published a unique book on this subject. The book almost covers all the Textile Auxiliaries and Chemicals with their formulae to provide detailed knowledge. Apart from these, we have also included many project profiles related with the same industry which will be helpful for the new entrepreneurs to set-up their own unit.

The book **Textile Auxiliaries and Chemicals with Processes and Formulations** covers almost all the basic and advanced details to setup own industry/unit. The new edition of the book is covering latest technology of textile auxiliaries chemical processes including: *Classifications and Chemistry, Manufacturing Processes of Textile Auxiliaries, Commercial Textile Auxiliaries, Formulations of Textile Auxiliaries, Classification of Surfactants, Details of Raw Materials, Anionic Surfactants, Cationic Surfactants, Nonionic Surfactants, and Miscellaneous Important Compounds.*

The book has been compiled for the benefit and to prove an asset and a handy reference guide in the hands of new entrepreneurs and well established industrialists.

Director
ENGINEERS INDIA RESEARCH INSTITUTE
Nai Sarak, New Delhi (INDIA)
E-Mail: eiribooks@yahoo.com

Contents-cum-Index

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4
FORMULATIONS OF TEXTILE AUXILIARIES .. 164-203

CHAPTER 5

CLASSIFICATION OF SURFACTANTS 204-228

CHAPTER 6

CHAPTER 7

ANIONIC SURFACTANTS 259-308

1

Classifications and Chemistry

CLASSIFICATION

The textile auxiliaries/chemicals in one way are classified depending on whether they are permanent or temporary, into two groups: viz. those which are used in textile processing and are removed from the textile material afterwards and those which form an integral part of the processed textile material. These two classes are called temporary and permanent textile auxiliaries. Temporary textile auxiliaries include a variety of products such as detergents, wetting agents, sizing agents, desizing agents, levelling agents, retarding agents, carriers, dispersing agents solution aids etc.

Permanent textile auxiliaries are usually applied in finishing processes. Softeners, water proofing and water repelling agents, crease resist finishing agents, flame retardants, rot proofing agents, antistatic agents, binders and fixers, dye fixing agents are some examples.

In another classification, the textile auxiliaries may be divided into essentially three groups:

- surface active compounds
- nonsurface active compounds
- water insoluble solids or water immiscible liquids, dispersed or emulsified in water with the help of dispersing agents or emulsifiers.

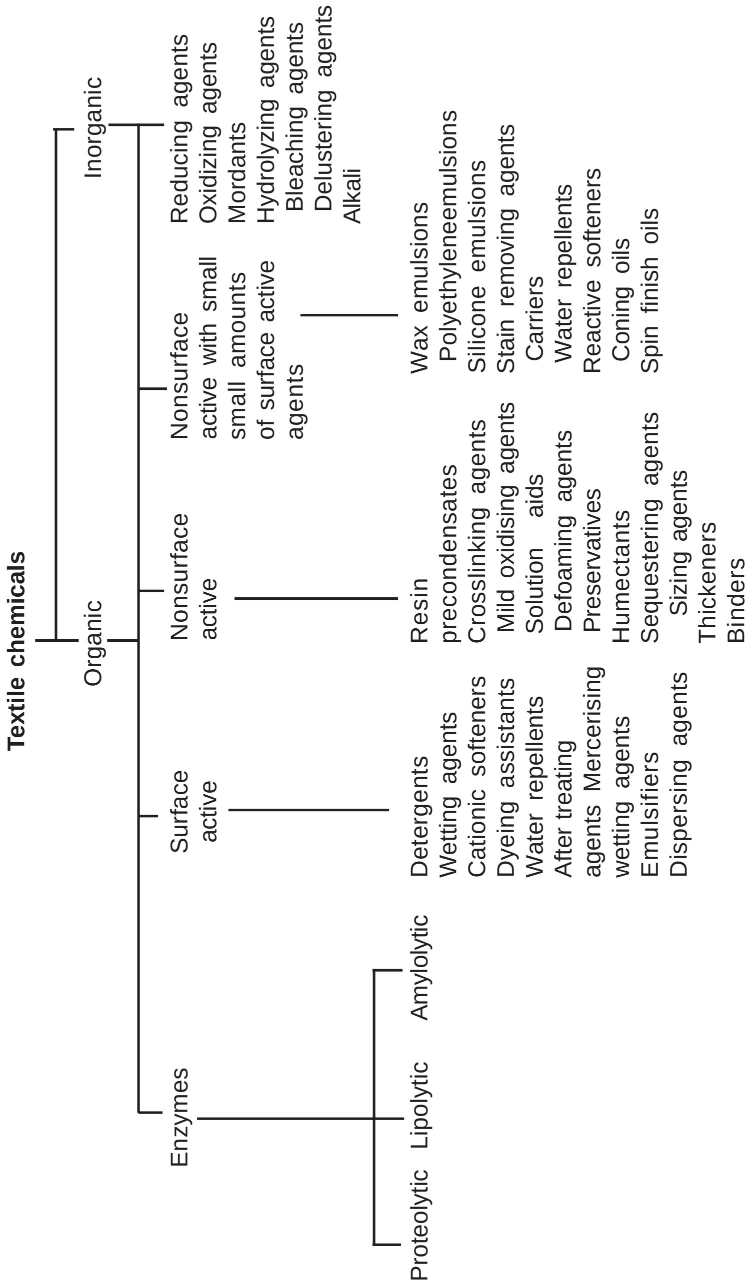


Fig 1.1: Classification of textile chemicals

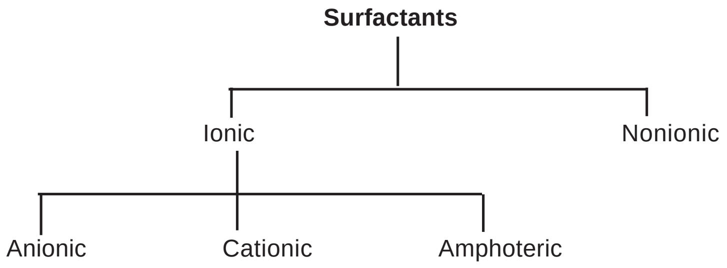


Fig 1.2: Classification of surfactants

Classifying textile chemicals based on the textile processes in which they are used is another method.

SPINNING ASSISTANTS

Cotton spray oils, coning oils, anti-static agents, lubricating agents etc.

Sizing Agents

Adhesives, lubricants, softeners, preservatives etc.

Desizing Agents

Mineral acids and enzymes

Scouring and Bleaching Aids

Wetting agents, detergents, emulsifying agents, mild oxidising agents, sequestering agents, rapid wetting agents, mercerising wetting agents, stain removers, etc.

Dyeing Assistants

Levelling agents, retarding agents, dispersing agents, carriers, after treating agents, dye fixing agents, stripping agents, rubbing fastners improves, detergents, sequestering agents etc.

Printing Aids

Thickeners, wetting agents, solution aids, hygroscopic agents, binders and fixers (in pigment printing), catalysts, discharging and resisting agents, complexing agents, mild oxidising agents, carriers and swelling agents, defoaming agents, emulsifying agents, dyefixing agents, detergents, sequestering agents, etc.

Table 1.1
Spin Finish Components

S.No.	Components	Products commonly used
1	Lubricants	Mineral oils and waxes, fatty acid esters, dicarboxylic acid esters, vegetable oils and waxes, neoalcohol esters, polyoxylkylene derivatives, silicone and modified silicone fluids
2	Fibre to fibre friction aids	Mineral oils, linear esters, branched esters, polyalkylene glycols, polyoxyalkylene monoethers
3	Antistatic agents	
	(a) Anionics	Alkyl alcohol sulphates, alkyl alcohol phosphates, alkyl alcohol ethoxylates (sulphate and phosphate)
	(b)	Nonionics alkyl phenol ethoxylates, alcohol ethoxylates, alkylamine ethoxylates, polyoxyalkylene glycol derivatives
	(c) Cationics	Imidazole quaternaries, alkyl quaternaries
4	Emulsifiers	
	(a) Anionics	Alkylbenzene sulphonates, alkyl alcohol phosphates, alkyl alcohol sulphates, alkyl alcohol ethoxylates (sulphate and phosphate) sulphosuccinates, fatty acid soaps
	(b) Nonionics	Alkyl alcohol ethoxylate, alkyphenol ethoxylates, fatty acid ethoxylate, sorbitol sorbitan, alkyl amine ethoxylates alkanolamides, alkanolamide ethoxylates
	(c) Cationics	Quaternary fatty amines, quaternary fatty amine ethoxylates, quaternary imidazoles

Finishing Agents

Resin precondensates and/or crosslinking agents, catalysts, anionic softeners, cationic softeners, nonionic softeners, reactive softeners, water repellents, waterproofing agents, sequestering agents, antistatic agents, rotproofing and mothproofing agents, flame retardants, rapid wetting agents, soil release agents, solid resisting agents, antisoil redeposition agents, stiffening agents, defoaming and antifoaming agents, emulsifying agents, stain removers, etc.

The auxiliaries are discussed in the ensuing paragraphs.

DETERGENTS AND SURFACTANTS

The term “detergency” is restricted to cleaning systems in which the following conditions prevail: (1) A liquid bath is present, and is the major cleansing constituent of the system. (2) The action of the bath involves more than a simple dissolving of the soil, although dissolving of some of the soil constituents may occur, and more than a simple hydraulic dislodging of the soil, although some action of this type inevitably occurs. (3) The enhanced cleaning effect is caused primarily by the presence in the bath of a special solute, called the detergent, which acts by altering interfacial effects at the various phase boundaries within the system. A typical detersive system thus consists of three major elements a solid object to be cleaned, called the “substrate”; “soil” or “dirt” attached to the substrate, which is to be removed in the washing process; and a liquid “bath” which is applied to the soiled substrate.

Bath considered is aqueous solutions. Among bath components, the solute that is effective in cleaning, usually a mixture of several components, is called the detergent. The term detergent is also used quite frequently in the restricted sense to mean a surfactant of high detersive power. In the great majority of fabric systems, the most important detersive component in the bath is a surfactant. Nonsurfactant components that augment the cleaning effect in these systems are called builders.

Detergents are formulated to suit the requirements of the soiled substrate to be cleaned and the expected range of washing conditions. Some detergents, for example, the familiar soap, consist essentially of onlly one component.

Inorganic Compounds

The more important inorganic detergent constituents are alkalies, phosphates, silicates, neutral soluble salts, acids and insoluble inorganic builders.

Caustic soda and sodium carbonate (soda ash) are more popular inorganic detergents. Trisodium phosphate is used with soaps, surfactants, or other alkalies. It precipitates many heavy metal ions.

Tetrasodium pyrophosphate ($Na_4P_2O_7$) is one of the most important primary detergents and builders for fabric substrates. It has high sequestering, suspending, and cleansing action.

Pentasodium triphosphate (sodium “tripolyphosphate,” $Na_3P_3P_{10}$) is the most widely used builder for heavy duty fabric detergents based on synthetic surfactants.

Sodium “hexametaphoshate” exerts powerful suspending and sequestering effects and are used where these effects are important.

The sodium silicates function primarily as alkalies and have been extensively used as builders for soap in laundering formulations.

Table 1.2
Important Detersive Systems

Soil		Mechanical action	Bath ratio	Detergent
	Fabric and fibrous systems			
Textile and allied manufacturing raw wool scouring	liquid at operating temperature	very gentle	high	organic surfactant
Wool yarn and piece goods surfactant	liquid	gentle	moderately high	organic
Scouring gray cottons	mostly solid; waxy and starchy	vigorous	low	built surfactant
Scouring mammade fabrics	mixed; oil lubricant sizing residues	moderate	medium	built surfactant
Laundering	mixed and variable	moderate	high	built surfactant
Household	mixed and variable;	vigorous	high	built surfactant
Commercial and industrial	heavier than household soil			
Rug cleaning plant surfactant	heavy solid	moderate gentle	medium to low	organic may be built
On location	heavy solid	vigorous, superficial brushing	very low, foam bath	organic surfactant foam

A commercially important detergent usually consists of a surfactants which helps to build foam, a sequestering agent, builders which assist cleaning and also economizes the price part, a bleaching agent and many a time optical brightening agent.

Surfactants or surface active agents are the heart of a detergent system. Besides being used as an important detergent constituent, they have other beneficial properties and end uses, e.g. wetting agents, emulsifying agent, softening agent etc.

The world surfactant is a condensation of the descriptive phrase surface active agent. Six fundamental characteristics of surfactants are considered for designating a surfactant.

1. The substance must be soluble in at least one phase of a liquid system in order to be classified as a surfactant.
2. Surfactant molecules are composed of groups with opposing solubility tendencies.
3. Surfactant molecules or ions form oriented monolayers at phase interfaces.
4. The equilibrium concentration of a surfactant solute at a phase interface is greater than its concentration in the bulk of the solution.
5. Surfactants form aggregates of molecules or ions called micelles when the concentration of the solute in the bulk of the solution exceeds a limiting value.
6. Solutions of surfactants exhibit some combination of detergency, foaming, wetting, emulsifying, solubilizing and dispersing.

A surfactant is an organic compound that encompasses in the same molecule two dissimilar structural groups, viz. a water soluble and a water insoluble moiety. Groups in relation to the overall molecular configuration determine the surface activity of a compound. The term amphipathy denotes a molecular structure in which one more groups have an affinity for the phase in which the molecule or ion is dissolved, together with one or more groups which are antipathetic to the medium. They are expelled by the phase and amphipathic structures are found in so many classes of organic substances and hundreds of thousands of surfactants are theoretically possible and thousands of individual compounds have been described. The groups which have affinity towards water are hydrophilic and those which are antipathic towards water are generally designated as hydrophobic.

Hydrophilic and hydrophobic groups

Surfactants are classified on the basis of their hydrophilic or "solubilizing groups" into four categories: anionics, nonionics, cationics, and amphoterics. The anionic solubilizing groups are carboxylates, sulphonates, sulphates, and phosphates. Nonionics are solubilized by hydroxyl groups and polyoxyethylene chains. Primary, secondary, and tertiary amines and quaternary ammonium groups are the cationic solubilizers. Amphoteric surfactants are solubilized by some combination of anionic and cationic moieties; nonionic solubilizing groups may also be part of amphoteric molecules. In addition to the primary solubilizing groups, other structural units contribute to the hydrophilic tendencies of molecules, e.g. ester linkages and amide linkages. The hydrophobic, i.e. lipophilic, moieties are almost invariably hydrocarbon or halogen substituted hydrocarbon groups. Olefin linkages are less hydrophobic than carbon to carbon single bonds.

Molecular weight

The molecular weight of surfactants ranges from a low of around 200 or slightly below, e.g. sodium hexylsulphate, to a high that is well up in the thousands for hydrophilic polymers. Nevertheless, a linear C_{12} hydrophobe solubilized by an anionic, cationic, nonionic or amphoteric group is an effective surfactant for a large proportion of surfactant applications involving dilute aqueous solutions. Extending the range of compositions to include C_{12} to C_{13} compounds and permitting branching of the hydrophobe provides substances that exhibit the full gamut of surfactant properties.

Solubility and surface activity

A surfactant solute usually displays maximum surface activity and functional effectiveness. When it is near the threshold of insolubility. Moreover, the solubility of surfactants is markedly affected by temperature and electrolyte concentrations. Thus for each set of conditions there is usually an optimum solubility balance for each type of surfactant. Relatively small changes in the composition of a surfactant are often sufficient to change its solubility, and hence its surface activity. There are many ways to effect such changes; for example the average molecular weight of the raw material mixture, i.e. hydrophobe, can be increased slightly or the degree of sulphation, sulphonation, or ethoxylation can be increased or decreased.

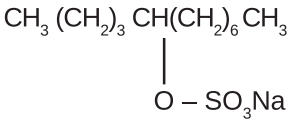
Nomenclature and chemical composition

Practical surfactant technology deals with mixtures of precisely specified properties but incompletely defined compositions. Many surfactant products are polydisperse in the meaning “a preparation containing molecules which are all the same type, but which vary only in chain length or in some other structural details.. as distinguished from a mixture of two different molecular species” Ethoxylated alkylphenols are typical polydisperse compositions. In surfactant chemistry the trivial names are used with a special denotation, e.g. “lauryl alcohol” is not a synonym for dodeeyl alcohol but rather designates a commercial product which contains dodeeyl alcohol as its main constituent but which varies in actual composition from a fairly narrow distillation cut to a broad fraction containing substantial proportions of lower and high alcohols. It is the same with the terms myristyl, cetyl, etc.

Sometimes expressions are descriptive of the origin of a product; for example, “coco acids” refers to the mixed fatty acids of coconut oil.

Wetting and detergent structures

Structures relating to strong wetting and strong detergent properties have been identified. The hydrophilic group of strong wetting agents is located at the middle of the hydrophobic chain or all the central branching point if the molecule contains two or more chains. Conversely, the hydrophilic group in strong detergents is located at the end of the hydrophobic chain. This may be illustrated by comparing two isomers, sodium 1 (n butyl) cetylsulphate and sodium n dodecylsulphate:



$$CH_3(CH_2)_3\underset{\substack{|\\ O-SO_3Na}}{CH}(CH_2)_6CH_3$$

Strong wetting

$CH_3(CH_2)_{10}CH_2-O-SO_3Na$

strong detergents

Although the wetting and detersive properties of unformulated anionic and nonionic compounds follow this structural pattern, usefulness of the generalization is limited to the selection of surfactants for a few specialized applications, e.g. textile wetting agents. This limitation is due to the pronounced superiority of formulated or “built” products over pure compounds for detergency, emulsification, etc. In formulations, detergency and wetting strength of individual components lose much of their significance. Textile wetting efficiency is not simply related to surface tension lowering. But dilute aqueous solutions of strong wetting agents characteristically have low surface tensions.

ANIONIC SURFACTANTS

The hydrophilic moiety in anionic surfactants is a polar group that is negatively charged in aqueous solutions or dispersions. In commercial products it is either a carboxylate, sulphonate, sulphate, or phosphate group.

In dilute alkaline solutions in soft water the solubilizing power of the sodium salts of the four anionic radicals is approximately equal and strong enough to balance the hydrophobic tendency of a 12 carbon saturated hydrocarbon group; the sulphate is actually a somewhat stronger solubilizer than the sulphonate. In neutral or acidic media or in the presence of heavy metal ions, the solubilizing power of the carboxylate is markedly less than that of the other groups.

The ionic environment associated with anionic surfactants influences the properties of their solutions. Sodium and potassium salts are generally more soluble in water and less soluble in hydrocarbons. Conversely, the calcium, barium, and magnesium salts are more compatible with hydrocarbon solvents and less so with water. Ammonium and amine salts, e.g. triethanolamine, improve the compatibility of anionics with water and hydrocarbons and are widely used in emulsification and detergent applications. Higher total ionic strengths are usually associated with lower solubilities of anionic surfactants. To offset this effect, the molecular weight of the hydrophobe is lower in products designed for use at high electrolyte concentrations. Micellar solubilization by anionics is markedly affected by total ionic strength and also be the identity of the associated cations.

Carboxylates

Soaps and a small volume of aminocarboxylates are the only commercial product types in the carboxylate class of surfactants. Soap has the general composition (RCOO)-(M)+ where R is an alkyl group, usually in the C_9 to C_{21} range and M is a metallic or amine ion. Although most soaps have surfactant properties, the term actually denotes the chemical composition rather than the use, and an appreciable volume of these products, particularly salts of polyvalent metals, go to nonsurfactant uses. The surfactant properties of soaps are excellent in soft water, but the heavy metal and polyvalent metal salts of soap, e.g. Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{2+}, and Al^{2+}, are insoluble in water and form “curds” or “lime soap” precipitates that reduce the effective concentration and adversely affect performance. Other types of surfactants are also used as lime soap dispersants and their relative effectiveness for this purpose can be compared by the method of Borghetty and Bergman. Organic sequestering agents such as ethylenediaminetetraacetic acid and nitrilotriacetic acid in make it possible to use soap as a surfactant in hard water.

Two types of aminocarboxylate surfactants, N-acylsarcosinates and acylated protein hydrolysates, are produced in small quantities as specialities. Both series of products are fatty acyl derivatives of aminocarboxylates. As compared to the corresponding soaps, the hydrophilic tendency of the amide linkages in these molecules is strong enough to significantly lessen inactivation of the carboxylate ions by the calcium and magnesium ions that are present in hard water.

Sulphonates

The most effective structure for an anionic surfactant is a sulphonate of the general formula RSO_3Na where R is a biodegradable hydrocarbon group in the surfactant molecular weight range. The R group can be alkyl or alkylarylene and the product can be a random mixture of isomers as long as it does not contain chain branching that interferes with biodegradability. The surface activity of the SO_3-group is not oversensitive to variations in the pH or to heavy metal ions and the C-S linkage is not susceptible to hydrolysis or oxidation under normal conditions of use.

Alkylbenzenesulphonates

Linear alkylbenzenesulphonates (LAB) rank first in total surfactant. This is biodegradable than the branched chain substituent. Commercial LAB sulphonic acid is a light coloured, viscous liquid that is used almost entirely as an intermediate for the manufacture of alkali metal slats. LAB sulphonate (sodium slat) is marketed as light coloured spray dried granules or flakes.

In comparisons of the performance of alkylbenzene-sulphonates to that of aliphatic sulphonates, the effect of the benzene right if often considered as approximately equivalent to three carbon atoms in an aliphatic chain. Alkylbenzenesulphonic acids are strong organic acids and form essentially neutral alkali metal salts that have a good solubility in aqueous solutions at use concentrations over the entire pH range. These acids are not sensitive to precipitation by the natural hardness of surface waters. The alkaline earth metal salts are less water soluble than the alkali metal and amine salts. The calcium salts are sufficiently soluble in hydrocarbons for use in these media. The alkylbenzenesulphonates are one of the most chemically stable types of surfactants. The sulphonic group is not susceptible to acidic or alkaline hydrolysis under normal conditions of storage or use. The compounds are stable to strong oxidizing agents in aqueous solutions at use concentrations and are stable in carefully formulated products containing oxidizing agents.

The surface activity of unformulated unbuilt alkylbenzene-sulphonate is sufficiently strong for the salts to be useful for their detersive, wetting, emulsifying, dispersing, and foaming properties, but they are not outstanding surfactants. The widespread usage of LAB stems from other factors which include their low cost, reproducible quality, adequate supply, light colour, low odour, and excellent response to formulation and builders.

Petroleum sulphonates

The petroleum sulphonates are the only large volume class of surfactants that are used predominantly in nonaqueous systems. They are available as coproducts of the refining of certain petroleum fractions. They are either water soluble types called green soaps or oil soluble types called mahogany soaps. The green soaps are of little use. The mahogany soaps are used in lub oil and greases.

Naphthalene-sulphonates

Four series of speciality surfactants make up the widely used but relatively low volume group of naphthalenesulphonate products, viz. salts of alklynaphthalenesulphonates; slats of sulphonated formaldehyde naphthalene condensates; slats of naphthalene-sulphonates; and slats of tetrahydronaphthalene-sulphonates.

In the concentrated dry form, most of the salts are almost odourless light gray solids. They are readily and highly soluble in water. In fact, except for the nonyl derivatives, the naphthalenesulphonates are generally too soluble to be strongly surface active in soft water. the naphthalenesulphonates are stable to be strongly surface active in soft water. The naphthalene-sulphonates are stable to hydrolysis in acidic or alkaline media and are not sensitive to oxidation by strong oxidizing agents under the use conditions.

The naphthalenesulphonates are used in many different applications as wetting and dispersing agents. Several members of the series are effective as stabilizing and suspending agents in disperse systems.

Olefin sulphonates

The increasing availability of relatively low cost linear alpha olefins in the C_{14} to C_{18} range has remitted in the use of their sulphonate derivatives. The sulphonate is referred to as alpha olefin sulphonate or AOS has detergency and foaming properties similar to $C_{11\text{-}14}$ LAB. It is superior is performance to similar products made from internal straight chain olefins. Biodegradability of the AOS is slightly better than LAB.

Sulphates

the hydrophilic group-OSO_3^-, of the half sulphate ester surfactants in $–SO_3–$ attached through an oxygen atom to a carbon tom in the hydrophobic moiety. The additional oxygen makes the sulphate a stronger solubilizing group than the sulphonate but the C-O-S linkage of the sulphates is more easily hydrolysed than the C-S linkage of the sulphonates. This susceptibility to hydrolysis, especially in acidic media, limits the utility of the sulphates. Solubilization of hydrophobes through the combination of ethoxylation and sulphation is frequently used to obtain the optimum solubility balance and also to utilize less expensive raw materials that cannot be solubilized sufficiently by sulphation alone, e.g. derived from tallow alcohols. The shift of the detergent industry to more biodegradable production has resulted in ethoxylated and sulphated aliphatic alcohols.

Alkyl sulphates (Sulphated alcohols)

Commercial production of alkyl sulphates are well established in speciality markets. The hydrophobes are obtained by reduction of fatty acids or esters or the synthetic primary alcohols. The alkyl sulphates are usually sold as light coloured pastes or almost colourless solutions at concentrations in the range from 25 to 40 wt % of active ingredient. Purified sodium lauryl sulphates are offered by several manufactures as light coloured powders or crystalline materials at activities of 90-99 wt %. Products with a low content of inorganic salts are almost odourless and tasteless. The stability of the alkyl sulphates to hard water is excellent.

Sulphated natural fats and oils

Ricinoleic acid, i.e. 12-hydroxy-9,10-octadecenoic acid, which contains one hydroxyl group and one double bond, is a desirable constituent of an oil for sulphation. Oleic acid is also satisfactory. Esters of these acids can usually be sulphated with a minimum of hydrolysis. Polyunsaturated fatty acid moieties are undesirable components of glycerides for sulphation since the resulting surfactants are usually dark in colour and sensitive to oxidation. The reaction of sulphuric acid with either – CH=CH- or-OH groups in natural fats and oils yields sulphate half esters which are neutralized with caustic soda.

The sulphated fats and oils are widely used as emulsifying agents, wetting agents, detergents penetrants, dispersants, textile softeners and textile lubricants. The examples are sulphated caster oil, sperm oil etc.

Sulphated alkanolamides

A typical product of this class would be the sodium salt of the half sulphate ester of lauric ethanolamide. Variations in the product type include mono and diethanolamides of all of the fatty acids in the range C_{12} to C_{18}. The degree of sulphation is adjusted to obtain the desired solubility in water. the alkanolamide sulphates are somewhat more stable toward hydrolysis at high temperatures, in alkaline or acidic media, and in hard water than the sulphates of fatty acid esters or glycerides. The products are effective detergents with good foaming and lathering properties. They add viscosity or "body" to aqueous solutions and are widely used in the formulation of textile auxiliaries.

Sulphated esters

Oleic acid and ricinoleic acid esterified with low molecular weight alcohols and then sulphated yield useful surfactants. A typical product of this type would be from the sulphation of an oleic acid ester in which the alcoholic part represents ethyl, propyl, butyl, or amyl group. Products of this type are marketed as clear yellow to brown viscous solutions with an active ingredient contents as high as 85 wt %. The balance is water and sometimes as much as 10 % of pine oil or terpineol. The sulphated esters have strong wetting and rewetting power combined with a lubricant effect on textile fibres. They also have good foaming, emulsifying, and detergent properties. The products are stable enough in hot solutions of dilute caustic soda for use as wetting agents in kier boiling and continuous bleaching processes.

Alkyphenols, ethoxylated and sulphated

Sulphated polyoxyethylene alkylphenols and sodium salts are widely used in retail and industrial detergent products. The salts of the sulphate ester of linear alkyl phenoxypenta (ethyleneoxy) ethanol are consumed in substantial volume.

The sulphated polyoxyethylenealkylphenols are marketed as colourless, odourless aqueous solutions at concentrations from 30 to 60 wt % of active ingredient. The more concentrated products often contain 12-15% of ethanol to reduce the viscosity and facilitate handling. These surfactants are high foaming detergents, strong wetters, and efficient emulsifiers and dispersants that perform effectively in hard as well as soft water. They are mild to the skin. Significant quantities are consumed in textile processing. The polyoxyethylene in the molecules in this product series improves their performance over the unethoxylated analogs by decreasing the sensitivity to hard water and by decreasing the skin irritation. It also makes the products more water soluble. Approximately 30-40 wt % of polyoxyethylene is the optimum proportion for most uses.

Nonionic Surfactants

A nonionic surfactant, as the name implies, bears essentially no charge when dissolved or dispersed in aqueous media. The hydrophilic tendency in a nonionic is due primarily to oxygen in the molecule which hydrates by hydrogen bonding to water molecules. The strongest hydrophilic moieties in nonionics are ether linkage and hydroxyl groups, but ester and amide linkages, which are also hydrophilic, are present in many nonionics. The contribution of each oxygen to solubilization is weak and nonionic molecules must contain a multiplicity of them in order to be water soluble.

Nearly all of the unmodified polyol surfactants are lipophilic and they are frequently used as coemulsifiers in combinations with more hydrophilic surfactants. One advantage of the nonionics is that they are compatible with ionic and amphoteric surfactants. Polyoxyethylene solubilization is the key to the substantial and continuing growing of the nonionics. Since the polyoxyethylene group can be introduced into almost any organic compound that has a reactive hydrogen, a wide range of organic substances can be solubilized by ethoxylation.

Polyoxyethylene Surfactants

The solubility of these products depends on recurring ether linkages in a polyoxyethylene chain, e.g. $–CH_2CH_2$-O-CH_2CH_2-O-CH_2CH_2-O-. A solubilized molecule may contain more than one such polymer chain. The hydrophilic tendency increases with the polyoxyethylene content of the molecule and 60-75% by wt is required on most surfactant hydrophobes for complete miscibility with water at room temperature. Another rule of thumb is that the hydrophilic strength of the one ethylene oxide unit, -CH_2CH_2-O-, is approximately equal to the hydrophobic strength of one methylene unit, -CH_2-. The water solubility of polyoxyethylene compounds decreases as the temperature increases, which is attributed to a decrease in the degree of hydration or to an increase in the size of the micelles. The temperature at which a second phase appears is called the cloud point, a practical solubility test that is not sensitive to concentration differences in the range between 0.5 and 10 wt %. A minor proportion of anionic mixed with a nonionic will often raise the cloud point several degrees. Surface activity and performance efficiency of polyoxyethylene nonionics are usually greatest at temperatures just below the cloud point. As would be expected from their composition, the surface activity of polyoxyethylene nonionics is not adversely affected by hard water. High electrolyte concentrations in which sodium ions are the predominant component decrease the solubility of polyoxyethylene compounds by a salting out effect, whereas hydrochloric acid and calcium ions increase their solubility. The polyoxyethylene surfactants are moderate foamers and do not respond to the conventional foam boosters.

Low foaming nonionics are prepared by terminating the polyoxyethylene chain with a less soluble group, e.g. polyropylene oxide. A significant advantage of solubilization by means of polyoxyethylene is the capability of attaining almost any hydrophilic hydrophobic balance. A shortcoming is that the polyoxyethylene nonionics tend to be liquid or low melting waxes that are difficult to incorporate into dry, free flowing powders. Flaked solid products containing a high ratio of polyoxyethylene are manufactured but their surface activity is low because they are too hydrophilic.

The conversion of an aliphatic alcohol, alkylphenol, or fatty acid into a polyoxyethylene derivative can be carried out by addition of ethylene oxide to the hydrophobe to form a monoadduct, followed by subsequent addition of ethylene oxide in a polymerization reaction. Ethoxylation of these hydrophobes are catalysed by bases.

Ethoxylation is normally carried out as batch reaction although continuous reactors have been designed and operator. The hydrophobe and a solution of catalyst are charged into a reactor. Air and solvent for the catalyst are removed by agitating and heating under a vacuum, or purging with nitrogen, or both. When the hydrophobe is at the reaction temperature, addition of ethylene oxide is started. The polymerization is exothermic (20 kcal/mole of ethylene oxide reacted) and the rate of ethylene oxide addition should be exceed the cooling capacity of the reactor since careful maintenance of the reaction temperature is essential for reproducible manufacture of products to specifications. The end point of ethylene oxide addition is often determined by testing the solubility of a sample for its cloud point in water, a salt solution, or a water solvent mixture. After the reaction is complete, the catalyst is neutralized and the product is discharged to storage or packaged.

Undiluted polyoxyethylated C_8 to C_{12} alkylphenols have a slight aromatic odour and very from pale yellow to almost colourless. Products with low polyoxyethylene content are liquids and their viscosity increases with the content of combined ethylene oxide. High ratios of polyoxyethylene to hydrophobe are waxes. The specific gravity at room temperature increases with polyoxyethylene content from <1 until it levels off at about 1.2. Physical properties of the polyoxyethylated higher alkylphenols, e.g. dinonylphenol and hexadecylphenol, are similar to those of the C_8 to C_{12} derivatives with the same wt % of combined ethylene oxide.

The solubility in water of the ethoxylated alkylphenols increases with the polyoxyethylene content. About 60 wt % of polyoxyethylene is required for complete miscibility in cold water, and above 75% of polyoxyethylene the products do not cloud out at the boiling point. Water hardness does not adversely affect the surface activity of the products. The solubility of polyoxyethylene alkylphenols in highly aliphatic mineral oils decreases faster with increasing polyoxyethylene content than the water solubility increases.

Ethoxylated Aliphatic Alcohols

The alkylpoly (ethyleneoxy) ethnols, are introduced as they are more biodegradable products. The hydrophobes are generally mixtures of straight chain alcohols in the range from C_{12} to C_{18} and that the mole ratios of combined ethylene oxide to hydrophobe vary from 1 to 50. The undiluted products vary in physical form from liquids to waxy solids. Viscosity in each homologous series increase as the polyoxyethylene content increases. The products have a slight odour characteristic of the hydrophobe the decrease as the polyethylene content increases. The liquids vary from pale yellow to almost colourless and the solids from yellow to white waxes; the products become lighter coloured as the polyoxyethylene content increases. Within each homologous series, the specific gravity at room temperature increases with the polyoxyethylene content from slightly less than 1 unit it levels off a little under 1.2. Solubility of the alkylpoly (ethyleneoxy) ethanols in water increases with the ethylene oxide content; about 65-70 wt % of polyoxyethylene is required for complete miscibility at room temperature. The water hardness does not impair the surface activity of the alkylpoly (ethyleneoxy) ethanols.

The alkylpoly (ethyleneoxy) ethanols have uses, such as textile-fibre lubrication, that are due to the properties of the hydrophobe and for which the polyoxyethylene alkylphenols are not applicable.

Ethoxylation processes and equipment for manufacture of the alkylpoly (ethyleneoxy) ethanols are similar to those described for the alkylphenols. However, the rate of reaction of primary alcohols with ethylene oxide is fast.

Carboxylic Esters

The carboxylic acid ester series of surfactants are polyol solubilized, polyoxyethylene solubilized, or both, and are based on several different types of hydrophobes.

Mono and diglycerol esters of the saturated fatty acids are light coloured solids with melting prints between 25 and 85ºC. The 1-monoglycerides are higher melting than the corresponding 2-monoglycerides. The glycerides of the unsaturated fatty acids are liquids at room temperature. The partial glycerol fatty esters have the characteristic odor of the fats from which they were derived. The polyol group of a monogylceride is not strong enough as a hydrophilic moiety to carry even an easily solubilized acid like oleic into aqueous solution. Despite their lack of water solubility the partial glycerol esters have commercially important and technically interesting surfactant uses.

The uses of the mono and diglycerides center around applications involving emulsification, dispersion, suspension, solubilization, and lubrication. The partial glycerol esters are used as components of textile mill processing oils and lubricant and softener formulations.

Polyethylene glycol esters

The polyoxyethylene esters of fatty acids and alicyclic carboxylic acid related to abietic acid comprise the polyethylene glycol series of surfactants. Properties and uses of these two groups of products differ markedly.

Commercial polyoxyethylene fatty acid esters are mixtures that contain varying proportions of the following components: monoesters $RCOO(OCH_2CH_2)_n OH$; diesters, $RCOO(OCH_2CH_2)_n OOCR$; and polyglycol, $H(OCH_2CH_2)_n OH$. The composition of the mixture can be forced toward the mono or diester by the ratio of reactants and process of manufacture. The descriptions of commercial products usually specify the acid esterified, whether it is predominantly a mono or diester, and either the mole ratio of polyoxyethylene to fatty acid or the molecular weight of the polyglycol esterified with the acid.

The polyoxyethylene ester of fatty acids range in consistency from free flowing liquids to slurries to firm waxes. Within a homologous series the products change from liquids to waxes as the polyethylene conent increases. Only low mole ratios of polyoxyethylene to unsaturated fatty acids or lower molecular weight acids yield liquid products. The odour of the products is characteristic of the fatty acid hydrophobe and decreases as the polyoxyethylene content increases. Odour and odour stability are important characteristics of these products because of their use in textile finishing. Colour stability is also important for the same reason.

The ester linkage is slightly hydrophilic and only about 60 wt % polyoxyethylene is required to solubilize the saturated fatty acids in water at room temperature. The surface activity of the fatty and acid polyglycol esters, e.g. wetting and surface tension lowering, is in the useful range but less than for ethoxylated alkylphenols or aliphatic alcohols. The products are low foamers in aqueous solutions, which is advantageous for certain uses. Emulsification is a key property of this series of compounds and its importance is reflected in the wide range of lipophilic solubilities that are available in commercial products. Susceptibility to hydrolysis in hot acidic or alkaline solutions in their principal limitation.

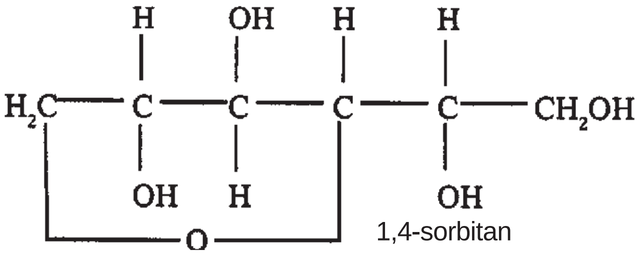
Two methods are used commercially for manufacture of the polyxyethylene acids. One is the alkali catalyzed reaction of a fatty acid wit ethylene oxide. The other is estrification of fatty acid with a performed polyethylene glycol in the presence of an acid catalyst. Some manufacturers claim that the properties are different for products of the same gross composition as prepared by the two methods. However, the ethoxylation catalysts also catalyze transesterification and the products of direct ethoxylation approach closely those obtained by esterification if the manufacturing process is directed to this end. Deodorization and decolourization treatments are commonly incorporated in manufacturing processes.

Abietic acid and related acids are a major constituent of rosin. Tall oil is a mixture of unsaturated fatty acid with alicyclic acids of the abietic family. Refined tall oil may be high in rosin acids or in unsaturated fatty acids, depending on the purification process. The polyoxeyethylene derivatives of the rosin acids (e.g. dehydroabietic acid) are generally similar to the corresponding polyoxyethylene fatty acid in surfactant properties and processes of manufacture except that they are surprisingly stable toward hydrolysis.

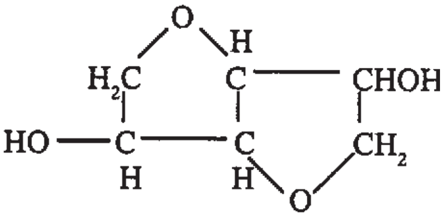
The chemical stability of the polyoxyethylene tallates together with their characteristic low foam generation at use concentrations makes them useful as components of consumer detergents for automatic clothes washing machines and for continuous high speed, industrial cleaning processes.

Anhydrosorbitol ester

Fatty acid esters of anhydrosorbitol are another important class of polyol solubilized surfactants. The important commercial products in the group are mono, di or triesters of sorbitan and fatty acids. Sorbitan is a mixture of anhydrosorbitols. The isomers shown below are the principal components of the mixture:



1,4-sorbitan



isosorbide

Fig 1.3

The sorbitan oleates and the monolaurate are pale yellow liquids. The palmitates and stearates are light tan solids. Sorbitan is not a strong hydrophilic group and its derivatives are not water soluble but they are soluble in a wide range of mineral and vegetable oils. The sorbitan esters are lipophilic emulsifiers, solubulizers, softeners, and fibre lubricants. An important application is in synthetic fibre manufacture and textile processing an antistats, fibre lubricants softener and emulsifiers of textile mill processing oils.

The anhydrosorbitol esters are prepared commercially by direct esterification of sorbitol with a fatty acid in the presence of an acidic catalyst at temperatures in the range 225-250ºC. Internal ether formation as well as esterification takes place under these conditions.

Ethoxylated anhydrosorbitol esters: Ethoxylation of the sorbitan fatty acid esters leads to a series of more hydrophilic surfactants. The structure of a representative component of polyoxtethlene sorbitan monostearate illustrates the composition of these products:

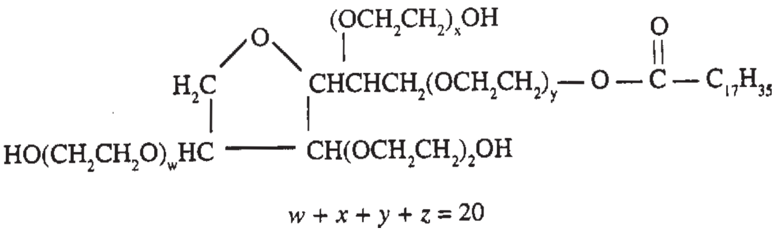


Fig 1.4: Polyoxyethylene sorbitan monostearate

Glycol esters of fatty acids

The ethylene glycol, diethylene glycol, and 1, 2 propanediol esters of fatty acids are widely used surfactants. The commercial products are mixtures of mono and diesters even though the stated composition usually refers only to the principal component. The mono and dilaurates and oleates of ethylene glycol, diethylene glycol, and propylene glycol are liquids. Stearates of these glycols are solids. The glycol esters are strongly lipophilic emulsifiers and pacifiers. They are normally formulated in combination with hydrophilic emulsifier. The monoesters of glycols can be manufactured by the alkali catalyzed reaction of ethylene or propylene oxide with fatty acids. Mono and diesters are also prepared by esterification of fatty acid with a glycol.

Natural fats, oils, and waxes, ethoxylated

Ethoxylated ester oil and ethoxylated lanolin derivatives are important surfactants. Castor oil is a triglyceride with a high content of esterified ricinoleic acid. Ethoxylation of it in the presence of an alkaline catalyst to a polyoxyethylene content 60-70 wt % yields water soluble surfactants. They are used as processing assistants and finishing agents in the manufacture of textiles.

Lanolin alcohols are derived from the fat that is, stripped from raw wool. They are a mixture of cholesterol, isocholesterol, and other high alcohols. Lanolin alcohols purified by bleaching, solvent extraction, crystallization or molecular distillation are ethoxylated to yield nonionic emulsifiers. The mole ratios of ethylene oxide to alcohols that are offered commercially represent a full series of lipophilic and hydrophilic products.

Carboxylic Amides

The usage of fatty diethanolamides is divided between "regular" (2/1, amine/acid) and "super" (1/1) amides. The 2/1 fatty dialkanolamides behave more like a compound than a mixture. The effect of the excess diethanolamine and its derivatives on the properties of the products is to increase their water solubility as compared to the super amides. A typical 1/1 super amide would contain 90% of the amide of the fatty acid, 7% unreacted diethanolamine, 2.5% amino esters and ester amides.

Foam stabilization and detergency are the most important functional properties of the fatty diethanolamides. The products are used in textile processing as detergents and dyeing assistants. Regular fatty diethanolamides are prepared by heating 1 mole of fatty acid with 2 moles of diethanolamine at 160-180ºC for 2-4 hrs. Superamides are prepared by heating a fatty acid methyl ester with an equimolar quantity of diethanolamine at 100-110ºC for 2-4 hrs. and distilling off the methanol that is formed.

Monoalkanolamine condensates

Coco, lauric, oleic, and stearic monethanolamides and monoisopropanolamides with amine ratios in the range from 2/1 to 1/2 are the principal surfactants in the monoalkanolamide group. They are generally water insoluble solids that are easily solubilized by hydrophilic surfactants. Except for solubility, their properties and uses are similar to the fatty diethanolamides. Manufacturing processes and product yields, are also similar to the fatty diethanolamides.

Polyoxyethylene Fatty Acid Amides

The mono and diadducts obtained by ethoxylation of a fatty acid amide are equivalent in gross composition to the mono and diethanolamide condensates of the corresponding fatty acid, but the condensates are more widely used than the adducts because they have better properties for most uses. Fatty acid mono and diethanolamide condensates, as well as fatty acid amides, can be ethoxylated by conventional technology. Ethoxylates of fatty acid amides are predominantly secondary amides.

CATIONIC SURFACTANTS

The hydrophilic moieties in cationic surfactants are amino or quaternary nitrogens. As the name implies, these hydrophobic moieties bear a positive charge when dissolved in aqueous media. The hydrophilic tendency the one amino nitrogen is approximately strong enough to solubilize a lipophilic group in the surfactant molecular weight range in dilute acidic solution; e.g. lauryl amine is soluble in dilute hydrochloric acid. To increase the water solubility, additional primary, secondary or tertiary amino groups can be introduced or the amino group can be quaternized with a low molecular weight alkyl group, e.g. CH_2-or $HOCH_2CH_2$-. Quaternary nitrogen compounds are strong bases that form essentially neutral salts with hydrochloric and sulphuric acid. Most quaternary surfactants are soluble even in alkaline aqueous solutions. Polyoxyethylated cationics behave like nonionics in alkaline solutions and like cationics in acidic solutions.

Cationic surfactants are widely used in acidic aqueous and nonaqueous systems as dispersants emulsifiers, wetting agents, dye fixing agents, textile lubricants, textile softeners, foam stabilizers, and corrosion inhibitors. This usage pattern parallels somewhat the widespread use of anionics in neutral and alkaline solutions. The negatively charged cationics are more strongly adsorbed than anionic or nonionic surfactants on a diverse group of substrates. This substantivity is the key to many applications for which the cationics are uniquely effective. The quaternaries are also combined with nonionics to form detergent sanitizers.

Polyoxyethylene alkyl and alicyclic amines

Ethoxylation is an economic route to the multiplicity of properties required by the numerous and sometimes smalls volume industrial uses of cationic surface active agents. Three series of products are represented: polyoxyethylene linear alkyl amines, polyoxyethylene aliphatic t-alkylamines, and polyoxyethylene dehydroabietylamines. Despite the wide range of chemical compositions, the polyoxyamines tend to have similar physical properties. They are generally yellow or amber liquids or yellow solids with low melting point. Specific gravities at room temperature range from approx 0.9 to 1.15. The ethoxylated amines have the characteristically greater solubility of cationics in acidic solutions as compared to neutral or alkaline solutions, but the different decreases as the polyoxyethylene content increases.

The polyoxyethylene amines are used as emulsifiers, dispersants, and wetting agents in neutral and acid solutions. Other uses are as textile softeners, lubricants and antistats.

Equipment and processes for ethoxylation of the amines are similar to those described earlier for reaction of ethylene oxide with alkylphenols and aliphatic alcohols. If there is no steric hindrance, ethylene oxide reacts with both hydrogens of a primary amine at a relatively low temperature (90-120ºC) in the absence of an added catalyst.

2 Alkyl 1 (hydroxyethyl) 2 imidazolines

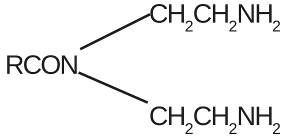
These materials are used in hydrocarbon and acidic aqueous media as wetting agents, dispersants, emulsifiers, corrosion inhibitors, and detergents. They are also useful antistats for application to textile fibres. The 1(2 hydroxyethyl) 2 alkyl 2 imidazolines are prepared by heating the salt of a carboxylic acid with hydroxyethylenediamine to obtain a substituted amide; raising the temperature to 200-250ºC then causes elimination of another mole of water to form the substituted imidazoline. In addition to their use as surfactants per se, these amines are further converted to yield three additional series of cationic surfactants. They are (1) ethoxylated to yield more hydrophilic products, (2) reacted with dimethyl sulphate for benezyl chloride to form quaternaries, and (3) treated with hydrogen peroxide to yield amine oxides. The second and third reactions involve substitutions on the 1 position in the imidazoline ring and the first reaction extends the oxyethylene chain that is already a monadduct on the nitrogen in the 1 position.

N,N.N’,N’ Tetrakis substituted ethylenediamines

The reaction of a 1, 2 alkylene oxide with ethylenediamine form the basis of an ether and an ester series of surfactants. The ethers, which are more important commercially, are weakly cationic products.

Amines Having Amide Linkages

The important products in this category are amide linked amines prepared by the condensation of a carboxylic acid with a di or polyamine. The type represents one approach in the search for a less expensive aliphatic amine in the surfactant molecular weight range. Formulas for typical amide linked amines are listed below:-



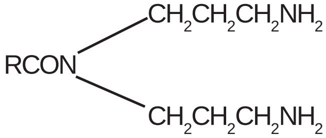
$$RCON\left\langle\begin{array}{l}CH_2CH_2NH_2\\ CH_2CH_2NH_2\end{array}\right.$$

Where R is derived from coconut, oleic, stearic, and tall oil acids;

$$RCONHCH_2CH_2CH_2N\ (CH_2)_2$$

Where R is from stearic acid;

$$RCONHCH_2CH_2CH_2NHCH_2CH_2CH_2NH_2$$



$$RCON\left\langle\begin{array}{l}CH_2CH_2CH_2NH_2\\ CH_2CH_2CH_2NH_2\end{array}\right.$$

Where R is from stearic acid; and

$$RCONHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$$

Where R is from stearic acid.

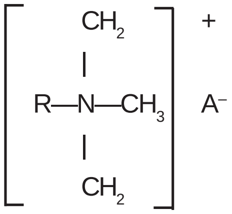
Fig 1.5 Amide linked amines

More water soluble polyoxyethylene derivatives are produced from most of the amide linked di and polyamines that contain one or more amino hydrogens.

Quaternary Ammonium Salts

The quaternary ammonium ion is a much stronger hydrophilic moiety than a primary, secondary, or tertiary amino group. The strong basicity or cationic activity of the quaternary ion will carry compounds in the surfactant mol wt range into solution even in alkaline media. The quaternaries also differ from other cationic types by being strongly absorbed on negatively charged substrates and by being less susceptible to yellowing on aging in the presence of air. They have textile-softening properties.

Stearmidomethylpryidinium chloride is the emulsifier and also an active ingredient in permanent water repellents. The water repellent composition which may also contain methylene distearamide $(C_{17}H_{33}CONH)_2\ CH_2$, is padded on the fabric that is to be rendered water repellent. The fabric is then dried and heat treated in an oven where the emulsifier is decomposed.



$$\left[\begin{array}{c} CH_2 \\ | \\ R—N—CH_3 \\ | \\ CH_2 \end{array}\right]^{+} A^{-}$$

Fig. 1.6 Alkyltrimethylammonium salts

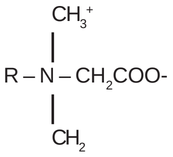
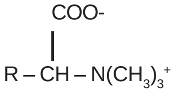
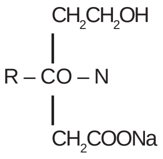
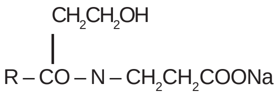
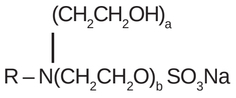
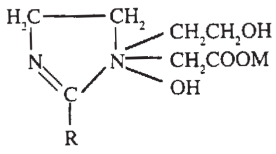
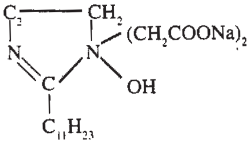
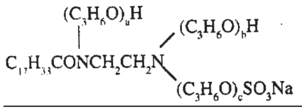
AMPHOTERIC SURFACTANTS

Amphoteric surfactants contain both an acidic and a basic hydrophilic moiety in their surface. These ionic functions may be any of the anionic or cationic groups that have been described in the preceding sections, and the molecule may contain several ionic functions. Many amphoterics also contain ether oxygens or hydroxyls that strengthen their hydrophilic tendency.

Table 1.3
Amphoteric Surfactants

Structure	Name
$RNHCH_2CH_2COOH/Na$	N coco 3 aminopropionic acid
	N coco 3 aminopropionic acid, sodium salt
CH_2CH_2COONa | R – N | CH_2CH_2COONa	N tallow 3 iminodipropionate, disodium salt N lauryl 3 iminodipropionate, disodium salt R: Lauryl/Tallow fatty radical

(contd.)

Structure	Name
 $R-\overset{\overset{CH_3^+}{\vert}}{\underset{\underset{CH_2}{\vert}}{N}}-CH_2COO-$	N Carboxymethyl N cocalkyl N dimethylammonium hydroxide N carboxymethyl N dimethyl N (9 octadecencyl) ammonium hydroxide R: Cocoalkyl/octadecenyl
 $R-\overset{\overset{COO-}{\vert}}{CH}-N(CH_3)_3^+$	(1 carboxyheptadecyl) trimethy lammonium hydroxide (1 carboxyundecyl) trimethylammonium hydroxide R: Heptadecyl/undecyl
 $R-CO-\overset{\overset{CH_2CH_2OH}{\vert}}{\underset{\underset{CH_2COONa}{\vert}}{N}}$	N cocoamidethyl N hydroxyethyglcine, sodium salt N hydroxyethyl N atearamidoglycine, sodium salt R: Cocoakyl/steryl
 $R-CO-\overset{\overset{CH_2CH_2OH}{\vert}}{N}-CH_2CH_2COONa$	N hydroxyethyl N lauramido b alanine, sodium salt N cocoamido N hydroxyethyl b alanine, sodium salt R: Lauric/cocoalkyl
 $R-\overset{\overset{(CH_2CH_2OH)_a}{\vert}}{N}(CH_2CH_2O)_b\,SO_3Na$	mixed alicyclic amines, ethoxylated and sulfated, sodium salt R: Alicylic radical
	2 alkyl 1 carboxymethyl 1 hydroxyethyl 2 imidazolinium hydroxide, sodium salt or free acid R = nonyl, undecyl, heptadencyl M = H or Na
	1, 1 bis (carboxymethyl) 2 undecyl 2 imidazolinium hydroxide, disodium salt
	Oleic acid-ethylenediamine condensate, propoxylated and sulphated, sodium, salt

SIZING

During the weaving process the warp threads are subjected to certain amount of friction as they move forward through the eyes of the healds and between the teeth of the reed. The friction during the vertical separation of the yarns to make the space or shed through which the shuttle passes is also there. Reinforcement and lubrication of the warp yarns are needed before it goes into the loom. This processes is known as sizing.

The sizing material must be an emollient adhesive substance, preferably with filmforming properties. The chief adhesive substances are gums, starches and glues. The softening and lubricating material is generally an oily or fatty substance such as glycerol, olive oil, etc. Hygroscopics substances such as glycol is also added to counteract any tendency to undue dryness of the sized yarns. Finally, an antiseptic substance is added to prevent mildew formation during storage. Zinc chloride, phenol or salicylanilide are used. The sizing preparation should be capable of readily being removed before the bleaching and dyeing of the cloth.

Practically all cotton warps are sized but many worsted warps are made of two fold yearns, so that the coarser types do not require sizing. The finer worsted and woolens are usually sized however, to maintain the clean state of the former and to avoid loss of fibre in the latter. In addition to the usual reasons; there appears to be a general tendency for the use of animal gluse for sizing worsted and woolens. Silk warps are often sized, but it is also possible to utilise the natural silk gum as a protective medium, and use warps of silk which has not been degummed. Rayons use linseed oil based size.

Starch, modified starch, natural gums carboxy methyl cellulose, tamarind Rernel powder are used as main ingredients of sizes for cotton. For synthetic fibres the usual size material is polyvinyl alcohol and acrylic polymers with other chemicals.

STARCH

Starch is a carbohydrate and is widely available in plants. Starch is obtained and extracted economically from maize, cassava, potato, wheat etc. Starches from different sources have different physical and chemical properties.

Table 1.4
Size Recipes (Parts)

	Cotton					Manmade fibre blends					
Recipe No.	1	2	3	4	5	1	2	3	4	5	6
Starch Maize, Tapioca	100			100							
Tamarind Kernel Powder (TKP)											
Thin Boiling Starch		100	100		100	55	55	50	50	50	
*Carboxy methyl cellulose (CMC)			10		10	6	6	6	5	5	
*Polyvinyl alcohol (PVA)					10	10	8	4	1	1.5	15
*Gum	2	3	2	7		2	2	2	1.5	1.0	
*Glue									0.8	0.8	
Softener: Mutton tallow	7.5	5	3	10	4	1	1	1.5	1.5	1.5	2
China clay				115							
Sodium silicate											
Preservative				2							
Magnesium chloride				5							
Antistatic agent						0.5	0.5	0.5			1

*can be replaced either partly or fully by polyacrylate/polyester

Table 1.5
Size Recipes and Add ons for Different Fabric Constructions

Recipe Number (Table 1.3)	Fibre	Counts	Fabric construction	Size add-on (%)
Cotton				
1	100% Cotton or less than 33% viscose or poly nosic Blended with cotton	Coarse Medium	Light and Light med.	8-10 10.12
2	do	Coarse Medium Fine	Med. Med. Light	10-12 12-13 12

(*contd. . . .*)

Table 1.5 *(Contd.)*

Recipe Number (Table 1.3)	Fibre	Counts	Fabric construction	Size add-on (%)
3	do	Coarse Medium Fine Superfine	Med. & Heavy Med. & Heavy Med. And Hy Lt. Md. and Hy	10.12 12-13 13-15 14-18
4	Grey Sort	Coarse Medium	Lt and Med. Lt. And Med.	As required As required
5	100% Cotton (Airjet loom)	Fine (about 40s)	Hy	12
		Man Made Fibre Blends		
1	Polyester Cotton (80/20)	40s to 50s	Md and Hy	18
2	Polyester Cotton (67/33)	40s to 50s	Md and Hy	18
3	Polyester Cotton (48/52)	40s to 50s	Md and Hy	15
4	Polynosic Cotton (67/33)		Md	12
	Or			
	Viscose Cotton (67/33)	40s to 50s	Md and Hy	12-14
5	Polyester Polynosic Cotton (15/52/33)	40s to 50s	Md and Hy	12-14
6	Polyester Cotton (67/33) (Airjet loom)	30s to 40s	Md and Hy	12-16

Starch is a high polymeric carbohydrate composed of glucopyranose units joined by alpha glucoside linkages. The approximate formula can be written as $(C_6H_{10}O_5)_n$ where n can be from a few hundred to a few million. Starch occurs in the form of white granules usually made up of amylose (linear polymer) and amylopectin (branched). The granules' size vary from 3 to 30 micron from cereals and 20 to 100 microns from tubers. The granules gelatinize in water when the temperature is raised to 60-70ºC. Each starch has a characteristic gelatinization range.

Table 1.6
Gelatinization Range of Starches

Starch source	Temperature range ºC
Wheat	58-64
Potato	59-68
Corn	62-72
Sorghum	68-78
Rice	68-78

The most important colloidal characteristics of starch in aqueous dispersion or solution are clarity, gel strength, adhesive and film forming properties. These characteristics make it a good sizing agent.

MODIFIED STARCH

Before the final dewatering operation, the starch slurry may be modified with chemical reagents at temperatures below the gelatinization point. The most important products are the thin boiling starches, which are made by a partial hydrolysis with acid, and the oxidized starches, which are made by treating the starch with hypochlorite. In making thin boiling starches, the starth is suspended in about 0.1 N sulphuric acid at 50°C for 6-24 hr, depending on the extent of modification of fluidity and desired. The action is topped by the addition to sodium carbonate, and the product is filtered, washed, and dried.

Manufacturing of oxidized starches consists essentially of the addition of predetermined quantities of sodium hypochlorite to the aqueous starch slurry. Alkali is added to maintain the pH at 8-10 throughout the reaction, and cooling is used to maintain the temperature in the desired range, usually 21-38°C. The amount of hypochlorite added is usually equivalent to between 0.5 and 6.0% available chlorine, based on starch, and is determined by the fluidity grade of starch to be made. The more reagent added, the less will be the viscosity of the starch when gelatinized. Following a reaction period of 5-24 hr, the slurry is neutralized and any free chlorine present is destroyed with sodium bisulphite. The starch is washed on continuous vacuum filters or centrifugal devices to remove soluble byproducts before it is collected on vacuum filters and dried.

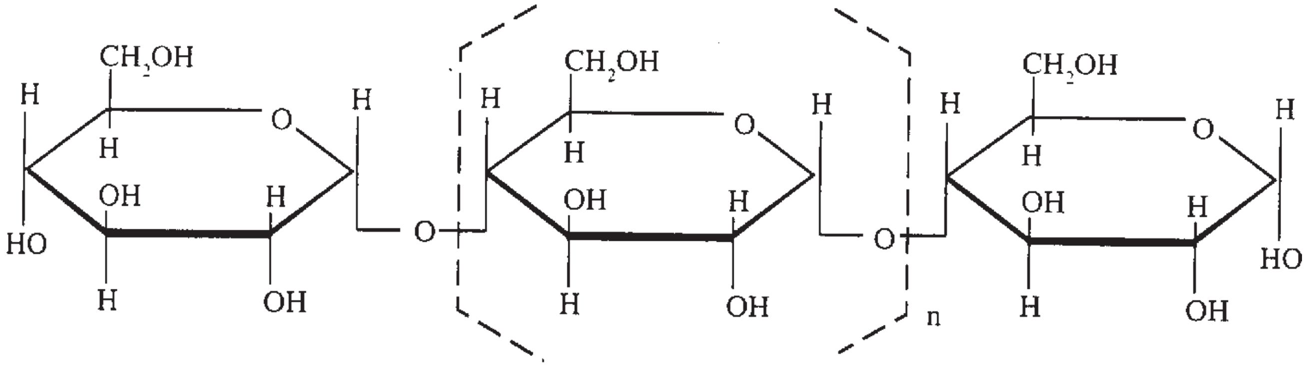


Fig 1.7: Amylose molecule

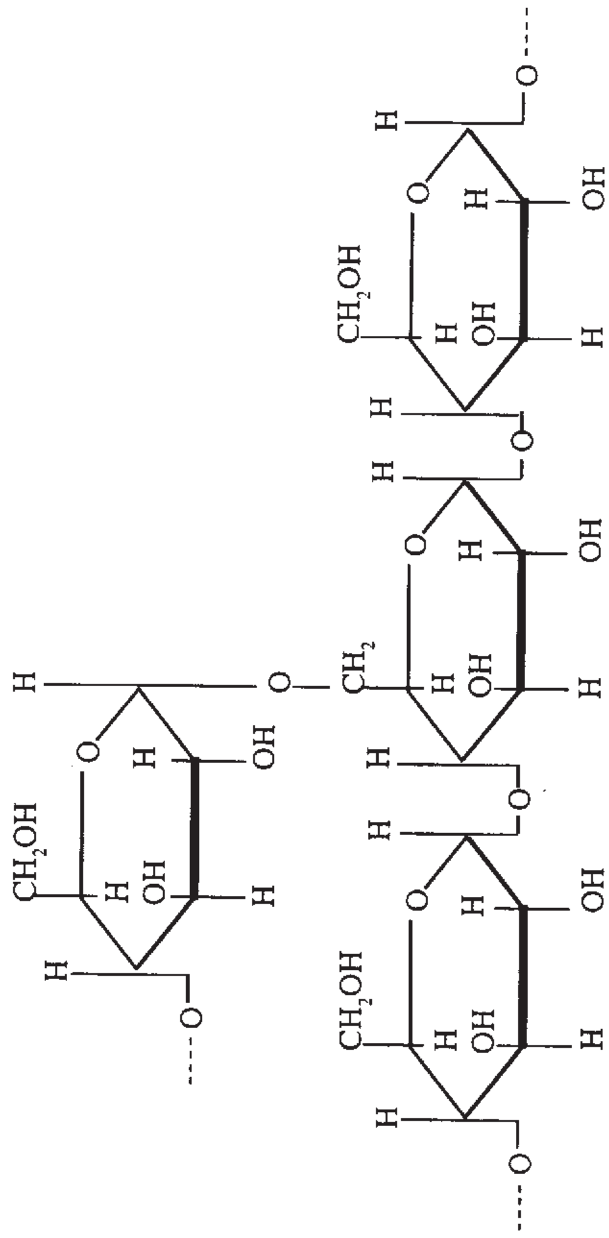


Fig. 1.8: Amylopectin molecule

Dextrins are made by heating, with or without the addition of chemical reagents. The resultant pyrodextrins, or torrefaction dextrins, are classified into three groups, depending on the amount of modification. The British gums are prepared by heating starch with agitation for 10-20 hr at 170-195ºC. the products have a buff to brown colour. Sometimes alkaline materials, such as sodium bicarbonate or ammonia, are added before pyrolysis. White dextrins are prepared by spraying a powdered starch with acid, usually dilute hydrochloric acid, before it is heated at 95-120ºC for 3-8 hr. The use of less acid and more strenuous conditions (150-180ºC for 6-18 hr) produces the yellow or canary dextrins.

Specifications of starch and starch products relate to purity and the extent of modification, if any, of the high polymer. Common impurities are ash, protein, liquids, as well as cold water extractives remaining in the starch. Excessive moisture may also be included in the list. Thus, for unmodified corn starch maximal limits may be; moisture, 12% ash, 0.1% protein, 0.4%; lipids (total of ether extractable material as well as adsorbed fatty acids), 0.90%; and cold water extractives, 0.2%. Modified starch products such as dextrins are often sold at lower moisture contents of 5-10%. The amount of water soluble material may increase to very high values as starch is modified. Thus, a dextrin may be almost completely water soluble; this solubility test may be used to determine the extent of the reaction, and specifications as accordingly.

Pure starch is white, and off colours are the result of extraneous materials such as ether extractives and gluten. Since the colour of starch is frequently improved by bleaching procedures, independent specifications may be set up, based on the degree of whiteness in reference to some standard such as magnesium oxide.

Because most starch applications involve the use of cooked pastes, the consistency of such pastes is of great importance. A number of different procedures have been devised based on rotational devices and flow through orifices. The most commonly used method to the Scott test for hot paste consistency. This test is performed by mixing a suitable amount of starch with 180 ml of water in a metal beaker and then immersing the beaker in coiling water. After this mixture has been stirred and heated under specified conditions, it is transferred to a Scott viscosity up. The number of seconds required for the delivery of the first 100 ml of paste is taken as the Scott viscosity. A sample weight is taken that will give a cooked paste delivering 100 ml in 40-80 sec.

Unmodified corn starch should have a minimum Scott test of 40 sec/100 ml at a concentration of 12g/280 ml. Modified starches, such as acid-hydrolysed and oxidized, have lesser Scott values. These viscometric tests are used by the manufacturer to control the extent of modification. Modified starches are generally classified according to fluidity number, an inverse measure of viscosity. It is determined on an arbitrary scale for commercial starches from 10 to 90, the lower the viscosity the higher the fluidity. Unmodified corn starch, gelatinized at a concentration of 5 g to 100 ml of 1% sodium hydroxide solution at 25%C, has a fluidity of one; water on this arbitrary scale has a fluidity of 100.

INDUSTRIAL GUMS

A number of naturally occurring gums are used as sizing agents. Because they are expensive, they are usually added to starch based sizes to improve upon their properties. These gums are gum Arabic, gum guar, locust beam gum tamarin kernel powder etc.

Gum Arabic

Gum Arabic is obtained as exudes from the Aeacia. There are five hundred different varieties of Aeacia. The best products is obtained from Aeacia Senegal. 85% of world supply comes from Senegal. The tree is 5 to 8 metre tall and lives for about 25 to 30 years. Gum production starts by creating would on the bark of the tree. It is a neutral or slightly acidic salt of a complex polysaccharide. Gum Arabic dissolves in hot or cold water forming a clear mucilaginous solution. It is used as a sizing components and also in printing and finishing formulations.

Guar gum

Guar gum is obtained from the seeds of Cyanaposis tetragonolobus. Guar is plenty available in India as a cultivated vegetable for human and animal consumption. For textile the gums or ethoxylated and propoxylated gums are used as size component and for making printing pastes. The active constituent is galactomannan.

Locust bean gum

Locust bean gum is obtained from locust beam botanically called Ceratonia siliqua or Carob. Carob is obtained only in the Mediterranean coastal areas. The chief growing areas are Spain, Italy, Greece, Cyprus, Algeria, Portugal, Israel and Turkey. It is an evergreen tree growing upto 6 m height and has luxuriant perennial foliage. The fruit that is the bean is a dark chocolate coloured pod 10-20 cm long 1.9 to 5 cm wide. The pods are collected crushed and kibbled. There are four grades of locust bean gums top high, normal high, industrial and technical. The gum and its derivatives are used as sizing agent addition and also as thickener in printing paste. It is also used to impart body and smooth touch to the fabric.

Tamarind kernel powder

Tamarind kernel powder is obtained tamarind tree widely grown in India. The pulp of the print is used as acidulent in food. The seed kernel powder is used for sizing. The seeds are decorticated and powdered. The powder is creamy white and contains mainly poly saccharides along with fibre, fat and salts.

Table 1.7
Typical Size Composition with TKP for Cotton Warp

Item	Kg
TKP	67
Sod. Silicate	6.7
Mutlon tallow	1.3
Sod. Silicofluoride	0.2
Water to make up	1000 litre

CARBOXY METHYL CELLULOSE SODIUM SALT

Sodium carboxymethylcellulose, a water soluble cellulose ether with ability to suspend solids in and control the viscosity of aqueous solutions and to form strong, tough films has accounted for the rapid growth of its use in industry since 1947. Sodium carboxy methyl cellulose was first used as a substitute for naural gums but new markets based on its own properties have since been developed. Large volumes of this cellulose derivatives are employed in paper, textile processing, detergents, drilling fluids, and protective coatings. The purified grade, known as cellulose gum, is used extensively in the pharmaceutical, cosmetic and food industries.

Some of the properties of CMC are listed below:

1. Sodium CMC is a white to cream coloured odourless powder, with a bland mucilaginous taste.
2. It is soluble in water at all temperature, yielding a clear solution with neutral pH.
3. It is insoluble in organic solvents.
4. The aqueous solutions of sodium CMC are stable in pH range of 5-10.
5. Specific gravity is 1.59.
6. Refractive index is 1.51.
7. Viscosities of 1% aqueous solution of sodium CMC varies in the range of 6 to 4000 cps. It is broadly divided into three viscosity grades low, medium and high.
8. It reacts with heavy metal salts to form films that are insoluble in water, transport, relatively tough and unaffected by organic chemicals.
9. Many of its colloidal properties are superior to those of natural hydrophilic colloids.
10. It is incompatible with many electrolytes.
11. Because of its anionic nature, sodium CMC is incompatible with quaternary ammonium compounds.
12. It is incompatible with strong acids, and heavy metal ions such as aluminium, zinc, silver mercury and iron.
13. Being physiologically inert, it is harmless when taken by oral route, and it can be safety injected.

Usages

Sodium carboxymethyl cellulose has received considerable attention in the textile industry because of its ready solubility and excellent film-forming characteristics. It has been particularly useful as a warp size for yarns and filaments. Sodium carboxymethylcellulose has replaced starch in many warp sizing operations because of its marked advantage in weaving efficiency and in reducing stream pollution at the finishing mill. Other advantages, such as reduced shedding on the loom, elimination of the need for desizing enzymes, and lowered water and steam consumption, have also been realized.

This cellulose ether has also been used successfully for many years as a thickener for textile printing pastes. It is not sensitive to acids or alkalies within the pH range of these pastes and can be used, therefore, with a variety of dyes. It dissolves readily in both hot and cold water, which facilitates formula preparation and removal of the gum after printing. Because viscosity can be closely controlled, sharper prints can be obtained at higher machine speeds.

Fabrics sized with sodium carboxymethylecellulose are difficult to soil and easy to clean. This unique property has sparked considerable interest in its utilization as a domestic laundry size. Other textile applications include it use as a scaffolding fibre, as a binder for nonwoven fabrics, and, when insolubilized, as a permanent finish.

Table 1.8
Designations of Carboxymethyl Cellulose Types

Grade	Viscosity	Degree of Substitution		Active matter content, % min	Designation
		Full form	Code		
T	EL	0.4 to 0.55	4	55	TEL-455
		0.55 to 1.0	8	55	TEL-855
T	L	0.4 to 0.55	4	55	TL-455
		0.55 to 1.0	8	55	TL-855
T	M	0.4 to 0.55	4	55	TM-455
		0.55 to 1.0	8	55	TM-855
T	H	0.4 to 0.55	4	55	TH-455
		0.55 to 1.0	8	55	TH-855
T	EH	0.4 to 0.55	4	55	TEH-455
		0.55 to 1.0	8	55	

(contd.)

Table 1.8 *(contd.)*

Grade	Viscosity	Degree of Substitution		Active matter content, % min	Designation
		Full form	Code		
T	SH	0.4 to 0.55	4	55	TSH-455
		0.55 to 1.0	8	55	TSH-855
P	L	0.4 to 0.55	4	92	PL-492
		0.55 to 1.0	8	92	PL-892
P	M	0.4 to 0.55	4	92	PM-492
		0.55 to 1.0	8	92	PM-892
P	H	0.4 to 0.55	4	92	PH-492
		0.55 to 1.0	8	92	PH-892

Note: Last two digits shall indicate the percentage of actual active matter content in the designation.

T = Technical, EL = Extra Low, P =Pure, L = Low, M = Medium. H = High, EH = Extra High, SH = Super High

Table 1.9
Viscosity Ranges

Type Technical	Viscosity cP	Type pure	Viscosity cP
Extra low	0 to 29	Low	0 to 99
Low	30 to 99	Medium	100 to 599
Medium	100 to 249	High	above 600
High	250 to 599		
Extra high	600 to 999		
Super high	above 1000		

SIZING OF BLENDED YARN

Polyester cotton or viscose blended yarns are differently sized. Synthetic sizes are used for them as the natural ones do not have adhering properties on the synthetics. The best synthetic size available for blends is PVA (Polyvinyl Alcohol) with degree of polymerization around 1700 and partially saponified (degree of saponification around 85-88%.)

PVA alone cannot meet the perfect size condition. The size mixture should contain Acrylic sizes to give adhesive properties, starch to reduce the cost of size and various other auxiliary agents like antistatic oil, dispersing agents and penetrants.

Table 1.10
Size Formulation

Ingredients	Quantity (parts)
Starch	3.5
PVA	17.8
Acrylic	2.5
Wax	0.8
Antistatic penetrants	0.26

When PVA and starch are used, they are used in the following proportions.

1) P.V.A. – 85-70% Starch – 15-30%
2) P.V.A. – 20-35% Starch – 80-65%

Acrylic sizes are usually added at 0.4-0.5% of size concentration. In case if strong adhesion is required. Increased proportion upto 0.8-1.0% can be used.

With PVA as the basic size, the auxiliary agents will be (0.08-0.01%) x concentration PVA size.

When starch is used as basic size, then the proportion of the auxiliary agents will be 0.08-0.9%.

Table 1.11
Size Formula

P.V.A.	0.9%
Starch	2.5%
Acrylic ester	1.05
Oil	0.8%
Size solution	13.3%

Acrylic Size

For polyester and Nylon filament yarn, the use of PVA alone is not sufficient to add to necessary strength and only with acrylic the size will be too hard. To tackle this problem, the addition of Acrylic size is necessary. Acrylic size gives the best adhesive strength to the hygroscopic fibres.

The film has softness and elasticity with good resistance to electrostatic charge. These size can easily be desized and their handling is easy. Acrylic sizes are (1) Polyacrylic ester (2) Polyacrylic acid (3) Polyacrylic sodium and (4) Polyacrylamide. Out of the above Polyacrylic ester is used most commonly.

Polyacrylic ester is not dissolved by water. It is saponified partly and made dissolvable in water. the higher the degree of saponification, the more will be its hygroscopic activity and the same way it is easy in desizing.

After waxing of sized yarns is also followed in some textile mills. Polyethylene glycol-4000 and tallow cakes are used as after waxing agents for polyester cotton blend and cellulosic yarns, respectively. The quantity of after waxing agent required is about 0.5% on the weight of yarn. To apply this much quantity the ratio, of the speed of the yarn to surface speed of the waxing roller should be about 80.1 for tallow cakes (viscosity equal to that of water) and about 200.1 for polyethylene glycol-4000 (viscosity equal to three times that of water). The temperature of waxing trough is around 85%C.

DESIZING

The size which is applied on the warp yarns must be removed prior to scouring and bleaching of the fabrics. These chemicals otherwise hampers the subsequent operations on textile fabrics.

The process of removing size from the cloth is termed desizing.

There are three methods desizing, namely the rot steep, an acid steep, and the enzyme steep. All of them depend on breaking down, by chemical means, the sizing preparation until it is soluble in water, but the cellulose must not be attacked during this process.

Rot steeping is the oldest method of desizing and depends on the presence in the air and in the fabric of starch-liquefying organisms with multiply in warm water. The cotton may be soaked in warm water for 24 hours at 35 to 40ºC, or overnight at 60ºC. Some of the natural impurities in cotton are also removed where these are water soluble.

The acid steep is favoured by many bleaches; about 0.5 to 1 per cent sulphuric acid solution is allowed to act on the size for 4 to 12 hours at 40°C, but great care is necessary in order to avoid any attack on the cellulose itself. A thorough rinsing afterwards is essential, for otherwise the cotton would be degraded if the acid is allowed to concentrate on drying.

Desizing can be done by using acids, alkalis, enzymes, hypochlorites and sodium bromite. Enzymes are most commonly used for desizing. The enzymes convert starch into soluble products which are then removed by washing with water. To accelerate wetting penetration, wetting agents are incorporated in the desizing bath. The selection of appropriate wetting agents incorporated in the desizing is important.

Table 1.12
Effect of Surfactants of Activity of Enzymes

Surfactant	% Losses in desizing activity	
	0.05%	0.1%
Octylphenoxy ethylene oxide	5	10
Sulphated fatty acid ester	15	40
Alkyl aryl sulphonate	-	80

Nonionic ethylene oxide condensates are better suited as wetting agents in desizing.

Sodium bromite oxidises starch very rapidly into alkali products which are removed by the subsequent scouring operation. The rate of desizing with sodium bromite is very rapid.

The nature of the desizing process depends upon the nature of the sizing materials to be removed. Most of the size mixing are combinations of starch, modified starches carboxymethyl cellulose (CMC) and natural gum, acrylic polymers and polyvinyl alcohol, wax or selfemulsifying wax, tallow or water dispersible oil.

Starch sizes can be removed by enzymes.

As a general rule, nonionics do not harm enzymes whereas anionics have a widely variable effect.

Hydrocarbon solvents such as xylene are used to facilitate removal of waxy components of the size. Common solvents do not have an adverse effect on enzymes but the emulsifier used should be properly selected. Fabrics should be desized at pH 7.

Acrylic copolymers are commonly added to starch sizes. Fabric may be preacidified or acetic acid may be added to be desizing bath. Acrylic copolymers giving a lower pH (about 8) are preferred. Polyvinyl alcohol has not tendency to inactive enzymes.

High temperature detergent scour followed by hot water rinsing and the usual alkali scouring and bleaching treatments remove polyvinyl alcohol. Scouring and rinsing are carried out at 70-80ºC. Nonionic surfactants are used.

Enzymes are organic substances produced by living cells, that posses the ability to catalyze specific chemical reactions. Enzymes synthesize or break down chemical compounds, or transform them from one type to another type, according to the ability built in them individually. Most enzymes are highly specific; they catalyze only one specific reaction or act upon only one isomer of a particular compound. Some enzymes are less specific and are able to catalyze several, usually related, reactions. Also, the same reaction may be catalyzed by a large number of enzymes, different in their specific characteristics, the produced by different types of cells.

Pure enzymes form the following four major groups with regard to the degree of specificity:

1. Absolute enzymes, catalyze the reaction of only one substrate,
2. Stereospecific enzymes, catalyse reactions with one type of optical isomer but may react on a series of related compounds of the same configuration.
3. General hydrolyzing enzymes, will react on a specific type of chemical linkage mostly respective of the associated groups.
4. Enzymes that attack certain specific points of a molecule.

Amylases: The most important carbohydrases, produced in far larger quantities than any other enzymes, belong to the group of amylase or diastase enzymes, which hydrolyze starch and its hydrolytic degradation products. Although all amylases hydrolyze the D-glycosidic linkage, they are different in many respects. Most of them hydrolyze only linkages between the carbons 1 and 4; others, in addition to the (1-4) linkage hydrolyze also bonds between the carbons 1 and 6. The enzymes which are used in desizing are alpha and beta amylases, bacterial and fungal protease and lysozyme.

For the production of industrial enzymes, cells (cultures) are selected from the groups of moulds, bacteria, or yeasts. Among moulds, strains of Aspergillus niger are selected for the production of amylases and amyloglucosidase. Strains of A. oryzae (A. flavus) are selected for the production of proteases. From bacteria, strains of Bacillus subtilis are selected for the production of proteases and heat stable alpha amylase.

Microorganisms used in the production of industrial enzymes must have good biological stability. Most organisms used for this purpose are obligate aerobes. Some organisms, under different conditions, will produce enzymes in different proportions. B. subtilis is used under different conditions to produce primarily either amylolytic or proteolytic enzymes.

The following organisms are known to be used in making industrial enzymes:

Amylases: Aspergillus oryzae, A. glavus oryzae, A. niger, Bacillus subtilis.

BLEACHING AND SCOURING OPERATION

Scouring of Cotton: After desizing, cotton materials are subjected to a process known as scouring. Natural cotton contains 80-85% cellulose and small amounts of nitrogenous matter, mineral matter, pectates waxes and colouring matter as impurities. Removal of these are important for further processing of textile fabric. The fabric material is treated with alkali. Kiers, continuous scouring plants like J-Box or other systems such as padroll are used for this purpose. in scouring sodium hydroxide is the main active ingredient and its function is to saponify some of the impurities present in cotton. The efficiency of caustic scour is improved by the addition of a surfactant.

The textile auxiliaries used in scouring must be stable to hard water, stable under alkaline conditions, have good wetting power and capable of emulsifying the impurities and maintaining them in the dispersed state over a wide range of temperatures during scouring and washing. Alkyl derivatives of naphthalene sulphonic acids, fatty alcohol sulphates, fatty acid amides, phosphate esters and nonionic ethylene oxide condensates are scouring auxiliaries.

The absorbency of caustic boiled cotton is much better when nonionic octylphenol ethylene oxide condensate is used as surfactant as compared to fatty alcohol sulphate or soap. A nonionic product with 12 units of ethylene oxide was found to give the best result. Phosphate ester surfactants are good scouring auxiliaries because of their excellent compatibility with alkali.

Bleeding of colour due to formation of the leu covat dye can be prevented by a mild oxidant such as m nitrobenzene sulphonic acid.

Scouring of Wool

Raw wool, contains grease, perspiration salts, dirt and vegetable matter as impurities. The scouring of wool to remove impurities can be done by suint scouring, solvent extraction, or emulsion scouring. Emulsion scouring is the most widely used method. A detergent used for wool scouring possess the properties of degreasing wool at low temperature, stabilise the emulsion of wool wax with water, remove soil efficiently, hold the fine dust in suspension and not have any detrimental action on wool.

Alkyl aryl sulphonates, alkyl sulphates, alkyl sulphonates and nonionic detergents are used in wool scouring. Nonionic also give a soft handle to scoured wool.

Carbonising

Raw wool contains a considerable quantity of foreign vegetable matter in the form of straws and burrs which are not removed by scouring. Wool is subjected to carbonising after scouring, to remove them.

Wool is treated with dilute solution of sulphuric acid and/or aluminium chloride, dried, baked and washed. Alkyl naphthalene sulphonate, cationic and nonionic wetting agents are used as wetting agents in carbonising. The addition of a surfactant also reduces significantly the loss of tensile strength of the treated wool.

Scouring of Silk

The scouring of natural silk of “degumming” to remove sericin, is carried out by repeated treatments with soap solution. A certain degree of alkalinity is necessary to dissolve sericin. This alkalinity is provided by the hydrolysis of soap and also alkali addition. Surfactants as wetting agents are used.

Scouring of Rayon

Scouring rayon to remove mill dirt and sizing agents are done by detergents. Nonionic detergents are efficient in continuous scouring of rayons. Mixture of nonionic and anionic detergent is also used.

Scouring of Synthetic Fibres

Scouring of synthetic fibres uses mild detergents. Synthetic surface active agents are used extensively. Nonionic and anionic detergents are suitable for scouring synthetic fibres.

The cleaning of cotton cloth form the coloured impurities is known as bleaching. The purpose of bleaching is to make the fabric amendable for subsequent processes of coloration and finishing. Bleaching is carried out after a gamut of operations which are performed in one or the other sequence depending upon the situation. Each operation is important and are carefully carried out so as to obtain satisfactory and consistent results.

Bleaching is usually carried out with oxidizing agents to oxidize the coloured impurities. The usual bleaching agents are sodium hypochloride, hydrogen peroxide, sodium peroxide, salts of per acids like sodium perborate etc. Wetting agents like non ionic or cationic or anionic surfactants are used during peroxide bleach. Stain removers like surfactants, trichloroethylene, perchloroethylenes are also used.

MERCERISING

Mercerisation of cotton material is carried out to improve its strength, lustre and dye adsorption. In this process, the goods are treated with 52-54º Tw sodium hydroxide, stretched and washed. A necessary condition for successful mercerisation is the rapid and uniform wetting of cotton by sodium hydroxide. A mercerising auxiliary has high stability in concentrated alkali and good wetting power and are readily removable from the fabric by a simple washing treatment. Phenolic compounds such as cresylic acid form the basis of most of the commercial preparations.

Ordinary wetting agents used in scouring are unsuitable as wetting agents in mercerising liquors and special wetting agents effective under these conditions have been developed. generally, there are two types-cresylic and non cresylic types of mercerising wetting agents to be used in mercerising liquors.

Mixture of ortho-, meta-, and para–cresols (cresylic acids), are not soluble in water but dissolve in strong caustic soda solution. These are found to be stable wetting agents in this solution. Their wetting power is found to be considerably improved by incorporating certain other additives like ethyl alcohol, polyhydric alcohols having C_{18} chain, butanol, 2-ethyl hexanol, polyethylene glycol etc. Some of these are not miscible with water, but dissolve in caustic soda solution.

A product, obtained by the distillation of pine oil as a fraction between turpentine and rosin, has excellent wetting, penetrating and emulsifying properties. It is dispersible in mercerising liquors and improves their penetration power so as to give mercerised cotton having more even dyeing properties. This fraction may be used together with cresols, which assist the dispersion of the pine oil distillate.

Cresylic wetting agents have strong phenolic odour and are known coloured liquids. Noncresylic wetting agents include sulphated lower aliphatic alcohols such as hexyl or alcohols. These mercerising wetting agents are free from phenolic odour and foam less. Piononic acid as mercerising auxiliary is as effective a wetting agent is cresylic acid. Mercerising auxiliaries based on a substituted diethylene glycol sodium sulphates in conjunction with a sparingly soluble alcohol and solution promoter of cellosolve type is a good mercerising wetting agent.

Special wetting agents suitable for adding to mercerising liquors which are sulphoxide compounds conform to the general formulae given below

Typical compounds are n-octyl-bid-(beta-hydroxyethyl)-sulphonium sulphate, n-octyl-(beta-hydroxyethyl)-sulphoxides, n-nonyl-(beta-hydroxyethyl)-sulphoxides and n-hexyldiethyl-sulphoxonium chloride.

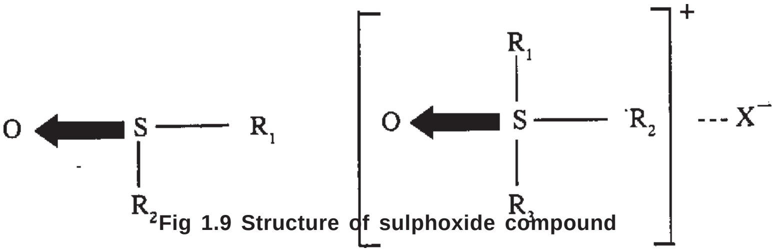


Fig 1.9 Structure of sulphoxide compound

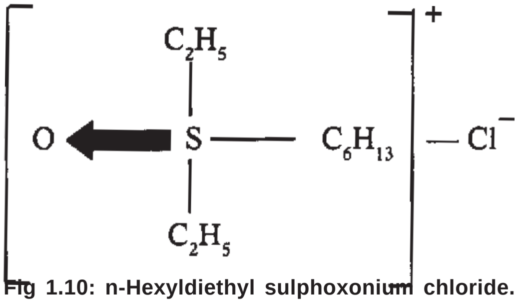


Fig 1.10: n-Hexyldiethyl sulphoxonium chloride.

These chemicals are more efficient than the cresylic type of wetting agents. Because of their good solubility in caustic liquor, there is no clouding of the mercerising liquor.

Mixtures of alkyl sulphonic acid having on an average one sulphonic acid group for 7 carbon atoms, alkyl dialkanolamine of general formula R-N $[(C_nH_{2n}O)_mH]_2$ in which R represents an alkyl radical of C_2 to C_5 n is either 2 or 3 and m is 1 or 2 and an ester of phosphoric acid with an alcohol having 4-8 carbon atoms are nonfoaming type and dissolve easily in mercerising liquor, giving clear solution. They are more efficient than the conventional wetting agents.

DYEING

Dyeing is production of coloured fabrics. A wide variety of dyestuffs are available and each class of dyes have different method of application. Chemicals (auxiliaries) are used in dying process to obtain satisfactory dyeing process. The auxiliaries used in dyeing are:

1. Wetting and penetrating agents
2. Dispersing agents

3. Levelling agents
4. Sequestering agents
5. Antifoaming agents
6. Accelerators
7. Migration inhibitor
8. Dye fixing agents
9. After washing agents
10. Stripping agents

Wetting agents

There are surfactants added to the dye bath to ensure penetration of dye liquor into the yarns and fabrics. Sulphated fatty alcohol, sulphated oil and anionic surfactants like sulphonic acids are used.

Dispersing agents

Dispersing agents are also surfactants used for uniform dye dispersion. These are particularly used in disperse and vat dyes. Sulphated fatty alcohol, alkyl aryl sulphonates, sulphated fatty acid amides are used.

Levelling agents

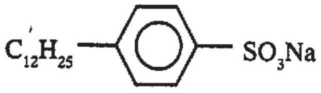
Levelling agents are added in dye bath to uniformly due the yarns or fabrics. An ionic surfactants like alkyl aryl sulphonates, fatty alcohol sulphates, fatty amide sulphonates are used. Non ionic surfactants are used for direct dyes, cationic surfactants and non ionic surfactants are used in vat dyeing.

In case of dyeing of acrylics, retarding agents like cationic and anionic surfactants are used as retarders. No ionic surfactants are used in polyester/blends dyeing as levelling agent.

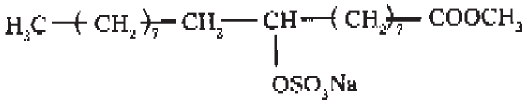
A. $H_3C-(CH_2)_{11}-OSO_3Na$

B. $H_3C-(CH_2)_{15\text{-}17}-OSO_3Na$

C.

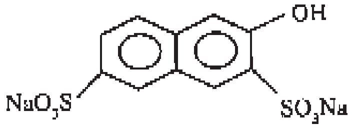


D.



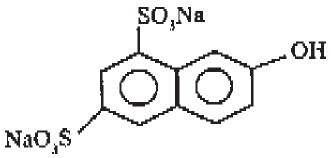
$H_3C-(CH_2)_7-CH_2-\underset{OSO_3Na}{CH}-(CH_2)_7-COOCH_3$

E.



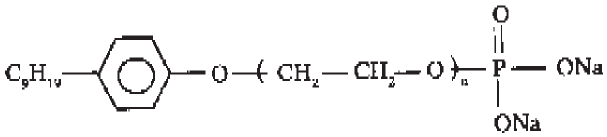
R - ACID

F.

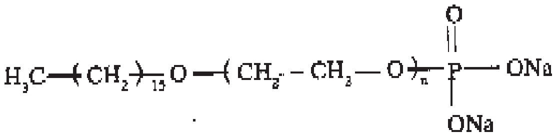


G - ACID

G.

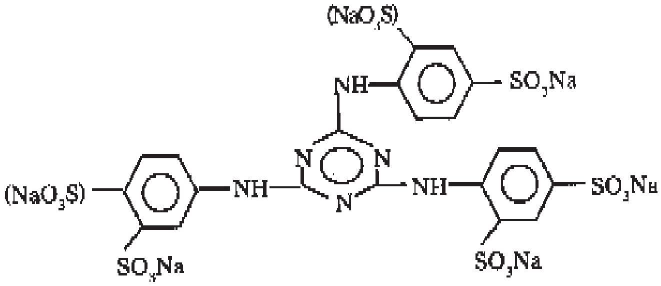


H.



$H_3C-(CH_2)_{15}-O-(CH_2-CH_2-O)_n-\underset{ONa}{\overset{O}{\overset{\|}{P}}}-ONa$

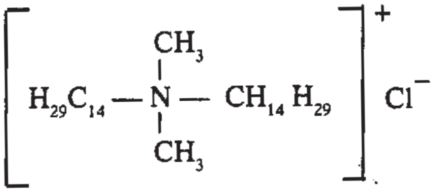
I.



J. Sulphated Castor Oil

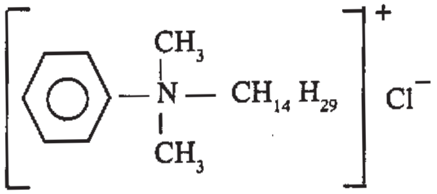
Fig. 1.11: Levelling agents for acid dyes on nylon

1.

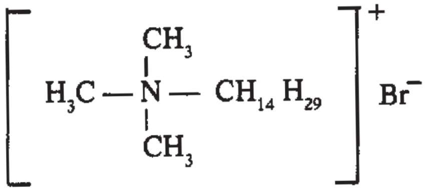


$$\left[H_{29}C_{14}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}-CH_{14}H_{29}\right]^{+}Cl^{-}$$

2.

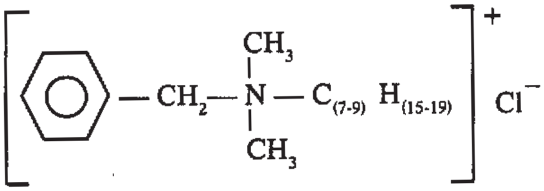


3.



$$\left[H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}-CH_{14}H_{29}\right]^{+}Br^{-}$$

4.



5.

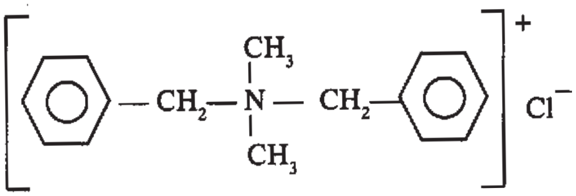


Fig. 1.12: Cationic retarders for level dyeing

Sequestering agents

Sequestering agents are chemicals which complexes heavy metal and do not allow these heavy metal to react with fibre or dyes. EDTA, NTA are common sequestering agents.

Antifoaming agents

Antifoaming agents are used in dye bath to prevent foaming of the bath which affects dyeing adversely. The best antifoaming agents are silicone polymers such as dimethyl polysiloxane with a viscosity of 100-500 centiposie at 25ºC. Polyamino alkyl substituted hydrocarbons are based organo poly siloxanes are also used as effective agents.

Carriers

Carriers are used in dyeing of synthetics particularly polyesters with disperse dyes. It imbibes deep shades on the polyester and blended fabrics. O phenyl phenol, monochloro o phenyl phenol, p phenyl phenol, diphenyl, mono methyl naphthalene, trichloro benzene, dimethyl pterephthalate, methyl salicylate etc. are good carriers.

Migration inhibitor

Migration inhibitor effects uniform dyeing of fabrics by preventing migration of dye molecules along with liquor during drying operation. Sodium alginate non ionic polyelectrolyests, carboxymethyl cellulose, ethoxylated and propoxylated guar gums are good migration inhibitors.

Dye fixing agents

Dye fixing agents fixes the dye on the yarns and fabric in a permanent fashion, so that their fastness properties are manifested properly. Usually cationic surfactants are used as dye fixing agents.

Stripping agents

Stripping agents are used for dye removal form bad dyed cloth produced by faulty dyeing. Quartery ammonium compound with long chain alkyl are effective. Poly vinyl pyrrolidone based agents are used for stripping vat sulphur and direct dyes.

Cetyl trimethyl ammonium bromide are efficient in stripping azoic dyes. These are usually effective in presence of oxidizing or reducing agents. Nonionic surfactants with caustic soda and hydrosulphite are formed useful.

Sulphoxylate of formaldehyde, polyvinyl pyrrolidone in presence of acetic strips disperse dyses from nylon. 1-20% diphenyl with 3-5% zinc sulphoxylate and 5% acetic acid at boiling temperature strips colour from polyester.

Printing is a process to decorate textile fabrics with colours and colour motif. Textile printing may be considered as a specialized dyeing process. It is a controlled application of dyes and pigments to exactly defined locations on the fabric leaving rest of the fabric essentially unaffected. There are three major methods of printing viz. direct printing, resist printing and discharge printing. In the direct printing method a paste of dyes and auxiliary chemicals are directly fixed on the fabric by a pattern block or silk screen. In discharge printing a reducing agent is used to destroy the oxidizing agent at the printed area needed to develop a particular dye (vat dye) or an acid is used to destroy the alkali needed for development and fixing of a dye. In discharge printing stable reducing agents are used to discharge the dye on the fabric. Vat dyes, pigments, basic dyes, are used for discharge printing.

The auxiliaries used for printing of textiles are thickeners, wetting agents, dispersing agents, antifoaming agents, hygroscopic agents, reducing and oxidizing agents, binders, after washing agents and miscellaneous auxiliaries.

Thickeners

These chemicals act as vehicles for carrying the dyes onto the cloth. The prevent the colour spread on the fabric beyond desired limit, starch, natural gums like locust bean, senegal, arabic, karaya, guar bean are used commonly. Modified starches like British gums dextrin, sodium alginate, sodium carboxy methyl cellulose are also used with satisfactory results. Kerosene, water emulsions with non ionic surfactants are also used.

Wetting agents

These are usually various surfactants compatible with other auxiliaries used for a specific printing formulation. These have already been discussed earlier.

Dispersing agents

Dispersing agents used are diethylene glycol, thio diglycol, sodium benzyl sulphanilate, nonionic surfactants are use for prevention of agglomeration of dye particles.

Antifoaming agents

Antifoaming agents are the same used for dye bath. They are usually siloxanes. Hygroscopic agents used are glycerine, diethylene glycol etc.

Oxidising and reducing agents

Oxidising and reducing agents are sodium chlorate, chromate, dichromate, nitrate, ferrocyanide hydrosulphite, bisulphite, glucose and stannous and ferrous salts.

Carriers

Carriers are the same chemicals used for dyeing with disperse dyes and already been discussed earlier.

Binders

Binders are used in pigment printing. It forms a film at the printed portion. The film should be colourless, clear have high resistance to washing liquids and chemicals, should have good adhesion with the fabric and should have good abrasion resistance.

Large number of synthetic resin based binders are used. They are vinyls, acrylics, melamine formaldehyde, UF precondensates, chlorinated rubbers etc. SBR, acrylonitrile, butadiene based binders are also used.

After washing

After washing removes thickeners and to bring out the true shades, usually mild detergents are used for after washing.

Finishing of textiles

This aspect has been discussed in earlier chapter. The auxiliaries used in finishing can broadly be divided as below:

1. Stiffening agents
2. Durable press/crease resistance agents
3. Optical brighteners
4. Softeners
5. Water repellents
6. Flame retardants
7. Antistatic agents
8. Soil release agents
9. Antipilling agents

10. Moth, mildew etc. proofing agents

Stiffening agents are applied on cloth in order to build up the apparent weight, impart thickness and to improve lustre. Their effect is temporary and once the fabric is washed most of the stiffeners are removed. The use of these temporary finishing agents is declining in recent years because of the growth of durable resins finishes.

A large number of substances are used as stiffeners. The important products are starch, modifies starches, natural gums, carboxymethyl cellulose etc.

Durable press or crease resistant finishing agents are usually polymer precondensate which are later allowed to set partially to provide wrinkle face characteristics to the cotton fabrics.

The majority of durable press agents used for imparting wash-and-wear finishes are:

(i) Urea formaldehyde derivatives.
(ii) Melamine formaldehyde derivatives,
(iii) Methylol derivatives of cyclic ureas,
(iv) Triazones, and
(v) Carbamates.

Urea and formaldehyde react under slightly alkaline conditions to give a mixture of monomethylol urea (MMU) and dimethylol urea (DMU).

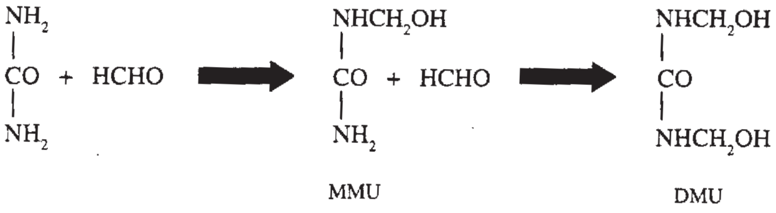


Fig 1.13: Synthesis of DMU

The precondensate contains mainly dimethylol urea and also small amounts of monomethylol urea. The precondensate is diluted to required solid contents. The treatment of fabrics with urea formaldehyde resin involves padding with a solution of precondensate and an acid liberating catalyst, drying, curing and washing. During curing the precondensate polymerises to impart wash and wear properties to the cloth.

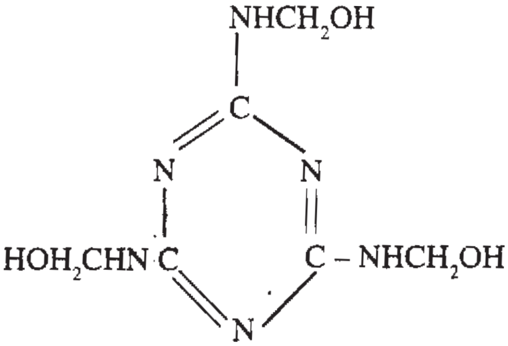


Fig. 1.14: Trimethylol melamine

Melamine reacts with formaldehyde to give methylol derivatives. It is possible to prepare hexamethylol melamine. The most commonly marketed product for wash-and-wear finishing is trimethylol melamine. The methylol melamines have good storage stability and when etherified with lower alcohols give finishes with good durability.

Methylol derivatives of cyclic ureas react with cellulose to give insoluble resin. The finished fabrics have a softer hand. The important members of this group are:

(a) Dimethylol ethylene urea,

(b) Dimethylol propylene urea,

(c) Tetramethylol acetylene diurea, and

(d) Dimethylol dihydroxy ethylene urea

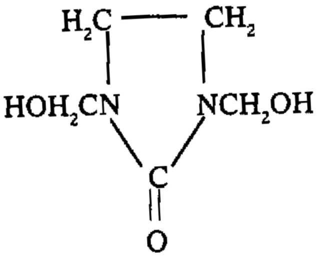


Fig. 1.15 Dimethylol ethylene urea (DMEU)

DMEU is prepared from formaldehyde and 2-imidazolidone commonly known as cyclic ethylene urea, which in turn is prepared from carbon dioxide and ethylene diamine. It can also be prepared by heating urea with ethylene diamine.

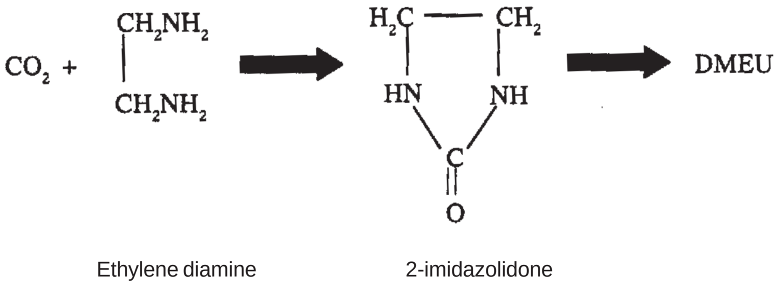


Fig. 1.16: Synthesis of DMEU

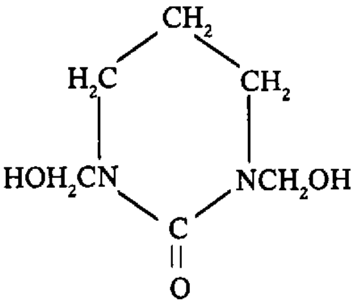


Fig. 1.17: Dimethylol propylene urea (DMPU)

DMPU prepared by reacting two moles of formaldehyde with one mole of propylene urea under alkaline conditions. Propylene urea is prepared by the reaction of urea with 1,3 diamino propane.

Dimethylol propylene urea gives good wrinkle recovery. The finish obtained is not susceptible to chlorine retention damage even after repeated hot alkaline launderings.

TMAD is prepared from acetylene diurea and formaldehyde. Acetylene diurea is obtained by the combination of urea and glyoxal. Tetramethylol acetylene diurea when applied to cellulose it has a strong tendency to combine with the fibre.

DMDEU is prepared by condensation of didhydroxy ethylene urea with formaldehyde. Dihydroxy ethylene urea is prepared by the reaction of glycol with urea.

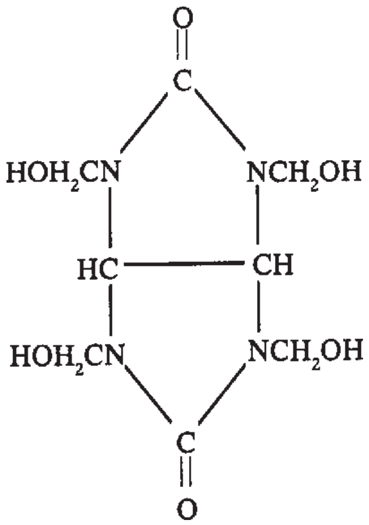


Fig. 1.18 Tetramethylol acetylene diurea (TMAD)

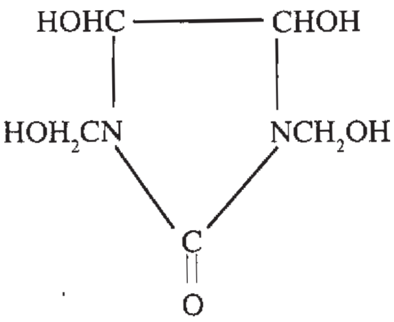


Fig. 1.19: Dimethylol didhydroxy ethylene urea (DMDEU)

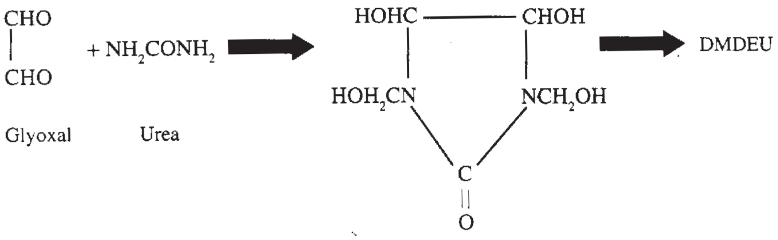


Fig. 1.20: Synthesis of DMDEU

The finish obtained with DMDEU urea exhibits excellent crease recovery and wash-and-wear properties. The finish is fast to repeated home launderings. Dimethylol dihydroxy ethylene urea dominate the field of colour durable press garments. It is an excellent reactant for the preferred cure process. Fabrics treated with this reactant will remain in the uncured state for a few months.

DET is readily prepared by treating dimethylol urea with ethylamine. The triazones are inexpensive agents. Their main advantage is resistant to chlorine damage.

Triazones dot not produce yellowing of cloth and hence are particularly suitable for finishing white goods.

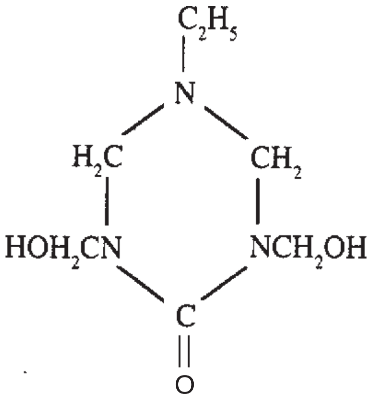


Fig. 1.21: Dimethylol ethyl triazone (DET)

The triazones give poor crease recovery compared to other resins. The finish is susceptible to acid hydrolysis below pH 5. Generally, triazoens require a hard cure, which may sometimes cause discolouration of the fabric.

In the crease resistance process, dimethylol methyl, dimethylol ethyl dimethylol hydroxyethyl, dimethylol isopropyl and dimethylol methoxyethyl carbamates are useful. Among these dimethylol ethyl carbamate is popular. In general, carbamates give good wash-and-wear properties when properly cured. The finish has a high stability towards hydrolysis during commercial and home launderings. Carbamates give a finish which is free from chlorine retention damage and has a reduced tendency to yellowing.

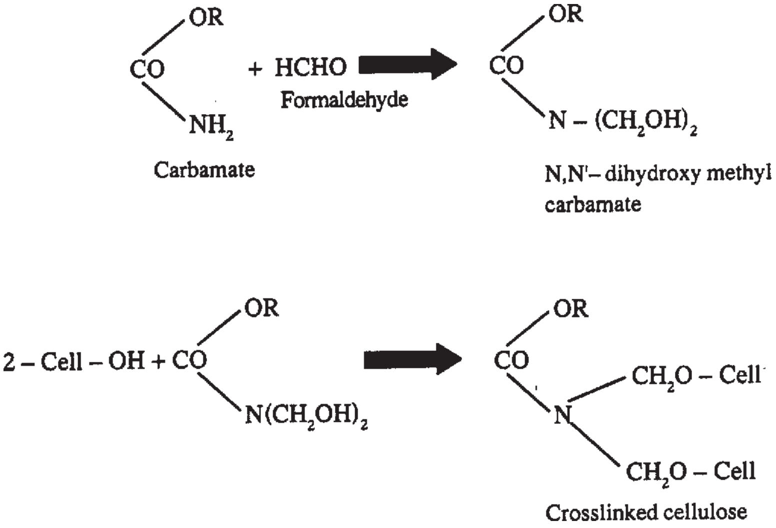


Fig. 1.22: Carbamate durable press compound

Acetals

Acetals are the reaction products of aldehydes with alcohols under acidic conditions. As in majority of cases the aldehyde used is formaldehyde, the acetals are also known as formulas. The most noted durable press agent to acetal class is glycol acetal which is prepared by the condensation of formaldehyde with diethylene glycol. This product is intended primarily for stabilisation of fabrics and gives only a slight improvement in crease recovery. It is generally applied in presence of magnesium chloride as catalyst. Because of the absence of nitrogen in glycol acetal there is no chlorine retention damage on hypochlorite bleaching.

Epoxides and epichlorohydrin

The advantages of epoxy resins are the complete freedom, from chlorine retention and stability to hydrolysis under both alkaline and acidic conditions.

The epoxy resins are capable of polymerisation as well as cellulose cross linking. However, the cross linking reaction predominates in the presence of cellulose.

Butadiene diepoxide is an important crosslinking agent of epoxy series.

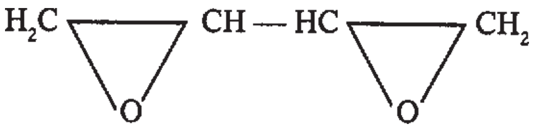


Fig. 1.23 : Butadiene diepoxide

When applied to cotton it gives a wash and wear product with a high moisture regain.

$$CH_2 = CH – SO_2 – CH = CH_2$$

Fig. 1.24: Divinyl sulphone

Divinyl sulphone was the first sulphone recommended for imparting wash and wear properties to cotton. It cross links two moles to cellulose in the presence of alkali, forming a cellulose ether. However, divinyl sulphone, is volatile, toxic and a very active skin dessicant. Harmless adducts of extremely low toxicity

$$Cell – O – CH_2 – CH – SO_2 – CH – CH_2 – O – Cellulose$$

Fig. 1.25: Cellulose adduct with divinyl sulphone

from sulphones are available Bis (hydroxyethyl) sulphone ($HOCH_2$ – CH_2 – SO_2 – CH_2 – CH_2 - OH) is prepared by the oxidation of thiodigylcol. The product has great commercial importance for imparting wash-and-wear properties to cotton.

OPTICAL BRIGHTENING AGENTS

All types of textile fibres, natural or synthetic, do not appear perfectly white but exhibit a yellow tinge because of the presence of certain coloured impurities which absorb some of the incident light in the blue end of the spectrum. Three methods are available to remove the yellow tinge. The first one is the destruction of the colouring matter by bleaching agents. This method is invariably used to remove most of the colouring impurities from the fibre but it is not possible to eliminate totally the slight yellowish tinge without degradation of the fibre itself. The second method employs the use of blueing agents on the bleached fabric. These agents correct the yellowness of the fabric by absorption of yellowness of the fabric by absorption of yellow light by the applied blue pigment. In this case the yellowish white fabric acquires a greyish white appearance.

The third method which is the most popular today involves the use of optical brighteners or fluorescent brighteners. The optical brightening agents are for the most part similar to dyes, and posses affinity for the fibre. They contain fluorescent chromophores instead of colour chromophores, and make the white fabric whiter without adversely affecting the strength and other useful properties.

Fluorescent brighteners, also known as fluorescent whitening agents, fluorescent dyes and optical brighteners, are special types of fluorescent organic compounds which are used to enhance the coloristic performance or brightness of the various materials such as natural fibres, synthetic fibres, textiles, polymers, papers and paints. In general, these molecules are capable of absorbing radiation of short wave length and high energy, normally invisible to the human eye and emitting the radiation of longer wavelength, i.e., in the visible light.

The textile industry being predominantly cotton oriented, the consumption of optical whiteners is preferentially for cellulosics. However, there is an increase in the trend for the production of polyester and polyester blended fabrics and, therefore, the demand for a whitener for synthetics is also increasing.

Optical whiteners are classified primarily into two large groups, direct whiteners and disperse whiteners.

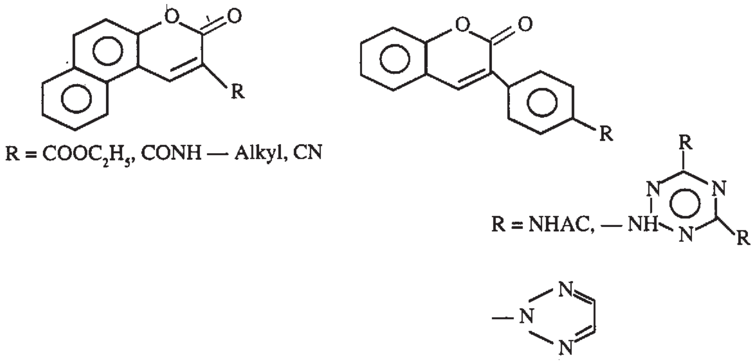
Direct optical whiteners are water soluble substances used mainly for the whitening of natural fibres, whereas disperse optial whiteners are water insolubles. As with disperse dyes, they are applied either to the coloured material from an aqueous dispersion or they can be used for mass colouration. They are mainly used for synthetic materials such as polyamide, polyester, poly-acrylonitrile, acetate silk and polyvinyl chloride.

In addition to this classification fluorescent pigments may either be organic or inorganic and claim more attention because of their wide applicability. From the chemical point of view optical whiteners are classified into derivatives of stilbene, coumarin, 1 diphenyl pyrazoline, naphthalane dicarbokylic acids, cinnamic acid and substances belonging to other chemical systems. Organic fluorescent pigments are basic dyes embedded in protective rasinous compositions. Today, most of the fluorescent pigments are prepared from commercial fluorescent dyes.

Coumarin derivatives: Efficient coumarin optical whiteners have their fluorescence maximum at 400 to 500 mm and those industrially most important are based on derivatives of 3 phenyl 7 amino coumarin. Coumarin derivatives are efficiently used today for animal textile materials and for synthetic fibres.

Amongst 3-substituted coumarin derivatives only 5,6 benzocoumarin 3 carboxylic acid and 3 phenyl coumarin derivatives are technically important. The structure are given in figure.

Malonic ester on condensation with 2 hydroxy 1 naphthaldehyde in the presence of piperidine or morpholine gives 5,6 benzocoumarin carboxylic acid, condensation of salicylaldehyde with p nitrobenzyl cyanide (Knoevenagel condensation) and a subsequent reduction of the nitro group gives 3 (p aminophenyl) coumarin, which forms the starting material for the synthesis of fluorescent brightening agents. 3 Aryl substituted coumarins can also be prepared by Perkin reaction, involving condensation of salicylaldehyde derivatives with phenyl acetic acid or its sodium salt in acetic anhydride and sodium acetate. The other method used is Meerwein arylation of coumarin with the aryldiazonium compounds in the presence of cupric slats. Important fluorescent brightening agents are obtained form 3 (p aminophenyl) coumarin by acylation, with methoxy benzoic acid chlorocarbonic esters, carbamic chlorides and chlorotriazyinyl compounds, e.g. 2 diethyl amino 4,6 dichlorotriazine and also by attachment of the amino group to an aryltriazole nucleus in the 2 position. Coumarin substituted in the 7 position by amino or alkylamino group are notable for strong blue fluorescence. The Pechmann coumarin synthesis is generally applied for the preparation of 7 amino coumarin. 7 diethylamino 4 methylcoumarin is industrially important, which is prepared from meta diethylaminophenol and ethyl acetoacetate in the presence of zinc chloride.



5,6 benzocoumarin
3 carboxylic acid derivatives

3 phenyl coumarin
derivates

Fig. 1.26

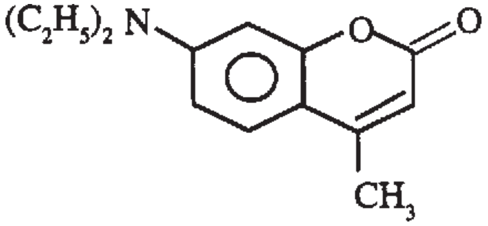


Fig. 1.27: 7 dimethyl amino 4 methyl coumarin

The product obtained is marketed under various names (Blankophor FBO, delft Weiss LS, Leukophor WC, Lencophor DC, Uvitx SWN, Uvitex SWR) and is used for the brightening of paper, cellulose acetate and synthetic fibres. Coumarin derivatives substituted in the 7 and 3 positions are important fluorescent brightening agents. Most of them are derived from 3 phenyl 7 amino coumarin.

In principle, it can be prepared according to Pechmann Synthesis by using b-keto carboxy acid derivatives like ethyl 3 hydroxy 2 phenyl acrylate or 3 hydroxy 2 phenyl acrylonitrile. The reaction proceeds in an inert solvent in the presence of lewis acid catalyst like aluminium chloride, boron trifluride or zinc chloride.

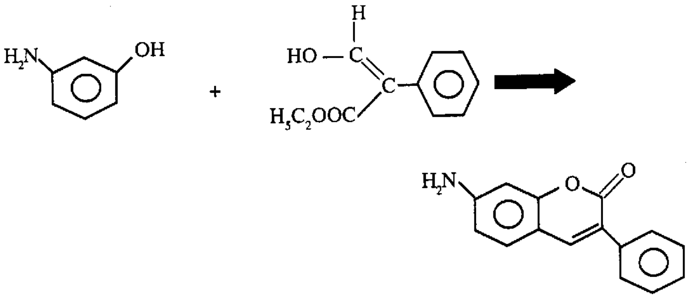


Fig. 1.28: 3 phenyl 7 amino coumarin

The N tetarylacetic acid and their nitriles, particularly those which are derived from nitrogen heterocylces such as 1,2,3 triazolyl 1 acetonitrile and 1,2,4 triazolyl 1 acetic acid can be reacted with 2 hydroxy 4 methoxybenzaldehyde, using the Knoevenagel procedure to form 3 N hetaryl 7 methoxy compounds. These compounds can be converted without any difficulty by alkalating agents such as dimethyl sulphate into cycloammonium salts which are excellent fluorescent brightening agents for polyarcylonitrile fibres.

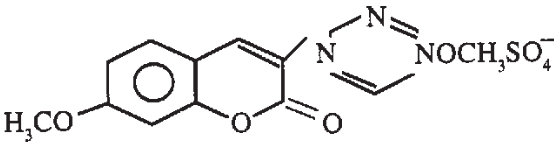
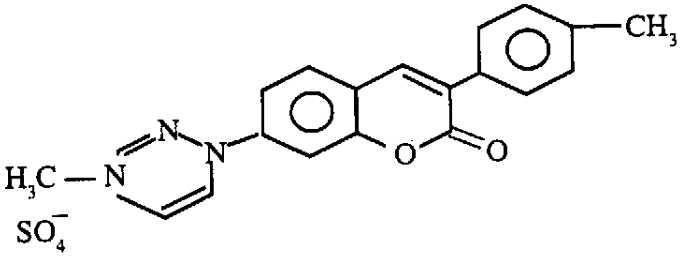


Fig. 1.29: Cycloammonium salt

7Amino 3 N hetaryl coumarins in which the N atom of the amino groups is built into a five membered heterocycle with two or three nitrogen atoms are of particular technical, and coloristic interest. The most important fluorescent brightening agent of this group for poylacrylonitrile is given below:



Red fluorescent dyestuff based on the coumarin system is obtained by condensing imino coumarin with malonoitrile under

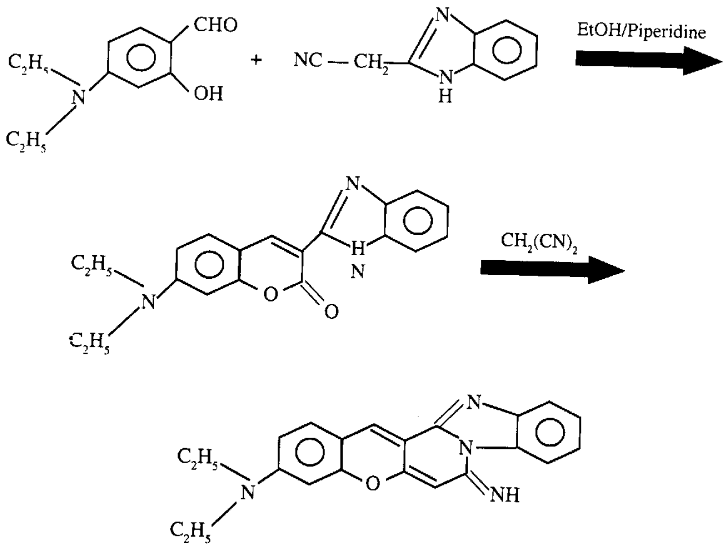


Fig. 1.31 Red fluorescent dyestuff

The same compound undergoes cyanation, leading to the formation of a greenish blue dyestuff exhibiting red fluorescence and the emission maximum being at 668 mm.

Pyrazoline Derivatives

Pyarzoline optical brightening agents display an intensive blue fluorescence. They are used mainly for the surface brightening of polyamide, cellulose acetate and polyacrylonitrile and as an addition into papers. They are unstable against oxidants.

A general method for the preparation of optical brighteners of the pyarzoline type involves the condensation of b-unsaturated carbonyl compounds with phenyl hydrazine as below:

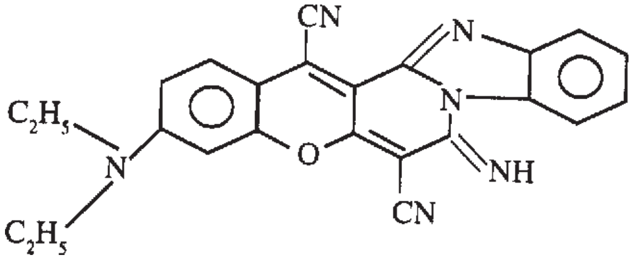


Fig. 1.32 Green blue dyestuff

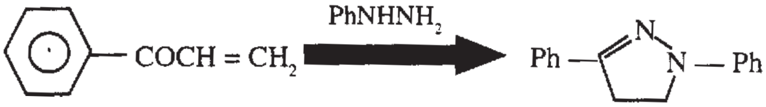


Fig. 1.33

Condensation of phenyl hydrazine with derivatives of phenyl, hydrazine with derivatives of phenyl vinyl ketone does not always take place well, because vinyl compounds are poorly stable and therefore this reaction is best carried out with tri (p benzoylethyl) amine hydrochloride which can be prepared by Tollen's reaction from acetophenone, formaldehyde and ammonium chloride.

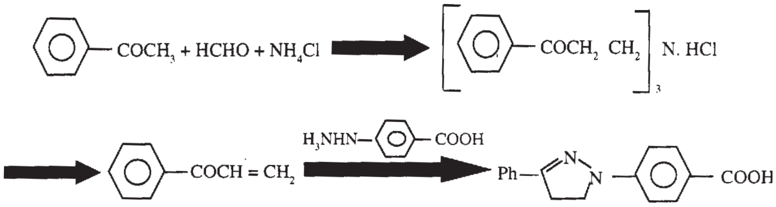
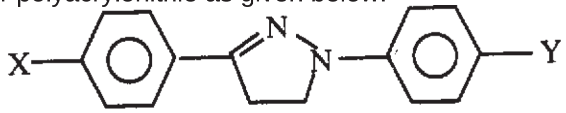


Fig. 1.34

Blankophor DCB or Blankophor FB 766 are prepared by this method. Some important optical whiteners of 1,3 diphenyl pyrazoline class having different substituents on phenyl ring are used for polyacrylonitrile as given below:



X = $NHCOCH_3CL$

Y = $COOH, SO_2NH_2, SO_2NH (CH_2)_3, N (CH_3)_3 SO_4CH_3$
$SO_2CH_3, SO_2CH_2CH_2O CH(CH_3) CH_2N (CH_3)_2$

Fig. 1.35: 1,3 diphenyl pyrazoline deriv.

Derivatives of Naphthalimide

Among the naphthalimides, 4 alkoxy and 4 alylamino substitution products are important from a commercial standpoint as fluorescent brightening agents.

The most interesting fluorescent brightening agent of this group is 4 methoxy N methyl naphthalimide known under the commercial name Mikowhite AT or Mikowhite ATN. This product gives a chlorite resistant fluorescent brightening effect in the thermosol dyeing process on cellulose acetate, polyacrylonitrile, polyolefins, polyoxymethylene and polyester fibres.

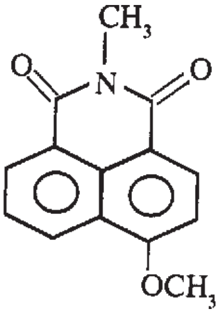


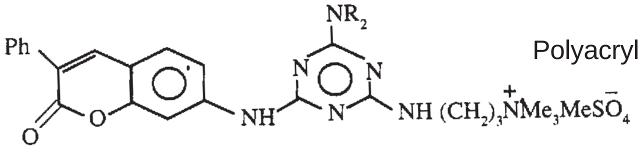
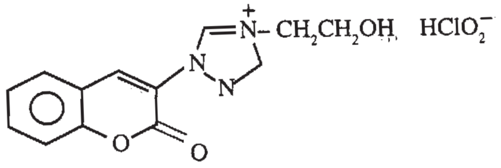
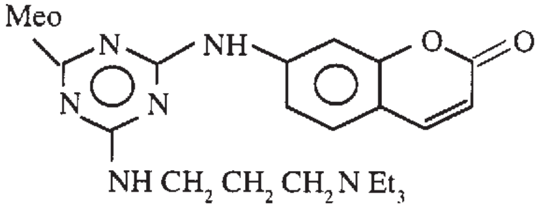
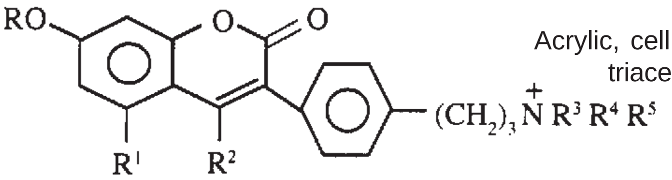
Fig. 1.36 4 methoxy N methyl naphthalimide

A general synthesis of this type of compounds involves replacing a 4 chloro, bromo, sulfo or nitro group of an appropriately substituted M methylimide of 1,8 naphthalene di carboxylic acid with a methoxy group. The most convenient and frequently used procedure involves heating 4 chloro or sulpho N Methylimide with methanol.

Softeners

All natural fibres are associated with some oily, fatty or waxy substances in the raw state. These substances give a soft feel to the fibre. However, on scouring and bleaching the material, these waxy substances are removed and the material becomes harsh. Certain colouring matters at higher concentrations, as well as finishing agents such as starches, china clay, etc., also impart an unpleasant handle to the cloth. It is, therefore, necessary to apply some softening agent to the textile so as to impart softness, smoothness, fullness, suppleness and flexibility. Although, many hundred of preparations are available for softening textile materials, it is noteworthy that most of these substances are based on long chain fatty compounds in one form or another. The softeners are of five types-

1. Anionic softeners
2. Nonionic softeners
3. Cationic softeners
4. Reactive softeners
5. Emulsion softeners

Sl. No.	Structure	Substrate
1.		Polyacrylonitrile
2.		Polyacrylonitrile
3.		Fibres, films moulding
4.		Acrylic, cellulose triacetate

$R = H, R^1 = H, R^2 = H, \overset{+}{N} R^3 R^4 R^5$ = Trialkyl ammonium

Fig. 1.37: Some of the recently developed coumarin based fluorescent compounds *(contd.)*

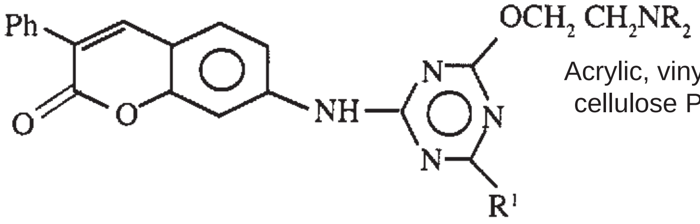
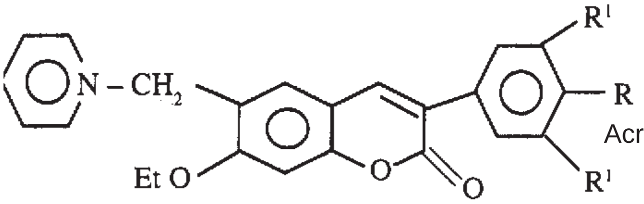
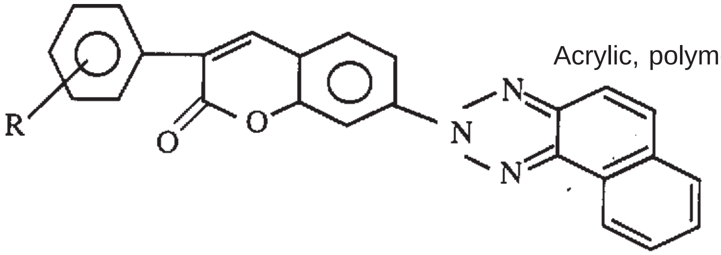
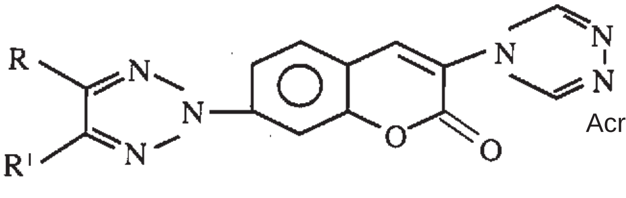
Sl. No.	Structure	Substrate
5.	 R = Me, R^1 = O Me	Acrylic, vinylon cellulose PVC
6.	 R = COOC$_2$H$_5$, R^1 = H	Acrylic fibre
7.		Acrylic, polymer
8.	 R = R^1 = H	Acrylic fibre

Fig. 1.37

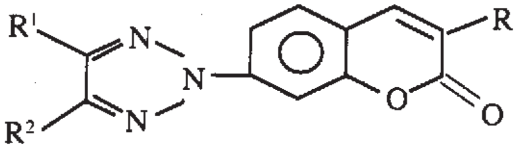
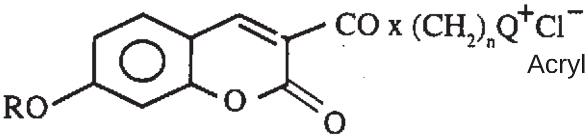
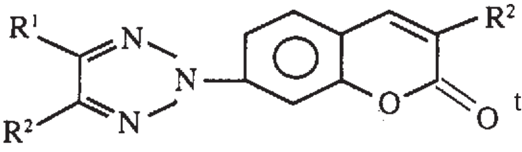
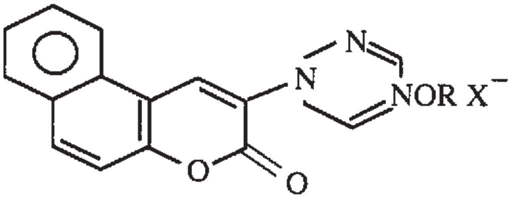
Sl. No.	Structure	Substrate
9.		Polyester
10.		Acrylic, fibre
11.	 R^2 = Carbethoxy	Polyethylare terephthalate
12.	 R^2 = Me, X = $MeSO_4$	Acrylic, fibres

Fig. 1.37: Some of the recently developed coumarin based fluorescent compounds

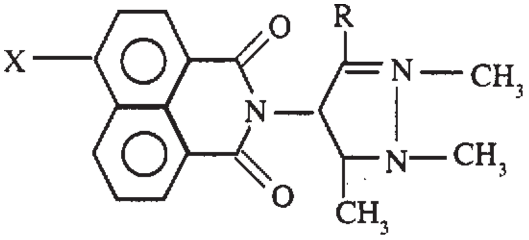
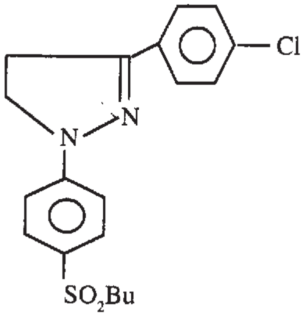
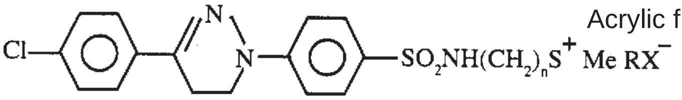
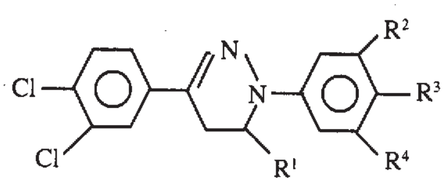
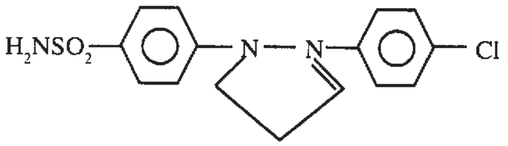
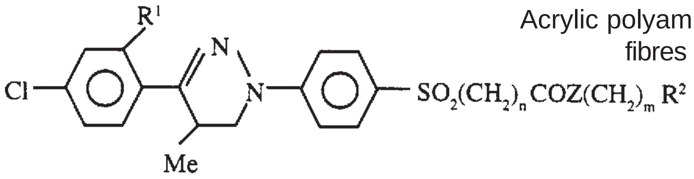
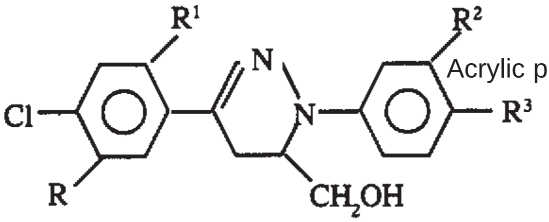
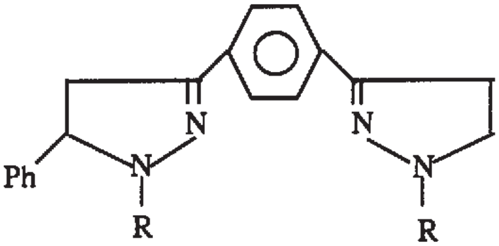
Sl. No.	Structure	Substrate
1.	 Y^- $X = OCH_3$ $R^1 = CH_3$ $Y = ½ ZnCl_4$	Acrylic fibre
2.		Cellulose triacetate Acrulic fibre
3.	 R = Me, n = 2, X = $MeSO_4$	Acrylic fibre
4.		Polyacrylonitrile

Fig. 1.38: Recently developed pyrazoline based fluorescent compounds

Sl. No.	Structure	Substrate
5.		Polyamide acrylic fibres
6.	 R = H, R^1 = H, R^2 = S^+ Z = O, n = 1, m = 2	Acrylic polyamide fibres
7.	 **R = R^1 = R^2 = R^3 = H**	Acrylic polyamide
8.	 R = H	Acrylic fibres

(contd.)

Fig. 1.38: Recently developed pyrazoline based fluorescent compounds

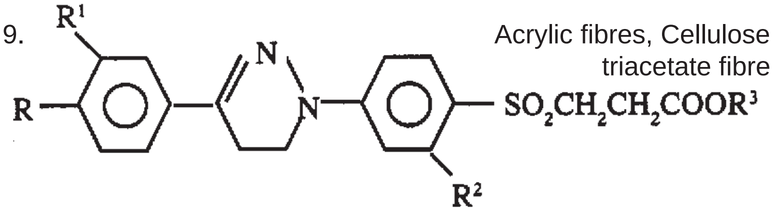
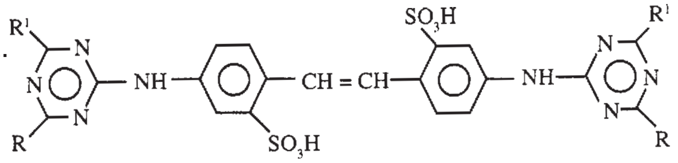
Sl. No.	Structure	Substrate
9.		Acrylic fibres, Cellulose triacetate fibre

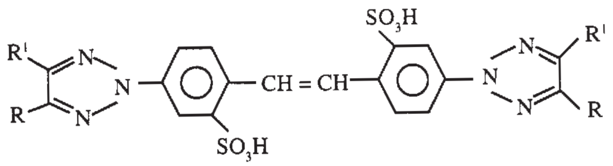
Fig. 1.38: Recently developed pyrazoline based fluorescent compounds

1.



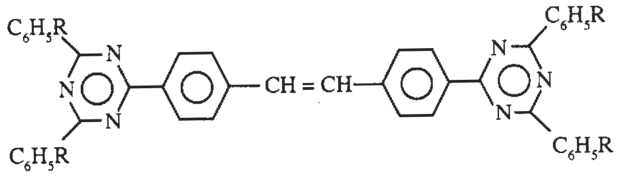
4,4' bis (triazinylamino) stilbene 2,2' disulphonic acids

2.



4,4' bis (v triazol 2 yl) stilbene 2,2' disulphonic acids

3.



4,4' bis (diphenyltriazinyl) stilbenes

Fig. 1.39: Some fluorescent brightening agents

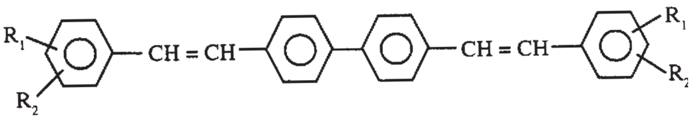
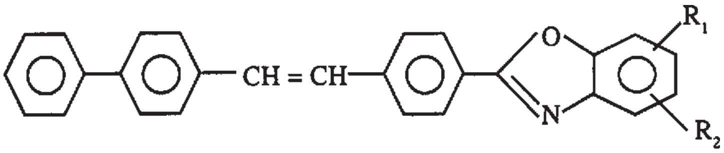
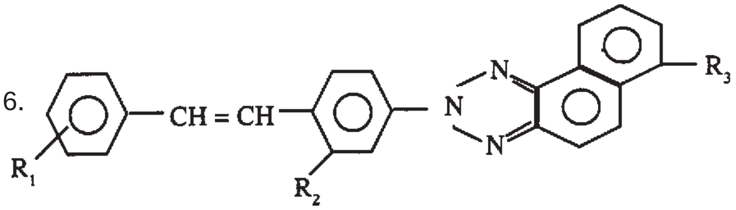
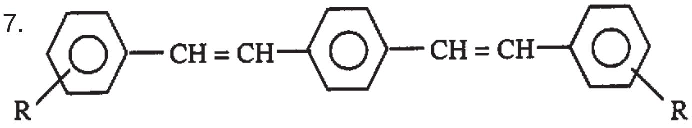
Sl. No.	Structure
4.	 4,4' distyryl biphenyl
5.	 **4 phenyl 4' benzoxazolyl stilbenes**
6.	 **Stilbenyl naphthotriazoles**
7.	 **4 Styrl stilbenes**

Fig. 1.39: Some fluorescent brightening agents *(contd.)*

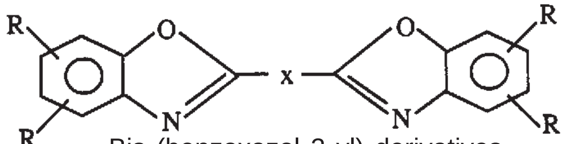
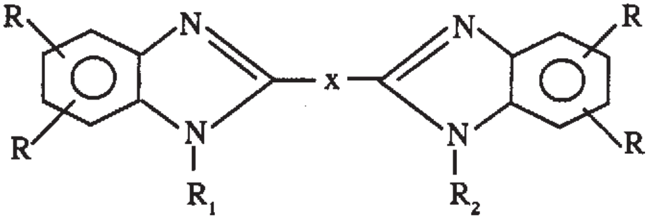
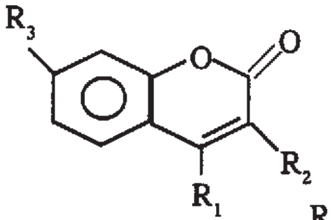
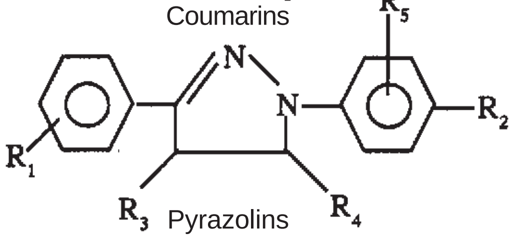
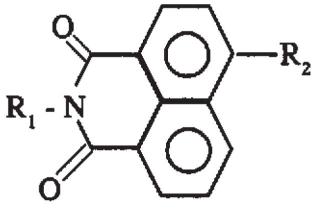
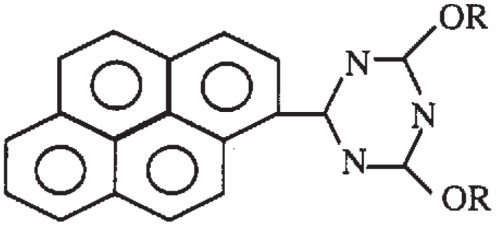
Sl. No.	Structure
8.	 Bis (benzoxazol 2 yl) derivatives
9.	 Bis (benzimidazol 2 yl) derivatives
10.	 Coumarins
11.	 Pyrazolins
12.	 Naphtalimides

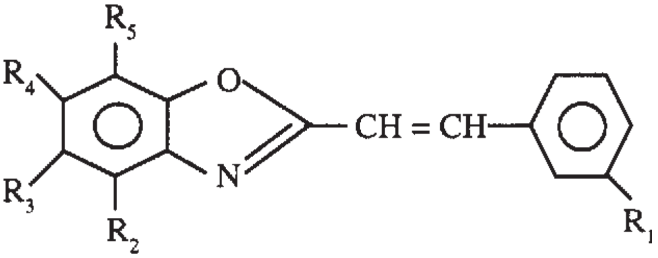
Fig. 1.39: Some fluorescent brightening agents

13.



Triazinyl pyrenes

14.



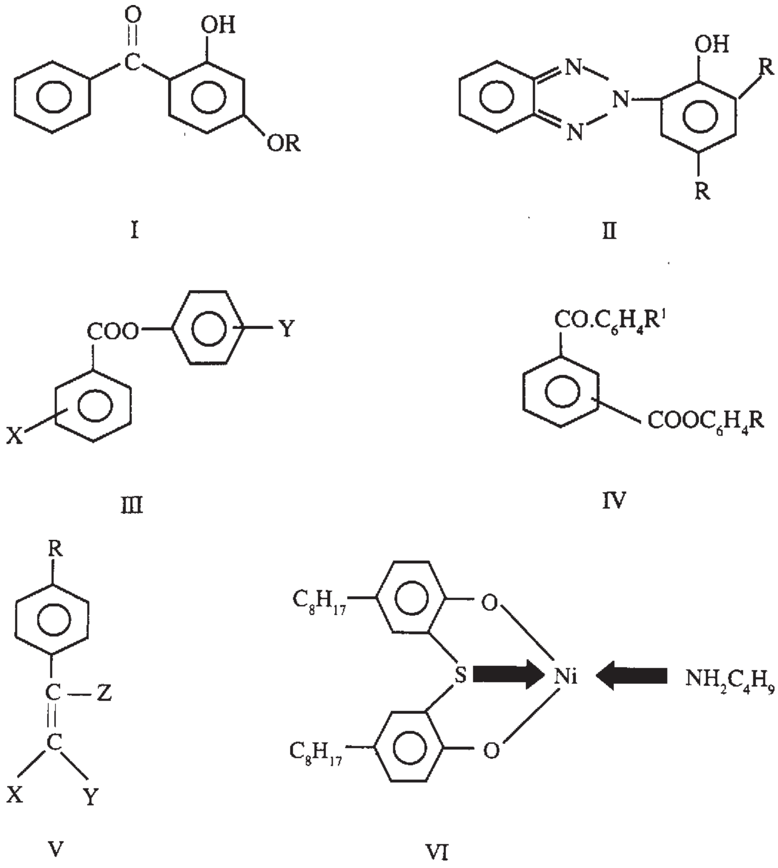
2 Styryl benoxazoles and naphthoxazoles

Fig. 1.39: Some fluorescent brightening agents

This group includes sulphonated oils, sulphonated tallow, fatty alcohol sulphates, fatty ester sulphates, sulphated mono-glycerides and hydrocarbon sulphonates. The anionic softeners do not possess substantivity to the fibre and are not washfast. They are not compatible with resin and cationic products. Hence, anionic products are used as softeners only in starch based temporary finishes.

Nonionic softeners

In this group of compounds, ethylene oxide condensates with stearyl alcohol and stearic acid are quite popular. Nonionic fatty amide type of products are also sometimes used. These softeners are characterised by their excellent stability against yellowing and good tolerance of catalysts used in resin finishing. Generally, they do not have any effect on shades of dyestuffs. However, nonionics also do not have any substantivity for fibres and are not fast to washing.



I II III IV V VI

Fig. 1.40: Speciality chemicals for imparting light stability to mammade textiles

Cationic softeners

Cationic softeners constitute a very important group of popular softeners. They are substantive to cellulosic fibres and therefore the treated textile remains soft for a few washes. These softeners impart a full and silk-like hand to the cloth. They have excellent stability in the resin finishing bath. But the major problem with them is of yellowing on white. Hence the treatment is done very carefully.

Reactive softeners

In order improve the durability of the soft finish, reactive softeners are developed. these softeners will react chemical with the hydroxyl groups of cellulose under suitable conditions. These softeners posses a reactive group attached to a long chain lubricating or softening group. “Velan PF” or “Zelan” is stearyl amido methyl pyridinium chloride. It is applied to the fabric in aqueous solution, usually buffered with sodium acetate. The fabric is dried and baked at 120-150ºC for a few minutes. During this baking the softener reacts chemically with cellulose giving off pyridine. The softener is expensive, toxic and yellows the treated fabric on curing.

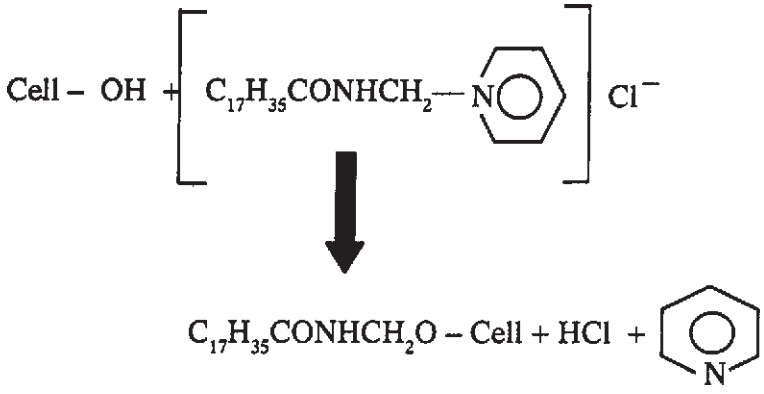


Fig. 1.41

Reactive softeners based on octadecyl ethylene urea have also been developed. A typical example is “Octex EM”, which reacts with cellulose in presence of diammonium hydrogen phosphate, giving a soft feel to the cloth.

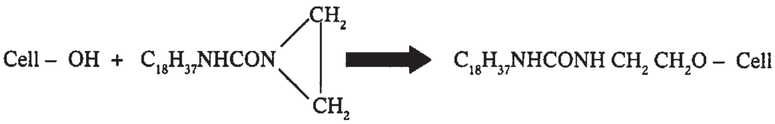


Fig. 1.42

Fatty acid substituted melamines have been put in the market. Fatty acid substituted triazones are also useful reactive softeners. The most recently developed reactive softeners are based on carbamates. These are prepared by condensing appropriate carbamates with formaldehyde.

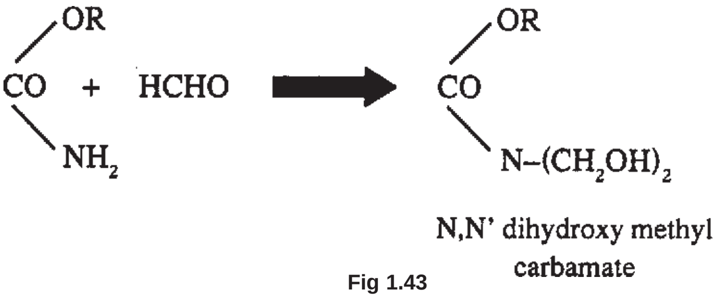


Fig 1.43

The substituent R in this case is a long chain fatty alkyl group.

Emulsion softeners

The emulsion softeners have gained popularity by virtue of their ability to reduce the losses in tear strength or resin finishing. These are prepared by polymerization of the monomer which has been emulsified in a water phase. The important products belonging to this group are polyethylene emulsion, polyester emulsion and so on. the emulsion softeners give excellent full hand with adequate fastness to washing.

Silicone softeners

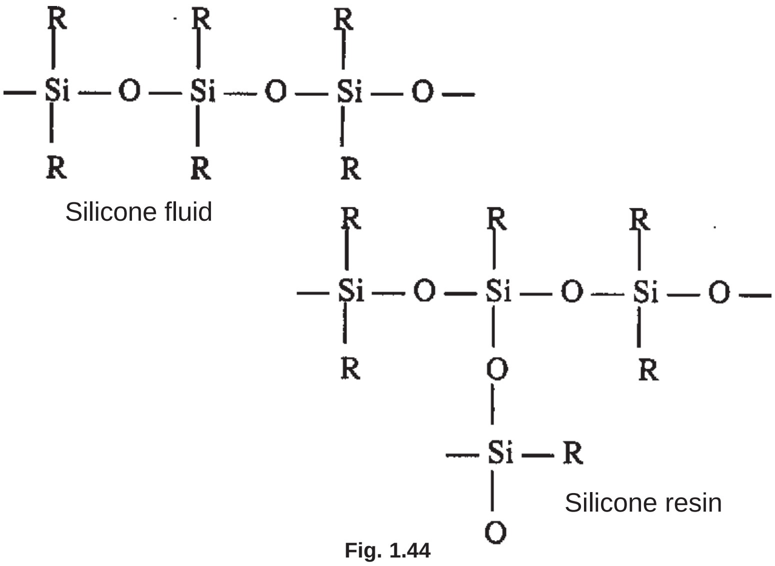
During last few years the use of silicone emulsions as softeners has increases considerably. The commercially important silicone polymers consist of a backbone of silicone and oxygen with organic substituents on the silicon atoms. Since silicon is tetravalent, two sites are available on each silicon member of the siloxane chain. When both the sites are substituted with organic groups a linear fluid polymer results. Network polymers or resins can be formed by selected branching along the siloxane chain with additional siloxane linkages

The first step in the manufacture of silicones is the preparations of the substituted chlorosilanes R_n-SiCi$_{(4-n)}$ where R is usually a methyl or phenyl group and n = o,1,2 or 3.

BIOPOLISHING

Biopolishing is the Novo Nordisk registered trade mark for a process of treating cellulosic fibres and blends with synthetics with cellulases to obtain the following effects.

- Antipilling of knitgoods.



Silicone fluid

Silicone resin

Fig. 1.44

- defluffing of terry fabrics.
- soft handle on viscose.
- defibrillation of Lyocell.
- surface effects on cotton, viscose and Lyocell.

Permanent antipilling of knitgoods

- best effects in overflow jets and winch becks.
- commercial cellulases show good effects.

Permanent defuzzing of cellulosic fibre terry fabrics

- best effects on overflow jets and winch becks.
- good effects in pad/ batch processes (bath cold for approx, 12-20 h or at 55ºC fir 2-4h).

Soft hand effects on viscose, Cupro (silk like)

- requires special machinery with vigorous wash action (e.g. airjets.)

Defibrillation of NMMO fibres (Lyocell, Tencel)

- relatively long processing times (up to 2 h) necessary.
- best effects in overflow jets and which becks.

- commercial cellulases do not give completely permanent effects.

Surface effects on cotton, viscose and Lyocell (e.g. peach skin)

- special machinery with vigorous wash action necessary (e.g. air jets).
- emerizing before or after treatment enhance the effect.

The cellulose products currently available were not specially developed for biopolishing of specific substrates. They mostly operate in a temperature range up to maximum 60ºC and pH value of 4.5 – 5.5 and give good effects on cotton.

Biopolishing process requires

- pH 4.5 – 9.5
- temperature upto 60ºC.
- 0.5 – 3.0 % cellulase.
- ½-1 h with discontinuous.
- 1-18 h with pad batch.
- deactivation at 70-80ºC or pH>9.

All treatments with cellulase carry a risk to some extent, i.e. since cellulase hydrolyses the beta 1,4 glucoside linkages of the cellulose a definite decomposition takes place. This decomposition results in weight and tensile strength losses in the substrate but not, however, in a reduction in DP (average degree o polymerisation). This risk can be held within limits with currently available cellulase products through appropriate process control, i.e. most importantly by timely termination of the enzyme action. Weight losses very seldom exceed 5% and the tensile strength losses are generally less than 10%.

Stone Washing

Almost 90% of all jeans on the market, and that was approx. 1 billion world wide in 1993, are treated with enzymes (cellulases) in order to obtain the typical “washed out” character. The proportion of combined processes, i.e. a combination of pumice stone and cellulases, is still very high (approx. 80%) but a very clear trend towards stone free processes can be observed. The use of stones bring obvious disadvantages such as:

- higher wear and tear on machinery

- handling and care of the stones
- reduced machine capacity through a high proportion of stones (up to 1 kg stones per kg jeans).

The action of the cellulases is essentially identical to the action of those which are used in biopolishing. By detaching cellulose particles from the fibre surface a prominence of adhering indigo dyestuff is also detached. Since indigo dyeings are typical sheath dyeings the lighter core of the fibre shines through more readily after this stripping process and this leads to the wash-down effects. Another factor plays an important role in the stone wash process with cellulases, namely the back staining of the fabric with indigo pigment.

In this case one can quite clearly detect the better performance, i.e. less backstaining, of the cellulases, which work in the neutral or slightly alkaline pH range compared to the cellulases which work in the acid pH range. Back staining is influenced by many factors and naturally just the pH value of the treatment bath alone has an undoubted influence.

Water Repellents

The earliest products used for water repellency were rubber latex, chlorinated rubber, linseed oil, etc. These agents make the cloth impermeable to air also and are not suitable for clothing as the treated material is uncomfortable to wear as well as heavy and stiff. Water repellents should:

- impart water-repellency to the fabric, which is fast to washing and dry cleaning,
- affect the porosity to air as little as possible,
- leave the wet soiling of the cloth unaltered,
- be compatible with other finishing agents,
- be easy to apply on cloth, and
- be inexpensive.

The important water repellents are:

- Aluminium compounds applied alone or with soap,
- Wax dispersions,
- Wax dispersions containing aluminium salts,

- Wax dispersions containing zirconium slats,
- Pyridinium compounds,
- Waxy thermosetting repellents,
- Silicones, and
- Fluorochemicals

Aluminium acetate

Aluminium acetate is used as, a water repellent. The cloth is padded with the aluminium acetate and batched. The process is repeated till a sufficient deposit of aluminium acetate is obtained. The cloth is then dried. The use of this repellent is not popular. A modification of this process involves the use of aluminium soaps.

Wax dispersions

Wax dispersions are anionic alkaline dispersions, used chiefly on nylon, polyester and acetate taffetas. They give no repellency on cotton of rayon. These are usually applied together with melamine or urea-formaldehyde resins to give a slightly crisp hand. A typical formula is:

10%	Wax dispersion
3%	Melamine formaldehyde resin
1%	Ammonia
0.5%	Ammonium sulphate

The cloth is padded, dried and cured. It gives a finish possessing good resistance to washing, particularly on nylon but resistance to dry cleaning is poor.

The use of aqueous dispersions of paraffin wax containing aluminium acetate or other salts has become quite popular for imparting water repellency to cellulosic and protein fabrics. The well known trade products ‘DipsaniV’, ‘WaxolW’, ‘Woxol PA’, etc., belong to this group. The pH of the dispersion should b maintained at 3.5 to 5.5

Wax dispersions containing zirconium salts are particularly valuable water repellents for wool and other animal fibres. They provide a pleasant full hand and good water repellency. However, on woolen fabric the finish has limited durability to washing and very little resistance to dry cleaning. Generally these are applied along with urea formaldehyde resins. A typical recipe is as follows:

8% Wax/Zirconium repellent

15% Urea formaldehyde resin

1.8% Amine hydrochloric acid catalyst

1% Acetic acid

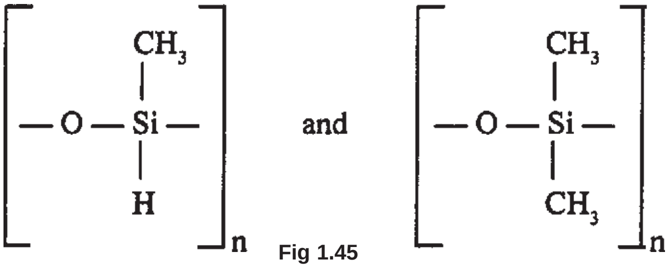
Pyridinium Type of Repellents

This group includes the well-known products – 'Velan PF', 'Zelan', 'Norane' etc. which are stearyl amido methyl pyridinium chloride. Instead of stearyl cetyl can also be present.

A large number of compounds have been developed consisting of quaternary ammonium salts of pyridine and containing a hydrophobic portion and polar group which is capable of forming a bond with cellulose.

Waxy thermosetting repellents vary widely in chemical structure and are available in anionic, cationic or nonionic forms. They are applied by pad, dry, cure process. Fatty acid substituted triazine, products based on methylolated carbamates, are useful as water repellents.

Silicones differ from most other repellents in that long chains of hydrocarbon or fluorocarbon are not present. Water repellency is provided by methyl groups oriented and attached to the fibre surface by silicon links. The silicones are mostly built up of one of the following two type of units. The first one is reactive and is generally used as water repellent mostly along with the other. Two of the most important polysiloxanes used in textile applications are methyl hydrogen and dimenthyl derivatives with the general formula



$$\left[-O-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{Si}}- \right]_n \quad \text{and} \quad \left[-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}- \right]_n$$

Fig 1.45

$$-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-$$

Methyl hydrogen polysioxane

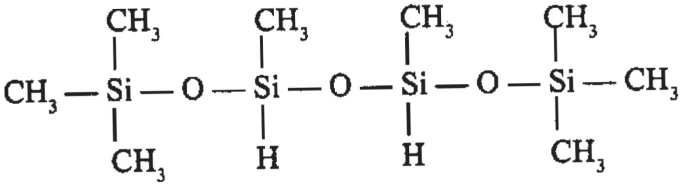
$$-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-$$

Dimethyl polysioxane

Fig 1.46

Polysiloxanes of low molecular weight are liable to undergo further polymerisation by the lengthening of the-Si-O-chain and also by cross-linking of adjacent-Si-O-chains. This is undesirable in textile application and is prevented by previously replacing the end hydrogen atoms by more inert substituents like methyl groups.

Methyl hydrogen polysiloxane end-blocked by trimethylsiloxane group.



$$\mathrm{CH_3}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$$

Fig 1.47

In general, siloxanes require the use of special catalysts, which are usually based on organo compounds of titanium, zirconium, tin, zinc and other metals. They are useful on cotton, rayon and nylon fabrics. For woolen material special silicone formulations containing organo titanium catalyst (pH 4-6) are avaialble which can be cured at a moderate temperature of 100ºC, and thus do not damage the fabric.

Some other types of silicones such as tetravinyl silane and thiouranium polysiloxane is applied under cold alkaline conditions and is particularly suitable for silk. Silicones are also available for finishing cellulose acetate.

Fluorochemicals

Fluorochemicals have revolutionised both water repellent and soil release finishes. They provide reference not only to water but also to oil. The drawback of fluorochemicals is that once the soil enters the finished cloth, it is very difficult to remove it. however, during recent years special products have been developed which facilitate the removal of ground in stains. Fluorochemicals are expensive and usually for obtaining water repellent finish they are used in conjunction with other water repellents called extenders. Flurochemicals give a finish with good resistance to washing and moderate resistance to dry cleaning.

A fluorochemical is an organic compound in which a high proportion of hydrogen attached to a carbon has been replaced by fluorine. 1,1 dihydro perfluoro octanol $C_7F_{16}CH_2OH$ polymerised the resulting acrylic monomer forms the poyacrylate as below:

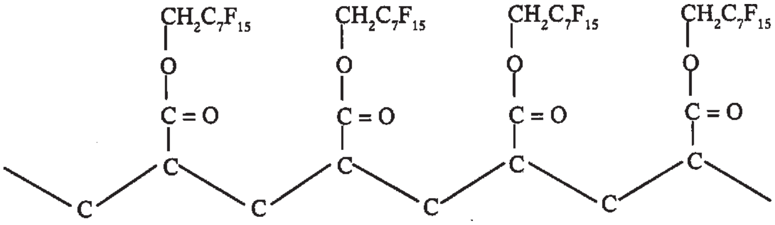


Fig 1.48: Fluoropolyacrylate

Such a compound will exhibit water and oil repellency when properly applied to a fibrous substrate. There are generally supplied as emulsions.

2

Manufacturing Processes of Textile Auxiliaries

STARCH

Starch occurs in most of the edible grains and tubers, such as rice, whet, maize, potato, cassava etc. Starch is most economically extracted from corn or cassava. Maize of corn contains about 70% starch on dry basis.

The starch located in the floury endosperm consists of large, round granules associated with a relatively small amount of protein. Separation of these granules in the milling process offers no serious problem. Smaller, polygonally shaped granules are tightly held in a water insoluble protein matrix in the horny endosperm region. The hydration and disintegration of the protein in order to lossen the starch, the separation of the starch from the finely dispersed protein and the accomplishment of these ends without damaging the more fragile granules of the floury region constitute the chief problems in milling. The wet milling process separates the four main parts of corn-germ, hull, gluten and starch in that order.

Shelled grain is prepared for milling in cleaners where air currents blow out light chaff and screens and magnets remove heavier pieces of foreign material. The cleaned corn is softened by soaking (steeping) for 30-50 hour in warm (50°C) water acidified with sulphur dioxide to a pH of 3 to 4. The dilute sulphurous acid controls bacterial fermentation and aids in the disintegration of the protein matrix so that starch and other components can be separated more easily. During steeping, the water content of the grain increases to 45%.

The softened kernels are separated from the steepwater and then coarsely ground with water from determinating or attrition mills. These mills tear the kernels apart, freeing the germ and loosening the hull. Care must be taken to minimize breaking the rubbery germ, for if oil is liberated from the germ a this step, it is absorbed by the gluten and is not recovered. The lighter germ floats to the surface where it is easily removed from the other particles. Separation is accomplished by use of hydroclones with the germ passing out in the overflow. The remaining mixture of starch, gluten and hulls passes out in the underflow.

The starch containing mixture is next finely ground in steel mills of special design. An attrition mill with special impact ring or an impact type mill are used. In the later, slurry dropped onto the rotation horizontal disc in spun with great force against both rotating and stationary pins. The coarser fibre particles are then removed by a screening operation. This is accomplished by passing the slurry over sieves made of metal or nylon fabric and supported on vibrating or rotating frames or by pumping the slurry over static screens of special design.

The mixture of starch and gluten which passes through the sieves as a slurry must still be separated; in most starch factories continuous centrifuges are used accomplish this separation. These machines, operating on the principle of cream separator, eject the heavier starch granules at the periphery of the centrifuge bowl while the lighter gluten particles flow but at the centre.

After separation from the gluten, the starch is filtered and washed or passed through washing hydroclones. At this point it may be dried and packaged for market.

DEXTRIN/BRITISH GUM

The nature of dextrin is determined by the source of the starch and its moisture content, the presence of contaminants, the rate of heating and agitation, concentration of catalyst, duration of heating. During dextrinization, solubility and fluidity is increased. Starch containing 5-12% moisture is charged into a kettle. The kettle is glasslined or rubberlined. Dilute hydrochloric acid is added. The mass is agitated and heated and cooked for several hours.

The heating is stopped. The excess acid is neutralized by ammonia. The product is then packed. The dextrin comes out of the cooker dry.

STARCH HYDROXY ETHYL ETHER

Ethylene oxide and propylene oxide react with commercially dried starch containing 5-10% moisture. Caustic soda, soda ash and other catalysts are used. In an autoclave starch is charged with the catalyst and ethylene/propylene oxide is charged under pressure. After the reaction is over, the mass is discharged and packed.

METHYL CELLULOSE

Cellulose or dissolving grade paper pulp is first treated with sodium hydroxide and water to get alkali cellulose. The alkali cellulose is then reacted with methyl chloride to obtain methyl cellulose.

HYDROXY ETHYL CELLULOSE

Cellulose is treated with alkalisation to get alkali cellulose. The alkali cellulose is reacted with ethylene oxide. The dispersion is heated to 30ºC and held for 1 hour. The temperature is raised to 35ºC and held for 3 hours. The reaction mass is then filtered to recover the product. The product is washed with methanol acetone solution and dried.

ETHYL HYDROXY ETHYL CELLULOSE

Manufacture of ethylhydroxyethylcellulose starts with a dissolving grade, bleached, sulphite pulp. Sheets of pulp are steeped in sodium hydroxide, pressed shredded and placed in an autoclave with a mixture of ethylene oxide and ethyl chloride. Ethylene oxide is more reactive than ethyl chloride and, with increasing temperature, ethoxylation of the cellulose chain takes place prior to ethylation. The raw product is washed with hot water, dewatered by centrifugation, ground, and dried.

SODIUM CARBOXY METHYL CELLULOSE

It is believed that each of the several companies that manufacture sodium carboxymethylcellulose employs different techniques to accomplish the reaction. Only one of these companies has disclosed its process. Essentially, this consist of concurrently spraying aqueous sodium hydroxide and monochloroacetic acid onto powdered cellulose as it passes slowly through a revolving drum. The resulting mixture is aged to complete the reaction, over-dried, and packed for shipment.

The traditional process is accomplished in a sigma-blade mixer. Either the cellulose is steeped in sodium hydroxide, pressed, and shredded, or the alkali cellulose is prepared entirely in the shredder. The sodium mono-chloroacetate or chloroacetic acid can be mixed with the cellulose either before or after the alkali is added. If a technical products is desired, the reaction mass is neutralised, dried, and packaged. The crude product can be purified by the use of alcohol-water mixtures to extract the salts without dissolving the gum.

GUM ARABIC

Gum production starts in breaks or wounds in the trees (Acacia Senegal) that are sometimes caused naturally but, more commonly, artificially. Originally, all gum Arabic marketed was the result of natural exudations, but about 60 years ago, tapping was introduced. A small axe is used to break the outer dark horizontally by making a shallow -cut 1.5 in (-3.8 cm) wide. The dark is then peeled one strip up and one strip down to form 2-3 ft. (0.6-1.0-m) wounds. Gum collects in the wound within 3-8 weeks, depending on weather conditions. Gum droplets formed are 0.75-3 in (1.9-7.5 cm) in diameter and gradually dry and harden on exposure to the atmosphere.

After collection, the gum is brought to villages and stored until there are sufficient quantities to transport to the marketing centre. Upon arrival at market, the gum is auctioned.

After auction, the gum is taken to cleaning sheds before shipment. Various cleaning techniques are used. The best grades of gum are hand picked to insure uniformity of colour and freedom from extraneous material.

Some gum is bleached by spreading it on sheets and exposing it to the sun for several weeks. The treatment develops many small cracks on the surfaces of the gum pieces so that the material is easily friable and has a uniform light colour or frosted appearance. The gum is available in several grades: natural, cleaned and sifted, bleached, and dust.

GUM KARYA

The best quality gum is collected during April, May and June before the monsoon season. As the weather becomes warmer, the gum yield increases. The gum quality, as well as yield, improves during this period. Early rains reduce the size of the crop by washing away much of the exudation before it can dry. In addition, the gum collected during a rainy season has low viscosity. In September, after the monsoons, the collected cycle is repeated. The gum gathered in the fall has a grayish colour and usually gives less viscous solutions than gum collected earlier in the year.

Gum exudes from Sterculia trees after they are tapped or blazed. Usually, only the younger trees are tapped. In trees over 3 ft. (1 m) in girth, blazes or chars not exceeding 1ft^2 (900 cm^2) are made with a maximum of two to a tree. The gum begins to exude immediately, and exudation continues for several days. the maximum amount of exudation occurs within the first 24 hr. The gum is in the form of large, irregular tears, some of which weigh several pounds. The dried tears are picked by natives and delivered to village collection points. Visiting dealers buy the gum for shipment to central processing houses. The yield of gum from mature trees is estimated to be 10 lb 1-4.5kg/per tree per season. The average tree can be tapped about five times during its lifetime.

The dark is removed from the large tears of field-grade gums. The tears are then broken up, and the fragments are sorted into grades on the basis of colour and amount of adhering dark.

The processor evaluates incoming raw materials according to impurity content, solution viscosity, and colour. Purification is accomplished by size reduction and air flotation of loose dark. There are also devices, such as Scutton-Steele tables, that remove both bark and small pebbles by a combination aerodynamic-specific gravity principle.

GUM TRAGACANTH

The plants are longitudinally incised with a sharp blade and the gum exudes spontaneously from these wounds or breaks and dries or hardness as ribbons or flakes. The bushes grow rather sparsely, and it is a time-consuming task to tap the roots and branches and then return later to collect the dried gum.

The ribbons occur in flattened, lamellated, frequently curved fragments or in straight, spirally twisted, linear pieces. They are white to off-white in colour, and 5-10 cm in length. The flakes are oval, thick, and brittle, varying in size from 1.25 cm in diameter. The better gum is milky white, whereas low viscosity gum is translucent and somewhat glassy in appearance and fracture. Gum tragacanth in odourless and tasteless. Collected gum is sorted and transhipped.

LOCUST BEAM GUM

Pods are harvested by shaking the twigs with poles and are then picked up from the earth by hand or with rakes. Farmers bring the fruit to the kibblers in bulk.

The pods are cleaned, then crushed and kibbled in kibbling machines. A pod consist of pulp, 90%; kernels, 8%; and other materials, 2%. The kernel is composed of husk, 30-33%; germ 23-25%; and endosperm, 42-46%.

The percentage of seeds contained in the pod as well as the gum portion (endosperm) contained in a seed depends upon the quality and origin of the crop. The dicotyledonous seed contains a central hard, yellow embryo surrounded by a corneous and comparatively large layer of white, semitransparent endosperm. This is the desired gum. The endosperm is turn is surrounded by a tenacious, dark brown husk.

Successful production of the gum (especially high-grade locust bean gum) involves separation of the endosperm from the embryo. The colour of the gum (white and with no brown specks) depends on efficient removal of the outer husk either by chemical attack or by mechanical abrasion.

The dehusked or decorticated seeds are split lengthwise, and the embryo is separated from the gum. The presence of yellow germ (embryo) in the gum increases the rate of fermentation of gum solutions. It is, therefore, important to have very clean endosperm. Finally, the gum is ground.

There are four main grades of locust bean gum: to high grade, normal high-grade industrial grade, and technical grade.

GUAR GUM

The hull of the guar seed is loosened by soaking in water. The hull is removed by grinding. Purification is done by repeated grinding and sieving. After the endosperm is separated from hull, it is ground to fine particle size and marketed.

TAMARIND KERNEL POWDER (TKP)

Preparation of TKP is a relatively simple operation and consists of decortication of the seeds and pulverization of the creamy white kernels. First, the seeds are thoroughly washed with water in order to free them from attached pulp. Hollow seeds, which float, are discarded. The seeds are parched in an oven or on hot sand at 150º for 10-15 min so that the inner kernels are not charred. The testae, which become brittle by this treatment, are removed by light pounding and winnowing.

For simultaneous decortication of seeds and pulverization of kernels, the seeds are ground directly. Here, advantage is taken of the fact that the testae and kernels have different degrees of pulverizability. The process, therefore, involves (a) breaking the seeds in a disintegrator running at such a speed (700-1100 rpm) that the testae alone are pulverized while the kernels remain in a crushed condition. (b) removing the testae, and (c) grinding the crushed kernels to a fine powder in a disintegrator running at a high speed (2000-2500 rpm).

TURKEY RED OIL

200 kg. of conc. Sulphuric acid is slowly added into castor oil (1600 kg) with continuous stirring in about four and a half hour. The temperature of the mixture is maintained between 25ºC-30ºC by circulating water in cooling coils and/or jacket. After stirring 1½ hour further, 130kg. of sulphuric acid is added slowly and with continuous stirring in over 3 hours and the batch is allowed stand for 13 hours without stirring. Finally a further quantity (50 kg) of sulphuric acid is added in about 1 hour and stirring is continued for another hour. The batch is then neutralized as quickly as possible by stirring with 40º Be caustic soda solution (860 kg). The temperature rises to 90 to 100ºC. The batch should now show an acid reaction to phenolphthalein. Live steam is now passed in for ½ hour. After standing overnight the aqueous salt layer is run off. The product is settled for 2 weeks, the aqueous layer is run off. It is then diluted by addition of requisite quantity of water.

SODIUM LAB SULPHONATE

Linear alkyl benzene (LAB) is charged into a jacketed glass lined or a stainless steel kettle equipped with an anchor type stirrer. Sulphuric acid is then slowly added to the sulphonating kettle at such a rate that the temperature of the mixture does not rise above 45ºC till half of the acid has been added in. In later half addition of the acid the temperature is allowed to go up to 55ºC. when sulphnating with 98º sulphuric acid it is advisable to warm the LAB to about 40ºC in order to start the reaction smoothly, otherwise when starting at too low temperature, the reaction might not begin until a very large quantity of acid is added and then it might be quite sudden with an excessive amount of heat which might cause the reaction to get out of control. Reaction should start immediately with the addition of acid, so that the time of acid addition and cooling together keep the reaction well within limit. After all the acid has been put in, the reaction mixture is agitated and maintained at 55ºC, to allow the reaction to go to sulphonation.

The batch is now neutralized with caustic soda solution. For this, the acid mix is carefully added with continuous mixing into the neutralizing kettle containing 540 kg. of caustic soda lye of 20% strength. The rate of addition of the acid mix to the caustic soda solution is so adjusted so as not to allow the temperature or the mixture to go about 55ºC. The final pH of the product should be 7.5 to 8. The slurry so obtained is drum dried or spray dried.

SODIUM LAURYL SULPHATE

Coconut fatty alcohol (185 kg.) were taken in a glass lined or stainless steam jacketed sulphonating vessel equipped with efficient stirring agent and coils for heating and cooling as required. The fatty alcohols are melted and brought to 28ºC temperature. Concentrated sulphuric is slowly added with constant stirring. The rate of acid addition and cooling is so adjusted that the temperature is maintained within the range of 30-35ºC. Lower temperatures cause partial crystallization of the alcohols and create difficulty in agitation. At higher temperature there is increased formation of colour bodies as well as by products, such as ethers. A contact time of 3 hours is satisfactory for completion of the reaction. The sulphation mass is poured in a thin stream into a solution o sodium chloride containing some ice, with good stirring. The mixture is allowed to stay overnight. The lower layer of saline water is carefully siphoned off and the upper cake is centrifuged to remove water as much as possible. The cake now contains some water, some sodium chloride, sodium sulphate, sulphuric acid sodium bisulphate and hydrochloric acid besides the sulphated alcohol. The cake is neutralized with sodium bicarbonate in wet condition and dried to give a product satisfactory for use.

DIBUTYL NAPTHALENE SULPHONATE

Napthalene and normal butyl alcohol are heated together to 100ºC with refluxing and constant stirring for an hour and cooled to room temperature. Concentrated sulphuric acid is slowly added to the alkylated napthalene slowly so as not to allow the temperature to go above 45-50ºC. on settling the product separates into two layers, spent acid is drawn off and the top layer is neutralized with caustic soda. This a good wetting agent.

ETHYLENE OXIDE CONDENSATE OF LAURYL ALCOHOL

186 kg. of Lauryl alcohol is charged to the kettle followed by 0.4 to 0.5 kg. of powdered caustic soda. A slow stream of nitrogen gas is started through the alcohol and the temperature raised to 150-160ºC. Ethylene oxide gas is admitted to the manifold and inside air is displaced. The nitrogen is vented to the atmosphere and the ethylene oxide is simultaneously introduced into the kettle.

Absorption takes place immediately with a rise in temperature. They ethylene oxide rate is increased to the point, where an occasional bubble of ethylene oxide escapes through the mass. The temperature is permitted to rise to 180-220ºC and is maintained within this range until the required amount of ethylene oxide has been absorbed (176 kg. equivalent to 4 kg mols). About 2 to 3 hours are required to absorb the above quantity.

In shutting down, the ethylene oxide is vented to air and the nitrogen is turned into the kettle and a slow stream maintained until all the ethylene oxide has been purged from the system. The contents are discharged into the tank and product.

OCTADECENOYL N METHYL TAURATE (IGEPON T)

930 kg of N-methyl taurine is dissolved and diluted to a total charge of 12,000 kg. with the help of water, in the reaction kettle. 30% solution of caustic soda equivalent to 172 kg. of sodium

hydroxide is added and well mixed. 2220 kg. of oleoylchloride and 295 kg. of sodium hydroxide in the form of a 30% solution and simultaneously added over a period of 4 to 6 hours as in the gel production.

The batch is stirred for one hour after the charging is completed. Then the charge is heated to 50ºC and neutralized with hydrochloric acid (to the brilliant yellow endpoint). Immediately after neutralization, 5200 kg. of common salt are stirred in and water is added to bring the total weight of the charge to about 26000 kg. At concentration of about 36% solids, the salt is completely dissolved. The pH after the addition should be 7.2 to 7.3 caustic soda or hydrochloric acid is added to adjust the pH within these limits.

The product is drum dried or spray dried. The yield is about 8200 kg. and contains from 30 to 32.5% cleoyl methyl taurine.

SODIUM BETA SULPHOETHYL ESTERS OF FATTY ACIDS

One such compound is made by condensing oleyl chloride with the sodium beta hydroxyethane sulphonic acid.

Oleyl Chloride

3000 kg. of oleic acid is run from a 30 cubic meter aluminium storage tank into a 7.5 cubic meter steel, lead lined reaction vessel with a conical bottom. The oleic acid is heated to 50ºC and 782 kg. of phosphorus trichloride is then run from a 11 cubic meter steel, lead-lined storage tank through a measuring vessel into oleic acid and takes about 1 hour, during which time the temperature rises a 55ºC, No stirring is employed. When all the phosphorus trichloride has been added the mixture is stirred for 5 minutes, after which it is allowed to settle overnight. The lower layer of phosphorus acid is then run off to waste through a lead pipe and the pipe is flushed with water.

After further stirring for a short period, the mixture is allowed to stand for one hour and any remaining phosphorus acid is run off. The finished fatty acid chloride is then run to a 4.5 cubic meter steel, lead lined storage receiver. Hydrochloric acid and fumes evolved during the reaction are absorbed in a rubber lined tower. The yield is 3315 kg. of Oleyl chloride (of 96% purity) in the form of a clear brown liquid.

Hydroxyethane Sodium Sulphate

It is made by the action of ethylene oxide on sodium bisulphate. A 15 cubic meter cast iron reaction vessel fitted with an anchor type stirrer working at 20-30 r.p.m., is charged with 11-12 tonnes of sodium bisulphite (38% strength) and 3000 litres of water. After heating the sodium bisulphite to 70ºC the air in the apparatus is displaced by nitrogen and the calculated amount of ethylene oxide run in through a weighing vessel at the rate of 70 to 80 kg. per hour, the precise rate of entry of ethylene oxide is regulated by reference to a mercury manometer, which indicates whether reaction has taken place or not. The reaction is exothermic and the temperature is kept down to 70ºC by intense water cooling. When reaction is complete, which is indicated by the mixture ceasing to be acidic by a colour change from light yellow to greying green, introduction of ethylene oxide is stopped and the reaction mixture is boiled for half an hour at 110ºC. The product is then adjusted to 43% hydroxyethane sodium sulphonate content (sp. gr. 1.125 at 80ºC), and impurities removed by filtering. It is then dried in a drier to 0.2% water content and sifted to a fine powder which contains 92-97% of hydroxyethane sodium sulphonate.

Sodium beta sulphothyl ester of oleic acid

The preparation is carried out in a 2 cubic meter lead lined condensation vessel fitted with a low pressure heating and cooling jacket. The stirrer which revolves at 15 r.p.m. is of specially heavy duty design, because the mixture becomes solid as the reaction proceeds.

185 kg. of hydroxyethane sodium sulphonate (calculated at 98-99% purify) charged into the reaction vessel and 3 atmosphere steam pressure applied. The manhole of the vessel is closed and 316 kg. oleic acid chloride run in from a measuring tank with stirring. The temperature is raised to 100ºC and after 15 minutes the reaction becomes vigorous with evolution of hydrochloric acid gas which is sucked into an absorption vessel. On continued stirring with heating to 110ºC, the thick pasty reaction mixture becomes a brittle solid and then breaks up into waxlike flakes. After cooling to 90-100ºC with continued stirring, gritty yellowish brown powder is formed. Sufficient solid sodium carbonate is then added to adjust the pH of 5% solution of the product from 7.2 to 7.5. The product is called “Igepon A Conc.” at this stage, yield is 460 kg. It is milled to give

“Igepon AP High Conc.” Which is a powder containing 75% active detergent. It is diluted with sodium sulphate to give “Igepon AP” and “Iegpon AP Extra”.

“Igepon A Paste” is prepared from “Igepon A Conc.” by dilution with water to 35% fat content which corresponds to about 43% active detergent.

Medialan A is y condensing oleyl chloride and the sodium salts of Sarcosine

$$C_{17}H_{33}CL + CH_3NHCH_2COONa \longrightarrow C_{17}H_{33}CI - N - CH_2\ CO\ ONa\ CH_3$$

(Oleyl cloride) (Sod. Salt of Sarcosine) (Medialan A)

Fig. 2.1

Sarcosine may be made by condensing the sodium salt of monochloro acetic acid with methylamine on the presence of methyl alcohol. “Medialan A” is used as a solubilizing agents for sulphur colours. It helps greatly in dissolving the dyestuff and does not foam excessively and is sufficiently stable in strongly alkaline dye-bath. It serves both as a pasting up and levelling agent.

Chloracetic acid 45 kg. and 380 kg. water are charged into a reaction vessel and 25.2 kg. of sodium carbonate are added slowly so that the temperature does not exceed 20ºC. Methylamine in the form of 20% solution is then added slowly over a period of 2 hours. The mixture is then heated upto 75ºC during a further 2 hours and maintained at this temperature for about 10 hours. The pressure is 2 to 3 atmospheres. The mixture is then cooled to 25ºC and 55 kg. of 40% solution of caustic soda is added to decompose the methylamine hydrochloride formed. The excess methylamine is then distilled off, the solution concentrated to contain 18 to 19% salt of sarcosine filtered and stored in a tank.

60 kg. of sodium salt sarcosine (18% solution) is taken into the reaction vessel along with 50 litre water and 6 kg and of caustic soda solution (33%). The mass is stirred and cooled to 25-30ºC.

LAURIC DIETHANOL AMIDE

Lauric acid is treated with di-ethanolamina in an dowthern heated stainless reactor fitted with an agitator and spurger pipe for the introduction of nitrogen gas for purging. The reaction is carried out at 160ºC for 5 hours. Nitrogen is introduced when the reaction mass has been heated to about 120ºC. The reaction is controlled by cooling water circulation.

In the same manner other fatty acid diethanolamide may be produced.

SUPERAMIDE

The starting material for super amide are methyl ester of fatty acids which may be obtained as follows:

The alcoholysis of a with monohydric alcohol of low molecular weight e.g., methyl or ethyl alcohol may be catalysed by either acid or alkali, but the alkali catalysed reaction is generally superior in speed, completeness and can be affected at relatively low temperature.

The coconut oil (fat) is heated to 80ºC and anhydrous methyl alcohol containing dissolved caustic soda is gradually added. After the addition of alcohol the mixture is stirred for a few minutes and then allowed to stand. The glycerol begins to separate almost immediately as it is heavier than other liquids and settles to form a layer at the bottom of the tank. Conversion of the oil to methyl ester is usually 98% complete at the end of about one hour. After drawing off the lower layer of glycerol, the upper layer which consists of the methyl ester, most of the unreacted alcohol, alkali and small amount of soap, is washed with warm water. The methyl ester may be fractionated to give pure methyl ester.

To the reaction vessel containing methyl ester and catalyst is added diethanolamine gradually, and the mass is heated to 105ºC and maintained at this temperature for 3 to 3½ hours. Methyl alcohol is liberated during the reaction and recovered for recycling. The progress, and completeness of the reaction is best controlled by collecting and measuring the liberated methyl alcohol. The reaction product is converted in the form of flakes by running the molten product over chilling rolls fitted with “doctor blades” for scraping off flakes.

SULPHATED ALKANOLAMIDES

Into a glasslined jacketed kettle equipped with an agitator and condenser, is charged 150 kg. of oleic acid and 50 kg. of 3 hydroxy 1 amino butane. The mixture is heated for six hours at 160ºC under mild vacuum to remove the water formed.

The sulphating medium is prepared by charging 37 kg. urea and 28 kg. formamide into a glasslined agitated vessel, cooled to –30ºC by chilled brine circulation. 140 kg. of sulphuric acid while keeping the temperature below 30ºC.

For sulphation 37.5 kg. of the amide is charged into the kettle. 22 kg. of sulhated mixture is then slowly added with constant stirring and holding the temperature at 30-40ºC by means of chilled water circulation through the jacket. The neutralization is carried out by charging 25 kg. of 50% soda caustic solution into a stainless steel kettle (equipped with an agitator and jacket), then slowly adding the sulphonated mass. The temperature is kept below 45ºC. Conc. paste containing 60% active ingredient is thus obtained.

The product has acid stability equal to alcohol sulphate and boiling with caustic soda solution does not decompose it.

UREA FORMALDEHYDE PRECONDENSATE

The best results are obtained by using a molar ratio of formaldehyde to urea of 1.6:1.

The preparation of the pre-condensate may be affected in either of the two ways (a) by boiling under a reflux condenser or (b) by allowing the mixture to react at room temperature. In both cases a slightly alkaline mixture of urea and formaldehyde is utilized.

The viscosity of the product is generally between 5 and 7 centipoises at 20ºC. The density of the condensate also increases during the initial reaction from 1.15 to about 1.17.

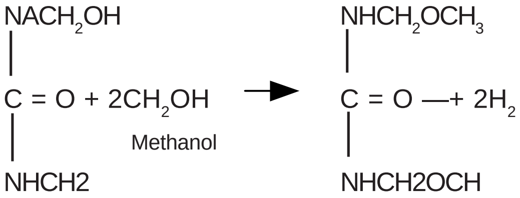
A solution is made by dissolving urea in formaldehyde at room temperature. To this is added the required quantity of ammonia with stirring. When urea is dissolved in formaldehyde solution there is fall in temperature, but the addition of ammonia is attended with development of heat. The solution is stirred periodically and its temperature be allowed to rise above 35ºC. About 4 to 6 hours is the minimum time for the formation of the precondensate at room temperature. Completion of the reaction is accompanied by crystallisation of the methylol urea from super saturated solution. The crystalline material is collected an dried.

BISMETHOXY METHYL UREA

The mixture of urea, formaldehyde and hexamine is heated on a water bath until a test sample exhibits no turbidity on cooling.

This takes longer time than time necessary for the preparation of precondensate for crease resisting purpose; which may be prepared by heating for 3 minutes to give a viscosity of 5 to 7 centipoise, whereas the far condensed solution required from 30 to 120 minutes and give a solution of 40 centipoises for the same density.

Treatment of a methylol urea with methanol in the presence of hydrochloric acid or magnesium sulphate results in the formation of a methoxymethyl urea.



$$\begin{array}{l} \mathrm{NACH_2OH} \\ \quad| \\ \mathrm{C=O} + \underset{\text{Methanol}}{\mathrm{2CH_2OH}} \\ \quad| \\ \mathrm{NHCH2} \end{array} \longrightarrow \begin{array}{l} \mathrm{NHCH_2OCH_3} \\ \quad| \\ \mathrm{C=O} \text{ —+ } \mathrm{2H_2} \\ \quad| \\ \mathrm{NHCH2OCH} \end{array}$$

Dimethylol urea Bis (Methoxy Methyl) urea

Fig. 2.2

Bis (methoxy methyl) urea is a water soluble wax like solid. It imparts to textile properties (crease resistance and shrinkage control) similar to those of methylol urea. The etherified material have better storage stability than unmodified methylol compounds and syrups.

MELAMINE FORMALDEHYDE PRECONDENSATE

18 kg. melamine and 12 kg. formaldehyde are agitated in an open vessel for a period of 1 to 1½ hour. Melamine dissolves in formaldehyde solution. The liquid mixture is withdrawn into agitated digestor operating at 150ºC and kept for 10 minutes. Form the digestor the mixture is transferred to an open flat pan and allowed to solidify for 24 hours. The solidified resin is removed from the pan pulverized and packed.

POLY VINYL ACETATE (FOR SIZING)

Vinyl acetate may be polymerized in aqueous dispersion to give a product in the form of emulsion. The process has the advantage of easy temperature control and absence of solvents. A typical run is carreid out as follows:-

Vinyl acetate	600	parts
Benzoyl peroxide	5.4	parts
Ethyl acetate		parts
Polystyrene-maleic acid		
Copolymer sodium salt	0.8	parts
Water	800	parts

Water and polysterene maleic acid copolymer sodium salt is taken in a jacketed and stirred reactor. The temperature is raised to 80ºC, then vinyl acetate when benzoyl peroxide and ethyl acetate are added in about 1½ hour. After about half the monomer has added, the reaction become quite vigorous and the charge must be cooled to hold the temperature at 80ºC. The monomer addition is controlled so that there is a gradual rise to 85ºC as the last portion of monomer is added. The temperature is finally raised to 93ºC, when the kettle is vented and blown with air to remove any unreacted monomer. The batch is discharged to a cooling vessel, where it is a cooled using first water then brine on the jacket to 4ºC, centrifuged, washed with water at 5ºC and dried in a try drier for 40 hours at 25 to 30ºC. The process produces a resin of about 25 cp. viscosity.

POLY VINYL ALCOHOL

Production of polyvinyl alcohol a multistep process since vinyl alcohol monomer is unstable, rapidly rearranging itself into acetaldehyde. Polyvinyl acetate resin from vinyl acetate monomer is put to alcoholysis to products polyvinyl alcohol.

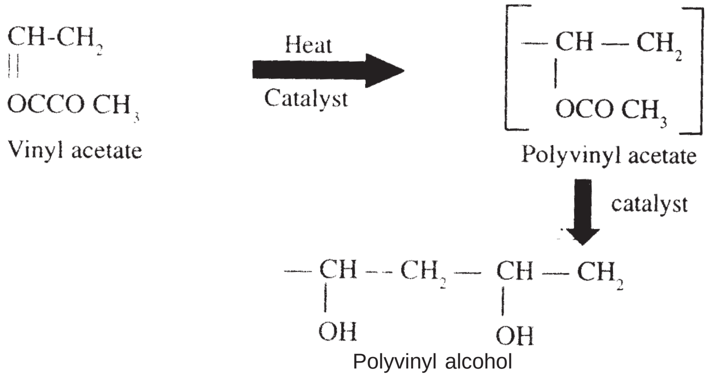


Fig. 2.3

(a) Preparation of Octadecyl Chloromethyl Ether

275 kg. of octadecyl alcohol are melted at about 60ºC along with 34.5 kg. paraformaldehyde. The operation is done in a kettle lined with phenolformaldehyde resin. The air in the kettle is removed and gaseous hydrochloric acid is introduced with good stirring at 2 atmospheric pressure until no more is observed. This takes about 4 hours. Stirring is continued for a further 3-4 hours while the temperature falls from 60ºC to 40ºC. The mixture is then allowed to stand for an hour. The hydrochloric acid layer is then run off. 3 kg. of silica-gel is now added and dry air or nitrogen is blown through to remove excess hydrochloric acid gas. The melt is finally filtered at 30ºC.

Polyvinyl acetate resins is dissolved in a solvent, usually methanol, and alcoholized by use of either an acid or alkaline catalyst. Polyvinyl alcohol, insoluble in the methanol and by-product methyl acetate, precipitates out and is then filtered, washed, dried, and packaged. The polyvinyl alcohol is characterized by the viscosity or degree of polymerization and the percent alcoholysis or degree of saponification.

Both viscosity and alcoholysis are controlled in the manufacturing process and are important in determining end-product characteristics. The molecular weight, a measure of polymer viscosity, is a direct function of the molecular weight of the precursive polyvinyl acetate resins fed to the alcoholysis reaction. This is normally controlled by use of “chain-breakers” during the polyvinyl acetate polymerization.

Polyvinyl alcohol is commercially available in four molecular weight ranges referred to as superhigh, high medium, and low viscosity polyvinyl alcohols. The average molecular weight of the four types are:

Superhigh viscosity, 250,000 to 300,000 high viscosity 170,000 to 200,000 medium viscosity, 120,000 to 150,000 and low viscosity, 25,000 to 35,000.

As the molecular weight of polyvinyl alcohol decreases, the water sensitivity or case of water solubility increases. Higher values for tensile strength, tear resistance, elongation, and flexibility are obtained with increasing molecular weight.

The percent alcoholysis is controlled by either allowing the alcoholysis reaction to go to completion or stopping at a desired level.

Changes in percent alcoholysis also affect product properties. As the percent alcoholysis increases, tensile strength, tear resistance and elongation increases. Water sensitivity is anomalous in that maximum sensitivity occurs at about 88 per cent alcoholysis.

POLY VINYL PYRROLIDONE (PVP)

1,4 Butanediol is dehydrogenated to butyrolactone. This when reacted with ammonia give 2 pyrrolidone. Acetylene is reacted with 2 pyrrolidone to obtain vinyl pyrrolidone which is polymerized to get PVP.

CETYL PYRIDINIUM BROMIDE (FABRIC SOFTENER)

Cetyl bromide is reacted with piperazine in presence of hydrobromic acid. The hydrobromic acid formed is distilled. The product is washed with mild alkali to make it acid free.

DIMETHYL PHENYL BENZYL AMMONIUM CHLORIDE (DYE DISCHARGING AGENT)

Dimethyl amine is stepwise amined by chlorobenzene and benzyl chloride, the hydrochloric acid formed is distilled off. The product is washed with alkali to remove excess acid. The product is then distilled to get the pure quaternary compound.

Dimethyl benzyl butyl ammonium chdoride used as a caion softener is prepared similarly.

M NITROBENZENE SULPHONIC ACID SODIUM SALT (MILD OXIDIZER)

Nitrobenzene is sulphonated with oleum is glasslined agitated vessel at low temperature of 30-35ºC with water cooling. Mono sulphonic meta derivatives are formed in large quantity. The mass is neutralized with alkali and washed. The meta isomer is fractionally crystallized.

STEARAMIDE METHYL PYRIDINIUM CHLORIDE

Stearamide is reacted with formaldehyde in presence of hydrochloric acid and pyridine. The product is washed with water and crystallized from it. It is used for water repellent finish.

SODIUM OLEYL PARA ANISIDINE SULPHONATE

Oleic and chloride is reacted with para anisidine. The product after purifying and recrystallisation is sulphonated with 20% oleum to produce the product.

POLYETHYLENE GLYCOL ESTERS

Fatty acids (Stearic, Mysystic, Oleolic) are reacted with ethylene oxide to give polyethylene glycol monoester. These are surfactants used for wetting, scouring, plasticizer for polyester fibres etc.

FATTY ACID ESTERS OF ANHYDROSORBITOL

Sorbitol is heated with fatty acids such as lauric, palmitic, stearic, and oleic. Two reactions take place simultaneously i.e. dehydration of sorbitol and esterification with fatty acids. The product has antifoaming properly and also are excellent lubricants and fabric softeners.

HIGHER ALCOHOL ESTERS OF METHACRYLIC ACID (POLYMERIZED)

Methyl methacrylate is inter esterified with stearyl/palmityl/oleyl/myristyl alcohols. The product is then polymerised in presence of organic peroxides to the required degree of polymerization. It is used as a binding agent in printing.

HIGH MOLECULAR WEIGHT FATTY AMIDE (STEARYL/CETYL STEARAMIDE)

Stearyl amine is reacted with stearyl chloride to get the product. It is used as a textile softener and emulsifying agent.

DIOCTYL ESTER OF SULPHOSUCCINIC ACID

Maleic acid/maleic anhydride is esterified with octyl alcohol/2 ethyl hexanol. The ester is digested with a concentrated solution of sodium bisulphite. The product is washed and distilled. It is an excellent wetting agent.

OPTICAL BRIGHTENING AGENTS

1. Sodium, 5,5’ Dichloro 4,4’ dinitrostilbene 2,2’ disulphonate

Sodium 5 chloro 4 nitrotoluene 2 sulphonate (22.8 g. 0.084

mole) was dissolved in 400 c.c. of water at 60º and 40 c.c. of 30% sodium hydroxide solution was added. Sodium hypochlorite solution, 100 c.c. (70% by weight active chlorine), was added dropwise over a period of 20 to 40 minutes at 60º with stirring. It is essential to maintain a positive starch iodide paper test at all times. It was stirred an addition 10 to 30 minutes until the starch iodide test became very faint. Salt (120 g) was added and the slurry was cooled to 20ºC, filtered and the cake was washed with five 10 c.c. portions of 20% salt solution. After drying at 60º, there was obtained 7.8 to 9.5 g (36-32%) of bright yellow needles. The 0 toluidine salt was obtained in the form of uniform needles after recrystallization from Pentasol, decomposition point above 360º.

2. 5,5' Dichloro 4,4' diaminostilbene 2,2' disulphonic acid

A slurry of 23.2 grams of barium 5,5' dichloro 4,4' dinitrostilbene 2,2' disulphonic acid in 100 c.c. of water was added dropwise over a period of 50 minutes to a vigorously stirred mixture of 170 grams (1,1 moles) of powdered iron, 200 c.c. of water and 2 c.c. of glacial acetic acid at boiling point. The mixture was heated under reflux for an additional 1.5 hours, cooled somewhat, made basic with solid sodium carbonate, filtered and the iron sludge was washed with water. the filtrate was cooled, acidified with hydrochloric acid, filtered, and the solid was washed with 25 c.c. of ice water and dried at 100º in vacuo. There was obtained 15.2 gram (93%) of cream coloured uniform needles.

4. Acylation of 5,5' dichloro 4,4' diaminostilbene 2,2' disulphonic acid

All the benzylations with substituted benzoyl chlorides were carried out essentially in the same way. The substitued benzoyl chloride, 0.03 to 0.06 mole, was added dropwise, slowly to a slurry of 4.4 gram (0.1 mole) of 5,5' dichloro 4,4' diaminostilbene 2,2' disulphonic acid in 150 c.c. of dry redistilled pyridine at the boiling point. The free amine test usually became negative within a few minutes; the test was made by diazotizing a test portion in the inverse manner and spotting as, an alkaline solution of 2 naphthol 3,6 disulphonic acid (R salt). The mixture was drowned in 150 c.c. of water and made basic by the addition of 10% sodium carbonate solution. the pyridine was removed by steam distillation and the residual slurry or solution, in the flask was cooled, or salted, to induce crystallization. It was filtered, the cake was washed with 2% salt solution, dried at 100º in vacuo, and recrystallized from water or aqueous alcohol solution, if necessary for purification.

5. Sodium 4,4’ Bis (phenylcarbamylamino) 5,5’ dichlorostilbene 2,2’ disulphonate

5,5’ Dichloro 4.4,’ diaminostilbene 2,2’ disulphonic acid (4.4 gram, 0.01 mole) was dissolved in 100 c.c. of water by the addition of sufficient 10% sodium carbonate solution to give a weekly basic test. Phenyl isocyanate (4.8 gram, 0.04 mole) was added dropwise and the mixture was stirred at 40º for 24 hours. It was cooled to 20º, filtered, and the cake was washed with four 25 c.c. portions of 2% salt solution and dried at 100 in vacuo. There was obtained 5.5 gram of a white solid which gave a negative free amine test. It was purified by solution in water, filteration and precipitation with salt.

6. Cyclohexylammonium 6,6’ Dichloro 4,4’ dinitrostibene 2,2’ disulphonate

Phenyl 2 chloro 4 nitrotoluene 6 sulphonate, 5.0 gram (0.015 mole), was dissolved in 300 c.c. of methanol. A rapid stream of oxygen was passed through the solution and rapid stirring was commenced. Potassium hydroxide solution (30 c.c. of 50% aqueous solution) was added, and the stirring and oxygen stream was continued for five minutes. The solution became a deep blue green, than an orange yellow, and considerable solid separated, most of which passed back into solution. The solid was removed by filtration, washed with methanol, and dried at 60º. It amounted to 0.8 gram and was apparently the diphenyl ester of the desired stilbene. The methanolic filterate was acidified with 35 c.c. of concentrated hydrochloric acid and the potassium chloride formed was removed by filteration. The filterate was evaporated to dryness. The residue amounted to 7.2 gram. The phenol was removed by steam distillation. The residual solution (150 c.c.) was cooled to room temperature and 30 c.c. of 1 N cyclohexylamine hydrochloride solution was added with stirring. The slurry was allowed to stand an hour, was filtered and the cake was washed with a little water and dried at 60º. There was obtained 2 gram of a light yellow solid.

GLYCEROL PHTHALIC ANHYDRIDE (PAN) CONDENSATE

Glycerol and PAN are reacted in a kettle to give a medium molecular weight polymer which is a yellow viscous liquid. This is an esterification reaction and proceeds in presence of sulphuric acid. The polymerisation is not continued beyond desired level otherwise cross linking takes place. This chemical is used as a crease resistant, durable press auxiliary.

o Methyl Cyclohexanol Stearate

o Methyl cyclohexanol is reacted with stearic acid in presence of dilute sulphuric acid in an esterification reaction. The liberated water is distilled off for completion of reaction. The product is then washed and distilled to obtain the ester. It is used as fabric softener.

TETRAHYDRONAPHTHALENE

It is prepared by catalytic hydrogenation of naphthalene under pressure. It is an admixture added to detergents for dyeing assistance and cleaning.

POLYVINYL BUTYRAL

Polyvinyl acetate is condensed with butyraldehyde in presence of alkali or acid as catalyst to produce polyvinyl butyral. This is a dispersing agent and also acts as wetting agent.

Dinaphthalene Methyl Disulphonic Acid

Beta naphthalene sulphonic acid is condensed with formaldehyde to give the product. It is a powerful dispersant in dyeing and printing.

POLYSTYRENE SUSPENSION

Styrene is undergone to controlled polymerization under emulsion condition. The product is a liquid with a total solid content of about 40%. It is used as a sizing material, as thickener, rayon textile, softener and rug and pile fabric finishing agent.

THPC THIOUREA CONDENSATION PRODUCT

244 parts of a 78% strength aqueous THPC solution (1 mol of THPC), 19 parts of thiourea (0.25 mol) and 200 parts of a xylene isomer mixture are heated to the boil, with rapid stirring, in a stirred vessel of 500 parts by volume capacity which is equipped with a

water separator and thermometer. At a boiling point of 105ºC, the azeotropic removal of the water from the aqueous THPC solution starts. After removal of this water (53.3 parts) the boiling point of the xylene is 130ºC.

A further 26 parts of water are now removed azeotropically by additional treatment at 130ºC, after which the condensation product forms a very highly viscous mass. The product is cooled to 90ºC and dissolved by adding 200 parts of water and the xylene is largely siphoned off. The aqueous solution is completely evaporated in vacuo at 70ºC. 160 parts of a very highly viscous yellowish condensation product are obtained and this is diluted to 80% active substance content with water to facilitate handling.

QUATERNARY ARYL AMINOALKYL PHOSPHONIUM SALT

Aniline (7.70 grams) was added to a solution of 3.83 grams of tetrakis (hydroxymethyl) phosphonium chloride (THPC) in 75ml of ethanol. There is a mild exotherm, followed immediately by the separation of solids. The mixture was stirred for 2 hours and then filtered, giving 9.15 grams (93.0% yield) of tetrakis (anilinomethyl) phosphonium chloride, MP 129º to 130ºC, as a white crystalline solid that yellowed rapidly on exposure to light. No further solids separated from the filtrate in the next 5 hours. The filtrate and washings, stripped under vacuum, left 1.15 grams of a yellow oil containing the remainder of the product and the unreacted aniline.

The product, which has the following structure $[(C_6H_5NHCH_2)_4P]$ ‘Cl’ was analyzed and found to contain 68.18% carbon, 6.88% hydrogen, 11.33% nitrogen, and 6.33% phosphorus. The calculated percentages of these elements are 68.49% carbon, 6.57% hydrogen, 11.41% nitrogen and 6.31% phosphorus in $C_{28}H_{32}ClN_4P$.

The infrared spectrum of the product, determined in a Nujol mull, showed a strong N-H absorption peak at 3.290 cm^{-1}. The nuclear magnetic resonance spectrum, determined in dimethylsulphoxide, d_6, showed a multiplet in the 3.3 to 5.0 region assigned to CH_2 and another multiplet in the 6.3 to 7.8 region assigned to N-H and aromatic C-H. The ratio of the protons in the two multiplets was 8:24, in agreement with the assigned structure.

The product was insoluble in water and in the common organic solvents, but dissolved in highly polar solvents such as dimethylformamide or dimethylsulphoxide. It dissolved readily in hot chloroform or acetone, giving yellow solutions that deposited gums on workup, and in hot methanol or ethanol, giving disproportionation products.

THPC AMMONIA CONDENSATION PRODUCT

125 parts of an 80% solution of tetrakis (hydroxymethyl) phosphonium chloride in water were added to 50 parts of water and 35 parts of ice. This solution was agitated as 10.1 parts of 28% aqueous ammonia were added gradually over a period of 50 minutes. The temperature rose to 35ºC. Formation of a water soluble condensation product was confirmed by thin layer chromatography (TLC). The amounts used correspond to a 3:1 molar ratio to tetrakis (hydroxymethyl) phosphonium chloride to NH_3.

POLY CONDENSATION PRODUCT

1,750 parts of a 78% strength aqueous solution of THPC (7.15 mol of THPC) and 1,000 parts of m xylene are heated to the boil, with rapid stirring, in a stirring flask of 4,000 parts of volume capacity, equipped with a reflux condenser, thermometer and water separator. The azeotropic removal of the water from the aqueous THPC solution starts at a boiling point of 104ºC. The calculated amount of water of 385 parts is obtained within 3 hours and the boiling point reaches 131ºC.

A further 145 parts of water are now removed azeotropically by additional treatment for a further 9½ hours at 135ºC, this water having been produced by self condensation of the dehydrated THPC, with simultaneous slight elimination of HCI. This amount of water corresponds to about 1.1 mols of water per mol of THPC. Thereafter, the mixture is cooled to 60ºC and diluted with 1,000 parts of methanol, whereupon the stringy viscous condensation product dissolves. The m xylene methanol mixture is thereafter removed in vacuo at 60ºC to 70ºC.

1, 127 parts of condensation product are obtained in the form of colourless, slightly cloudy, highly viscous resin. The product contains 18.6% of phosphorus (THPC=16.3%) and is soluble in water in any proportion to give a clear solution. The viscosity at 25ºC is 2,030 poises.

The addition of an aqueous solution of sodium lauryl sulphate to the aqueous solution of the condensation product causes precipitation, thereby confirming the higher molecular cationic character of the condensation product manufactured according to the process. Water insoluble condensation products cannot be obtained with ammonia.

1,3,2 DIAZAPHOSPHOLIDINE COMPOUNDS

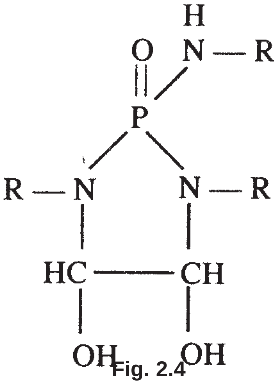


Fig. 2.4

Where all R substituents are identical and are methyl or ethyl.

The compounds can be prepared by the reaction of a trialkylphosphoric triamide and aqueous glyoxal at a pH of about 7 with moderate heating. In a preferred case, trimethylphosphoric triamide (TPA) is employed, resulting in a product where the R group of the above structure is methyl, the product being 1,3 di methyl 2 methylamino 2 oxo 4,5 dihydroxy 1,3,2 diazaphospholidine.

A typical preparation of the monohydrate of 1,3 dimethyl 2 methylamino 2 oxo 4,5 dihydroxy 1,3,2 diazaphospholidine is set forth in the following example.

Filtered 40% aqueous glyoxal (159 grams) was weighed into a 500 millilitre flask. The flask was equipped with a magnetic stirring bar, a thermometer and pH electrode which had been standardized against pH 7 buffer. The pH of the solution was adjusted to 7.0 with a 50% aqueous sodium hydroxide solution.

TPA (150 grams) was then added to the flask and the pH was maintained at 7.0, with stirring. The pale yellow solution was then heated slowly to 65°C with dropwise addition of sodium hydroxide to maintain the pH at 7.0 The contents were held at this temperature for 8 minutes and then quenched in ice to 25°C. The solution was still pale yellow but no solid formed until after 3 to 4 hours.

The crystals were filtered and washed with small quantities of an 80/20% tetra hydrofuran/ethanol solution and dried in a nitrogen stream. With 98 grams of product recovered, this amounted to a

42% yield based on 233 grams theory for the compound shown below:

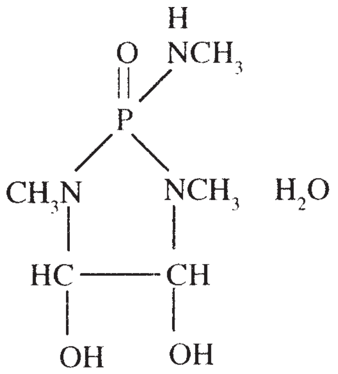
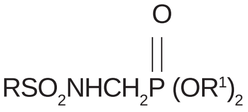


Fig. 2.5

These offwhite crystals melted at 160° to 115°C and could be recrystallized from hot water to give a snowwhite solid melting at 107° to 115°C but having substantially identical analytical data and spectra. The molecular weight of the recrystallized product was found to be 202 by vapour pressure osmometry in methanol versus a theoretical of 213. The product is soluble in water, methanol and ethanol but insoluble in tetrahydrofuran and chloroform.

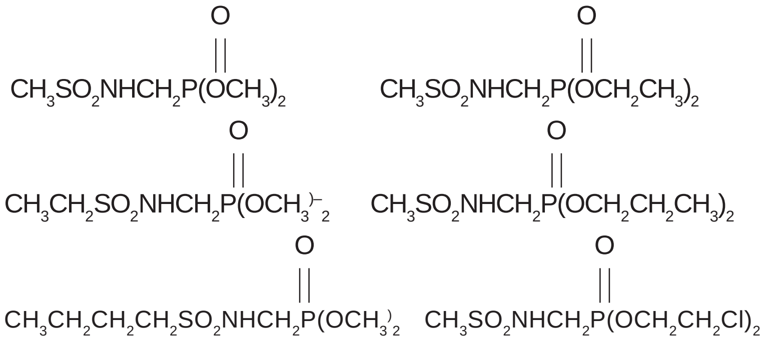
ALKYL AND ARYL SULPHONAMIDOMETHYL PHOSPHONATES



$$RSO_2NHCH_2\overset{\overset{O}{\|}}{P}\ (OR^1)_2$$

Fig. 2.6

Where R is selected from the group consisting of lower alkyl of 1 to 6 carbon atoms, phenyl and alkyl substituted phenyl and R is selected from the group consisting of phenyl, lower alkenyl and halogen substituted and unsubstituted lower alkyl of 1 to 6 carbon atoms. Illustrative examples of the process include, for instance, compounds such as:



$$CH_3SO_2NHCH_2\overset{\overset{O}{\|}}{P}(OCH_3)_2 \qquad CH_3SO_2NHCH_2\overset{\overset{O}{\|}}{P}(OCH_2CH_3)_2$$

$$CH_3CH_2SO_2NHCH_2\overset{\overset{O}{\|}}{P}(OCH_3)_2 \qquad CH_3SO_2NHCH_2\overset{\overset{O}{\|}}{P}(OCH_2CH_2CH_3)_2$$

$$CH_3CH_2CH_2CH_2SO_2NHCH_2\overset{\overset{O}{\|}}{P}(OCH_3)_2 \qquad CH_3SO_2NHCH_2\overset{\overset{O}{\|}}{P}(OCH_2CH_2Cl)_2$$

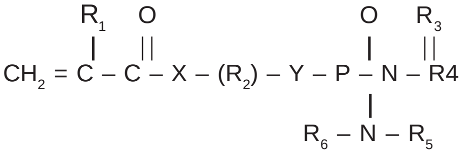
Fig. 2.7

The synthesis of the compositions of the process is accomplished by reacting an N-hydroxymethyl sulphonamide of the formula RSO_2NHCH_2OH with a trialkyl phosphite of the formula $(R'O)_3P$ where R and R' are as previously described, in a suitable solvent with an excess of the phosphite, or without solvent. Typically, the reaction is continued for about 1 to about 12 hours. Temperatures are generally about 50ºC to about 160ºC. Preferably reaction is continued from about 3 to about 6 hours at a temperature of about 80ºC to about 120ºC. The solvent or other volatiles are thereafter stripped, or otherwise removed from the product. Suitable solvents include benzene, toluene, xylene, the glymes, dimethylformamide and aliphatic or aromatic hydrocarbons. In the following example which illustrate the process, all parts and percentages are by weight unless otherwise specified.

A 1 litre flask, equipped with a mechanical stirrer, thermometer and reflux condenser, was charged with 171.2 g (1.0 mol) of p toluenesulphonamide, 30 g (1.0 mol) of paraformaldehyde and 200 ml methanol. Sodium methoxide was added to the solution to obtain a pH of 10 and thereafter the solution was refluxed for 48 hours and cooled. 150 g (1.2 mol) of trimethyl phosphite was added to the cooled reaction mixture (N hydroxymethyl p toluene sulphonamide) and, after an introduction period of about 5 minutes, a vigorous exotherm ensued causing the reaction mixture to reflux. After the exotherm had subsided the reaction solution was heated at reflux for 15 hours and then cooled to room temperature.

On standing, colourless crystals separated from the solution. The crystals were filtered off the solution and dried resulting in a yield of 179 g. A further concentration of the mother liquor, after filtration, yielded a further 40 g of crystalline material. Total yield of production was 219 g of a colourless crystalline solid analyzed as essentially pure N dimethyl phosphonomethyl p toluene sulphonamide. Elemental analyses – Calculated: C, 41.0% H. 5.5%; N. 4.8% P,10.6%. Found: C, 40.6%; H, 5.7%; N, 4.6%; P. 10.5%.

PHOSPHORUS CONTAINING ACRYLIC MONOMERS



$$CH_2 = \overset{\overset{R_1}{|}}{C} - \overset{\overset{O}{||}}{C} - X - (R_2) - Y - \underset{\underset{R_6 - N - R_5}{|}}{\overset{\overset{O}{|}}{P}} - \overset{\overset{R_3}{||}}{N} - R4$$

Fig. 2.8

where R_1 is hydrogen or methyl; R_2 is a lower substituted or unsubstituted alkylene group, R_3, R_4, R_5, and R_6 are selected from the group consisting of methyl and ethyl; X = O or -NH-; and Y = O or –NH.The flame retardant monomers defined by the general formula when graft copolymerized onto a cellulosic substrate impart flame retardancy to the resulting graft compolymerized product. With reference to the general formula, R_2 is a lower alkylene group connecting the X and Y atoms and preferably has 1 to 3 carbon atoms. This alkylene group can be substituted or unsubstituted with substituents such as halogen or other substituents that do not prevent the flame retardant ability of the monomer when grafted onto cellulosic substrates.

The grafting of a monomer of the above general formula onto a cellulosic fibre or fabric results in a permanently fire retardant cellulosic product that is capable of withstanding at least about 50 home launderings or dry cleanings. The particular method employed for grafting the monomer onto the cellulosic substrate is not critical and there are many known techniques for grafting such monomers onto cellulosic substrates.

A 4 neck 1 litre flask equipped with stirrer, condenser, pressure equalizing separatory funnel and a thermometer was charged with 500 ml dry diethyl ether; 76.5 g (0.5 mol) phosphorus oxychloride; 50.5 g (0.5 mol) dry triethylamine; and 68 g (0.5 mol) dry 2 hydroxyethyl methacrylate. During the addition of reagents, the temperature of the flask's contents was controlled in the –10º to 10ºC temperature range. After stirring the reaction mixture at room temperature for a suitable reaction time (72 hours), triethylamine hydrochloride was filtered off at an essentially quantitative yield. The filtrate was placed back into the reaction flask without isolation of the dichlorophosphatoethyl methacrylate intermediate.

The reaction flask was then charged with 101 g (1 mol) dry triethylamine and 45 g (1 mol) dry dimethylamine. The addition of the two amines was accomplished in the –10º to 10ºC range and afterwards the reaction mixture was stirred at room temperature for a suitable reaction period (72 hours). The reaction mixture was next filtered to remove the triethylamine hydrochloride byproduct and the volatile impurities; then diethyl ether was removed by distillation. Methacryloxyethylorthophosphorotetra-methyldiamidate was obtained at a yield of 60% of the theoretical for the two step reaction sequence. This is a compound of the general formula in which R_1, R_3, R_4, R_5, and R_6 all equal $-CH_3$; X and Y = O; and R_2 is $-C_2H_4$-.

HALOGENATED POLYPHOSPHONATES

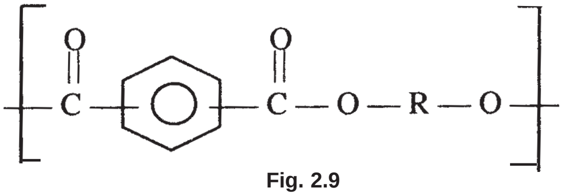


Fig. 2.9

R represents a linear or branched alkylene radical containing 2 to 6 carbon atoms. The process is characterized in that there are incorporated into these polyesters 0.5 to 40 wt %, preferably 1 to 20 wt %, based on the weight of the polyester, of a polyphosphonate possessing a plurality of units of the general formula.

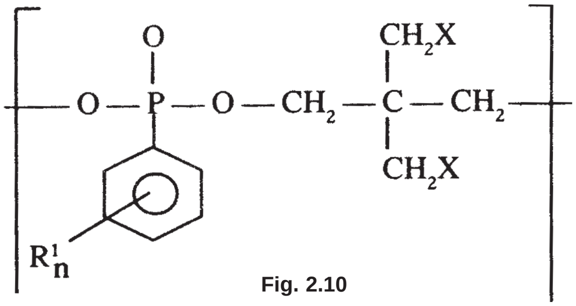


Fig. 2.10

R' represents a hydrogen atom, a halogen atom (chlorine, fluorine or bromine) or an alkyl radical containing 1 to 4 carbon atoms, e.g., methyl, ethyl, or propyl, optionally substituted by one or more halogen atoms such as chlorine or bromine; n represents an integer from 1 to 3 and X a chlorine or bromine atom.

It has been found that, in addition to their excellent capacity for flame proofing polyesters, the polyphosphonates possess the property of reducing the tendency of the polyesters to form drops when they are subjected to intense heat, and especially to a flame. Furthermore, because of their polymeric nature, the polyphosphonates do not posses the disadvantages of nonpolymeric adjuvants, such as the tendency to crystallize, to sweat or to volatilize, which manifest themselves by rapid removal of the adjuvant with consequent loss of fire resistance.

The polyphosphonates of formula can be produced by various known processes. A preferred process consists of reacting substantially equimolar amounts of an arylphosphonyl dihalide and 2,2 bis (halogenomethyl) propane 1,3 diol. This reaction can be carried out in bulk, optionally in the presence of catalytic amounts of metal salts such as $MgCl_2$ $ZnCl_2$ or $CaCl_2$, at a temperature of between 100º and 300ºC, or in solution in organic solvents such as benzene, optionally in the presence of a stoichlometric amount of a proton acceptor such as tertiary base, e.g., pyridine.

Preparation of 2,2 Bis (Bromomethyl) Propane 1,3 Diol Poly phenylphosphonate – 157.2 g (0.6 mol) of 2,2 bis (bromomethyl) propane 1,3 diol are introduced into a 1,000 cm_3 cylindrical glass reactor, equipped with a stirring system, a heating device, a dropping funnel and tube for removing the gaseous reagents, and the diol is melted by heating at 100ºC. 117 g of phenyl phosphonyl dichloride (0.6 mol) are then added dropwise with stirring over 1 hour. As soon as the addition is complete the temperature is raised gradually to 225ºC and is maintained at this temperature for 2 hours, after which it is brought back to 70ºC in order to empty the contents of flask onto a stainless steel plate; the product obtained is then left to cool to ambient temperature. The composition of this product corresponds to that of polymer consisting essentially of recurring units of the formula.

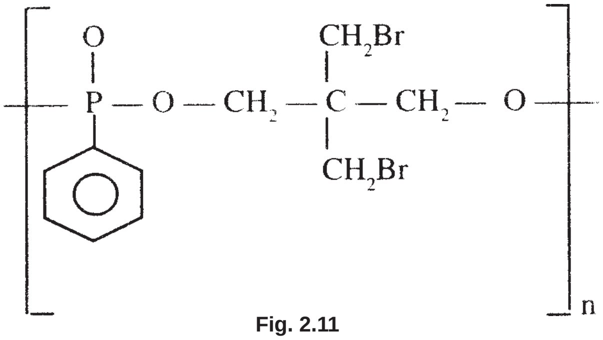


Fig. 2.11

This polymer has a softening point of 60ºC and specific viscosity of 0.2 measured at 25ºC as a 1 wt % solution in dimethylformamide. It is soluble in dimethyl formanide, dimethylacetamide, dimethylsulphoxide, N methylpyrrolidone and methanol.

DIMETHYL a, ac BIS (DIETHYL PHOSPHONO) ADIPATE (D)

This is a flame retardant as well as gives wrinkle resistance. The isomeric meso form of dimethyl a, ac dibromoadipate (100 g.0.3 mol) and triethyl phosphite (150 g. 0.9 mol) were heated at 150º to 180ºC. Nitrogen was swept through the system to facilitate the removal of ethyl bromide. The reaction mixture was heated for 3 hours, after which the evolution of ethyl bromide ceased. This occurred after collecting 90% of the theoretical amount of ethyl bromide.

The reaction mixture was fractionally distilled to give (D) (90 g. 0.2 mol); BP 192ºC (0.09 mm); and n_D^{20} 1,4572. Additional (D) can be obtained from the adjacent fractions to give a total yield of 75 to 80%. (D) solidified to a waxy white solid.

The compounds described below are durable press agents.

2,4,6 TRIS (CARBAMOYLMETHYLAMINO) 1,3,5, S TRIAZINE

2,4,6 tris (carbamoylmethylamino) 1,3,5, s triazine, referred to as TCMT, and its methylol derivatives are useful in their application to cellulosic textiles to impart wrinkle recovery. The resins are particularly useful to impart wrinkle recovery to cotton textiles or cotton and polyester blends.

TCMT is prepared by the reaction of 2,4,6 tris (carbethoxymethylamino) 1,3,5, s triazine with ammonia. This is represented by the following equation:

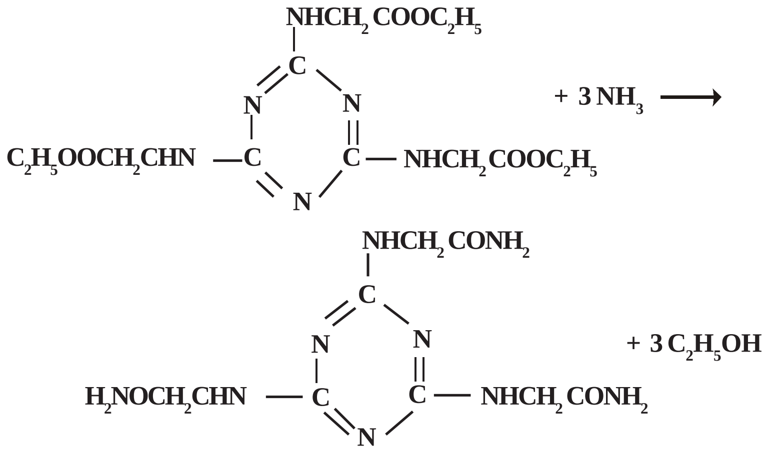


Fig. 2.12

The triazine ester in the above equation may be conveniently prepared by the reaction of cyanuric chloride with glycine ethyl easter hydrochloride in the presence of potassium carbonate. The reaction of ester may be carried out at about 20º to 30ºC for period ranging from 26 to 66 hours. It is preferable to carry out the reaction in excess aqueous ammonia because when alcoholic ammonia is used a mixture of products is obtained. It is also preferable to carry out the reaction at 27º to 29ºC for about 26 hours.

In the preparation of the methylol derivatives of TCMT, the reaction of TCMT with formaldehyde is carried out in alkaline aqueous solution by boiling until the TC MT dissolved. This requires from 2 to 5 minutes, depending on the mol ratio of TCMT to formaldehyde, the rate of heating and the quantity of solution. The mol ratio of TCMT to formaldehyde may be varied from 1:3.5 to 1:9. The preferred ratio is 1:3.5. At this mol ratio the solution consists primarily of the trimethylol derivative of TCMT.

In the application of the trimethylol derivative to textiles a latent acid catalyst is required. The catalyst may be any suitable catalyst such as $Zn(NO_3)_2$. $6H_2O$, $MgCI_2.6H_2O$. The textile is impregnated with the solution and dried at 60º to 85ºC for 3 to 7 minutes and cured at 150ºC from 3 to 5 minutes. The treated textiles have improved wrinkle recovery properties as measured by the AATCC Test Method 6-6-1968.

ANIONIC POLYURETHANE RESIN EMULSION

Anionic resinous aqueous emulsions useful for the treatment of fibre as made by reacting an isocyanate terminated urethane prepolymer with an excess of a polyalkylene polyamine to form a polyurethane urea polyamine, then reacting a part of the amino groups in the polyurethane urea polyamine with a compound selected from the group consisting of alkyl isocyanates in which the alkyl group has 12 to 22 carbon atoms and a-olefin epoxies containing 12 to 22 carbon atoms, to introduce a long chain alkyl group into the molecule, reacting the thus formed product having the remaining amino groups unreacted with a cyclic dicarboxylic acid anhydride, and mixing the resulting reaction product with an aqueous solution of a base. When the polyurethane emulsion prepared according to this process is used for the treatment of fibre containing products, it imparts to the fibrous products not only elasticity and crease resistance, but also a soft touch.

34.8 parts (0.2 mol) of 80:20 mixture of 2,4 tolylene diisocyanate and 2,6 tolylene diisocyanate and 90 parts of benzene were added to 202 parts (0.1 mol) of dehydrated polytetramethylene ether glycol (having an OH value of 55.3), and the mixture was agitated at 80ºC for 1 hour. Then, the mixture was allowed to cool in air to room temperature (18ºC to 25ºC) to obtain a solution of a urethane prepolymer having an isocyanate group content of 2.50%.

A four neck flask was charged with 250 parts of methyl ethyl ketone and 3.83 parts (0.037 mol) of diethylenetriamine, and while the temperature of the charge was maintained below 10ºC by external cooling with ice, 100 part (0.030 mol) of the above prepolymer solution was gradually added dropwise to the charge of the flask over a period of 2 hours under agitation to obtain a poly urethane urea polyamine solution.

4.44 parts (0.015 mol) of octadecyl isocyanate was added under agitation to the above polyurethane urea polyamine solution, and the temperature was elevated to 50ºC and the reaction was conducted for 30 minutes. Then, 3.62 parts (0.037 mol) of maleic anhydride dissolved in 50 parts of methyl ethyl ketone was added to the reaction mixture at a temperature lower than 10ºC under vigorous agitation over a period of times as short as possible. The temperature was gradually elevated to 60ºC over a period of about 1 hour to complete the reaction.

Then, a solution of 1.5 parts of sodium hydroxide in 600 parts of water was added to the reaction mixture to effect neutralization and they were mixed sufficiently. The solvent was removed at 60ºC under reduced pressure, and water was added to the residue to adjust the concentration. Thus, there was obtained a stable low-viscosity aqueous emulsion having a resin content of 10%.

The compounds given below are oil and water repellents and soil release finishes.

PERFLUORO TERTIARY ALKYL ETHERS

A perfluorocyclic monoether in which one of the vicinal carbon atoms is completely substituted with perfluoroalkyl radicals is decyclized in contact with hydrogen fluoride with or without the presence of a decyclization catalyst under conditions such that the cyclic ether chain is opened to produce the corresponding tertiary alcohol. The perfluorocyclic monoethers can be decyclized in the presence of catalysts, such as antimony pentafluoride, cesium fluoride, activated carbon and pyridine. The temperature conditions utilized are from about 20º to 350ºC and pressures utilized are atmospheric or substantially elevated.

The perfluorocyclic monoethers as the starting compounds of this process are designated perfluoroisoakylene oxides, 1,2 and the preferred ethers are represented by the following typical formula in which R_f is defined as a perfluoralkyl radical of less than 10 carbon atoms, preferably of 1 to 4 carbon atoms, and preferably at least one R_f is a perfluoromethyl radical. Examples of perfluorocyclic monoethers falling within the scope of the starting compounds include perfluoroisobutene oxide 1,2; perfluoro 2 methylbutene oxide 1,2; and perfluoro2 methylpentene oxide 1,2.

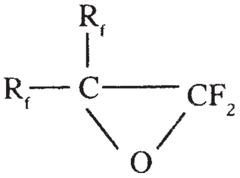


Fig. 2.13

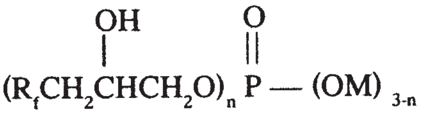
In accordance with the process the perfluoro tertiary alcohols are converted to useful organic condensation products containing a perfluoro tertiary alkyl group in which the alkyl group contains at least one, preferably at least two, perfluoro methyl groups, and the perfluoro tertiary alkyl group has not more than 20, preferably 10, carbon atoms.

The condensation products are obtained by reacting the above perfluoro tertiary alcohol with an anionogenic organic compound of not more than 20 carbon atoms (an organic compound which is normally unionized but which is capable of generating a negative ion, anion, during the condensation reaction) by heating a mixture of the same, preferably in the presence of an organic solvent or liquid reflux medium. Particular examples of condensation products of the perfluoro tertiary alcohol are the esters of organic acids (including anhydrides or acid halides) and ethers of aliphatic halides.

To 10 ml of acetone and 31 grams of 30% hydrogen peroxide at 0º to 5ºC, in a two neck, one litre glass flask with a magnetic stirrer and dry ice condenser was added 27 grams (0.135 mol) perfluorisobutene. Water, 75 ml, containing 15 grams Na_2CO_3 and 16 grams Na_2HPO_4 was added dropwise during 2 hours. Stirring was continued for an additional 20 minutes. The product was obtained 13.3 grams of product, a 46% yield. Infrared spectroscopy indicated about 95% perfluoroisobutene oxide and no olefin.

POLYFLUOROALKYL HYDROXYPROPYL PHOSPHATES

The polyfluoroalkyl hydroxypropyl phosphates are those represented by the formula:



$$(R_fCH_2\overset{\overset{\displaystyle OH}{|}}{C}HCH_2O)_n\overset{\overset{\displaystyle O}{||}}{P}—(OM)_{3-n}$$

Fig. 2.14

where R_f is a polyfluoro-alkyl group having 1 to 24 carbon atoms, n is an integer of 1 to 3 and M is a hydrogen atom, alkali metal, ammonium radical or substituted ammonium radical.

The phosphates having the above formula, when applied to fibrous materials, impart excellent sizing effect or water and/or oil repellency to the material treated therewith. It is to be noted that the phosphates are those derived from difunctional polyfluoroalkane diols and contain at least one functional alcoholic hydroxyl group in the molecule. Due to the presence of the functional alcoholic hydroxyl group the compounds display unique properties useful as sizing agents, water and/or oil repellency agents etc.

The polyfluoroalkyl hydroxypropyl phosphates, of the above formula can be prepared by various method. According to one of the preferred methods, the phosphates having the above formula in which M is a hydrogen atom can be obtained by reacting phosphoric acid with the corresponding polyfluoroalkyl propylene epoxide having the formula:

where R_f is the same as defined before. The phosphate in the first formula thus obtained in the form of free acid (M=H) is converted into a salt by neutralization with an appropriate base, if necessary.

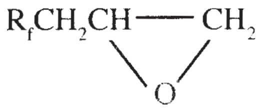


Fig. 2.15

In a 500 ml three necked flask equipped with a reflux condenser were placed 100 parts of perfluoro isononyl propylene epoxide of Formula (Fig. 2.16).

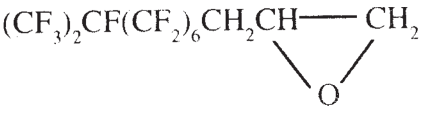


Fig. 2.16

200 parts of isopropyl alcohol and 11 parts of

orthophosphoric acid having a concentration of 85%. The mixture was heated under refluxing condition to effect esterification reaction. The reaction was terminated after 3 hours, when the epoxide was found to be completely consumed in the reaction by gas chromatography.

The resulting reaction mixture was evaporated to dryness and the residue was pulverized and washed with water repeatedly, until PO_4 was not detected in the washings, followed by drying a 30ºC in vacuo whereby 105 parts of product was obtained. The product was found to be di(3 perfluoro isononyl 2 hydroxy propyl) phosphate by elementary analysis and infrared absorption analysis.

20 parts of the phosphate thus obtained was dissolved in 80 parts of isopropyl alcohol, and 5 parts of the resulting solution was diluted with 95 parts of water to obtain 1% aqueous solution of the phosphate. Polyester/cotton blended broad cloth was dipped in the solution and squeezed to 100%. After being dried at 80ºC for 10 minutes, the cloth was heated at 150ºC for 5 minutes. No change was observed in appearance. The cloth thus treated was tested to determine water repellency and oil repellency in accordance with AATCC 22-1952 and 118-1966T respectively. The best results are as follows: water repellency, 80 and oil repellency, 6.

HYBRID TETRACOPOLYMERS BASED ON FLUOROACRYLATES

The copolymers which confer stain repellency and soil release on surfaces are obtained from (1) fluoraliphatic radical containing components in combination with (2) hydrocarbyl radical containing component, together conferring controlled oleophobicity and hydrophobicity in air, and (3) a balanced combination of hydrophilic components conferring oleophobicity in water.

A preferred group of these copolymers consists essentially, in percent by weight, of 40 to 70% fluoroaliphatic, radical containing acrylate or methacrylate, 5 to 15% lower alkyl acrylate or methacrylate and a balance of a least two hydrophilic polyoxyalkylene acrylates or methacrylates, one of which is polyoxyethylene acrylates or methacrylates amounting to 20 to 30% of the tetrapolymer and another of which is polyoxypropylene or polyoxytetramethylene acrylate of methacrylate amounting to 5 to 15% of the tetracopolymer.

A tetrapolymer of the process is prepared as follows. In a suitable size sealable container, e.g., a bottle of about 115 ml capacity, are combined 12.0 grams of N methyl perfluoro octanesulphon-amido butyl acrylate, 2.0 grams of ethyl acrylate, 4.0 grams of 40% esterified polyoxyethylene methacrylate (MW 4,000), 2.0 grams of 75% esterified polyoxytetramethylene methacrylate (MW 2,000), 20.0 grams of ethyl acetate, 0.15 gram of azobis isobutyro nitrile, and 0.4 gram of octyl mercaptan.

The bottle is flushed with nitrogen and sealed and is then agitated at 65ºC for 16 hours. The polymer solution contains 50.5% solids and is emulsified in water using approximately 0.5 gram (2.5% of polymer solids) perfluoro octanesulphonamido propyl trimethyl ammonium chloride to give an aqueous emulsion containing 15.3% solids.

VINYL ETHER REACTIVE ORGANOPOLYSILOXANE ADDITION PRODUCTS

Vinyl Ether Reactive Organopolysiloxane Addition Products give oil repellency of water repellence to fibre materials in which the fibre materials are impregnated with a liquor containing homopolymer and/or copolymer having a plurality of perfluoralkyl groups of at least 4 carbon atoms per alkyl group and as extender, an addition product of (a) an unsaturated compound which is an olefin, a vinyl or allylester of an aliphatic straight or branched chain acid, an allyl ether whose alkyl radical has at least 4 carbon atoms, and/or a vinyl halide with (b) an Organo polysiloxane which contains hydrogen atoms bonded to silicon atoms, the addition product containing on average more than 7 carbon atoms in the alkyl radical and at least 0.20 mol of unsaturated component (a) per gram atom of hydrogen in the siloxane component (b) and thereafter the impregnated fibre materials are dried and heated.

The resulting treated fibre materials have good oil and water repellency and a good handle. The homopolymers and copolymers having a plurality of perfluoro alkyl groups with at least 4 carbon aoms which can be used are know.

300 grams of methyl hydrogen polysiloxane consisting of units of the formula-$Si(HCH_3)$-O-(viscosity 30 cp. at 20ºC), 1.5 mols of vinyl isobutyl ether and 0.5 mol of vinyl octadecyl ether were mixed

in a 1 litre vessel. 125 grams of the mixture were placed in a 1 litre, three necked flask, equipped with a stirrer, thermometer, reflux condenser and supply vessel, and heated to 60º to 75ºC. After removing the source of heat, 0.3 ml of hexachloroplantinic acid solution (0.5% in isobutanol) were added to the mixture, whereupon a strongly exothermic reaction and foaming of the reaction product occurred.

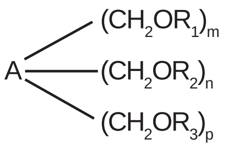
The temperature of the contents of the flask rose as a result to 170º to 180ºC. Thereafter, the remainder of the mixture was added from the supply vessel over a period of about 1 hour, during which time a temperature of 160ºC was maintained in the flask.

The mixture was then kept for another 30 minutes at 140ºC, a water jet vacuum was applied to remove residual monomers and stirring continued for another hour at this temperature. After cooling the mixture to 80ºC, 0.6 gram of an inactivator for the catalyst (propylene oxide glycerine adduct esterified with thioglycolic acid and of the molecular weight of about 4,000) was added and the flask contents cooled under vacuum to 20ºC.

A viscous, slightly cloudy light coloured product was obtained, which had viscosity of about 600 cp. (measured with measuring element 2 of the Epprecht viscosimeter) and an alkaline hydrogen cleavage of about 132 ml/g.

ALKYLENE OXIDE MODIFIED AMINOPLAST COMPOUNDS

These imparts antisoiling properties on cellulose and synthetic fabrics. The compounds have the general formula:



$$A\begin{cases}(CH_2OR_1)_m\\(CH_2OR_2)_n\\(CH_2OR_3)_p\end{cases}$$

Fig. 2.17

in which A is a radical resulting from the removal of at least 3 atoms of hydrogen replaceable by methylols on atoms of nitrogen of a compound capable of supplying aminoplasts; R_1 is either a hydrogen atom or an alkyl or acyl radical comprising less than 4 atoms of carbon; R_2 is an aliphatic alkyl or acyl radical with a long chain comprising at least 10 atoms of carbon or an alkyl radical comprising at lest 2 atoms of carbon and at least one halogen substituent; R_3 is a radical which results from the removal of a hydroxyl from the alcohol group of the addition product of 5 to 30 molecules of identical or different alkylene oxides

Table. 2.1
Ethylene Oxide Adduct Carbamates

Sl. No.	Ethylene oxide adduct -	Grams of adduct	Grams of urea	Temp ºC	Time hours	Carbamate hydroxy	Methyl carbamate
1.	Polyoxyethylene (4) lauryl alcohol	200	35.6	155	13	0.67	1.2
2.	Dioleate of polyoxyethylene (20) sorbitol	60	5.8	150	9	0.62	1.2
3.	Polyoxyethylene (15) castor oil	500	5.8	160	6	0.66	1.2
4.	Polyoxyethylene (20) tall oil	200	13.4	160	9	0.6	1.2
5.	Dioleate of polyoxyethylene (20) glycerol	106	5.3	150-160	5.5	0.69	1.2
6.	Polyoxyethylene (20) ether or lanolin	200	7.8	160	7	0.27	1.2
7.	Monopalmitate of Polyoxyethylene (20) glycerol	200	21.2	115-160	7.5	0.83	1.2
8.	Polyoxyethylene (40)-N-stearyl-12-hydroxystearamide	200	5.4	160	6.5	0.42	1.2
9.	Polyoxyethylene (20) ether of sorbitol monooleate	200	17	155-160	6.5	0.64	1.2
10.	Polyoxyethylene (30) stearic acid	200	10.4	160	4	0.51	1.2
11.	Polyoxyethylene (5) ARMEEN SD	100	26	155-165	6.5	0.83	1.2
12.	Polyoxyethylene (14) cocoamine	100	16.6	150	5.5	1	1.2
13.	Polyoxyethylene (20) sorbitan monolaurate	100	33	150	7	1	1.2
14.	Polyoxyethylene (20) sorbitan monostearate	100	27.6	150	5	0.95	1.2
15.	Dioleate of polyoxyethylene (20) sorbitol	100	15	150	7	0.8	1.2
16.	Polyoxyethylene (5) octadecylamine	100	24	150-160	12	0.6	1.2
17.	Polyoxyethylene (20) ARMEEN TD	100	19.8	155	6	0.6	1.2

18.	Polyoxyethylene (25) hydrogenated caster oil	100	8.4	155	6	0.5	1.2
19.	Polyoxyethylene (54) castor oil	100	6.6	155	7.5	0.88	1.2
20.	Polyoxyethylene (81) castor oil	100	4.5	150-165	10	0.6	1.2
21.	Polyoxyethylene (150) hydrogenated castor oil	100	3.2	155	6.5	0.75	1.2
22.	Polyoxyethylene (50) octadecylamine	100	6	150	12	0.77	1.2
23.	(3)	100	24	170-175	6.5	0.8	1.2
24.	Polyoxyethylene (25) hydrogenated castor oil	100	5.6	155	7	0.53	1.7
25.	Polyoxyethylene (25) hydrogenated castor oil	100	10.1	155	7	1	1.5

on an alcohol or an acid; and m, n and p are equal to or greater than 1.

The compounds are prepared by the usual method from the compounds $A(CH_2OR_1)_{m+n+p}$ by reacting the latter, successively with R_2OH and then R_3OH in the presence of an acid catalyst, the compounds R_2OH and R_3OH being utilized according to a number of mols corresponding respectively to n and p.

The nitrogenous product which form the radical A is preferably a product capable of supplying aminoplasts, such as for example, glycoluril, melamine, an alkyl or aryl diamino 4,6 s traizine, dicyandiamide, biuret and the like. The radical R_1 is preferably a methyl or acetyl radical, the radical R_2 is an octadecyl radical, stearoyl or perfluoro heptyl methyl and the radical R_3 represents the chain of alkylene oxides obtained by the addition of ethylene oxide, propylene oxide or a mixture of the two on methanol or ethanol.

The following compounds are **softeners and lubricants**.

FATTY, METHYLOLATED POLYOXYALKYLENE CARBAMATES

Carbamates are esters of carbamic acid, N methylol carbamic acid, or N,N dimethylol carbamic acid and an ethylene oxide adduct of a fatty acid, fatty alcohol, fatty acid ester of a polyol, fatty amine, or fatty acid amide. The carbamates contain at least one oxyethylene group, at least one fatty group, and at least one carbamate group. The carbamates are useful as textile treating agents or as intermediates for the preparation of textile treating agents. The following examples illustrate the process. All parts of percentages are by weight unless otherwise stated.

Urea and ethylene oxide adduct are charged to a three necked flask and the contents of the flask heated to the indicated temperature for the indicated length of time. The reaction product is filtered to remove any unreacted urea. The filtrate is the carbamate of the starting ethylene oxide adduct. The recovered carbamate is the mixed with a 37% aqueous solution of formaldehyde and heated to about 50ºC for 10 to 12 hr to form the methylolated carbamate.

The carbamates containing at least one methylol group may be used to treat textile material to impact thereto improved physical characteristic such as softness. It has been found that if the methylolated carbamates of the process are applied to textile material along with a textile resin catalyst for methylolated carbamate and the textile material heated to an elevated temperature, the methylolated carbamate will be attached to the fibre so that the softening properties imparted to the fabric will not be removed by subsequent washing or drycleaning.

POLYETHYLENE GLYCOL MODIFIED TRIAZINE MPOUNDS

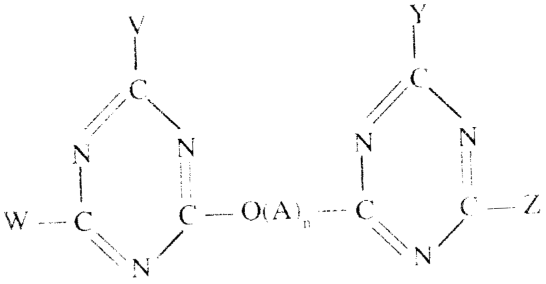


Fig. 2.18

A represents an ethenoxy; propenoxy; 1,2 or 2,3 butenoxy group or a combination thereof, V, W, Y, Z represent halogen, -OH,-NRR$_1$ or-OR$_1$ providing that at least one of V, W and at least one of Y, Z is halogen and at least one of V, W, Y, Z is –OR$_1$ or-NRR$_1$, R represents a C$_{12}$, C$_{30}$ linear or branched chain alkyl group, n = 1.80.

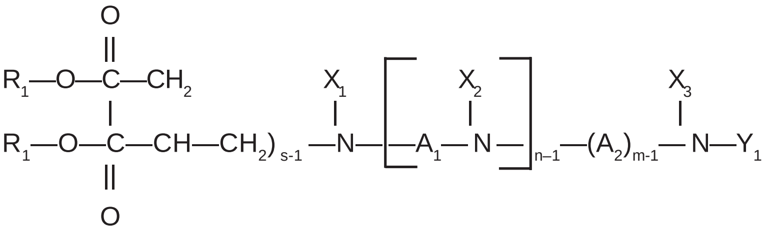
The term, O(A)$_n$, covers a polyethylene glycol, a polypropylene glycol, a polybutylene glycol residue or a copolymer residue containing any combination of ethenoxy, propenoxy or butenoxy units. The compounds of the process are prepared with the aid of a C$_2$-C$_4$ alkylene glycol, a poly (C$_2$ –C$_4$ alkylene) glycol or a derivatives which is introduced directly into each of the two triazine rings. The poly (C$_2$ – C$_4$ alkylene) glycol is preferably a polyethylene glycol having a molecular weight ranging form 600 to 1,000 or a copolymer of similar molecular weight containing propylene oxide units together with a majority of ethylene oxide units.

Preparation of Alpha, Omega Bis(Distearylamino, 6 Chloro Triazin 2 yl) Polyethylene Glycol 600 –12.2 g cyanuric chloride (0.066 mol) was dissolved in 50 ml dry acetone and the solution cooled to 5ºC in an ice water bath. 20g (0.33 mol) polyethylene glycol having an average molecular weight of 600 (referred to henceforth as polyethylene glycol 600) and 8.0 g collidine (0.006 mol) were dissolved in 50 ml dry acetone and the solution added dropwise to the cyanuric chloride sodium with stirring over a period of 2 hr.

The temperature was slowly raised to ambient, the precipitate of collidine hydrochloride was filtered off and the acetone solution was evaporated on a rotary evaporator at 30ºC. An oily liquid remained (29.0 g, 98% yield) which analyzed as: C,45%; H, 6.3%; N, 9.1%; Cl, 14.4%. The desired intermediate alpha, omega bis(4,6 dichlorotriazine 2yl) polyethylene glycol 600 requires; C,42.6%; H, 5.7%. N, 9.9% and Cl, 16.8%.

4.5 g of the above product (0.005 mol) was dissolved in 20 ml pure dry chloroform, 5.2 g distearylamine (0.01 mol) and 1.2 g collidine (0.01 mol) were dissolved in 20 ml pure dry chloroform and added dropwise with stirring over a period of 30 min at 25ºC. The reaction mixture was then stirred for 2 hr at 35 to 40ºC and the chloroform then distilled off under vacuum. 50 ml acetone was added to the residue, the insoluble collidine hydrochloride was filtered off and the acetone subsequently evaporated from the filterate. The resulting product (8.8 g, 100% yield) analyzed as: C, 69.7%; H, 10.4%; N, 6.8% and Cl 4.7%. Alpha omega bis (4 distearylamino, 6 chloro triazin 2 yl) polyethylene glycol 600 requires: C, 67.0%; H, 10.7%, N. 6.4%; and Cl, 4.0%.

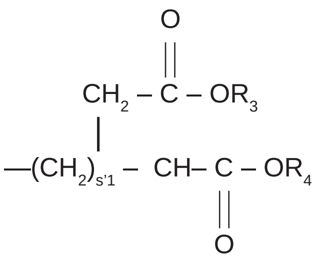
DIESTER AMINE ADDUCTS



$$\begin{array}{l} R_1{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_2 \\ \qquad\quad\;\; | \\ R_1{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH{-}CH_2)_{s-1}{-}\overset{X_1}{\overset{|}{N}}{-}\left[{-}A_1{-}\overset{X_2}{\overset{|}{N}}{-}\right]_{n-1}{-}(A_2)_{m-1}{-}\overset{X_3}{\overset{|}{N}}{-}Y_1 \end{array}$$

Fig. 2.19

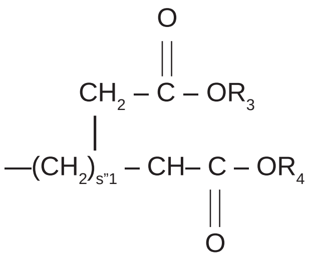
where A_1 and A_2 each denote alkylene with 2 or 3 carbon atoms or 2 hydroxy n propylene, X_1, X_2 and X_3 each denote hydrogen alkyl with 1 to 4 carbon atoms or hydroxyalkyl or hydroxyhalogenoalkyl with 2 to 4 carbon atoms or a radical of the formula,



$$-(CH_2)_{s'1}-\underset{\displaystyle CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OR_3}{\overset{|}{CH}}-\underset{\underset{\displaystyle O}{\|}}{C}-OR_4$$

Fig. 2.20

and, if n is 3 or 4, the individual X_2 radicals are identical or different, Y_1 denotes hydrogen, alkyl with 1 to 4 carbon atoms or a radical of the formula,



$$-(CH_2)_{s''1}-\underset{\displaystyle CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OR_3}{\overset{|}{CH}}-\underset{\underset{\displaystyle O}{\|}}{C}-OR_4$$

Fig. 2.21

where R_1, R_2, R_3, R_4, R_5 and R_6 each denote alkyl or alkenyl with 12 to 22 carbon, m, s, s' and s" denote 1 or 2 and n denotes 1, 2, 3 or 4, with the ratio of the diester groups to the nitrogen atoms being at most 1:1. The adducts may be in the form of the free bases, acid salts or quaternary ammonium salts and are useful as agents for imparting a soft handle to organic fibrous materials, especially textiles.

3

Commercial Textile Auxiliaries

FOREIGN

1. Shirlan

(I.C.I., LTD.)

A powder or 50% paste form of salicylanilide, insoluble in water but soluble in alkalis. Used in textile sizes and finishing compositions or may be directly applied to textile materials to prevent mildew under damp conditions.

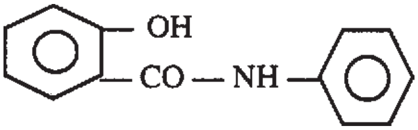


Fig. 3.1

2.Mercerol

(Sandoz Products LTD.)

Aromatic hydroxyl containing agents soluble in concentrated aqueous solutions of caustic alkalis, particularly mercerising liquros, and sold as brown coloured liquids.

Reference

B.P. 523549 279784

Mercerol (various brands with slightly differing properties) is soluble in, and much increases the penetrating power of caustic soda mercerising liquors so that it is satisfactory to mercerise without previously scouring or otherwise removing starch and natural fatty impurities from the cotton yarn and fabric: it facilities the production of high lustre goods having even-dyeing properties.

When the spent caustic soda liquors are recovered and strengthened by evaporation in vacuo it is recommended to use MERCEROL BP as it is nonvolatile.

Mercerol GS is especially recommended for the ordinary mercerisation of cotton piece goods but when cellulose rayon fibres are present, and must be protected by the addition of common salt to the mercerising liquor, it is better to use MERCEROL G or GWS.

A special feature of certain Mercerol grands, which are based on cresol, is that they are non poisonous and practically odourless.

3. Teepol

(Shell Chemicals LTD.)

The sodium salts of a mixture of higher alkyl sulphates made from olefine fractions produced by cracking selected petroleum derivatives. Sold in the form of liquid and powder or under the name of (TEEPEX) as a paste. It is distinguished from the linear type alkyl sulphates (R-O SO_3 Na) made from fatty alcohols by the branched chain in its formula where R_1 represents a short linear carbon chain and R_2 a long chain.

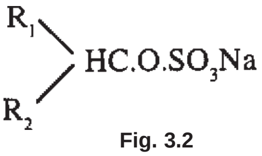


Fig. 3.2

Teepol is anion active and has good wetting out, dispersing and penetrating properties so that is suitable for use in scouring, dyeing and finishing liquors (important for wool). No insoluble lime soaps are formed in hard water and it has strong dispersing action on lime soaps present from any other source. It is compatible with most dyestuffs, the exceptions being a few basic dyestuffs.

Teepol is stable to acids, alkalis and chlorine so that it can be added to acid carbonising and to active chlorine bleaching liquors. Its scouring and grease removal properties are frequently increased by the presence of an electrolyte such as common salt. Used with Epsom and/or urea it gives a soft, full and weighted finish on cotton and cellulose rayon materials.

Teepodol is a noninflammable mixture of Teepol with a high boiling organic solvent having powerful degreasing properties. It is particularly useful as an addition to scouring liquors where heavy or persistent grease is encountered. It can also be used for prespotting grease and oil stains on fabrics.

4. Amoa Solo-Prufe

(Amoa Chemicals Co. LTD.)

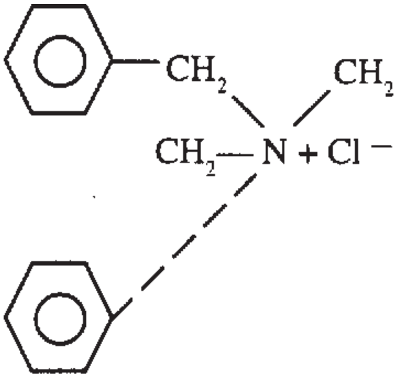
A wax emulsion containing softeners which is sold as a smooth white jelly readily soluble in hot water.

Used for waterproofing all types of textile materials by a onebath padding method followed by drying at as high a temperature as a fibre allows (up to 140ºC, for cotton and viscose rayon and up to 80ºC for silk and acetate rayon). If desired, additions of aluminium acetate or China clay or glue or mixtures of these may be added to the padding liquor to secure an increased effect or a fuller handle with additional weight.

5. Metabol O

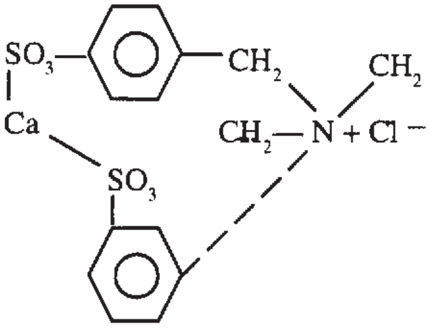
(I.C.I. LTD.)

A cream coloured powder (turns green by exposure to light and air) which is very soluble in water and consists of dimethyl phenyl benzyl ammonium chloride, being thus equivalent to Leucotrope O of I.G.



Metabol O

Fig. 3.3



Metabol WS

Fig. 3.3

Metabol O is used in producing orange discharges of indigo grounds and for resists under vat dyes in textile printing. In such discharges the Metabol O combines with the dye reduction products to give yellow orange substances fast to more influences.

Metabol WS (equivalent to Leucotrope W of I.G.) results from the sulphonation of Metabol O and is sold as a buff coloured powder very soluble in water to give solutions stable to acids, alkalis and hard water. Used to assist the production of resists under vat dyes and improved white discharges of indigo and other dyes when formaldehyde sulphoxylate discharging agents are used. In such discharges the metabol WS combines with the dye reduction products to give alkali soluble substances which can be easily washed out.

6.Mitin FF

(Geigy Co. LTD.)

A white odourless, nontoxic (to humans) powder used for mothproofing wool and having for its active component a substitute urea containing dichlorodiphenyl ether such as:

References

B.P. 547871, 547874 and 627549

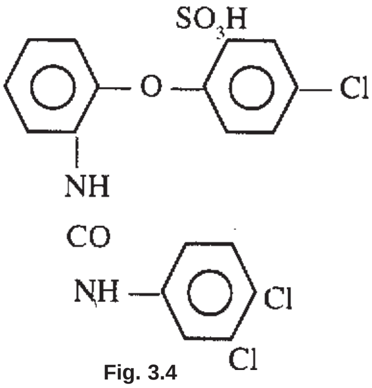


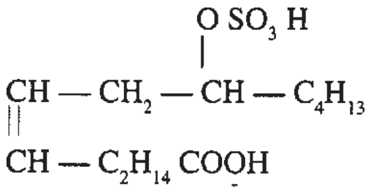
Fig. 3.4

Mitin FF is colourless acid wool dye which can be applied with other wool dyes (not basics) by the usual methods and it then gives protection to carpets, blankets and like materials against attack by moth, carpet and furriers' beetles. It is fast to most influences including washing, dry cleaning, milling, cross dyeing, carbonising, potting, sea water, perspiration, light, chlorination, and sulphur dioxide and hydrogen peroxide bleaching. Its presence in wool does not adversely affect the shade of bleached and dyed wools or harm their fastness properties.

7.Aquasols

(American Cyanamid Co.)

Light coloured oils containing 50%, 75% and 90% of highly sulphonated castor oil and useful as wetting, dispersing, and softening agents in textile processing. Allied to Turkey Red Oil.



$$\begin{array}{l} \qquad\qquad\qquad\quad O\,SO_3\,H \\ \qquad\qquad\qquad\quad | \\ CH - CH_2 - CH - C_4H_{13} \\ \| \\ CH - C_2H_{14}\,COOH \end{array}$$

Fig. 3.5

References

1. Sunder (Sealed Note No. 2595); Bul. Soc. Ind. Mulhouse, 1930, 96, 635.
2. Parks; J, Phys. Chem., 1931, 35, 488.
3. Anon; Chem. Trade J., 1925, p. 163.
4. German P., 454458.

Aquasol AR is resistant to acids and has good emulsifying power which makes it useful in degumming silk.

Aquasol M is a double sulphonated castor oil and is less resistant to acids.

Aquasol W is not resistant to acids.

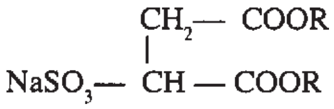
8.Aerosol OT

(and various homologues)

Formerly ALPHASOLS

(American Cyanamid Co.)

sold as pure solids, pastes or aqueous solutions (25%) and consisting of dialkyl sodium sulpho succinates



$$\begin{array}{rl} & CH_2-COOR \\ & \;| \\ NaSO_3- & CH-COOR \end{array}$$

Fig. 3.6

In Aerosol

OT, R represents 2 ethylhexyl (C_8H_{17})

MA, R represents hexyl (C_8H_{12})

AY, R represents amyl (C_8H_{17})

IB, R represents isobutyl (C_4H_8)

References

1. U.S.P., 2028091.
2. U.S.P., 2181087 and 2265944.
3. B.P. 446568.

All the Aerosols are powerful anion active wetting agents having textile applications. They differ from most other agents in being soluble (especially the OT brand) in numerous organic solvents.

Aerosol OT retains its wetting power in moderately strong alkaline liquors if soap is also present. All the Aerosols the stable in hard water. Any objectionable foaming of a liquor containing an Aerosol can be depressed by adding an aliphatic alcohol or a mineral oil or both. Aerosol OT has most all round usefulness.

9.Ammonyx BC

(onyx international U.S.A.)

Cation active alkyldimethylbenzylammonium chloride.

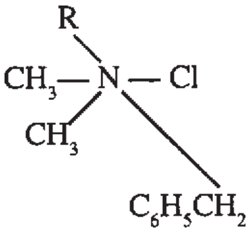


Fig. 3.7

R is a mixture of C_{12} – C_{18}

Ammonyx BC is used to soften textile materials and give direct cotton dyeings increased fastness to water.

10. Lissolamine A and V

(I.C.I. LTD.)

Lissolamines A and V, a neutral light buff powder and a slightly acid grey paste respectively.

Lissolamine A is a cetyl trimethyl ammonium bromide, and Lissolamine V is a cetyl trimethyl ammonium bromide fatty compound.

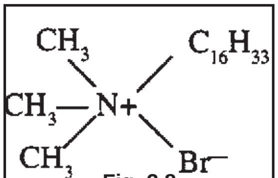


Fig. 3.8

References

1. Rowe and Owen; J. Soc. Dyers and Col., 1936, 52, 205.
2. B.P. 400239, 422466, 422556 and 444169.
3. Lawire; J. Soc. Dyers and Col., 1934, 50, 314.
4. F. P. 771349.

Lissolamines A and V are water soluble and stable in hard water and dilute acids and alkalis. They are used, in the presence of sodium hydrosulphite, to assist the stripping of insoluble azoic and vat dyeings by agglomerating the extracted dye particles and so making if difficult for them to be reabsorbed during the stripping action.

Lissolamine A is for stripping insoluble azoic dyes from cellulose fibres (in alkaline conditions) and silk (in acid conditions) and it will reduce Turkey red to white. Lissolamine V is for stripping vat dyes from cellulose fibres in alkaline conditions, but neither Lissolamine is useful for stripping vat dyes from silk. These products are also effective in stripping with oxidising agents such as active chlorine and hydrogen peroxide.

11. Nervanase and Gelatase

(Norman Events & Rais LTD.)

Nervanase, sold as an aqueous solution (Nervanase lx) or as a powder (Nervanase 3x and 10x) is a diastase or starch liquifying enzyme produced by a bacterial fermentation process. It is claimed to be superior to malt, pancreatic and mould diastases in retaining its activity at considerably higher temperatures even, for short periods at 100ºC.

Nervanase converts insoluble starch into soluble starch, dextrins, and sugars and is thus useful for preparing starch sizing compositions and for desizing all types of textiles materials without affecting their strength or colour, when more drastic processing is undesirable. Its low sensitivity to heat enables Nervanase to be used (preferably at 75ºC) in continuous desizing processes and although it can be “poisoned” it is not affected adversely by hard water or weak alkalies.

Gelatase is a protein liquefying enzyme which is used similarly to Nervanase, but for desizing textile materials containing glue, gelatine and similar substances; it is preferably employed in neutral conditions at the optimum temperature of 50ºC.

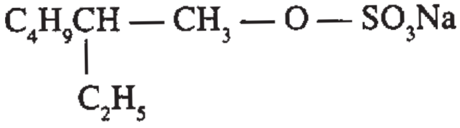
Nervanase and Gelatase can be used together when required.

12. Tergitols 08, 4 and 7

(Union Carbide International Co., U.S.A.)

The Tergitols are 25% to 40% slightly alkaline aqueous solutions of the sodium salts of sulphated long carbon branched chain alcohols and have high wetting power and excellent stability to acids, alkalis hard water, solutions of electrolytes and bleaching (oxidising) liquors. The alcohols from which they are made by sulphation are synthesised by aldol or ketol condensations followed by dehydration and reduction. Thus 2-ehtyl hexanol used for Tergitol 08 is made by condensing two molecules of butyraldehyde.

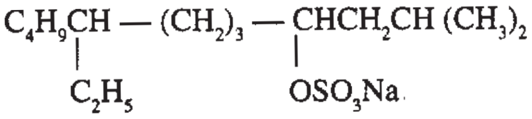
Tergitol 08, especially useful as it is effective in liquors containing more than 5% of dissolved solids and is strong acid and alkaline (mercerising) liquors is a 37% to 39% solution of sodium 2 ethylhexyl sulphate:



$$\begin{array}{l} C_4H_9\underset{\displaystyle \begin{array}{c} | \\ C_2H_5 \end{array}}{CH} - CH_3 - O - SO_3Na \end{array}$$

Fig. 3.9

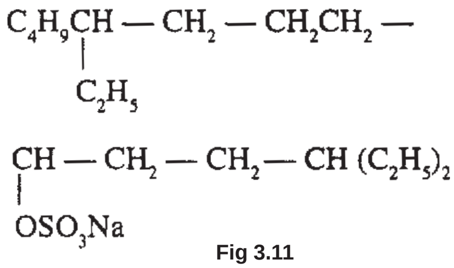
Tergitol 4, effective in liquors containing 1% to 5% of dissolved solids, particularly wool carbonising liquors, is a 24% to 26% solution of sodium 7 ethyl 2 methylundecyl 4 sulphate:



$$C_4H_9\underset{\displaystyle \begin{array}{c} | \\ C_2H_5 \end{array}}{CH} - (CH_2)_3 - \underset{\displaystyle \begin{array}{c} | \\ OSO_3Na \end{array}}{CH}CH_2CH\,(CH_3)_2$$

Fig. 3.10

Tergitol 7, most effective in liquors containing less than 1% of dissolved solids and of general utility in kiering, scouring, dyeing, hypochlorite and hydrogen peroxide bleaching, is sodium 3:9 diethyl tridecyl 6 sulphate:



$$C_4H_9\underset{\substack{|\\ C_2H_5}}{CH} - CH_2 - CH_2CH_2 -$$

$$\underset{\substack{|\\ OSO_3Na}}{CH} - CH_2 - CH_2 - CH\,(C_2H_5)_2$$

Fig 3.11

and has powerful emulsifying properties towards water insoluble, low viscosity organic liquids such as toluene, petroleum, and the chlorinated hydrocarbons including trichloroethylene.

13. Avi-Meral L24

(Produits Chimiques De La Mer-Rouge, France)

A sulphonated fatty alcohol product having a neutral reaction and consisting of sodium cetyl sulphate.

$$C_{16}\,H_{33} - O - SO_3Na$$

Fig. 3.12

Avi-Meral L24 is stable to acids and alkalis within the pH range 3 to 13 and has moderate stability in hard water. It is used as a softener in the treatment of freshly spun cellu lose rayon yarns.

14. Velan PF

(I.C.I. LTD.)

A cream coloured powder containing about 60% of cation active stearamidomethyl pyridinium chloride which partly dissolves (methylated spirit assists dissolution) in water at 40ºC to give a slightly acid opalescent viscous solution having fair stability in the cold, but precipitated by alkalis such as caustic soda, soda ash, and borax, and also by boric acid, sulphonated oils and fatty alcohols, soap, and various wetting and dispersing agents.

Velan PF is used to produce soft of soft water repellent finishes on all types of cotton, wool and rayon (not acetate rayon) textile materials by padding them with its solution (up to 1 Ib. per 100 gallons for water repellency combined with softness), drying at to 105ºC, baking for 5 to10 minutes at 120ºC, or for 1½ to 3 minutes at 150ºC, followed by thorough washing and drying. About 30% (calc. on the Velan PF) of sodium acetate should be added to the padding liquor to neutralise any free acid formed during baking and which might tender cellulose fibres.

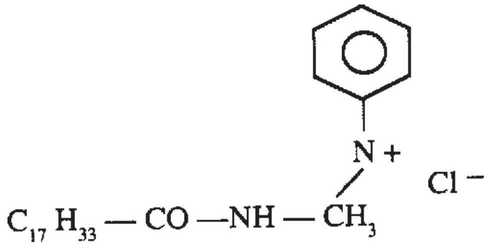


Fig. 3.13

Velan PF can be used as a softener in Epsom salt weighted finishes and in anti crease treating liquors as it is stable in such conditions. It is substantive towards cellulose and animal fibres. The soft water repellent effects are highly resistant to repeated washing and dry cleaning (faster to white spirit than to chlorinated hydrocarbons such as trichloroethylene and perchloroethylene) and the soft effects produced without baking are resistant to repeated washing.

The shade of coloured materials may be changed by Velan PF treatment, particularly if the dyes present are sensitive to acids. Wool made unshrinkable by chlorination or other means has its original softness and water repellency restored by treatment with Velan PF. Velan PF can also be used for delustring rayons in conjunction with resin dispersions such as Catalac VA (I.C.I.).

15. Nilo (Various Brands)

(Sandoz Products LTD.)

the Nilos are neutral or alkaline oils and pastes consisting of sulphonated fatty alcohols or esters which are especially useful for emulsifying oils, fats, and waxes to give aqueous emulsions for use in textile processes such as spinning, winding, sizing and finishing.

Nilo EM and EMC are similar, the EMC brand being three times more efficient than EM and especially recommended for emulsifying liquid oils and fats.

Nilo FO is for emulsifying vegetable and animal oils, fats and waxes (except castor oil and Japan wax) and is most useful in making linseed oil sizes.

Nilo MO is for emulsifying mineral oils as used for making rayon winding oils. Nile S has similar users but it usually emulsifies without then need for vigorous stirring.

Nilo T is for emulsifying vegetable and animal oils, fats and waxes, but being of it's a fatty compound it adds materially to the fat content of the resulting emulsion.

Brands specially adapted for different oils are also available. A new preparation of this kind is Nilo VO which works with ease and can be applied at exceptionally low concentrations, with a wide rang of different mineral oils.

16. Celanol A

(Consortium De Produits Chimiques Et De Synthese, France)

An amber coloured liquid containing 33% of a nonionic ether of polyethylene glylcol

$$R – O – CH_2 – CH_2(O – CH_2 – CH_2)_n – OH$$

Fig. 3.14

where R represents a fatty alcohol.

17. Nonic 218

(Sharples Chemicals Inc., U.S.A.)

A straw coloured neutral liquid containing nonionic polyethylene glycol tert dodecyl thioether.

$$C_{17}H_{33} – S – (CH_2 – CH - O)_n – CH_2 – CH_2 - OH$$

Fig. 3.15

Nonic 218,easily soluble in water and many organic solvents such as ethyl alcohol, acetone, and pyridine, and stable in hard water, is useful in textile wet processing as a powerful detergent and wetting agent. It is stable to alkalis, and has limited stability to acid and oxidising substances (for instance, hydrogen peroxide and benzoyl peroxide). In certain conditions it causes decomposition of hypochlorite bleaching liquors, but it is compatible with many anion and cation active products. The detergent action of Nonic 218 is improved by the presence of carboxymethyl cellulose or alkaline builders such as tetrasodium pyrophosphate, sodium hexametaphosphate, sodium tetraphosphate and trisodium phosphate.

Nonic 218 mixes with water and mineral oils such as kerosene and white oil to give stable gels having detergent and lubricating properties so that they may be used as “self scouring” lubricants for wool in its preparation for spinning or other manufacturing operations.

18. Resloom M-75 and HP

(Monsanto Chemical Co., U.S.A.)

Resloom M-75 and HP are water soluble melamine formaldehyde near condensed raisins and are substantially monomeric dimethylol melamine products:

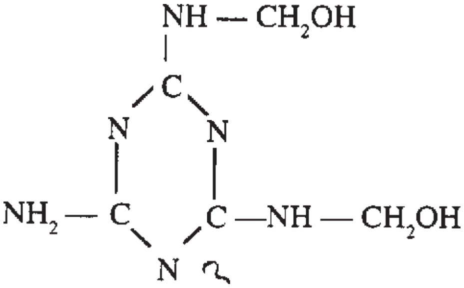


Fig 3.16

They are used for the impregnation of woolen and worsted materials followed by drying at a moderate temperature and by baking at 280ºF to 300ºF to reduce or largely eliminate the felting properties of the wool, and so give these wool materials dimensional stability (resistance to shrinkage in washing).

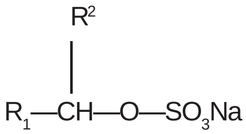
Resloom M-75 is a clear aqueous 60% resin solution and a 5% solid deposit in the wool gives a soft shrink resist finish. Resloom HP is a free flowing 100% resin powder and a 10% to 15% solid deposit in the wool gives a combined crease and shrink resist finish. An acid catalyst AC is used in applying Resloom HP. Both types of finish have excellent fastness to washing and this improved fastness may be extended to may dyes present in the wool.

Both brands of Resloom penetrate the wool material and 30% of solids may be deposited without producing a coating effect. The treated materials acquire a fuller handle and they allow various stains to be more easily removed.

19.Lenka

(Shell Chemicals LTD.)

A fairly strongly alkaline product containing the sodium salt of a higher alkyl sulphate



$$R_1{-}\overset{\overset{\displaystyle R^2}{|}}{CH}{-}O{-}SO_3Na$$

Fig 3.17

where R^1 represents a sort linear carbon chain and R^2 a long chain

and having strong detergent and wetting dispersing power so that it is useful for purifying heavily soiled cotton and other cellulose fibre materials (not wool or other protein fibres). It is useful as an addition to kier liquors where it exerts a mild bleaching action, but is not suitable for use in dye liquors. Lenka can be used for cleaning the metal part of scouring, dyeing and other machines, it is stable in hard water.

20.Rhonite 609 (and Various Brands)

(Rohm & Has Co., U.S.A.)

The Rhonite are water soluble near condensation products of urea and formaldehyde closely related to dimethylol urea which are suitable (together with an acid forming catalyst and optionally also with a softener such as TRITON K-60) for impregnating cotton, linen, and cellulose rayon piece goods (to the extent of 10%-20%) to be followed by baking for a few minutes at 140-155ºC to produce (according to the amount of Rhonite applied) resistance to creasing and shrinkage with an accompanying increase of wet strength for rayons. Coloured treated materials may have their shade and fastness properties changed. Often the fastness to washing is improved.

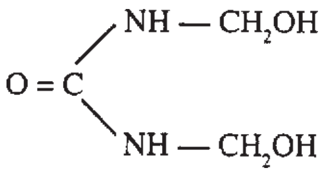


Fig 3.18

Rhonites may also be used to make starch and protein filling and weighting substances insoluble in textile materials and so make the resulting finish fast to laundering.

Rhonite 609 is a white amorphous powder which is stable when stored cool but rapidly becomes insoluble and infusible when heated.

Rhonite 610 is a 60% paste of Rhonite 609.

Rhonite 313 is a 45%-50% aqueous solution of a modified urea formaldehyde condensate. It gives a crisp full handle to fabrics treated with it and may be used with Rhonite 609 for this purpose.

Rhonite 414 is a water clear aqueous solution containing 50% of a further condensate of urea and formaldehyde which gives a full wool like handle to spun rayon materials. It is useful for insolubilising starches and may be used together with the other Rhonite.

Rhonite R-1 is a very stable clear white to pale yellow liquid containing 50% of a modified methylol urea resin which it is claimed gives an exceptional degree of dimensional stability (comparable to that produced by a formaldehyde treatment) and resistance to creasing which is more durable in repeated washing than the corresponding finishes which can be produced by use of the conventional urea and melamine formaldehyde resins. Rhonite R-1 is applied to cellulose fibre materials in the form of an impregnating liquor also containing oxalic acid or a special catalyst A to promote insolubilisation of the resin during the final baking treatment for 3to 5 minutes at 140-155ºC, and this liquor has outstanding stability. It requires 6%-10% of Rhonite R-1 to give both dimensional stability and crease resistance but only 3-4% for dimensional stability without appreciable increase of resistance to creasing.

21.Lubrol Mo

(I.C.I. LTD.)

A light brown thick oily liquid containing a fatty alcohol ethylene oxide condensation product (nonionic) which is insoluble in water but completely miscible with mineral oils.

$$R - CH_2 - O - CH_2 - CH_2 - (O - CH_2 - CH_2)_n - OH$$

Fig 3.19

where R represents a long linear chain of carbon atoms. It is useful for preparing stable aqueous emulsions of mineral oils (preferably formed in the cold) which can be employed for lubricating textile materials.

22. Gardinol WS and CS Paste

(Gardinol Chemical Co. LTD.)

Gardinol Ws, the sodium salt of sulphated lauryl alcohol (this alcohol is obtained from hydrogenated coconut oil), has strong detergent, wetting and emulsifying properties which it does not lose in contrast to similar products based on higher fatty alcohols) in cold and warm liquors. It is useful as an addition to scouring and dyeing (to promote levelling) liquors but is not compatible with basic dyes. In wool scouring, Gardinol WS $C_{12}H_{25} – O – SO_2Na$ does not cause felting but assists the subsequent washing out of any soap used. It is stable in hypochlorite bleaching liquors.

It is also valuable for wet processing and washing cellulose and cellulose acetate rayons and synthetic fibres (such as nylon) particularly at low temperatures.

Gardinol CS paste is a mixture of the sodium salts of sulphated oleyl and cetyl alcohols and has good wetting, fat solvent and emulsifying properties. It is stable to acids, alkalis and hard water and is especially useful in the wet processing of wool and wool union goods as for example in scouring and as an addition to the alkaline or acid milling processes.

$$C_{18}H_{35} – O – SO_3Na$$

Sulphated oleyl alcohol

$$C_{18}H_{35} – O – SO_3Na$$

Sulphated cetyl alcohol

Fig 3.20

Gardinol CS paste can, in acid conditions be absorbed by wool fibres and may thus brighten and lubricate them if previously robbed of their usual natural fat content.

Gardinol CS paste is also suitable for wet processing and washing cellulose and cellulose acetate rayons and synthetic fibrs, such as nylon, and for producing a soft a supple handle to the finished fabrics.

23. Glydote A

(I.C.I. LTD.)

a neutral clear colourless liquid completely miscible with water and consisting of thiodiethylene glycol

Glydote A is hygroscopic and has solvent action for vat dyes in their leuco and sulphuric acid ester states and also for basic dyes in the form of their tannic acid lakes so that it is useful as an addition to printing pasts in the application of these dyes. It assists the production of deeper shades.

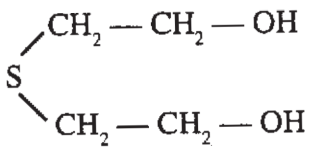


Fig 3.21

Glydote A can also be used in restoring the lustre of acetate rayon which has been previously delustred in a boiling soap liquor.

According to U.S.P. 1968926 thiodiethylene glycol gives diethylene glycol on oxidation and this

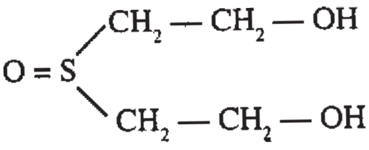


Fig 3.22

24. Igepal (Various Brands)

(General Dyestuff Corp., U.S.A.)

Igepal CA Extra, Igepal CA Extra High Conc., Igepal HC Extra High Conc. Igepal CO Extra High Conc., and Igepal CO Extra are sold as nonionic liquids having surface active properties very useful for emulsifying, wetting, dispersing and scouring in textile processing. They are aromatic polyglycol ethers conforming to the general formula

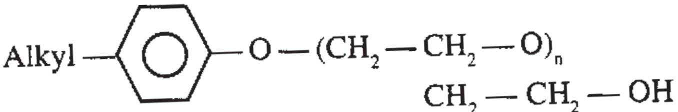


Fig. 3.23

The Igepal Co, CA and HC Types are stable to strong acid and alkalis, also to hard water and electrolytes. Igepal HC Extra High Conc., is especially effective at high temperature. Igepal CO Extra High Conc., and Igepal CO Extra Conc., are special deodourised products similar to Igepal CA Extra High Conc., and Igepal CA Extra Conc., respectively.

The nonionic character of these products allows them to be mixed with anion and cation active textile auxiliaries.

25. Lissapol C (Paste and Powder)

(I.C.I. Ltd.)

These neutral paste and powder products, readily soluble in warm water, and in hot and cold methylated spirit, pyridine, pine oil and hot cyclo hexanol, are anion active and contain as their active ingredient the sodium salt of oleyl sulphate

$$CH_3\ (CH_2)_7\ CH = CH\ (CH_2)_7\ CH_3 - O - SO_3Na$$

Fig 3.24

26. Lissatan AC

(I.C.I. LTD.)

Lissatan AC is a pale buff coloured powder which is readily soluble in water, has good wetting power, and consists of naphthalene formaldehyde sulphonic acid.

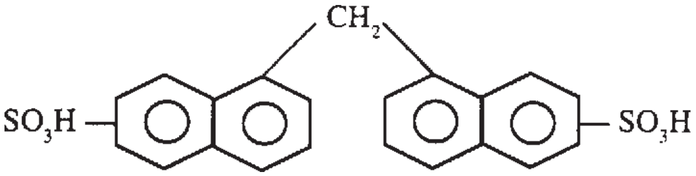


Fig 3.25

27. Textol Wax

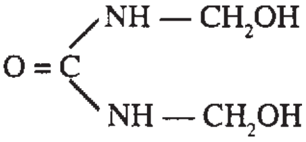
(Gardinol Chemical Co. LTD.)

Textol Wax is a neutral product consisting of a mixture of a synthetic fatty alcohol and a small proportion of an emulsifying agent so that is immediately emulsifies in water without requiring other assistance. Dilute aqueous dispersions of Textol Wax are useful in finishing textile materials (they are strengthened, and there is no risk that rancidity will develop during storage) and are especially recommended for treating flannelettes either before raising to facilitate the production of an even nap, free from fluffing, or after raising to improve their handle and appearance. It is best applied from a padding bath.

28.Formaset (Various Brands)

(Warwick Chemical Co., U.S.A.)

The Formasets are water soluble stabilised near condensation products of urea and formaldehyde closely related to methylol urea which are suitable for application (together with a catalyst) to cotton and rayon materials so that on subsequent baking ("curing") an insoluble resin is produced which gives the textile material resistance to shrinkage and also, in some instances, resistance to creasing.



$$O=C(NH-CH_2OH)_2$$

Fig 3.26

Formaset 10-D is a near condensate recommended for giving dimensional stability to cotton and rayon materials.

Formaset S is a slightly further condensate having the same uses as a Formaset 10-D, but capable of conferring a firmer handle.

29. Norane R

(Warwick Chemical Co., U.S.A.)

A water soluble long carbon chain pyridinium salt, reputed to be stearoyl methyl pyridinium chloride which by application to textile materials followed by a baking for a few minutes at a temperature exceeding 100ºC confers permanent water repellency. It is cation active.

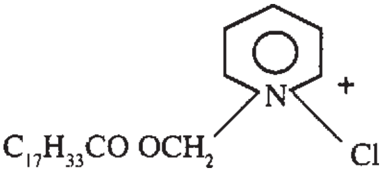
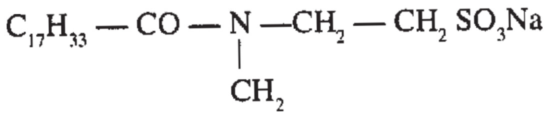


Fig. 3.27

(General Dyestuff Corp, U.S.A.)

30. Igepon T Powder, T Gel, TFS Conc.

Igepon T Powder is a neutral anion active powder containing about 32% of the sodium salt of oleyl taurate and having excellent wetting, dispersing and detergent properties which make it useful in the wet processing of textile materials, particularly in kiering and boiling off of cotton and manmade fibres. It is stable in aqueous acids, alkaline and hypochlorite (bleaching) solutions.



$$C_{17}H_{33}-CO-\underset{\displaystyle CH_2}{\underset{|}{N}}-CH_2-CH_2\,SO_3Na$$

Fig 3.28

Igepon T gel (16% active) and TFS Cons., (76% active) are additional brands of Igepon, Igepon T types have the power to disperse lime soaps in hard water.

31. Triton NE and N 100

(Rohm And Haas Co., U.S.A.)

Triton NE is a 33% aqueous solution and Triton N 100 is a 100% concentration of an aryl alkyl polyether alcohol having wetting and emulsifying properties, and which is nonionic, readily soluble in cold and somewhat less soluble in hot water. It is soluble in most organic solvents such as glycerine and alcohol, but not the aliphatic hydrocarbons.

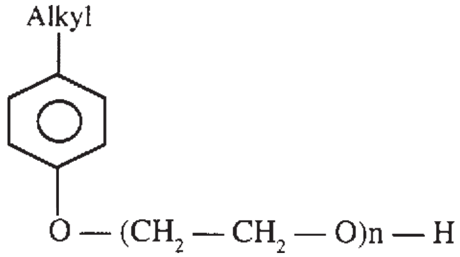


Fig 3.29

Both Triton NE and Triton N 100 are compatible with acids and bases, with anion and cation active substances, and are not precipitated by high concentrations of electrolytes. They are recommended for use in textile processing when ordinary anion and cation active auxiliaries are unsuitable and especially for use together with Triton K 60 for softening fabrics previously made crease-resistant by application of RHONITE resins.

32. Rhozyme PF

(Rohm And Haas Co., U.S.A.)

Rhozyme PF is a buff coloured, powder which is soluble in water and stable in cool dry conditions. As a proteolytic enzyme product has no adverse affect on vegetable or animal fibres, but is able to solubilise gelatin, casein, glue, and similar protein substances such as are commonly used in textile sizing compositions. It is used in desizing textile materials, particularly cellulose and acetate rayon fabrics, and is most effective within the pH range of 6.5 to 7.5 at the optimum temperature of 120ºF.

33. Triton K 60

(Rohm And Haas Co., U.S.A.)

A 25% aqueous dispersion of stearyl dimethy benzyl ammonium chloride which is cation active, and in neutral or acid solution (its activity increases as the acidity rises to pH 3.0-3.5) it acts as a powerful permanent softening agents for textile materials and for which it has substantive properties.

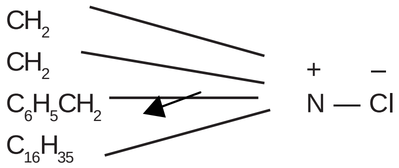


Fig 3.30

Triton K 60 is very useful for softening fabrics previously made resistant to creasing by application of Rhonite resin, as a mordant for Rhoplex resin dispersions, and for increasing the water fastness of dyeings on cellulose fibres made with direct cotton dyes. Its is not precipitated by aluminium salts or water proofing agents containing such salts.

34. Triton 770 Conc. and X-301

(Rohm And Haas Co., U.S.A.)

Triton 770 Conc., is a clear 23% solution (in aqueous isopropyl alcohol) with 30% active ingredient and Triton X-301 is a 20% paste (no isopropyl alcohol) of the sodium salt of an aryl alkyl poly ether sulphate having the following or a similar formula:

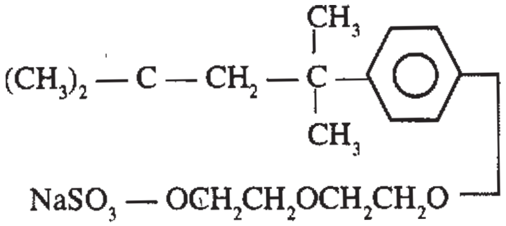


Fig 3.31

Both Triton 770 and Triton X-301 are anion active and have detergent, wetting and emulsifying properties which make them useful in all kinds of textile scouring processes. They are effective in neutral, highly alkaline, and acidic conditions and are not adversely affected by calcium, magnesium, and iron slats.

35. Rhozyme BB and C

(Rohm And Haas Co., U.S.A.)

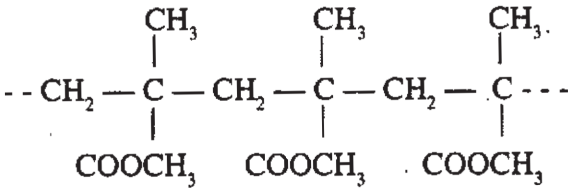
These are diastatic enzyme products useful for liquefying of solubilising starch either in the preparation of starch sizing and thickening compositions or of the desizing of textile materials. Both Rhozyme BB and C have a useful high resistance to high temperatures.

Rhozyme BB is especially recommended for converting pearl corn starches into low viscosity gums having a low sugar content and Rhozyme C is particularly designed to "convert" pearl root starches.

36. Calatac MMN and MMP

(I.C.I. LTD.)

Calatac MMN and MMP are aqueous dispersions of thermoplastic methyl methacrylate polymers which



$$\cdots CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}}\cdots$$

Fig 3.32

are useful in textile finishing to produce a fuller and crisper handle or to retard slipping of the threads in rayon and nylon goods so as to prevent fraying.

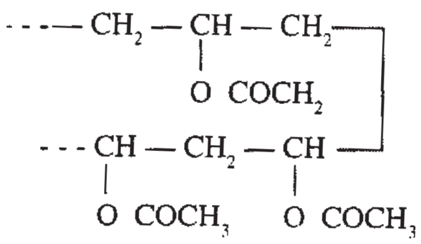
Calatac MMN is anion active and contains 33% of polymer including a plasticiser. It is stable in hard water and in moderately acid and alkaline liquors, but is unstable to high concentrations of electrolytes such as Epsom salts and aluminium and zinc salts. Calatac MMN is substantive to wool in the presence of sulphuric acid.

Calatac MMP contains 17% of polymer in the form of positively charges particles. It is unstable to anion active substances such as soaps and sulphated fatty alcohols, and is recommended for the antisnag and nonslip finishing of nylon hosiery and fabrics.

37.Calatac VA

(I.C.I. LTD.)

A 50% aqueous dispersions of a thermoplastic vinyl acetate polymer which is readily miscible with water and is stable in the presence of small amounts of acid or alkali. It is used for imparting a full stiff finish to textile fabrics, as a binder for pigments in textile printing, and (together with a cation active agent such as Velan PF) for delustring rayon materials.



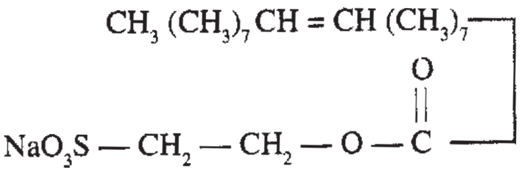
$$\cdots - CH_2 - \underset{\substack{| \\ O\ COCH_2}}{CH} - CH_2 -$$
$$\cdots \underset{\substack{| \\ O\ COCH_3}}{CH} - CH_2 - \underset{\substack{| \\ O\ COCH_3}}{CH} -$$

Fig 3.33

38.Igepon AP Extra Conc.

(General Dyestuff Corp., U.S.A.)

An anion active powder containing 85% of the sodium salt of oleyl isethionic acid having wetting and deter-gent properties useful in textile wet processing, laundering and cleaning metals.



$$CH_3\,(CH_3)_7\,CH = CH\,(CH_3)_7 -$$
$$NaO_3S - CH_2 - CH_2 - O - \overset{\substack{O \\ ||}}{C} -$$

Fig 3.34

39.Lanoc CN

(I.C.I. LTD.)

A pale cream coloured powder almost insoluble in cold but 1½ soluble in boiling water and consisting of the sodium salt of dihydroxy pentachlor triphenylmethane sulphonic acid which is used for mothproofing wool.

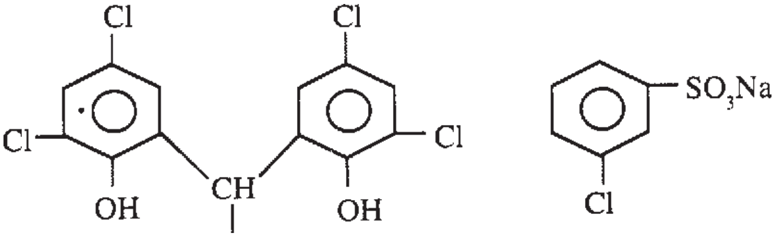


Fig 3.35

Lanoc CN may be considered as a colourless acid wool dye but can be applied by most method used for dyeing wool either separately for simultaneously with dyeing, Maximum fastness is ensured by application at the boil. It has no adverse influence on the shade and fastness properties of dyes. Being less soluble in hard water it is preferred to apply Lanoc CN using soft water.

Lanoc CN is fast to most influences including light, washing dry cleaning, rubbing stoving, chlorine, perspiration, bleaching, carbonising, decatising, chroming, and moderate milling. About 2% on the wool is required to give permanent mothproofing.

40.Alkylene B and IP

(Doittau-Produits chimiques, France)

These products are white pastes, easily soluble in water and having excellent wetting and dispersing properties. They are stable in hard water and also in alkaline and acid liquors such as are used in textile processing.

Alkylene B is the sodium salt of polybutylene naphthalene sulphonic acid:

Fig 3.36

and alkylene IP is the sodium salt of polyisopropylene naphthalene sulphonic acid:

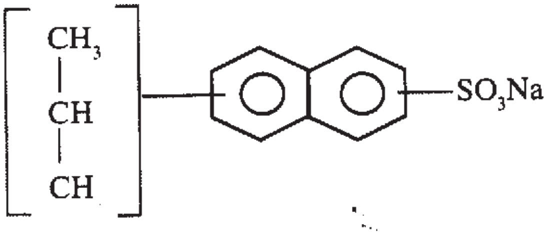


Fig 3.37

Both products exert their wetting power a high and low temperatures and are useful in all forms of textile wet processing such as scouring and dyeing cotton with all classes of dyes. They can be added to hypochlorite bleaching liquors.

41. Zelan AP Paste

(E.I. Du Pont De Nemours And Co. Inc., U.S.A.)

Zelan AP paste is a durable water repellent consisting essentially of high molecular weight nitrogen compounds such as stearamide methyl pyridinium chloride which is made by reacting stearamide with formaldehyde in the presence of hydrogen chloride and pyridine. It is used to impart water resistant or water repellent finishes to cotton, linen, viscose and cellulose acetate rayon, nylon and orion (poly acrylonitrile) fibre fabrics. Such finishes are fast to laundering and dry cleaning.

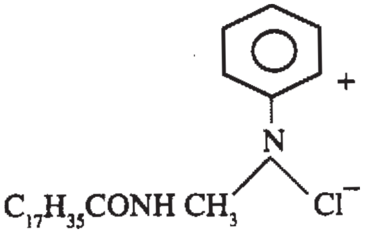


Fig 3.38

Zelan AP is applied from a water dispersion buffered with sodium acetate. The fabric is padded with the dispersion at 90ºF to 110ºF so that 2% to 6% of the product is left in the fabric (cotton require a higher concentration than the synthetic fibre materials). The padded fabric is dried at 150ºF to 325ºF, cured or heat treated for a short time at 275ºF to 400ºF, neutralised and rinsed to remove chemical byproducts, and is finally dried at 275ºF to 350ºF.

During the curing stage, the product undergoes a chemical change to form a complex substance on the fabric which repels water and which is very resistant to removal by laundering or dry cleaning. Pyridine and pyridine compounds are liberated. The nature of the reaction is complex, but it appears to be a combination of chemical reaction (etherification) with the fibre substance and physical bonding between the fibre and certain insoluble reaction products such as methylene distearamide derived from the Zelan AP. In this stage the sodium acetate neutralises any hydrochloric acid which may be formed and which otherwise would produce tendering of the fabric.

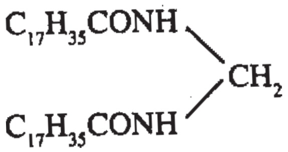


Fig 3.39

Fabrics treated with Zelan AP may afterwards be Sanforized without impairing their water repellency. The shade and light fastness properties of certain dyes are changed, but the majority of dyes, especially vat dyes, are effected only slightly or to a negligible extent. In treating white fabrics vat tinting pigments may be added (if desired) to the Zelan AP padding liquor. It is satisfactory to use Zelan AP in conjunction with certain of the thermosetting resins used for imparting crease and dimensional stabilisation.

42. Aridex L Conc. and Aridex WP Water Repellents

(E.I. Du Pont, De Nemours And Co. Inc., U.S.A.)

The Aridex products are stable, white acidic, aqueous dispersions of mixtures of wax and aluminium salts such as the acetate or formate. The are applied to textile materials by padding or exhaust methods, followed by drying at an elevated temperature in the range of 175ºF to 300ºF to give a water repellent finish. The high temperature drying serves to melt the wax components of the products which results in better coverage of the fabric and consequently better repellency.

Aridex L Conc. is preferred for application by the padding method to cotton, linen, rayon, nylon, and acrylic fibre fabrics, using a padding temperature of 140º F to 180ºF.

Aridex WP is preferred for application to wool and silk materials, preferably by means of an exhaust method using a moderately long bath at 70ºF to 110ºF. Drying of the textile at 170ºF to 250ºF develops maximum repellency.

43. Resist Salt L

(I.C.I. LTD.)

A cream coloured powder readily soluble in water to give slightly alkaline solutions stable to acids, alkalis, and hard water. It consists of the sodium salt of metra nitrobenzene sulphonic acid and possesses mild oxidising power revealed in neutral or alkaline conditions and which can be utilised in textile printing and in kiering coloured cotton goods.

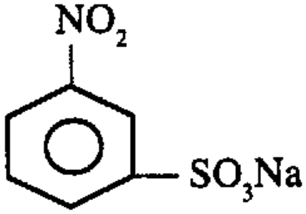


Fig 3.40

Light and medium resist effects may be obtained under vat dyes subsequently over printed using alkali and Formosul by employing Resist Salt L in the resist printing paste.

In discharge printing vat dye patterns on previously dyed fabric there is a possibility that excess of discharge paste may be transferred from the printing roller to those parts of the fabric between the printed pattern and so there make “bare” the ground shade. This can be prevented by impregnating the dyed fabric with ½% solution of Resists Salt L before printing.

By adding a small amount of Resist Salt L to the usual alkaline kier liquor bleeding of vat coloured stripes, etc., in the cotton fabric can be prevented as the sodium meta nitro benzene sulphonate oxidises those reducing impurities which are extracted from the cotton and which could otherwise solubilize the vat dye.

Vat dyed and printed fabrics which are finished with dextrine or similar reducing substances are liable to lose colour in washing and laundering treatments. This can be counteracted by adding Resist Salt L to the washing liquor.

By previous impregnation of viscose (or cotton) acetate rayon mixture fabric with Resist Salt L. or by adding this auxiliary to the priting paste (this contains caustic soda to saponify the acetate rayon and makes possible its fixation of a direct cotton dye) it is possible to print solid patterns on both fibres with azo direct cotton dyes; if the Resist Salt L is omitted the azo dye is destroyed on the cellulose fibre so that this is left uncoloured.

44. Merid T

(Societe Produits Chimiques De La Mer-Rouge-France)

A white powder completely water soluble and consisting of sodium lauryl amido N ethyl sulphate having wetting, emulsifying, softening, and especially detergent properties.

$$C_{17}H_{35} - CONH - CH_2 - CH_2 - O - SO_3Na$$

Fig 3.41

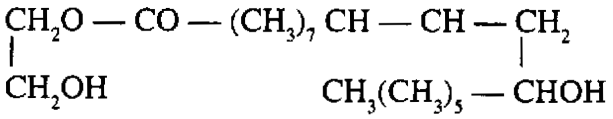
Merid T is stable in hard water and to acids and alkalis within the limits of pH 3 to 13. It is recommended for scouring greasy textile materials such as raw wool, degreasing sheepskins, scouring linen and cotton and other cellulose fibre materials, and as an addition to liquors used in dyeing, and in rinsing dyed materials. Merid T may be used for softening scoured and dyed combed wool.

45. Glycol Fatty Acid Esters (Including Diglycol Oleate S, Diglycol Stearate S, S147, S151, S152, S137, S1003, And Aldo 25)

(Glyco Products Co. Inc., U.S.A.)

These products comprise a large number of fatty acid esters made by reacting one or other of three glycols (ethylene, diethylene and propylene glycols) with equimolecular proportions of a fatty acid selected from lauric, oleic, ricinoleic, and stearic acids. They are nonionic surface active substances and are useful in textile processing on account of their wetting, emulsifying, detergent, softening and lubricating properties.

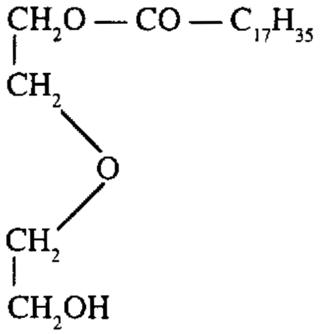
Typical chemical formulae for these three groups of glycol fatty acid esters (they represent the pure esters whereas the commercial products may be mixtures and only technically pure and in the instance of Diglycol Stearate S be modified by the presence of some free acid) are given below (See Fig on net page):-



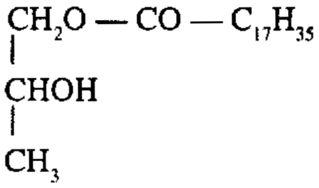
$$\begin{array}{llll} CH_2O - CO - (CH_3)_7\ CH - CH - & CH_2 \\ | & | \\ CH_2OH \quad CH_3(CH_3)_5 - & CHOH \end{array}$$

Ethylene glycol mono ricinoleate

S137



Diethylene glycol mono stearate
(Diglycol stearate S)



$$\begin{array}{l} CH_2O - CO - C_{17}H_{35} \\ | \\ CHOH \\ | \\ CH_3 \end{array}$$

Fig 3.42

The range of Glycol Fatty Acid Esters now available comprises:

Ethylene Glycol Mono laurate (S.147) – a cream-coloured semi-sold.

Ethylene Glycol Mono ricinoleate (S.152) – an amber-coloured liquid.

Ethylene Glycol Mono stearate (S.151) – a cream-coloured waxed solid.

Diethylene Glycol Mono laurate (Glaurin) – a straw-coloured liquid.

Diethylene Glycol Laurate (Diglycol Laurate S) – a straw-coloured liquid.

Diethylene Glycol Oleate (Diglylcol Laurate S) – a straw-coloured liquid.

Diethylene Glycol Stearate (Diglycol Stearate S) – a white waxy solid.

Propylene Glycol Mono laurate (S. 1003) – a yellow liquid.

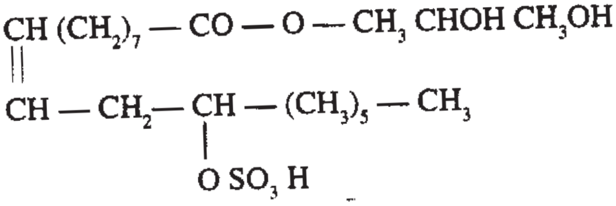
Propylene Glycol Mono stearate (Aldo 25) – a white waxy solid.

Many of these Glycol Fatty Acid Esters are soap modified to make them more easily dispersible in water. They are all in varying degree, soluble in organic solvents including methyl and ethyl alcohols acetone, toluene, and mineral and vegetable oils. They can be made into dry cleaning soaps, the used for emulsifying oils, fats, waxes, and mineral oils to yield products suitable for softening textiles in finishing and for lubricating rayon, worsted and nylon yarn, and also be used for a substitute for vegetable gums) for thickening, printing and finishing pastes. Most of these products have antifoaming properties.

46. Doittau 32 – Huile Universol R

(Doittau-Produits Chimiques, France)

A clear yellowish oil containing a high proportion of a especially sulphonated mono glyceride of ricinoleic acid



$$\begin{array}{l} CH\,(CH_2)_7-CO-O-CH_3\,CHOH\,CH_3OH \\ \| \\ CH-CH_2-\underset{\displaystyle OSO_3H}{\underset{|}{CH}}-(CH_3)_5-CH_3 \end{array}$$

Fig 3.43

Huile Universol R or Doittau 32 has good wetting and softening properties combined with a stability in hard water which is claimed as being superior to that of ordinary and related Turkey Red Oil products. It readily emulsifies oils and fats, it disperses various dyes, and has many uses in dyeing and finishing textile materials.

47. Perminal BX, WA and EML

(I.C.I. LTD.)

These products are all anion active and contain the sodium salt of an alkylated naphthalene sulphonic acid together with a colloid, (in Perminal ELM) are common salt, (in Perminal WA, which is also somewhat hygroscopic).

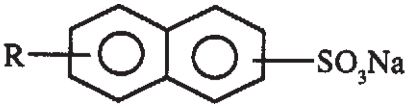


Fig 3.44

Both Perminal BX and Perminal WA are pale fawn to cream coloured powders and are wetting agents which readily dissolve in water to give slightly acid solutions which are stable to acids, dilute alkalis, and most common metal salts. They are useful in textile wet processing (for example, as additions to desizing and wool carbonising liquors) on account of their penetrating and dispersing power. In laundering, the use of Perminal WA allows destarching and washing to be effected in one stage instead of the two stage treatment otherwise necessary to remove the old starch before the wash or boil.

Perminal WA has no affinity for any textile fibre and is therefore not absorbed in textile wet processing; this makes the control of continuous processes easier.

Perminal EML is a viscous brown liquid which is easily soluble in water to give neutral solutions (not harmful to acetate rayon) which are stable to hard water, acids and alkalis. It is recommended for emulsifying vegetable oils and fats to give oil in water emulsions useful in textile finishing and for oiling raw wool in spinning operations.

48. Lissapol LS paste and powder

(I.C.I. LTD.)

A light fawn coloured paste or yellowish cream powder containing the anion active sodium oleyl para anisidine sulphonate which dissolves in water (including sea water) to give neutral solutions possessing strong wetting, detergent, and lime soap dispersing power combined with exceptional stability towards acids, alkalis, hard water and common electrolytes. It retains its detergent power in acid, neutral, and alkaline conditions, and in the presence calcium and magnesium salts but is not recommended for use in hypochlorite bleaching liquors. Lissapol LS is stable to salts such as zinc sulphate, zinc chloride, magnesium sulphate, magnesium chloride, aluminium sulphate, copper sulphate and bichromates such as may be used in textile finishing.

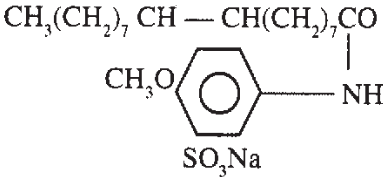


Fig 3.45

Lissapol LS is useful in washing or soaping printed fabrics and textile materials which have been dyed with azoic or vat dyes. Formation of scum due to the presence of traces of metal salts used in the dyeing or printing is thus prevented. It is very useful for scouring all kinds of wool materials including woolen yarns oiled with oleine x mineral oil or olive oil, and also wool piece goods. It is useful for improving penetration and level dyeing in dyeing wool with acid and chrome mordant dyes, cotton with direct sulphur and vat dyes, and viscose and acetate rayons.

Lissapol Ls is very stable to boiling alkalis and so can be added to the caustic soda or lime liquors used for kiering cotton piece goods.

49. Leucaphor O

(Doittau-Produits Chimiques, France)

A yellowish liquid containing a nonionic condensation product of a fatty alcohol such as lauryl or octadecyl with several molecules of ethylene oxide.

$$R - O - (CH_2 - CH_2O)n\ H$$

Fig. 3.46

where R represents a fatty alcohol residue.

Leucaphor O has strong wetting, dispersing, and emulsifying properties and readily dissolves in water to give solutions stable to moderate concentrations of acids and alkalis, to hard water, and to copper and chromium salts. When used in small amounts in vat dye liquors it assists level dyeing, but in larger amounts it retards due absorption and can be used for stripping vat dyeings.

Leucaphor O is related to Peregal O.

50. Cellofas C

(I.C.I. LTD.)

Cellofas C is a white fibrous solid which differs from Cellofas B in being insoluble in water but soluble in alkalis such as 3% to 9% aqueous solutions of caustic soda. It is used for the production of permanent, stiffened finishes in textile materials and consists of sodium carboxymethyl cellulose of the type:

$$[C_6H_9O_4 - O - CH_2COONa]_a$$

Fig 3.47

Cellofas C is available in higher and lower viscosity types, a 7% solution of the higher in 7% aqueous caustic soda has a viscosity of 40 to 80 poises and a similar solution of the power has a viscosity of 10 to 25 poises. Finished effects obtained with the lower viscosity type Cellofas C are softer but less durable than those obtained with the higher viscosity type and the higher type of Cellofas C is more generally recommended.

Cellofas C is recommended for application to textile materials, notably cotton, rayon, and linen fabrics, to secure durable laundry fast stiffened finishes accompanied by increased strength and resistance to abrasion, improved dimensional stability, greater surface smoothness, and tendency to wash whiter (due to the soil repelling power of the sodium carboxy methyl cellulose attached to the fibres). Fabrics finishsed with that Cellofas C may be bleached. In these uses it has to be remembered that Cellofas C forms insoluble salts with metals such as iron, lead, aluminium, tin and zinc.

In applying Cellofas C to fabrics to secure a stiff finish, the fabric is impregnated with an alkaline solution of Cellofas C, then run through an acid precipitating with such as 3% to 5% sulphuric acid (acetic acid gives a softer handle), followed by neutralisation of the acid and drying. Cellofas C may be applied to cotton fabric and there fixed, as part of the process of mercerisation.

4

Formulations of Textile Auxiliaries

SCOUR FORMULATIONS

Non-Solvent Formulations

Components	%			
	A	B	C	D
Water	83	81	57	60
IPA	-	-	2	5
Hexylene glycol	-	-	3	3
EDTA	2	2	3	2
Nonyl phenol	5	-	10	20
DEA	10	17	25	10
Water	80	80	70	60
IPA	5	5	5	10
Soap	-	-	15	10
Nonyl phenol	6	5	-	-
DEA	3	-	-	10
Sulfoscuccinate	6	10	10	10
Water	55	55	55	75
Butyl Cellosolve	10	10	10	5
Hexylene glycol	5	5	5	5
Phosphate ester NP-10	10	10	10	10
Nonyl phenol (EO 10)	10	-	5	-
DEA	10	10	5	5
Coconut soap	-	10	10	-

DEA: Diethanolamine

Solvent Formulations

Intermediate	Percentage
Orthodichlorobenzene	30
IPA, 10%	10
Sulphonated red oil	10
Sulphonated propyl oleate	10
Sulphonated caster oil	15
Water	25
TEA	to clear
Odourless mineral spirits	22
Orthodichlorobenzene	14
Phosphate	5
Butyl Cellosolve	5
TEA	2
Water	50
Silica flour	3
Odourless mineral spirits	80
Isopropyl amine	10
Tall oil EO adduct	8
IPA	2
Deodorized kerosene	6
Odourless mineral spirits	6
IPA	28
Water	60
Pine oil	35.0
Tall oil	9.0
IPA	6.0
Flaked potassium hydroxide	1.5

ACTIVATED BLEACH

a. Spandex/Cotton Bleach

   a. Pre-scour: Nonionic 3.00%

   Scour cold and drop. Rinse cold.

b.	Bleach: Chemic	12-15.00%

Run cold for 30 minutes. Drop. Rinse cold

c.	Antichlor: Peroxide (35%)	8.00%
	Sodium silicate	4.00%

Raise temperature to 180ºF and run for 20 minutes. Drop cold rinse

d. Optical Tinopal 4 BMA	1.25%

e. Finishing: Extract-tumble partially dr. Board at 15# psi (220ºF)

b. Scouring and Bleaching of spandex (Lycra) – Hosiery

a. Prescour (make up bath at 100-120°F)

Pine oil scour	5-8.00%
Built detergent	1-2.00%
Soda ash	1-2.00%
TSPP	1-2.00%
Sequestrant	1.00%

Raise temperature to 170ºF and run for 15 minutes. Drop. No rinse.

b.	Bleach: Chemic (12-15%) available chlorine	12.00%
	Soda ash	0.50%
	TSPP	0.50%

Run cold for 10 minutes. Raise temperatuer slowly to 115ºF. Run for 15 minutes. Drop bleach bath and give rinse for 15 minutes.

c.	Antichlor: Peroxide, 35%	6-8.00%
	TSPP	2.00%
	Built detergent	0.25%
	Sequestrant	0.25%
	Blancophor	0.25%

(Add at 120ºF)

Bring slowly to 170ºF for 20 minutes. Give warm rinse and soften.

c. Bleach on Cotton Socks

a. Scour:	Pine oil gel	5.00%
	Built detergent	2.00
	DTPA	1.00%

Heat at 80ºC for 15 minutes

d. Borax bleaching formula for Smith Drum Machine (cotton bleaching)

a. Take 100 lb dry cotton and add:

Water	220 gal
Borax	1 lb
Nonionic	½ lb
H_2O_2 (15%)	33 lb

Raise temperature to 130ºF and maintain for 10 minutes. Don't dump, but add:

Sodium silicate 43º Be	6 lb
Peroxide, 35%	½ lb
Optical dye	10 oz

Raise the temperature to near oil and maintain for 30 minutes. Drain and rinse at 180ºF for 10 minutes and then rinse with softener at 110-120ºF.

e. Tub Bleach (Hose or Piece Goods) – Cotton

a. Fill tub with water to dye level and add:

Pine oil gel	2.00%
Soda ash	1.00%

Load tub and run for 5 minutes or until wet. Add:

Chlorine	20.00%

Run cold for 5 minutes. Bring to 120ºF and run for 15 minutes. Bring to 140ºF in 30 minutes. Drop. No rinse.

b. Follow with: Peroxide	2.00%

Run for 10 minutes cold and then add:

Blancophor or Tinopal	0.50%

Bring to 180-190ºF and run for 30 minutes. Drop. Add softener. Run a 120ºF for 20 minutes.

f. One Bath Bleach for Bedspread (All percentages are OWG):

Pine oil gel	2.00%
Built detergent	1.00%
Chlorite	30.00%

Start cold and raise temperature to 120ºF for 20 minutes. Raise temperature at 180ºF and add:

Peroxide, 35%	2.50%

Run for 25 minutes at 180ºF and add:

Optical	0.50%

Run for 10 minutes. Drop. Wash

g. Activated Bleach on Cotton in Package Form (500-550 lb of Goods)

a. In bath, ad:

Solvent scour	7.5 lb
Chlorite	20.0 lb

Run at 130°F for minutes. Drop. Refill. No rinse.

b. Set second bath and add:

Silicate	15.0 lb
Peroxide, 50%	2.0 gal
Sequestering agent	2.0 lb
Caustic, flake	5.0 lb

Heat to 195ºF and run for 15 minutes. Add:

Tinopal	3.75 lb

Run for additional 1¼ hours at 195ºF. Drop to 180ºF and rinse for 10 minutes. Drop to 160ºF and rinse for 10 minutes. Drop and rinse 5 minutes in and 5 minutes out. Then add:

Acetic acid	1.0 pint

Run at 120º-130ºF for 20 minutes

STARCH SIZE

Surfactant	3.30
Calgon	0.02
CMC	0.12
Water	98.22

Water at 100ºC	
Mix. cool and add butane	5.00

STARCH SIZING

Item	Parts by weight
Starch	6.00
Borax	0.85
Formaldehyde	0.15
Polyglycol	0.50
U.V. Brightener	0.10
Water	12.50
Solvent	

DURABLE FINISH FOR COTTON AND RAYON

UF adduct	34
Polyvinyl alcohol, Medium viscosity	62
Sodium carbonate, anhydrous	4
Water	1900

It is insolubilized by heat (150ºC for 5 min)

"WASH AND WEAR" COTTON FINISH

UF adduct	140 lb
Magnesium chloride, Hexahydrate	28 lb
Nonionic wetting agent	1 lb
Water to make a 100-gal mix	

After padding the fabric is dried ideally to a moisture content of less than 5%

CREASE RESISTANT FINISH FOR COTTON

a.	Polyvinyl alcohol 50-42 (5% solution)	100.0 lb
	Wax activator	20.0 lb
	Eponite 100	100.0 lb
	40% aqueous zinc fluoborate	12.5 lb
		100.0 gal mix

Polyvinyl alcohol 50-42 (5% solution)	100.0 lb
Wax activator	20.0 lb
Surfactant	75.0 lb
50% ethylene urea-formaldehyde resin	60.0 lb
40% aqueous zinc fluroborate	13.0 lb

The cotton goods should contain less than 0.1% alkal

CREASE RESISTANT RAYON FINISH

Polyvinyl alcohol 50-42 (5% solution)	100.0 lb
Activated wax	16.0 lb
Surfactant	62.0 lb
50% ethylene urea-formaldehyde	62.0 lb
40% aqueous zinc fluoborate	11.5 lb
	100.0 gal mix

RAINPROOFING POLYESTER COTTON FINISH

4.0%	Isopropanol
1.2%	Water repellent
0.3%	Water repellent catalyst
0.3%	Acetic acid
1.0%	Cationic softener
4.5%	Cross linking resin
20.0%	Reactant for deferred cure
1.7%	Cross-linker catalyst
4.0%	Fluochemical oil/water repellent

FLAME PROOF CREASE RESISTANT FINISH

THPC	250 g/l
NaOh 100%	25 g/l
Urea	50 g/l
Polyethylene emulsion	20 g/l
Carbamate nonionic wetting agent	1 g/l
Resin, dimethylolmethoxyethyl	70 g/l

The fabrics are padded at 80ºF with this flame retardant finish, at 80% wet pick up, dried at 220ºF, then cured for 3 min a 320ºF. The fabrics are neutralized by padding at 80ºF with a solution of:

Ammonium sulphate	60g/l
Sodium bicarbonate	30 g/l
Sodium carbonate	36 g/l

Left standing for 15 min, soaped at 180ºF for another 15 min with:

	on weight of fabric
Nonionic detergent	1%
Sodium carbonate	4%
Sodium perborate	4%

and hen rinsed and dried

FLAME PROOF, SOFTENING AND ANTICREASE FINISH

Chlorinated Paraffin	362
DiOctyl Phthalate	362
2% Sodium carboxy methyl cellulose	100
Emulsifying agent	16
Water	600
Antimony oxide	364
Polyvinyl chloride latex	1500
Silicone antifoam	1

The liquor is applied to the fabric by padding, and any surplus is expressed by adjustment of the nip to give a desired wet “add-on” which is a direct function of the final dry “add-on”. The treated fabric is then dried, an cured a 120-140ºC for 2-4 min. Washing and treatment with an appropriate softening agent may then be carried out if necessary in conventional plant used for this purpose.

In special circumstances the emulsion may be applied by brush or spray. For example, the hessian backing of a carpet can be flameproofed after manufacture by spraying or brushing the emulsion on to the reverse side, subsequently drying and curing. However applied, the emulsion is absorbed by the fibres, and thus a continuous surface coating of the fibre is formed.

FLAME PROOF FINISH (COTTON)

Tetrakis hydroxymethyl phosphonium chloride	22.3
Dimethylol cyanoguanidine	12.7
Na_2HPO_4	3.0
Urea	2.0
Softener	1.0
Wetting agent	0.1
Water	58.9

Fabric treated with this formulation has approximately a 17% add-on a 75% wet pickup. A lower and higher percent add-on is obtained by changing the percent of THPC and DMCG, while maintaining a mole ratio of 1:0.75.

CRUSH RESISTANT FINISH

(100 Gallons Finished Volume)

Gum Arabic (4.7% solution, approx.)	40 lb
Cationic softener (1.9% solution, approx.)	16 lb
50% Solid urea formaldehyde (10% Solution, approx.)	80 lb
or	
80% Solids melamine formaldehyde (7% Solution, approx.)	60 lb
Suitable catalyst for resin used	

A typical formulation for imparting dimensional stability, crush-resistance, and durable hand to a light weight fabric such as shirting or dress goods consists of:

(100 Gallons Finished Volume)

Gum Arabic (1.5% to 3% solution, approx.)	12 to 25 lb
Cationic softener (1.2$ solution, approx.)	10 lb
50% Solid urea formaldehyde resin (10% solution, approx.)	80 lb
or	
80% solids melamine formaldehyde resin (7% solution, approx.)	60 lb
Suitable catalyst for resin used.	

TEXTILE SOFTENER AND WATER REPELLENT

Emulsifiable can be formulated readily into later type emulsions either by the water to wax or wax to water methods. In the water to wax method, for example, 100 kg of Wax is melted at 105ºC together with 25 kg of a nonionic emulsifying agent. After the melt has cleared, add in small portions 6 kg of a 20% KOH solution with vigorous agitation to minimize frothing. After 15 minutes add 400 litre of hot water (95-100ºC) in small portions. To complete the emulsification agitate for an additional 15 minutes at 95-100ºC, then allow to cool to room temperature while slow agitation is maintained continuously.

Strain the cooled product, and store the homogeneous colloidal emulsion in polyethylene lined containers to prevent contamination. The resultant latex emulsion will have a pale, opalescent appearance and will be free of suspended solids. A typical emulsion should be stable several months at room temperature, but should be protected from freezing. Similar emulsions may be prepared with a reduced amount of emulsifying agent if desired. While potassium hydroxide is the preferred alkali, triethanolamine may be used if an emulsion with larger particle size is required.

TEXTILE BLEACH

	Parts
Prewet at 60ºC	
Hydrogen peroxide - 50%	3.0
Sodium silicate	2.0
Caustic soda (NaOH)	0.80
Potassium perphosphate	0.50
Nonionic detergent	0.10
J-box temperature	100ºC
Saturation temperature	Room temperature
Time (min)	80
Defoamer	2-6 oz
Lubricant	0-1.5 lb

Water to:	100 gals
Draw two-thirds the amount of water	60 gal
Add sodium carbonate	3.0 lb
Heat to 80ºC	
Add polymer emulsion with agitation	80 lb
Add defoamer	2-6 oz

Thickening Dye Pastes

Acid Dye

Water	97.0
"Vialan" fast yellow CL (dye)	2.0
CMC	1.0
Sodium hydroxide, 10% sol.	q.s.

Dispersed Dye

Water	57.5
CMC	0.4
Sodium hydroxide, 10% sol.	0.9
Dispersing agent	0.95
"Celliton" fast scar;let BA extre (dye)	2.0
Mineral spirits	38.25

TEXTILE WARP SIZING

	Formula a.
Water	150 gal
Soda ash	2½ oz
1% Copper sulphate solution	50 cc
Tapioca starch	100 lb
35% Hydrogen peroxide	68.6 fl oz
Tallow	5 lb

In a copper kettle, these ingredients are added in the order given and with constant stirring. With full steam heating, the gel point (165ºF) is reached in 12 minutes and the processing temperature of 202ºF, in 18 minutes. The batch is kept a 202ºF for another 20 minutes. The initial pH of the cold slurry is 8.3 and the end pH of the cooked batch (determined on a cooled sample) is 6.5. The starch paste is used to size 22/1 warps on the slasher at 204ºF and the yarn dried to 5.25% regain. The copper content of the yarn is approximately 0.0001%.

b.	Water	150 gal
	Soda ash	5 oz
	1% Copper sulphate solution	50 cc
	Corn starch	80 lb
	35% Hydrogen peroxide	135.4 fl-oz
	Tallow	1 lb

WATERPROOFING FINISH

a.	Octadecylethylene urea	4
	Melamine	1
	Sulphated castor oil	3
	Water	92

Immerse the cloth, wring, dry, and iron to give permanent waterproofing.

a. Silicone Textile Waterproofing Emulsion

a.	Methyldichlorisilane	4 cc
	Benzol	5 cc
b	Water	166. Cc
	Sodium acetate $3H_2O$	5.5 g
c.	Water	100 cc

Mix *a* and add 2cc slowly with good mixing to b; then pass through a homogenizer and dilute with c.

Treat the cloth with this emulsion at room temperature for 5 minutes. Dry at 100ºC. Wash well with water; dry and cure 2 hours at 100ºC.

MILDEW RESISTANT AND WATERPROOFING AGENT

6% Copper naphthenate	2.5
Linseed oil	1.0
Aluminum stearate	2.0
High flash naphtha	94.5

Mix the first two ingredients. Heat slowly in a steam-jacketed kettle to 150ºF, and add the aluminum stearate with agitation. Increase the temperature to 175ºF by the time all the aluminum stearate is in. Hold at 175ºF until homogeneous.

TEXTILE SIZINGS

a. Twill suiting (2.75 yd/lb)

Corn starch	20 lb
Tapioca starch	10 lb
Avitex C	11 lb
Water	100 gal

This finish is full and pliable.

b. Filling sateen (4.40 yd/lb)

Corn starch	20 lb
White dextrin	12 lb
Avitex C	10 lb
Avitex assistant	1 lb
Water	100 gal

Schreiner calender finish.

This finish is soft and silky.

c. Printed twill suiting (2.75 yd/lb)

Tapioca Starch	50 lb
Corn Dextrin Gum	80 lb
Avitex C	18 lb
Water	100 gal

Plain calender finish.

This finish is full and pliable.

d. Printed twill suiting (2.25 yd.lb)

Tapioca Starch	25 lb
Dextrin	30 lb
Avitex C	11 lb
Water	100 gal

Pre shrunk finish.

This finish is full and pliable.

e. French Patent 810,688

Maltose	50 kg
Dextrose	35 kg
Dextrin	15 kg
Water	to suit

f. French Patent 841,162

(Non-Oxidizing Benzene Soluble)

Colza Oil	200
Rosin	800
Paraffin wax	100
Borax	10

Heat together, mixing well.

g. U.S. Patent 2,188,167

Gelatin	12½ lb
Sulphonated Olive Oil	1½ lb
Wetting and Mildewproofing Agent	
Sodium Isopropylnaphthalenesulphonate	10.0 g
Orthophenylphenol	2.2g
Water	71.5 g
Ethylene Chlorohydrin	6.0 g
Alcohol	10.0 g
Sodium salt of sulphated lauryl alcohol	½ lb
Glycol bori-borate	1 lb

h.	Gelatin	13 lb
	Triethanolamine salt of sulphated oleyl	
	Alcohol	1 lb
	Mineral oil	¼ lb
	Glyceryl bori-borate	1 lb

Rot Proofing

Textiles are impregnated with

a.	Zinc naphthenate	60.0 oz
b.	Mineral scripts	17.5 oz
c.	Emulsifying agent	2.5 oz
d.	Water	20.0 oz

a is dissolved in b and add slowly with vigorous mixing to c and d (mixed) and mixed until emulsified. The emulsion is diluted, as desired, with water before use.

CREASE PROOFING CELLULOSE ACETATE

Immerse fabric in acetic acid	25-30%
Urea	5-10%
Pyridin	5-10%
Water to make	100%

for 10-20 minutes at 20-30ºC; squeeze and dry at 20-40º; heat at 140-190ºF for 1 hour; wash and dry.

CREASE RESISTING VISCOSE CREPE

Viscose crepe is padded with a hot solution (pH 9) of

Borax	15 lb
Lactic acid	3 lb
Sulphonated cetyl alcohol	1 lb
Ammonia	1 lb
Water and stretched and dried.	80

FABRIC SIZING (AEROSOL)

CMC	2.0
Blancophor	0.2

Silicone (35%)	0.2
Sodium Benzoate: Sodium Nitrite 5:1	0.2
Total solids	2.6
Water	97.4

Crush Resistant Finish

(for rayon velvet or plushes)

Alkyl quaternary ammonium chloride	75
MF resin finish	12
Isopropanol	18
Softener	1
Water	7
Magnesium chloride $6H_2O$	15
Colour and perfume	To suit

Pad this mixture on the fabric, brush to raise the nap, and cure at 300º to 325ºF for these minutes.

Resin Treatment For “Dacron” Polyester Marquisette

	Formula 1	**Formula 2**
Methylated methylol melamine	9.9 oz/gal	-
Resin	9.9 oz/gal	9.9 oz/gal
Modified cyclic ethylene urea	4.9 oz/gal	-
Epoxy resin	-	6.8 oz/gal
Polyvinyl alcohol	0.8 oz/gal	0.8 oz/gal
Softener	1.0 oz/gal	1.0 oz/gal
Zinc fluoborate 40%	-	2.3 oz/gal

TEXTILE FABRIC FINISH (ANTICREASE WATERPROOF)

Formula 1

Hydroxethyl cellulose	1.0
Silicone emulsion (35%)	0.6
Borax	0.4
Formaldehyde	0.05
Water	97.95
Perfume	As desired

Formula 2

Dimethylol ethyleneurea (50%)	14.0
Magnesium chloride hexahydrate	2.0
Polyethylene emulsion (30%)	1.5
Water to makeup	

VAT COLOUR PRINTING PASTE

	Stock thickening	*Reduction thickening*
CMC	7 kg	5 kg
Cold water	61 litres	75 litres
Dissolved the CMC in the water, then add Rongalite	10 kg	6 kg
Potash	16 kg	10 kg
Glycerin	6 kg	4kg

About 700 grams of the stock thickening are required per kg of printing paste. This formula can be used both for roller printing and screen printing.

TEXTILE DELUSTERANT

Polyoxyethylene Laurate	180
Lecithin	90
Alcohol	20
Water	20
Acetic acid (30%)	190
Titanium dioxide	500

TEXTILE SOFTENER

Formula 1

*Nekal	4
Castor oil	30
Soft soap	20
Water	46

*Alkyl naphthalene sulphonate

Formula 2

Lecithin	500
Urea	250
Water	500

KAPOK SOFTENER

Mineral oil	10
Castor oil	4
Soda ash	1
Tallow	2
Water	100-200

NYLON YARN CONING OIL

White mineral oil	28
Diglycol laurate S	10
Polyethylene glycol	

TEXTILE PRINTING PASTE THICKENER

Formula 1

British gum	5 oz
Wheat starch	14 oz
Potassium carbonate	1¾ lb
Glycerin	¼ pt
Olive oil	¼ pt
Formosul (sodium formaldehyde sulphoxylate	1¼ lb

Water, sufficient to make 1 gallon of thickening.

The above is for thickening a strong printing paste; one suitable for a weak paste has the following composition:

Formula 2

British gum	5 oz
Wheat starch	12 oz
Potassium carbonate	8 oz
Glycerin	3/16 pt
Olive oil	3/16 pt
Formosul	6 oz

Water, sufficient to make 1 gallon of thickening

In making the printing paste itself, a mixture is made (for a strong colour) of 3 parts of the thickening and 1 part of the vat dye paste, or (for a weak colour) the strong colour paste is suitably diluted with the thickening.

SEMISTIFF COLLAR

Aqueous dispersion of polyvinyl chloride	
Resin containing 25.0% resin	71.2
Titanium dioxide pigment ground in dictyl phthalate in the ratio of 1:1	26.2
Dioctyl phthalate	2.6

FLAMEPROOF, WATERPROOF AND MILDEWPROOF COATING FOR TEXTILES PIGMENT COMPOSITION

Formula 1

Antimony oxide	12.0
Zinc oxide	1.5
Black iron oxide	1.2
Olive drab composite	15.3

Non-volatile vehicle

	Formula 1	**Formula 2**
Chlorinated paraffin wax	16.2	16.2
Polychlorphenol	1.8	1.8
Resin	10.2	-
Soft wax B	1.8	-
Nevtex 90 resin	-	11.1

Volatile Solvent

	Formula 1	**Formula 2**
Solvent	40.0	..
Xylol	..	32.0
Isopropanol	..	8.0

Resin

Polyvinylbutyral resin	10.0
Xylol	90.0

PRINTING PASTE

(Block Printing Dye)

Acid dye	310 g
British gum, powdered	325 g
Glycerin	75 g
Potassium chlorate	25 g
Sodium oxalate	130 g
Ammonium hydroxide	130 g
Water	5.1

TEXTILE DULLERS (DELUSTERANTS) FOR HOSIERY

Formula 1

Barium chloride	40
Dextrin	3
Starch	16
Hydrous aluminum sulphate	36
Anhydrous sodium acetate	5

Formula 2

Barium chloride	40
Zinc sulphate (Anhydrous)	16
Dextrin	16
Starch	14
Aluminum sulphate	14

Formula 3

Barium chloride	48.0
Starch	2.5
Aluminum sulphate	43.5
Sodium acetate (Anhydrous)	6.0

All ingredients should be powdered finely and intimately mixed

Formula 4

Sodium stannate	58.0
Sodium aluminate	8.0
Titanium dioxide	2.5

Water	18.5
Glucose	13.0

Formula 5

Sulphuric acid	4 g
Water	17 l
Bentonite	3 kg
Neutral soap	300 g
Water	2.7 l

TEXTILE SOFTENING CREAM

Stearine	20
Tallow	24
Coconut oil	16
Caustic potash (10% by weight)	18
Water	22

Melt fats, saponify with caustic potash with constant stirring by using adequate heat; dilute with water while hot. If softer consistency is desired, additional water may be used. It gives a soft finish to all kinds of textiles when used in 1-5% concentration.

This should not separate while standing overnight, and must keep its milky consistency. A gelatinous, soapy compound indicates the use of too much alkali. It must give a neutral reaction to phenolphthalein when tested cold.

For use as a softening agent soak textiles into this textile cream solution at approximately 100ºF for ½-2 hours. Thereafter the water is drained from the goods. Do not rinse. Do not rinse. Dry at moderate heat.

TEXTILE SCOURING AGENTS

Formula 1

Sulfatate	10
Sulphonated castor oil (75%)	20
Oleic acid	34
Caustic potash (30º Be)	6
Water	30

Mix sulphonated castor oil and oleic acid, add caustic solution under constant stirring. Dissolve sulfatate in water and blend together.

Formula 2

Sulphonated castor oil (75%)	13
Oleic acid	40
Caustic potash (30º Be)	7
Water	40

Blend sulphonated easter oil and oleic acid, add ½ of caustic, dissolve in water, add second half of caustic, stir well, do not heat.

Add to 2 parts of sulphonated castor oil and 1 part of sulphonated olive oil, 1 part of petroleum solvent. Mix in cold, add ammonium hydroxide (sp. gr, 0.910) until it changes to a gelatinous to a gelatinous consistency.

TEXTILE PRINTING PASTE

Ethyl cellulose	5.00
Naphtha	77.00
Ammonium oleate	12.18
Oleic acid	0.70
Water	5.12

The above is mixed 1.2 times its weight of water.

SILK PRINTING DISCHARGE

Formula 1

Stannous chloride	15
Methylated spirits	10
Urea	30
Sodium thiocyanate	5
Citric acid	1
Gum Arabic (50%) or gum tragacanth solution (10%)	2.9
Water	10

Formula 2

Stannous chloride	10
Methylated spirits	10

Sym-dimethyl urea	20
Sodium thiocyanate	5
Gum arabic thickening	55

TEXTILE PRINTING RESIST

Albumin	50
Titanium dioxide	160
Barium chloride	75
Sodium sulphate	50
Glycerin	50
Castor oil	30
Gum tragacanth solution (6%)	260
Water	325

The addition of a suitable discharging agent, such as hyposulphite, to the resistant produces white effects on coloured backgrounds.

STRIPPING DYE FROM WOOL

(per 100 lb of Wool)

Formula 1

Sulfoxite S concentrated	
(Zinc solfoxylate formaldehyde)	1½ lb
Acetic acid (28%)	5 lb

Formula 2

Sulfoxite C (Sodium sulfoxylate formaldehyde)	3 lb
Acetic acid 28%	5 lb

In either case the chemicals are dissolved in 250 gallons of water. The cloth, previously wetting-out is entered into this bath, the temperature raised gradually to the boil in ½ hour, and boiling continued for ½ hour.

STRIPPING DYED COTTON

Cotton dyed with para red is stripped by:

Glucose, or sodium sulphide	2.0
Sodium carbonate	1.0

2-Sulphonic acid	0.1

Anthraquinone at 80º in ¼ hour.

FLAMEPROOF, WATERPROOF AND MILDWPROOF TEXTILE COATING

	%
Non-volatile vehicle	29-32
Pigment and fillers	28-31
Volatile vehicle	43-37
Non-volatile vehicle:	
Chlorinated paraffin	22-24
Resin	7-8
Pigment and fillers: Antimony oxide	7-8
Calcium carbonate	8-8.5
Iron oxide	8-9
Colouring pigments	4-4.5
Mildwproofing agent	1-1

Volatile Vehicle
Ketones
Mineral spirits
Solvent
Oxylol

WATERPROOFING AGENT

Paraffin wax	3.70
Aluminum stearate	3.40
Urea-formaldehyde butanol ether	2.30
Butanol	3.90
Ethyl cellulose	0.11
Xylol	0.25
Solvent naphtha	29.80
Acetic acid	0.30
Water	To make 100.00
Basic aluminum formate	30 kg

Water, hot	60 l
Paraffin wax	20 kg
Mineral oil	10 kg
Oleic acid	3 kg

Mix until uniform

For use dilute with hot water.

ANILINE BLACK PRINTING PASTE

Yellow prussiate of potash	8 oz
Chlorate of soda crystals	5 oz
Dissolved in hot water	2 pt
And added to aniline salt	12 oz
Previously dissolved in hot water	1 pt
And stirred into starch tragaeanth thickening printing paste	5pt

VAT PRINTING COLOUR

Paste vat colour	10 lb
Glycerin, dynamite	3½ lb
Carbonate of potash	14 lb
Sodium formaldehyde sulphoxylate	7 lb
British gum thickening	7 gal

The following recipe for a colour for the brush printing of viscose rayon plush will furnish an indication of the proportions of substantive dyestuff and other ingredients used in preparing the print colours:

Diphenyl brown BBN extra	8 oz
Direct orange G	3 oz
Chrysophenine G	8 oz
British Gum (Dry)	8 oz
Glycerin	10 oz
Phosphate of soda	12 oz
Condensed water	1 gal

TEXTILE PRINTING PASTES

Wheat starch thickening

Wheat starch	12 oz
Water	6 pt
Boil and add chlorate of potash	6½ oz
When dissolved add yellow prussiate of potash	8 oz
Aniline salt	12 oz
Aniline oil	½ tumbler
Printing paste	1 gal

TEXTILE WATERPROOFING

Formula 1

Paraffin wax (M.P. 48-52ºC.)	17.0
Bone glue	2.5
Alumina	3.0
Formic acid	7.0
Rosin	0.7
Caustic potash (50º Be)	0.2
Water	To suit

Formula 2

Bleached montan wax	6.3
Paraffin wax (M.P. 48-50ºC)	6.3
Stearic acid	3.2
Formic acid	12.0
Alumina	8.0
Zirconium oxychloride	10.0
Water	to suit

Formula 3

Paraffin wax	26
Bone glue	11½
Sodium tetralinsulphonate	2

Add water to suit before use.

Organdie Finish For Textiles

Cotton lawn is impregnated with:

Polyvinyl alcohol	25

Glycerin	5
Formaldehyde	5
Ethylene chlorhydrin	1

Squeeze, dry at 105ºC and wash with a soap solution at 60ºC.

DELUSTERANT FOR TEXTILES

Water	46
Castile soap	1
High boiling petroleum hydrocarbons	14
Castor oil	1

To this is add:

Egg albumin	1
Titanium dioxide	1
Water	6

COTTON FILLING COMPOSITIONS

Formula 1

Corn starch	56 lbs
Paraffin wax emulsion	1½ gal
China clay	5 lbs
Glycerin	8 lbs
Water	100 gal
Bluing	To suit

Formula 2

Corn starch	35 lbs
Dextrin, white	12 lbs
Paraffin wax emulsion	8 lbs
Sulphonated castor oil	4 lbs
Water to make	65 gal

Fine Cotton Size

Potato starch	75 lbs
Tallow	7½ lbs
Pine oil or turkey red oil	1 lb

Water	830 lbs

Cotton Size

Wheat starch	4 lbs
Narobin	1 lb
Water	25 gal

SIZING RAYON AND SILK

Rayon and silk are sized to give firmness, elasticity and suppleness by a solution in water of

Formula 1

Stearic acid	15 gm
Glue	35 gm
Gum Arabic	8 gm
Soap	32 gm
Glycol stearate	18 gm
Borax	2 gm
Pepsin	0.15 gm

Formula 2

Lauric acid	20 gm
Gelatin	34 gm
Soap	30 gm
Gum arabic	8 gm
Ethylene glycol	6 gm
Borax	2 gm
Trypsin	0.05 gm

TALLOW EMULSION FOR TEXTILE SOFTING

Formula 1

Water	7 lbs
Soap	3 lbs
Tallow	1 lb

Formula 2

Tallow	100 lbs
Caustic potash (45%)	30 lbs

LUBRICATIONS FOR SYNTHETIC TEXTILE FIBRES

Triethanolamine oleate	1lb
Diethylene glycol	9 lbs
Fugitive colour	Trace

THREAD AND YARN LUBRICANT

Pass the thread or yarn through a bath of

Gelatin	4 gms
Dextrin	5 gms
Glycerin	2 gms
Olive oil	½-1 gms
Hexylresorcin	½ gms
Water	100 cc

Allowing the yarn to take up 5% of its weight of solid materials.

HOECHST COMPOSITION OF PRINTING PASTE

Dye	X
Urea	30-50 g
Warm water	Y
Sodium alginate (4%)	500-600g
Reduction inhibitor	10g
Total	1000

After printing with the above paste and drying, fixing treatment is carried out. (In order to prevent hydrolysis of printing paste, if paste is kept at pH 4.5-5, it can be preserved for a long time). U type or V type vats of special design are used.

Composition of fixing liquors

a.	Sodium silicate 47ºBe or	
b.	Salt	100 g/l
	Sodium carbonate	150 g/l
	Potassium carbonate	50 g/l
	Sodium hydroxide	70-100 cc/l
	Sodium silicate	10-20 g/l

Formula (Example)

Dischargeable acid dyes	X	
Glyceine A	20-30 g	After padded and dried, it is Printed with coloured resist and discharge paste
Water	Y	
Ammonium sulfate	10-20 g	
Thickening 301(10%)	30-50 g	
	1000	

Coloured resist and discharge printing (example)

Undischargeable acid and metal-containing dyes	X	
Glyecine A	20-30 g	After printed, it is steamed at 100-103ºC for 30 minutes, and then washed with water.
Water	Y	
Thickening 301 (10%)	600-650 g	
Stannous chloride	50-70 g	
	1000	

Coloured discharge printing (vat dyes) example

Vat dyes	80-159 g
Glyecine A	30 g
Decroline soluble conc.	120-160 g
Water	X
Lame crystal gum (25%)	500-600 g
]1:1	
Thickening 301 (10%)	1000

Formula for white discharge paste

Decrolin soluble conc.	150-200 g
Glyecine A	30-50 g
Zinc oxide	50 g
Fluorescent dye	10 g
Lame crystal gum (25%)	600 g
]1:1	
Thickening 301 (10%)	1000

Formula for coloured discharge paste

Dyes	X

Glyecine A	30 g
Water	Y
Decrolin soluble conc.	150-200 g
Lame crystal gum (25%)	600 g
]1:1	
Thickening 301 (10%)	1000

Printing paste with disperse dyes (example)

Disperse dyes	X	Thickener*	
Warm water	Y	Meypro gum NP	100 g
Glyecine SB	20 g	Luprintan ATP	30
Thickener*	600	Ludigol	15
Inhibitor GFN	20	Etingal A	3
(anti-gasfading agent	Water X		
	1000	1000	

Thickener*	**I**	**II**
Locust-beam gum	80-90 g	80-90 g
Etherified starch	20-10	20-10
Urea	20-50	-
Thiourea	-	2-30
Ammonium sulphate or ammonium tartarate	10-2010-20	
Water	X	X
	1000	1000

Formula for printing paste (example)

Cationic dyes	X	Thickener*	
Glyecine A (BASF)	20-30 g	Meypro gum NP	800-100 g
Acetic acid (48%)	20-30 g	Tartaric acid	10.20 g
Hot water	Y	Luprintan OFD	20-30
Thickener*	600-700 g	$NaClO_3$ (1:2)	10-20

Composition of printing paste (Example)

Printing paste	
Acidic dyes or metal complex dyes	2-50 g

Glyecine A (BASF) or Glyecine BC	20-30
Hot water	X
Thickener*	600-700

A. White discharge printing (Example)

Rongalit or Decroline	100-200
Titanium white (1:1)	30-60
Or Fluorescent whitening agent	5-10
Stock paste	500-700
Total	1000

B. Coloured discharge printing (Example: pigment)

Pigment resin colour	10-50
Binder	100-200
Reducer	X
Decrolin	100-150
Total	1000

BLOTCH PRINTING FORMULATION

Stock paste

Starch (10%)	600 g
Sodium alginate (4%)	400
Total	1000

Printing paste

Stock paste	600-700 g
Water water	X
Dyestuff (paste)	10-120
Total	1000

Reducing paste for blotch

Flashgen (7%) (Made by Nihon Denpun)	350 g
Water	X
Caustic soda (35%)	150-200 g
Hydrosulphite	50-7- g
Total	1000

VAT PRINTING PASTE

Formula 1

Corn Starch	55 lbs
Dark burnt British gum	220 lbs
Potash, calcined	220 lbs
Hydrosulphite, lumps	160 lbs
Glycerin	5 gals
Hydrocarbon oil	2 gals
Water to make	100 gals

Formula 2

Corn starch	60 lbs
Light burnt British gum	180 lbs
Potash calicined	220 lbs
Hydrosulphite, lump	160 lbs
Glycerin	5 gals
Textile gum	5 gals
Glycerin	5gals
Hydrocarbon	2 gals
Water to make	100 gals

Formula 3

Wheat starch	40 lbs
Gum Tragacanth paste (6%)	30 lbs
Glycerin	8 gals
Soda ash	160 lbs
Hydrosulphite, lumps	125 lbs
Water, to make	100 lbs

MANUFACTURE OF 'SOROMINS'

It is an emulsion made form a mixture of triethanolamine salt of the condensate product of oleic acid chloride and sarcosine, the triethanolamine salt of the condensation product of stearic chloride and sarcosine, Igepon T and water.

Triethanolamine salt of oleic sarcoside	19%
Triethanolamine salt of stearic sarcoside	14.7%
Igepon T powder	6.6%
Water	59.7%
The mixed sarcoside are prepared by reacting	0.555 mol
Proportion of oleic acid chloride plus	0.445 mol

Proportion of stearic acid chloride with sarcoside as in the preparation of medialan A (details of manufacture given earlier) and neutralizing the free acid with triethanolamine. "Soromine S" is finished at 20% fatty matter content, which corrsponds to 35% active matter content. It is applied in the dye bath and finds considerable use in the finishing of cuprammonium rayon knitted goods, hosiery. It imparts a smooth handle, is fast to rinsing and is reasonably stable to stable to hard water.

SOROMIN WF

It is an emulsion of medialan A, tallow, poly-glycerol ester, alkyl phenol condensate, 20 molecules ethylene oxide and water.

Medialan A	25%
Tallow polyglycerol	21.5%
Alkyl phenol condensate	3.75%
Water	49.75%

The tallow polyglycerol is made by heating 66.7 kg. of tallow with 27.2 kg polyglycerol at 200ºC and finally raising the temperature at 260ºC for 30 minutes to complete the reaction. Completion of the reaction is indicated by the solubility of the mixture in alcohol. Six grams of sodium hydrosulphite is generally used as a catalyst along with tallow and polyglycerol, but the reaction proceeds almost as well without it. Soromin F" is applied to the cloth in the dye bath. It imparts a very full finish and also aids levelling and penetration of the dye

"SOROMIN F"

Sod. Salt of stearic sarcosine	27.3%
Igepon T powder	7.7%
Water and a little salt	65.0%

It is applied to the fabric in the dye-bath and is used especially with light dyeing and for printed goods.

"SOROMIN DM"

Tallow polyglycerol ester	21.5%
Alkyl phenol condensate (with 20 mol. Of ethylene oxide)	3.75%
Water	74.75%

"Soromin DM" is not applied form the dye-bath but as an after treatment. It imparts an especially smooth finish and gives perhaps the fullest handle of all soromins.

WATERPROOFING AGENT

Wax emulsion containing aluminium salts

Paraffin wax (m. pt. 48-52ºC)	17.0
Glue	2.5
Aluminium oxide	3.0
Formic acid	7.0
Colophony	0.7
Caustic potash 50º Be	0.2
Water	69.6

The glue after swelling in water in dissolved by heating to 40-50ºC and the colophony dissolved in caustic potash is added to this glue solution. The solution is heated to 60-70º and the wax, previously heated to 60-70ºC is run in with vigorous stirring. Aluminium formate is made by dissolving the powdered aluminium oxide in formic acid (85%) plus water to give about a 15% solution of aluminium oxide. The wax emulsion is added with stirring to be the aluminium formate solution and the whole passed through a homogenizer.

ANTISTATIC AGENTS

		Parts
a)	Triethanolamine sebacate	1
	Triethanolamine caprate	1
	Water	100

The above composition may be applied on nylon or cellulose acetate fabrics by spraying or exhaustion technique followed by centrifuging or squeezing and drying to get antistatic effects.

b) A mixture of an ester of a carboxylic acid (molecular weight not greater than 100) and a polyglycol (molecular weight at least 200) has been recommended. The first part of the mixture may be glyceryl diacetate or ethylene glycol monomethyl ether acetic ester (CH_2-O-CH_2-CH_2-OOC-CH_2) and the second component may be polyethylene glycol or polypropylene glycol. A mutual solvent such as diethylene glycol or glycol ether is also added. A suitable composition is given below:

	Parts
Diethylene glycol	46
Diethylene glycol monoethyl ether acetic ester	34
Polyethylene glycol (molecular weight 400)	20
Distilled water	20

		Percent
c)	Polyethylene oxide wax (M.W.6000)	1
	Turkey Red Oil	7.5
	52 parts spindle oil	
	45 parts Turkey red oil	
	10 parts oleic acid partially	7.5
	Neutralised with ammonia	
	Water	8.4

The product may be applied by pad-dry technique.

SYNTHETIC TEXTILE FIBRE LUBRICANT

Mineral oil (colourless)	64.3%
Tricresyl phosphate	11.6%
Oleic acid	10.9%
Triethanolamine	5.7%
Sulphonated olive oil	5.0%
Sperm oil	2.5%

RAYON LUBRICANTS

Diethylene glycol	50 lbs
Glycerin Mono-oleate	50 lbs

COTTON SPRAYING OIL

a)	Light lubricating oil	99.5-95 oz
	Butyl acetyl ricinoleate	0.5-5 oz
b)	Mineral oil (55-sec. Saybolt)	70 parts
	Oleic acid	15 parts
	Sodium petroleum sulphonates	15 parts
c)	Mineral oil (55 sec. saybolt)	82 parts
	Oleic acid	3 parts
	Sodium petroleum sulphonates	5 parts
	Lard oil	10 parts
d)	Xylol or Toluol	15 parts
	Paraffin oil (28ºBe’)	78 parts
	Red oil	2 parts
	Alcohol	3 parts
	Caustic soda solution 27ºBe’)	1 parts
	Water	1 parts

TEXTILE SOFTENERS

a)	150 lbs.	Water, add
	180 lbs.	Castor soap oil, add
	½ gal.	Caustic soda (25º Be’), and add

80 lbs. Stearic acid, and heat up and cook slowly until the stearic acid is melted, mixing the contents meanwhile.

		lbs.
b)	Double pressed stearic acid	65
	Ammonia	10
	Formaldehyde	1
	Water	450

c) Parts

(a) Stearamide	40
stearic acid	10
(b) Ammonia (23%)	10
Water	940

Heat the mixture (a) to 80°C and add to (b) which has also been heated to 80ºC.

d) Tallow Emulsion for Textile Softening

	lbs
Water	7
(a) Soap	3
Tallow	1
(b) Tallow	100
Caustic potash (45%)	30

e) Wax Emulsion

	oz
(a) Paraffin wax	12
(b) Stearic acid	5
(c) Trigamine	3
(d) Water	80

Melt a and b at 65-70ºC and add c and d at same temperature, slowly, while mixing with a high speed agitator.

f) Coconut Oil Softener

	lbs
Coconut oil	2060
Soda ash	135
Caustic soda 39º Be	1090
Dilute to produce	9000

These products are finish off alkaline or neutral as desired and are exceptionally well suited for use in hard water or in mixes containing excessive amounts of salts, such as Epsom and others. Their excellent solubility, moreover permits of easy removal on washing when this is necessary. Coconut oil soaps almost invariably become rancid with age, although this can be retarded by complete saponification.

Softeners made from the completely neutralized fatty acids are less liable to this fault than those made from the oil itself. The great fluidity of the soap with its capacity for holding water enhances the value of this material as a softener, as well as for the lustrons sheen imparted on calendering. A shirting formula containing this oil is given below:

g)	Shirtings	
	Wheat starch	1 lb. 10 oz
	Potato starch	15 lbs
	Talc	60 lbs
	Stearic acid softener	2 lb. 8 oz
	Coconut oil softener	13 oz
h)	Nekal AEM	4 parts
	Castor oil	30 parts
	Soft soap	20 parts
	Water	46 parts
i)	Lecithin	500 parts
	Urea	250 parts
	Water	500 parts
j)	Lecithin	5-10 oz
	Cyclohexanol	50-100 oz
	Tetralin	500-1000
	Water	1000 oz
k)	Water	7 lbs
	Soap	3 lbs
	Tallow	1 lb
l)	Tallow	100 lbs
	Caustic potash (45%)	30 lbs

Glaze Paste

	kg.
Stearic acid	16
Sodium dodecyl benzene sulphonate	3
Triethanolamine	1
Water	80
	100

5

Classification of Surfactants

The textile industry uses natural and/or man-made (semi-synthetic and synthetic) textile fibres and filaments as its basic raw materials. These are subjected to various mechanical processes to convert them first into yarns and then into woven or knitted fabrics. Occasionally, these processes are aided by the physical deposition of certain chemicals in the fibre assembly, so as to facilitate the mechanical processing and/or to protect the fibre from getting damaged during such processing. Coning oils, antistatic compositions and sizing ingredients fall under this group of chemicals used for the purpose. Generally, after the fabric is made (it is known as grey cloth at this stage), all these chemicals are removed from the fabric, since they interfere with the subsequent processes, such as bleaching, dyeing, printing, finishing etc., involving physical and/or chemical processes, using a still larger number of chemicals. Thus, in the entire process of conversion of fibres into the finished fabric, ready to be introduced onto the consumer market, a wide variety of chemicals, variously known as **textile auxiliaries, textile chemicals, textile process chemicals, textile auxiliary products, speciality chemicals, etc.,** are used. The term, “textile chemicals” will be used in the following. These chemicals may be classified based on various considerations as described below:

In one, these chemicals are classified, depending on whether they are permanent or temporary, into two groups: (1) those which are used in textile processing to serve some purpose or purposes and after these purposes are served, they have to be removed from the textile material, being processed at a suitable stage of processing; and (2) those which continue to form an integral part of the textile material, being processed, by way of either chemical reaction with, or mechanical deposition of water-soluble or water-insoluble substances in the textile material and are expected to remain on, or in the textile material, more or less permanently, withstanding the subsequent rigorous action of varying degree, exerted on the end-products during their use by the consumers. These two classes may be called temporary and permanent textile chemicals respectively. The temporary textile chemicals may be defined as those which are helpers or assistants and are additives to the usual processing solutions used in scouring, bleaching, dyeing, after-treating, finishing, etc., for improving the efficiency of the process and/or the effect obtained on the textile material being processed. Thus, under the category of temporary textile auxiliaries is included a variety of products, having diverse properties. **Detergents**, used in kier-boiling or scouring of cotton fabrics, and **wetting agents** used in the mercerising liquors, especially in the mercerisation of grey cloth help caustic soda to come into intimate contact with the cotton fibres by efficient wetting and penetration of the liquors into the fabric to bring about either the saponification of the fatty matter present in the fibres or on the warp yarn (kier-boiling), or swelling and subsequent merceristion of the fabric (mercerising). After these processes are carried out, the detergent and the wetting agents are removed from the fabric, along with the caustic soda used, and the impurities removed from the fabric. **Levelling agents or retarding agents** used in dyeing acid dyes on nylon, or normal dyeing (In class of) vat dyes on cotton, or **carriers** and **dispersing agents** used in the dyeing of polyester fibres wiyh disperse dyes, and **solution aids** used in dissolving sparingly soluble dyes in printing pastes, which normally contain a small amount of water, are some examples of temporary textile chemicals. Their presence in the processing media (dye solutions or printing pastes) is absolutely necessary from the point of view of obtaining level shades, good depth and optimum colour value in dyeing and printing.

Textile chemicals belonging to the second group, the permanent ones, are usually found in finishing processes. Thus softeners, water proofing and water repelling agents, crease resists finishing agents, flame retardants, rot proofing agents, antistatic agents, binders and fixers used in pigment printing and dye-fixing agents are some examples of types of products falling in this group of textile chemicals. In this group, we find that some are semi-permanent and some permanent. Deposition of water-insoluble chemicals to impart a particular finishing effect is the basis of the use of semi-permanent textile chemicals, while chemical reaction with the fibre substances forms the basis of producing permanent or durable effects in textiles. In these cases emphasis is laid on the production of finishes, which last 25 or 50 home launderings or repeated dry cleanings.

In another method of classification, the textile chemicals may be divided into essentially three groups:

(A) surface active compounds and their formulations which are also surface active,

(B) non-surface active compounds and their formulations, and

(C) water insoluble solids or water immisicible liquids, which are dispersed or emulsified in water with the help of small amounts of (surface active or non-surface active) dispersing agents or emulsifies respectively.

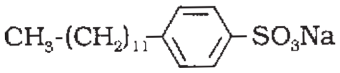
(A)SURFACE ACTIVE AGENTS

A surface active agents or surfactant is one: (1) which has balanced solubility in water and in oil, (2) which preferentially gets oriented at the interface between air and water, in which it is dissolved, and (3) which lowers the surface tension of water substantially, when dissolved in it in the concentration range 0.1-10 g/l at the room temperature (27º-30ºC). Since all the surface active agents belonging to textile chemicals are based on organic compounds such as alkyl benzenes, fatty acids, fatty alcohols, fatty amines, esters, ethers, amides, formaldehyde condensates etc., these surface active agents may be called organic surface active agents (OSA).

Usually a surface active agent consists of two parts within one molecule. One part is hydrophilic, and the other, hydrophobic. The hydrophilic part is generally hydroxyl, carboxyl, sulphonated, sulphate, phosphate etc. and the hydrophobic part is a long aliphatic chain or alkaryl chain. When the acid groups (-COOH, -SO_3H, -OSO_3H etc.) are neutralised with an alkali like sodium hydroxide, the corresponding ionisable groups (-COONa, - SO_3Na etc.) are formed and the solubility in water increases considerably. On the other hand the hydrophobic nature of aliphatic chain increases as the number of carbon atoms increases.

Other solubilising groups also confer surface activity on aliphatic groups when attached to them. Some of the resulting compounds are shown below:

$$CH_3\text{-}(CH_2)_{11}\text{-}OSO_3Na$$



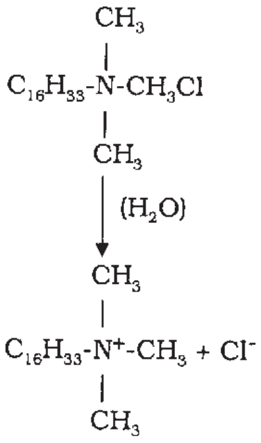
When dissolved in water, these ionise into long anions and small sodium cations:

$$CH_3\text{-}(CH_2)_{11}\text{-}OSO_3Na$$

$$\Big\downarrow (H_2O)$$

$$CH_3\text{-}(CH_2)_{11}\text{-}OSO_3^- + Na^+$$

Such compounds are called anionic surfactants. In contrast, there are cationic surfactants, such dissolved in water to give long cations and small anions. Thus cetyl trimethyl ammonium chloride ionises as follows:



$$C_{16}H_{33}\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}\text{-}CH_3Cl \xrightarrow{(H_2O)} C_{16}H_{33}\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}\text{-}CH_3 + Cl^-$$

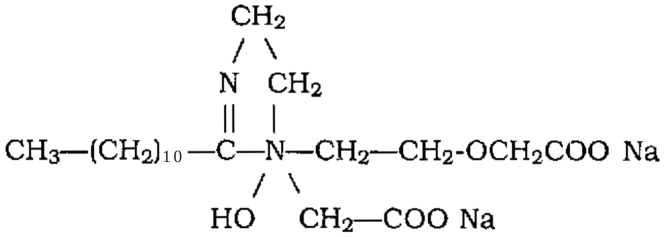
AMPHOTERIC SURFACTANTS

Then there are amphoteric surface active agents, which when dissolved in water ionise and produce large segments carrying both anionic and cationic charges (these segments are called zwitterions).

Thus aminocarboxylic acids, in which amino and carboxylic acid groups are situated at the molecular chain ends, dissolve in water to give zwitterions:

$$H_2N - (CH_2)_n\ COOH \xrightarrow{(H_2O)} H_3N^+\ (CH_2)_n - COO^-$$

The following is another example



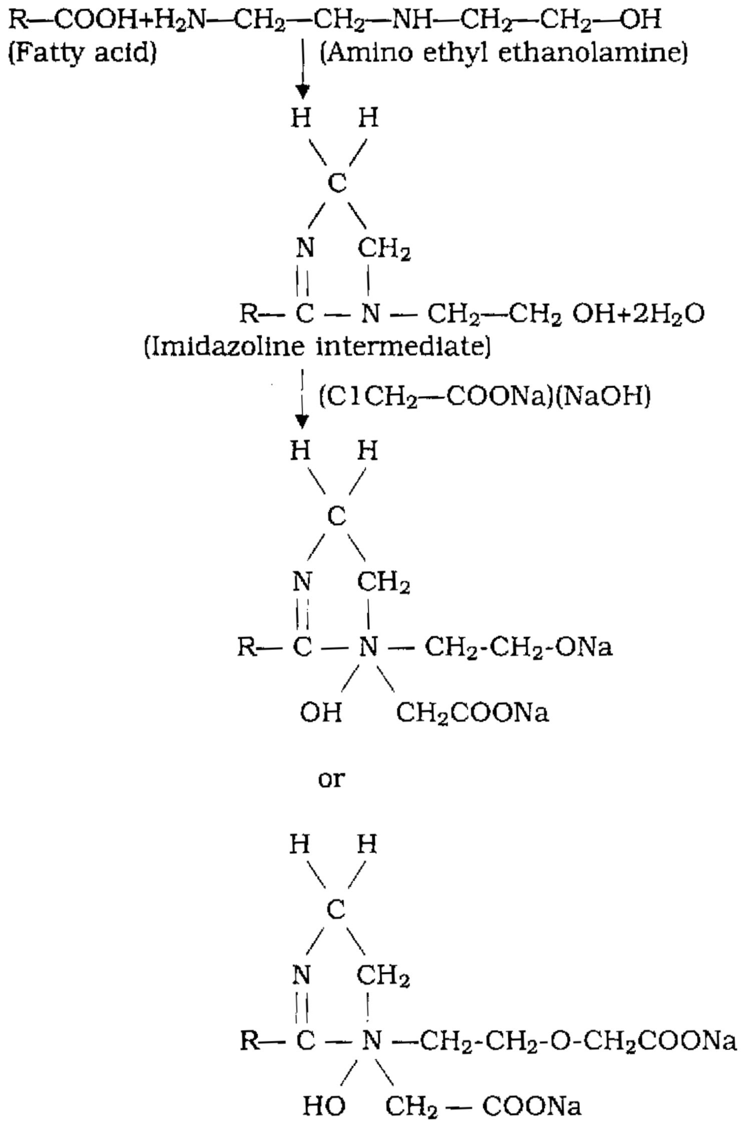
The amphoteric surfactants have one outstanding feature that they can behave like cationic surfactants without the disadvantage of being incompatible with an anionic surfactant. They have affinity for wool and cellulosic fibres and have lubricating properties.

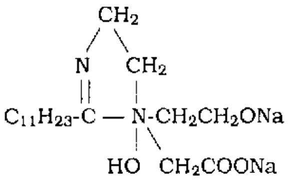
In alkaline solutions, they behave like anionics and in acidic solutions, like cationics. At pH close to 7, they act like non-ionic surface active agents. They are compatible with acids, alkalies and monovalent electrolytes. They get precipitated by calcium and magnesium salts present in hard water.

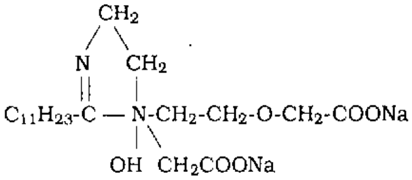
One of the basic methods of production of amphoteric detergents is the reaction between a fatty acid and substituted ethylene diamine.

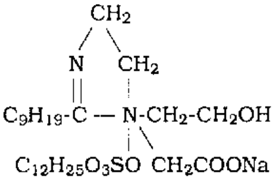
Some of the commercial amphoterics have the following formula.

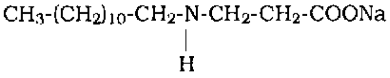
Anionic, cationic and amphoteric surface active agents are together called ionic surface active agents. There are other surfactants, which are soluble in water and reduce the surface tension of water. however, they do not generally ionise when dissolved in water. Hence these are called non-ionic surfactants. For example, when stearic acid is condensed with ethylene oxide (mole ratio, 1:6) a polyether ester is formed.


R—COOH+H2N—CH2—CH2—NH—CH2—CH2—OH
(Fatty acid)
(Amino ethyl ethanolamine)
R— C — N — CH2—CH2 OH+2H2O
(Imidazoline intermediate)
(C1CH2—COONa)(NaOH)
R— C — N — CH2-CH2-ONa
OH
CH2COONa
or
R— C — N —CH2-CH2-O-CH2COONa
HO
CH2 — COONa

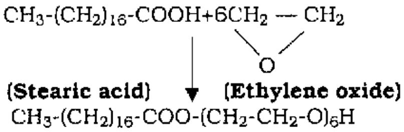






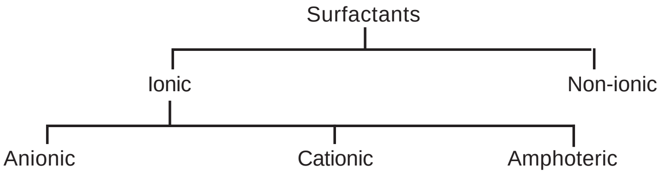


$CH_3\text{-}(CH_2)_{10}\text{-}CH_2\text{-}\underset{\displaystyle H}{\underset{|}{N}}\text{-}CH_2\text{-}CH_2\text{-}COONa$



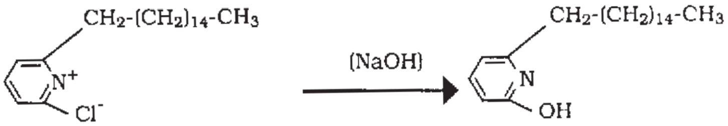
The oxygen atom of the oxyethylene unit (there are six such units in the molecule of the polyether ester) is sufficiently hydrophilic and six such atoms provide the required degree of hydrophilicity to balance the hydrophobic nature of the compound. With this balanced water solubility and water insolubility, the resulting compound acquires surface activity even though it does not ionise when dissolved in water.

Thus surfactants may be classified as follows:



If solutions of anionic and cationic surfactants are mixed, the large ions of opposite charges (anions and cations) combine with each other, get their charges mutually neutralised resulting in the precipitation of the anionic-cationic complex and losing their surface activity. Therefore, anionic and cationic surfactants should not be mixed with each other. In other words, anionic surfactants are not compatible with cationic surfactants. On the other hand, non-ionic surfactants are compatible with either anionic or cationic surfactants and hence may be mixed with them without the danger of either of them losing their surface activity.

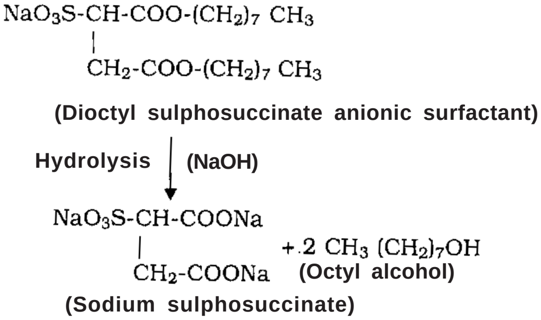
Generally, cationic surfactants are not stable to highly alkaline liquors, since under these conditions the free base of the quaternary ammonium compound, which may not be soluble in water, is formed:



(Cetyl pyridinium chloride) (Cetyl pyridinium hydroxide)

Similarly, anionic surfactants are not compatible with acidic solutions of extreme acidity. This when sodium stearate (soap) solution is acidified, insoluble stearic acid is formed.

On the other hand, anionic surfactants are generally compatible with alkaline liquors and cationic surfactants are compatible with acidic solutions. Non-ionic surfactants are stable over a wide range of pH (from acidic through neutral to alkaline solutions). However, ester type of anionic and non-ionic surfactants are not stable to highly alkaline solutions, when the ester gets hydrolysed, producing the acid and the alcohol:



$$\begin{array}{l} NaO_3S\text{-}CH\text{-}COO\text{-}(CH_2)_7\ CH_3 \\ \qquad\quad | \\ \qquad\quad CH_2\text{-}COO\text{-}(CH_2)_7\ CH_3 \end{array}$$

(Dioctyl sulphosuccinate anionic surfactant)

Hydrolysis $\downarrow$ **(NaOH)**

$$\begin{array}{l} NaO_3S\text{-}CH\text{-}COONa \\ \qquad\quad | \qquad\qquad\qquad + 2\ CH_3\ (CH_2)_7OH \\ \qquad\quad CH_2\text{-}COONa \end{array}$$

(Octyl alcohol)

(Sodium sulphosuccinate)

(I) Anionic Surfactants

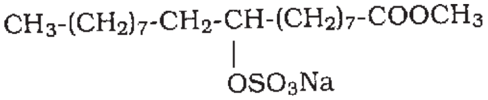
Wetting agents, detergents, emulsifying agents, scouring agents, mercerizing wetting agents, levelling agents antistatic agents etc. belong to this group of surfactants. Some of the important chemical types are given in the following:

1.Sulphated vegetable oils

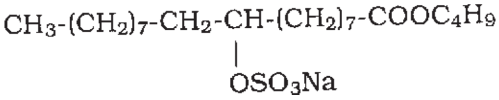
Sulphated castor oil (Turkey Red Oil) is a good wetting agent. Its main constituent is sulphated rincinoleate.

2. Sulphated fatty acid esters

Sulphated methyl oleate (or butyl oleate) belongs to this group. This is also a good wetting agent:



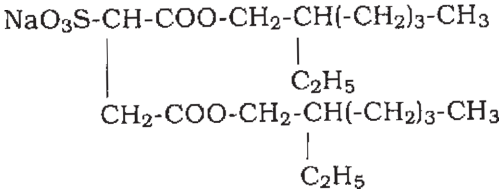
$$CH_3\text{-}(CH_2)_7\text{-}CH_2\text{-}\underset{\substack{|\\ OSO_3Na}}{CH}\text{-}(CH_2)_7\text{-}COOCH_3$$



$$CH_3\text{-}(CH_2)_7\text{-}CH_2\text{-}\underset{\substack{|\\ OSO_3Na}}{CH}\text{-}(CH_2)_7\text{-}COOC_4H_9$$

3. Sulphated esters of low molecular weight aliphatic acids:

The most powerful wetting agent (rapid wetting agent) belongs to this group. Dioctyl sulphosuccinate (octyl being obtained by 2-ethyl hexanol) is a representative of this class:



$$\begin{array}{l} NaO_3S\text{-}\underset{|}{CH}\text{-}COO\text{-}CH_2\text{-}\underset{\substack{|\\ C_2H_5}}{CH}(\text{-}CH_2)_3\text{-}CH_3 \\ \phantom{NaO_3S\text{-}}\overset{|}{CH_2}\text{-}COO\text{-}CH_2\text{-}\underset{\substack{|\\ C_2H_5}}{CH}(\text{-}CH_2)_3\text{-}CH_3 \end{array}$$

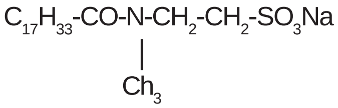
4. Fatty acid esters of sulphonated alcohols:

An important detergent belongs to this group and is made by reacting oleyl chloride with isothionic acid ($HO\text{-}CH_2\text{-}CH_2\text{-}SO_3Na$):

$C_{17}H_{33}\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}SO_3Na$

5.Sulphonated substituted fatty acid amides:

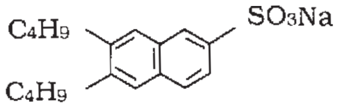
Another important detergent made by condensing oleyl chloride with N-methyl taurine, belongs to this group:



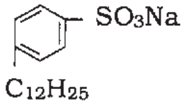
$$C_{17}H_{33}\text{-CO-}\underset{\substack{|\\ Ch_3}}{N}\text{-}CH_2\text{-}CH_2\text{-}SO_3Na$$

6. Alkyl aryl sulphonates

Dibutyl naphthalene sulphonate and dodecyl benzene sulphonate belong to this group and the latter is the most widely used detergent:



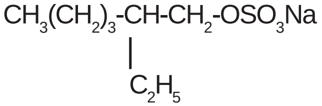
(Dibutyl naphthalene sulphonate)



(Dodecyl benzene sulphonate)

7.Aliphatic alcohol sulphates:

Lower aliphatic alcohol sulphates are powerful wetting agents in mercerizing liquors and higher fatty alcohol sulphates are good detergents:

a) 

$$CH_3(CH_2)_3\text{-}\underset{\substack{|\\ C_2H_5}}{CH}\text{-}CH_2\text{-}OSO_3Na$$

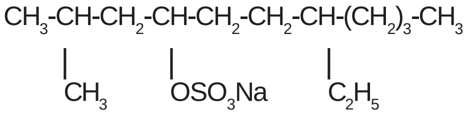
(2-ethyl hexyl sulphate)

b) $CH_3(CH_2)_{11}\text{-}OSO_3Na$
Laurly sulphate)

c) Cetyl-oleyl alcohol sulphates
$CH_3\text{-}(CH_2)_{15}\text{-}OSO_3Na$
$CH_3\text{-}(CH_2)_7\text{-}CH = CH\text{-}(CH_2)_7\text{-}CH_2OSO_3Na$

8.Secondary alcohol sulphates:

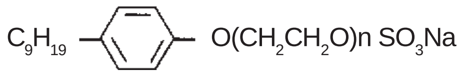
Some detergents are made form secondary alcohols, a typical example being sulphated 7-ethyl-2-methyl unde-canol-4:



$$CH_3\text{-}\underset{\substack{|\\ CH_3}}{CH}\text{-}CH_2\text{-}\underset{\substack{|\\ OSO_3Na}}{CH}\text{-}CH_2\text{-}CH_2\text{-}\underset{\substack{|\\ C_2H_5}}{CH}\text{-}(CH_2)_3\text{-}CH_3$$

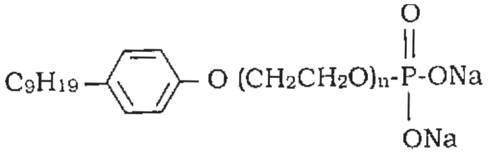
9. Sulphated alkyl phenol-ethylene oxide condensates

Levelling agents used in anionic dyeing belong to this group, a typical compound is shown below:



10. Phosphate esters:

Antistatic agents for hydrophobic fibres are available in this group. A typical example is shown below:

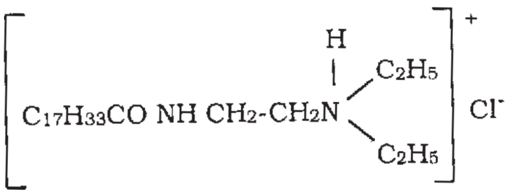


(II) Cationic Surfactants

Softeners, dye-fixing agents, cationic retarding agents used in dyeing acrylic fibres, water repellants etc. belong to this group of surfactants. Important cationic surfactants are given below:

1. Fatty acid amides and their derivatives:

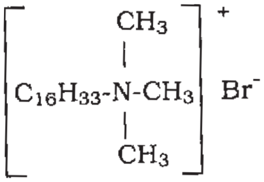
Water repellents and softeners belong to this sub-group. Suitable salts of oleylamido diethyl ethylene diamine are typical examples –



2. Quaternary ammonium salts:

A large number of products belong to this sub-group some of them are shown below:

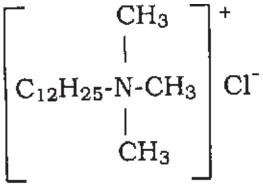
(a)



$$\left[\begin{array}{c} CH_3 \\ | \\ C_{16}H_{33}\text{-}N\text{-}CH_3 \\ | \\ CH_3 \end{array}\right]^{+} Br^{-}$$

(cetyl trimethyl ammonium bromide)

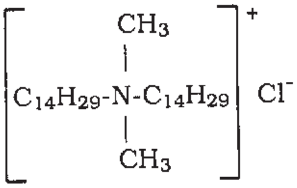
(b)



$$\left[C_{12}H_{25}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}-CH_3 \right]^+ Cl^-$$

(Lauryl trimethyl ammonium chloride)

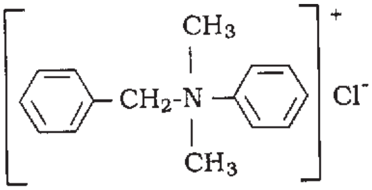
(c)



$$\left[C_{14}H_{29}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}-C_{14}H_{29} \right]^+ Cl^-$$

(Dimyristyl dimethyl ammonium chloride)

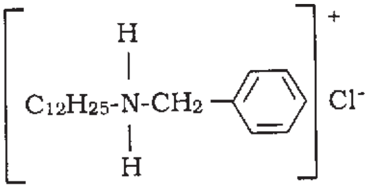
(d)



(Benzyl phenyl dimethyl ammonium chloride)

3. Fatty amine salts:

A typical example of the surfactants belonging to this sub-group is shown below:

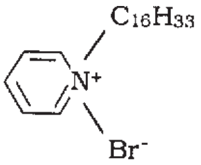


(Lauryl benzyl ammonium chloride)

4. Pyridinium and substituted pyridinium salts:

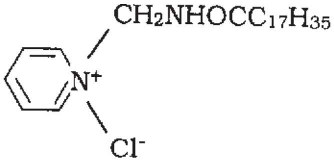
Water repellents and dye-fixing agents belong to this group. Some of them are shown below:

(a)



(Cetyl pyridinium bromide)

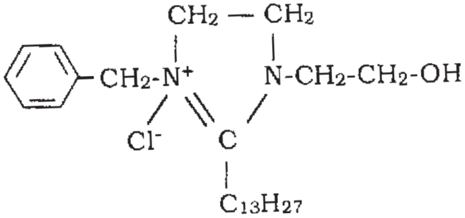
(b)



(Stearamido methyl pyridinium chloride)

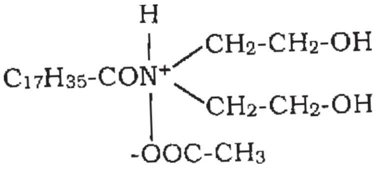
5.Cyclic (imidazolinium) derivatives:

A typical examples is tridecyl benzyl hydroxyethyl imidazolinium chloride:



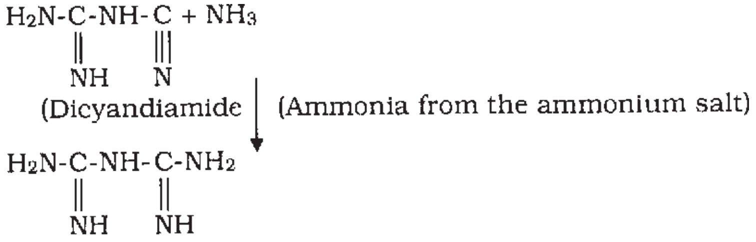
6. Alkylol amide salts:

Cationic softeners can be found in this sub-group. Stearic acid-diethanolamine condensate, solubilised by salt formation is one of the largely used cationic softeners:

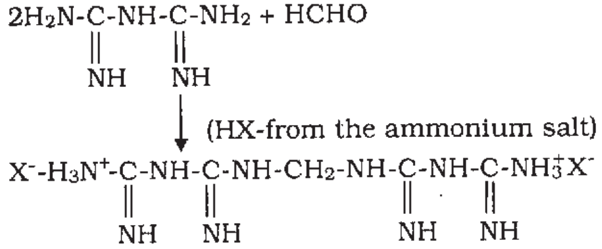


7. Dicyandiamide-formaldehyde condensate:

Cationic dye-fixing agents, widely used in aftertreating direct and reactive dyeings and prints belong to this sub-group. The condensation is carried out in the presence of an ammonium salt, which also takes part in the reaction.



$$\underset{\text{(Dicyandiamide}}{H_2N\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{N}{|||}}{C}} + NH_3 \xrightarrow{\text{(Ammonia from the ammonium salt)}} H_2N\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH_2$$



$$2H_2N\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH_2 + HCHO \xrightarrow{\text{(HX-from the ammonium salt)}} X^-\text{-}H_3N^+\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}CH_2\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH_3^+X^-$$

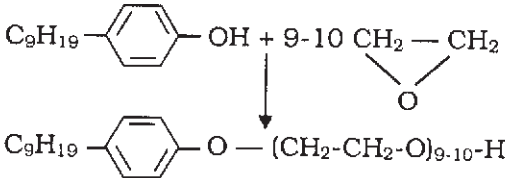
(III) Nonionic surfactants

Wetting agents, detergents, emulsifying agents for siliconces, polyethylene, kerosene, levelling agent in vat dyeing, azoic rubbing fastness improvers, softening agents, scouring agents, fixation accelerators in the fixation of polyester printing, levelling agents in polyester dyeing etc. are found in this group of surfactants.

These are generally made by condensing ethylene oxide or propylene oxide with compounds containing active hydrogen atoms or by reacting polyethylene glycol or polypropylene glycol with active hydrogen-containing compounds. Some important examples are given below:

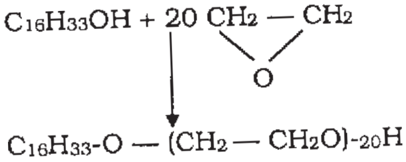
1. Alkyl phenol condensates:

The most important nonionic surfactant with detergent, wetting, emulsifying and other properties belongs to this sub-group. This is made by condensing an average of 9-10 moles of ethylene oxide with one mole of nonyl phenol:



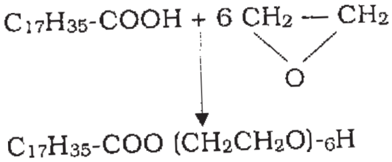
2. Fatty alcohol condensates:

Vat levelling agents and azoic rubbing fastness improvers are made by condensing ethylene oxide with cetyl alcohol:



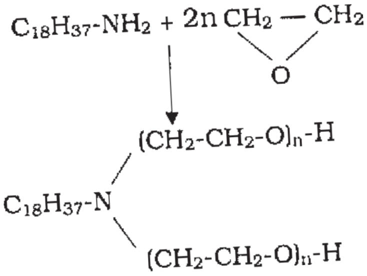
3. Fatty acid condensates:

Kerosene emulsifiers, nonionic softeners etc. are found in this sub-group. A typical examples is stearic acid-ethylene oxide condensate:



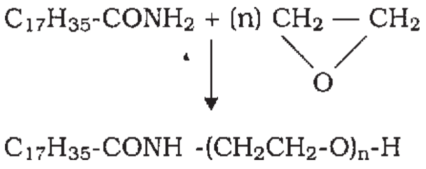
4. Fatty amine condensates:

Stearamine may be condensed with several moles of ethylene oxide: (both the hydrogen atoms attached to nitrogen take part in the reaction):



5. Fatty amide condensates:

Stearamide may be condensed with several moles of ethylene oxide: (only one hydrogen atom attached to nitrogen takes part in the reaction):



(B) Non-Surface Active Compounds

A number of textile chemicals are used in textile processing. These chemicals do not exhibit surface active property. For example, mild oxidising agent (sodium m-nitrobenzene sulphonate), solution aid (sodium benzyl sulphanilate), preservative (pentachlorophenol) and its sodium salt, humectants (glycerine, glucose), antifoaming agents and defoaming agents (octyl alcohol, lauryl alcohol etc.), resin pre-condensates and crosslinking agents (DMU, DMEU, DMPU, DMDHEU etc.), flame retardants (THPC, THPOH, etc.), finishing agents (polyvinyl alcohol), sequestering agents (EDTA, NTA) etc. belong to this group of textile chemicals.

(C) Non-surface active agent formulations containing small amounts of surface active agents:

Various water-insoluble solids and water-immiscible li-quids find extensive use in textile processing. Thus, wax, polyethylene, silicone oil, reactive softener, carriers used in polyester dyeing (di- or tri-chlorobenzene), mineral oil, organic solvents (trichloroethylene, perchloroethylene, carbon tetra-chloride, etc.) are the main components of the various formulations used as softening agents, water repellent compositions, wax emulsions, polyethylene emulsion, silicone emulsions, coning oils, carriers, stain removers etc. Since the main component is immiscible with water, they have to be emulsified in water with the help of emulsifying, agents, generally of the nonionic type. Even though the emulsifying agents are organic surface active agents, and the finishing formulations like wax emulsion, polyethylene emulsion, silicone emulsion, etc. do contain emulsifying agents, the finishing formulations themselves cannot be considered as organic surface active agents, since the finishing formulations are used mainly for the active ingredients like wax, polyethylene, silicone oil etc. (which are not surface active compounds as they are not at all soluble in water they contain.)

However, all of these emulsions do fall under the group of textile chemicals. In fact, both cationic softener (which is an organic surface active agent) and silicone emulsion (the active component of which is not an organic surface active agent) impart softness and water repellency to cotton fabrics when properly applied, though the degree of softness and water repellency may vary in the two cases. Summarising, organic textile chemical may be classified as follows:

Organic Textile Chemicals

Surface active	**Non-surface active**	**Non-surface active with small amounts of surface active agents**
Examples	**Examples:**	**Examples:**
Detergents	Resin precondensates	Wax emulsions
Wetting agents	Crosslinking agents	Polyethylene emulsions
Cationic softeners	Mild oxidising agents	Silicone emulsions
Dyeing assistants	Solution aids	Stain removing agents
Water repellents	Defoaming agents	Carriers
After-treating agents	Preservatives	Water repellents
Mercerising wetting agents	Humectants	Reactive softeners
	Sequestering agents	Coning oils

A yet another way of classifying textile chemicals is based on the textile processing in which they are used. Thus, there are spinning assistants, sizing agents, desizing agents, scouring and bleaching aids, dyeing assistants, printing aids and finishing agents. However, some of the textile chemicals fall in different classes. The various groups are sown below:

I. Spinning assistants

Cotton spray oils, coning oils, antistatic agents, lubricating agents etc.

II. Sizing agents

Adhesives, lubricants, softeners, preservatives etc.

III. Desizing agents

Bacterical and pancreatic desizing agents

IV. Scouring and bleaching aids

Wetting agents, detergents, emulsifying agents, mild oxidizing agents, sequestering agents, rapid wetting agents, mercerising wetting agents, stain removers, etc.

V. Dyeing assistants

Levelling agents, retarding agents, dispersing agents, carriers, after-treating agents, dye-fixing agents, stripping agents, rubbing fastness improvers, detergents, sequestering agents, etc.

VI. Printing aids

Thickeners, wetting agents, solution aids, hygroscopic agents, binders and fixers (in pigment printing), catalysts, discharging and resisting agents, complexing agents, mild oxidising agents, carriers and swelling agents, defoaming agents, emulsifying agents, dye-fixing agents, detergents, sequestering agents, etc.

VII. Finishing agents

Resin pre-condensates and/or crosslinking agents, catalysts, anionic softeners, cationic softeners, non-ionic softeners, reactive softeners, water repellents, water-proofing agents, wax emulsions, silicone emulsion, polyvinyl acetate emulsions, polyvinyl alcohol, sequestering agents, antistatic agents, rot-proofing and moth-proofing agents flame retardants, rapid wetting agents, soil release agents, soil resisting agents, anti-soil re-deposition agents, stiffening agents, de-foaming and anti-foaming agents, emulsifying agents, stain removers, etc.

HYBRID SURFACTANTS

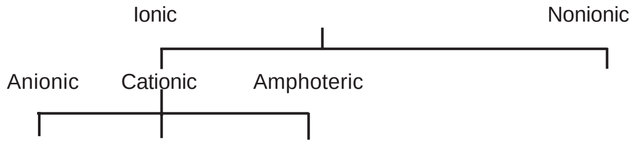
Surfactants are generally classified into ionic and nonionic surfactants, and ionics are futher sub-divided into anionic and cationic surfactants. Thus, there are three distinct classes of functional groups:

1. Anionic (sulphate, sulphonate, carboxylate, etc.).
2. Cationic (quaternary nitrogen, quaternary phosphorus etc.), and
3. Nonionic (polyoxyethylene, polyoxypropylene or mixed, etc.).

The name “hybrid surfactants” is proposed for surfactants, which contain multiple functional groups. Amphoteric surfactants, containing both anionic and cationic functional groups in the same molecule fall under “hybrid surfactants” and are known for long. An attempt is made in the following to describe other hybrid surfactants, though these surfactants are already well known, and some of them are widely used as textile speciality chemicals.

The dictionary meaning of ‘hybrid’ (The Concise Oxford Dictionary, V Edn, 1963) is “offspring of two animals or plants of different species or varieties; it also means heterogeneous”. Perhaps it may also be applied to compounds having two (or more) different, and at times opposite, types of chemical group. The expression "Hybrid Surfactants" has been proposed in the present article to denote surfactants having two or more different functional groups in their molecules. In the classical classification of surfactants, we come across ionic and nonionic surfactants and in ionic surfactants, we have anionic and cationic ones. Amphoteric surfactants have both anionic and cationic groups in the same molecule and this compound may be included in the group hybrid surfactants, as per the above description, though they have not being given that name in the literature. There are other surfactants too, qualifying for inclusion under the hybrid surfactant class. Many of these surfactants are of great commercial importance in textile processing. Some of these are described in the following. The classical classification of surfactants or surface active agents is as follows:

Surfactants

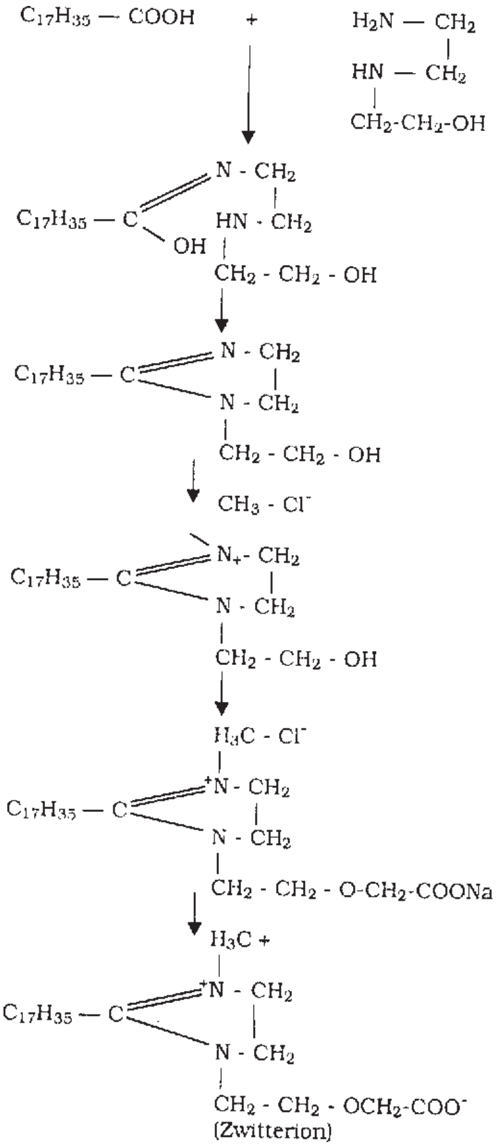


SURFACTANTS

Surfactants are generally made from fatty compounds, such as fatty acids, fatty alcohols, fatty amines, fatty acid amides, etc., which provide the long chain hydrophobic portion (C_{12} – C_{18} saturated chains or with one double bond). In anionic surfactants, solubilising groups like – COONa, - SO_3Na, - OSO_3Na, - PO_3Na_2, - OPO_3Na_2 etc., are present.

In aqueous solutions, ionization of these surfactants takes place and the long chain has a negative charge, with sodium counterions in the vicinity to neutralize the anionic charges. In cationic surfactants, generally a quaternary nitrogen atom is attached to the long chain alkyl (fatty) group, (again, C_{12}-C_{18} saturated chains or with one double bond). Thus, there is a cationic charge on the long chains, with small counter anions, like chloride, bromide, methosulphate, etc., in the vicinity to neutralise the cationic charge.

In nonionic surfactants, the same hydrophobic chains are used and water solubility of the surfactants is achieved by attach-ing the required number of ethylene and/or propylene oxide moles. The hydrophobes are selected from fatty alcohols, fatty acids, fatty amines, fatty acid amides, nonyl or octyl phenol, castor oil, etc.

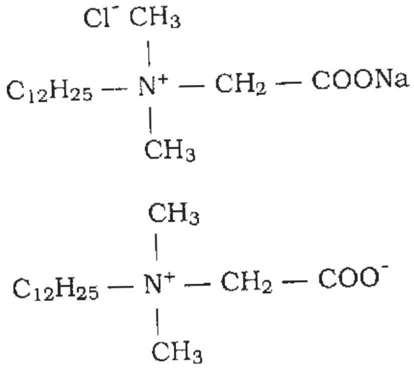


Structure 1

HYBRID SURFACTANTS

Amphoteric surfactants belong to this class and are known for long. A typical product is made by condensing a fatty acid with hydroxyethyl ethylene diamine, followed by cyclisation at high temperature, and quaternising with methyl chloride then reacting the hydroxy group with sodium monochloro acetate: (see Structure1) .

(Carboxy methyl) dodecyl dimethyl ammonium chloride is another amphoteric surfactants, which can exist in the zwitterion form: (see Structure 2).



$$C_{12}H_{25}-\overset{Cl^{-}\ CH_3}{\overset{|}{N^{+}}}\underset{\underset{CH_3}{|}}{}-CH_2-COONa$$

$$C_{12}H_{25}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N^{+}}}-CH_2-COO^{-}$$

(Zwitterion)

Structure 2

Alkyl betaines are the simplest amphoterics, and are made from alkyl dimethyl amines and sodium monochloro acetate:

$$R-N\,(CH_3)_2 + Cl-CH_2-COO\,Na$$

$$\downarrow$$

$$R-N^{+}\,(CH_3)_2-CH_2-COO^{-} + NaCl$$

where R can be COCO – alkyl, decyl, cetyl, lauryl, oleyl, etc.

Structure 3

Relatively inexpensive alkyl dimethyl amines, containing an amide group can be made from fatty acids and 3-diemthyl aminopropyl amine. Further reaction with sodium monochloroacetate yields acylaminopropyl betaine:

$$R-COOH + H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2$$

$$\downarrow$$

$$R-CONH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}N\,(CH_3)_2$$

$$\downarrow$$

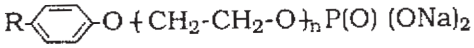
$$R-CONH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}N\,(CH_3)_2\text{-}CH_2\text{-}COO^{-}$$

where RCO – is cocoyl, lauroyl, iso-stearoyl, myristoyl, palmitoyl etc.

Structure 4

NONIONIC-ANIONIC HYBRIDS

The nonionic surfactants, based on ethylene oxide/propylene oxide, have a primary hydroxy group at one of the ends. This group can be converted into an anionic group by reaction with monochloroacetic acid (sodium salt), sulphamic acid, sulphur trioxide (and then neutralised with sodium hydroxide), phosphoric acid (and then converted into sodium salt). A few examples of this class are shown in Structure 5.

1. $R - O(CH_2\text{-}CH_2\text{-}O)_n CH_2COONa$
2. $R - O(CH_2\text{-}CH_2\text{-}O)_n SO_3Na$
3. 
4. $R - O(CH_2\text{-}CH_2\text{-}O)_n P(O)\,(ONa)_2$

Structure 5

Depending on 'R' and 'n' the resulting surfactants have different uses in textile processing.

Specifically, polyalkoxy carboxylates are made by:

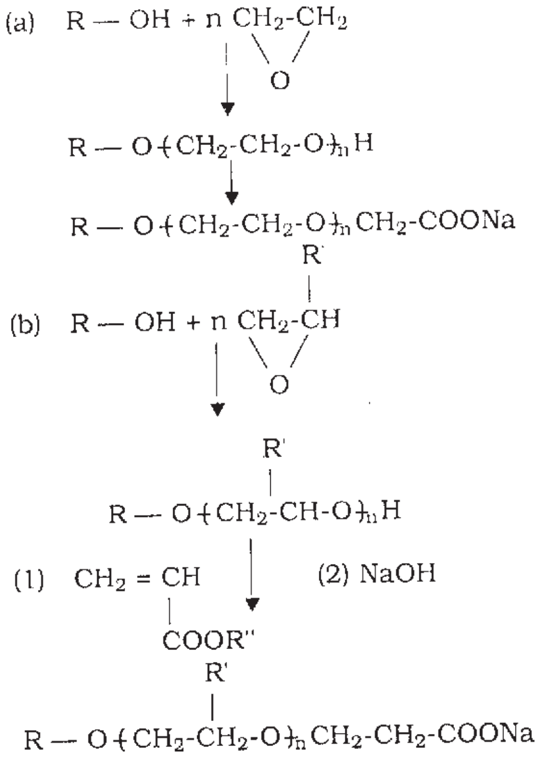
a) Reaction of monochloroacetate with an alcohol polyethoxylate, or

b) From an acrylic ester and an alcohol polyalkoxy compounds:

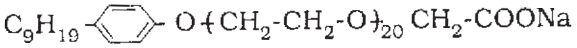
Because of the presence of ethylene oxide linkages, the above products have somewhat nonionic character, which manifests in greater compatibility with cationic surfactants. These may be called crypto anionic surfactants. Some of the commercial products belonging to this group are shown in Structure 7.

Instead to carboxy methylation, the terminal hydroxyl group of the nonionic surfactants may be sulphated to give another set of nonionic anionic surfactants. These have several advantages over alcohol sulphates, such as lower sensitivity to hard water, with respect to foaming and detersive effectiveness; less irritating to the skin and eyes, and higher water solubility. Sulphation of alcohol ethoxylates is carried out in high yields with oleium, chlorosulphonic acid, sulphamic acid, amido sulphuric acid, and gaseous sulphur trioxide, that last being the preferred one:

where R can be C_{12-14} (linear, mostly lauryl, branched tridecyl; C_{12-15} (linear, primarily myristyl, caprylyl/capryl); n is 1-5 and generally



Structure 6

1. $C_{13}H_{27}\text{-}O(CH_2\text{-}CH_2\text{-}O)_7\ CH_2\text{-}COONa$
2. $C_{16}H_{33}\text{-}O(CH_2\text{-}CH_2\text{-}O)_{12}\ CH_2\text{-}COONa$
3. iso - $C_{18}H_{37}\ \text{-}O(CH_2\text{-}CH_2\text{-}O)_5\ CH_2\text{-}COONa$
4. 

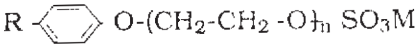
Structure 7

$$R-O(CH_2\text{-}CH_2\text{-}O)_nH + H_2N\text{ - }SO_3H$$
$$\downarrow$$
$$R-O(CH_2\text{-}CH_2\text{-}O)_n\text{ - }SO_3H$$

Structure 8

3; and the sulphonic acid is converted into its sodium or ammonium salt.

Allied products are made form alkyl phenol ethoxylates by sulphation:



where R can be octyl, nonyl (alkyl) with n = 4 and M is sodium, ammonium or triethanoalmine.

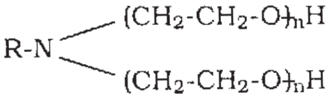
These are available as colourless, odourless aqueous solutions of 30% or higher. The presence of ethylene oxide in the molecule increase the resistance to hardness ions and reduces skin irritation. Phosphate esters of alcohol ethoxylates are another set of hydrid surfactants:

$$R\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\ P(O)\ (OM)_2$$

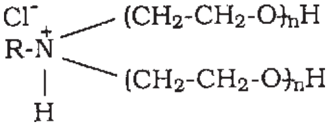
where R can be butyl, 2-ethyl hexyl, dodecyl, tridencyl, 9-octadecyl, etc., and M can be sodium, potassium, magnesium, diethanolamine, etc.

NONIONIC-CATIONIC HYBRIDS

These too are known for long and include fatty aminethylene oxide condensates. In this case, both the hydrogen atoms attached to the nitrogen atom are equally active and hence take part in the condensation reaction:

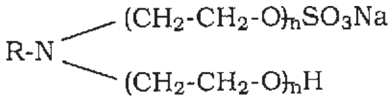


In acidic medium, the nitrogen atoms gets protonated and develops a cationic charge



CATIONIC-NONIONIC-ANIONIC HYBRIDS

These are interesting surfactants, in the they have all the three groups in the same molecule. They are made by reacting a fatty amine with ethylene oxide, followed by sulphation of the end hydroxy group of one of the polyoxyethylene chains. If both are sulphated, the two solubilising groups (sulphate groups) disturb the balanced water solubility water insolubility of the compound (since there is only one hydrophobic group in the molecule), which then loses surface activity. A typical compound is shown below:



Such surfactants find use as levelling agents in dyeing acid dyes and 1:2 metal-complex dyes on wool and nylon fabrics. Finally, hybrid surfactants may be defined as those surfactants, which contain two or three different functional groups in the same molecule, i.e. those containing: (1) anionic and cationic groups; (2) anionic and nonionic groups; (3) cationic and nonionic groups and (4) anionic, cationic and nonionic groups. In other words, they are heterobifunctional or heterotrifunctional surfactants.

6

Details of Raw Materials

FATTY ACIDS

The fatty acids are obtained from vegetable and animal fats. The composition of some fats and oils are given below in Table 6.1

Tables 6.1
Fatty Acid Composition (%) of Some Natural Oils And Fats

	Oil							
Fatty acid	Coco-nut	Palm	Plam kernel	Soya bean	Sun-flower	Lin seed	Castor	Beef tallow
Caprylic (C8)	6	-	3	-	-	-	-	-
Capric (C10)	6	-	4	-	-	-	-	-
Lauric (C12)	47	-	51	-	-	-	-	-
Myristic (C14)	18	1	17	-	-	-	-	3
Myristoleic (C14/Cl18*)	-	-	-	-	-	-	-	1
Palmitic (C16)	11	48	8	11	11	6	2	26
Palmitoleic (C16/C18*)	-	-	-	-	-	-	-	6
Stearic (C18)	3	4	2	4	6	4	1	17
Oleic (C18*)	7	18	13	25	19	22	7	43
Linoleic (C18/2*)	2	9	2	51	53	16	3	4
Linolenic (C18/3*)	-	-	-	9	1	52	-	-
Ricinoleic	-	-	-	-	-	-	87	-

*- double bond

There are four main types of animal fats-edible tallow, inedible tallow, lard and inedible grease. Typically, tallow is the fat of cattle, and lad and grease are the fats of hogs. These are the primary sources of stearic and oleic acids.

Coconut oil is an important raw material for fatty acid and fatty ester production, because of its high C8, C10 and C12 fatty acid content.

Stearic acid **$C_{17}H_{35}$ – COOH Mol.wt.284**

This is the most common naturally occurring fatty acid, and is obtained from animal and vegetable oils and fats. Commercial stearic acid contains about 50% stearic acid, 45% palmitic acid and 5% oleic acid. It is a colourless, odourless wax-like solid. It is soluble in alcohol, ether, chloroform, carbon tetrachloride, etc., but not in water. It has a melting point of 69.6ºC and boiling point of 360ºC. Stearic acid is combustible, but non-toxic. It is made from high grade tallow by wahsing, hydrolysis, boiling, distilling, cooling and pressing. It is also made by hydrogenating oleic acid.

Stearic acid is used in the manufacture of stearamide, softeners, aluminium stearate (water-proofing agent), etc.

Oleic acid $C_{17}H_{33}$ – COOH Mol. Wt. 282

This is a mono unsaturated, straight chain C18 fatty acid (double bond in between C9 and C10). It occurs in almost all natural fats. Most oleic acid is obtained from animal tallow or vegetable oils. It is a yellow to red oily liquid, with a lard-like odour and darkens on exposure to air. It is immiscible with water but miscible with alcohol, ether and other organic solvents. It is a solvent for oils, fatty acids and oil-soluble compounds. The fatty acid is obtained from fats by hydrolysis followed by steam distillation and separation by crystallisation or solvent extraction. Filtration from the press cake gives the oleic acid of commerce (red oil). It is used in the manufacture of oleic acid-triethanolamine soap, which is an emulsifier for mineral oil. Oleic acid-polyethylene glycol condensation products are kerosene emulsifiers. After esterifying and sulphonating, wetting agents and levelling agents can be made from oleic acid.

When stearic (or other fatty acid) or its ester is reacted with amino alcohols (mono-,di-or triethanolamine), alkanolamides are produced, which find application as antistatic compounds, softening agents and levelling agents in dyeing. Commercial alkanolamides vary in nature and composition, arising from the choice of the amino alcohol, ratio of reactants and the carboxylic derivative used. Reasonably pure monosubstituted amides from amino alcohols can be made from the fatty acid or its methyl ester with or without a catalyst. These are normally produced in 6 to 10 hours at 140º to 160ºC. The manufacture of diethanol-amides is more difficult. The products are known as “Kritchevsky-type” amides. This is made using the fatty acid and diethanolamine in the mole ratio 1:2. The resulting product is a water-soluble mixture of N,N-bis (hydroxyethyl) amide, amino ester, amido ester, etc. and the unreacted diethanolamine. If the methyl esters of the fatty acid is reacted with diethanolamine in the presence of alkali metal oxide catalyst, about 90% pure amide is obtained.

Cationic softeners generally contain a stearic acid residue as the hydrophobic portion of the molecule. They are made form amides of stearic acid and polyamino compounds, like hydroxyethyl ethylene diamine and diethylene triamine. The resulting amino amides are made water-soluble by quaternisation or salt formation. In the latter process, the product is treated with acetic acid or acetic anhydride. For quaternising diethyl sulphate, methyl chloride, dimethyl sulphate and triethyl phospite are used. Quaternisation is a better method since it removes the amino group, which is the cause of yellowing of the softened goods. Many cationic softeners cause yellowing, the degree of yellowing depending on the amount and type of the free amino groups present and the temperature of drying the goods after the application of the softener.

Nonionic softeners do not produce the degree of softness and yellowness obtained with cationic softeners but are not durable to laundering. However, because of their greater resistance to yellowing and compatibility with other finishing ingredients of any ionic nature, they are also widely used, especially in resin finishing, where high curing temperatures are employed, and cationic softeners, if used, turn yellow to an objectionable degree. Dispersions of stearic monoglyceride, dispersed with polyethylene glycol stearate as the dispersing agent or polyethylene glycol stearate itself can be used as non-ionic softener.

Anionic softeners based on fatty acids are mixtures of stearic acid monoglyceride with stearic acid soap as the dispersing agent. These have good resistance to yellowing and can be used as yarn finish, because of their additional lubricating property. Stearic acid itself is a good softener. In the commercial products based on this, the acid is partly neutralised with sodium hydroxide or potassium hydroxide to form sufficient soap, to emulsify the free stearic acid.

Stearic acid is used in the manufacture of water repellents. One type is based on stearamide or methylol stearamide, applied along with a thermosetting resin like trimethylol melamine. When cured under acidic conditions, the methylol group of trimethylol melamine reacts with stearamide, which also reacts with cellulosic hydroxyls and produces durable water repellency. Sometimes, methylol stearamide is applied as a self-finish to produce softening effect, rather than water repellency, in which case, it is called a reactive softener. This needs curing in the presence of acidic catalyst, like magnesium chloride.

The second type o durable water repellent is based on stearoxymethyl pyridinium chloride, prepared by hydro-chlorination of methylol stearamide and reacting the resulting chloromethyl derivative with pyridine.

Fibres are mechanically procssed to produce yarns, fabrics and knitted goods. In such cases, the fibres have to be lubricated. Synthetic fibres need antistatic finishing also. Yarn lubricants are generally mineral, vegetable or synthetic oils mixed with emulsifiers with or without an antistatic agent (sometimes the emulsifier acts as an anti stat also). Polyglycol stearates are used for the purpose. The coconut fatty acid esters of polyethylene glycol have excellent emulsifying as well as antistatic properties. Synthetic oils, used as lubricants, include fatty acid esters like butyl stearates and glycerine trioleate and fatty alcohols such as oleyl and cetyl alcohols, sulphated glycerine trioleate. (Sulphation is carried out at the double bond).

Dispersions of fatty acid esters in protein emulsifiers (stearates of oxyethylated butanols in casein solutions) are commonly used as scrooping agents for imparting the resulting crackle of silk fabrics to synthetic fibre fabrics.

(B) ALIPHATIC HYDROXY COMPOUNDS AND THEIR DERIVATIVES

1. Octyl alcohol $C_8H_{17}OH$ Mol. wt. 130

Of the various octyl alcohols (straight chain and branched chain), 2-ethyl hexanol is the most important raw material for the manufacture of textile auxiliaries. This is a colourless liquid, miscible with most organic solvents, but immiscible with water. it boils at 183ºC and has a specific gravity of 0.83. it is combustible and has low toxicity. Its oral LD_{50} value in rats in 12.46 ml/kg. It is used in the manufacture of dioctyl sulphosuccinate, which is the rapid wetting agents; for producing non-cresylic wetting agent in mercerising liquors, after sulphation and neutralisation. Octyl alcohol is also a defoaming agent when used as such.

2. Lauryl alcohol $C_{12}H_{25}OH$ **Mol. wt. 186**

This is a straight chain aliphatic alcohol, also called dodecyl alcohol. This is a colourless solid, with a melting point of 24ºC and a boiling point of 259ºC. It is immiscible with water. It has low toxicity. It is made by the reduction of coconut oil fatty acids (which contain about 47% lauric acid). After sulphation and neutralisation, it produces sodium lauryl sulphate (SLS), which is a detergent, as well as a levelling agent in dyeing acid dyes on nylon. Lauryl alcohol can be used as a defoaming agent.

3. Cetyl alcohol $C_{16}H_{33}OH$ **Mol. wt. 242**

This is the straight chain C16 aliphatic (saturated) alcohol; also called palmityl alcohol. It is combustible and is non-toxic. It is a white waxy solid with a faint odour and melts at 49.3ºC and boils at 344ºC. Cetyl alcohol is partly miscible with ethyl alcohol and ether but is immiscible with water. It is made by saponifying spermaceti with caustic soda or by reducing palmitic acid.

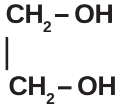
4. Oleyl alcohol $C_{16}H_{31}OH$ **Mol. wt. 240**

Oleyl alcohol is the unsaturated straight chain alcohol derived by the reduction of oleic acid. Technical oleyl alcohol contains linoleyl, myristyl and cetyl alcohol as impurities.

A mixture of cetyl and oleyl alcohols is used in the manufacture of detergents of alcohol sulphate type in the paste form.

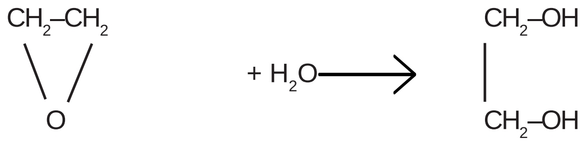
When reacted with ethylene oxide (about 20 moles of ethylene oxide per mole of cetyl alcohol), a very useful product is obtained, which can be used as an emulsifier, rubbing fastness improver for azoic dyeing, nonionic levelling agent in vat dyeing etc.

5. Ethylene glycol **Mol. wt. 62**



$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$

This is made by hydrating ethylene oxide with dilute hydrochloric acid in the presence of excess of water at 200ºC under a pressure of 20 atmospheres.

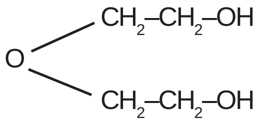


Ethylene glycol is a colourless syrupy liquid, which is hygroscopic and toxic in nature. It boils at 197ºC. It mixes freely with water or alcohol, but is sparingly miscible with ether and hydrocarbons.

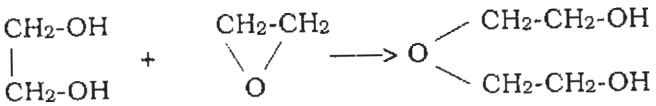
Its oral LD_{50} values in rats and guinea pigs are 8.54 and 6.61 gm/kg and in mice, 13.79 ml/kg. *Human toxicity*: Constitutes a hazard when ingested. Transient stimulation of central nervous system, followed by depression, vomiting, drowsiness, coma, respiratory failure, convulsion, kidney damage and death. Lethal does in humans in about 1.4 ml/kg or about 100 ml.

It is a solvent for ballpoint pen ink and can be used to removes the stains of this ink form clothes. It is used to make its monoethyl ether (cellosolve) or monobutyl ether (butyl cellosolve).

6. Diethylene glycol Mol. wt. 106



This is made by reacting ethylene glycol with ethylene oxide.

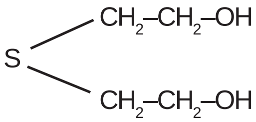


Diethylene glycol also called diglycol, is a clear, colourless syrupy liquid, which is practically colourless and has a sweet taste. It is extremely hygroscopic. It is miscible with water, ethanol, ether, acetone, toluene and carbon tetrachloride. It boils at 245ºC, is combustible and has low toxicity.

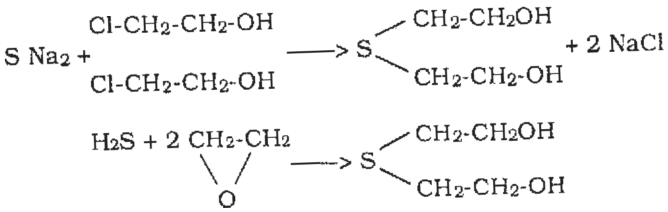
LD_{50} orally in rats and guinea pigs: 20.76 and 13.21 g/kg. *Human toxicity*: Symptoms on ingestion are similar to those of ethylene glycol.

It is used as a hygroscopic agent and a solvent for dyes in textile printing and also in dyeing and printing of phthalogen blue.

7. Thiodiethylene glycol **Mol. wt.122**



Thiodiethylene glycol, also called thiodiglycol, is made by reacting ethylene chlorohydrin with sodium sulphide or form hydrogen sulphide and ethylene oxide:

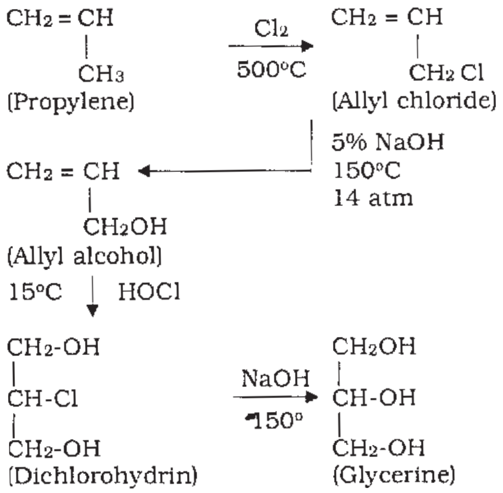


This is a syrupy, colourless liquid with a characteristic odour. It boils at 283ºC and is miscible with acetone, ethanol, chloroform and water. it is combustible and has low toxicity. This is an excellent solvent for basic, direct, acid, and disperse dyes and is used in textile printing paste to assist the dissolution of these dyes and promote the production level and deeper printed patterns. It has also hydroscopic property and solvent action on vat dyes in their water soluble leuco form.

8. Glycerine (Glycerol) **Mol. wt. 92**

CH_2 – OH
|
CH – OH
|
CH_2 – OH

Glycerine is obtained: (1) as a by-product in soap manufacture, (2) by reaction of propylene with chlorine to form allyl chloride, followed by conversion into dichlorohydrin by reacting with hypochlorous acid and finally reacting with sodium hydroxide to get glycerine.



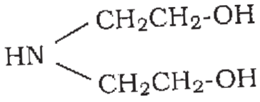
Glycerine is a clear, colourless, odourless, syrupy liquid with a sweet taste and is very hygroscopic. It boils a 290ºC and is combustible. It is miscible with water, benzene and chloroform.

LD$_{50}$ in rats > 20 ml/kg orally, and 4.4ml/gk i.v.

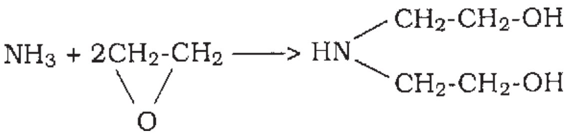
Contact with strong oxidizing agents, such as $KClO_3$ or $KmnO_{4-}$ may produce an explosion.

Glycerine is used as a hygroscopic agent in textile printing and as a humectant in sizing.

9. Diethanolamine **Mol. wt. 105**



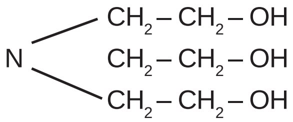
This is made by reacting ethylene oxide with ammonia.



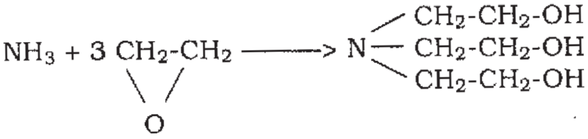
It is available as colourless crystals or liquid and has a melting point of 28°C and boiling point of 217ºC at 150 mm. It is miscible with water and alcohol, but immiscible with benzene and ether. It is combustible. Oral LD$_{50}$ value in rats is 12.76 g/kg.

Diethanolamine is used in the manufacture of cationic softener by reacting with fatty acids, especially with coconut oil fatty acids, followed by salt formation with acetic acid or acetic anhydride.

10. Triethanolamine **Mol. wt. 149**



This is made by reacting ethylene oxide with ammonia.

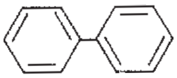


It is a colourless, viscous, hygroscopic liquid with a slight ammoniacal odour. It boils at 335ºC and is miscible with water, alcohol, chloroform and is slightly miscible with benzene and ether. Commercial triethanolamine contains up to 25% mono-ethanolamine. It is combustible and has no toxicity. When it is used to neutralize fatty acids (to get triethanoalmine soaps) detergents and emulsifying agents are produced. It is used in scouring wool and also in making anionic softening agents.

It forms an emulsifying agent for emulsifying dichlorobenzene or trichlorobenzene in water, after reacting with dodecylbenzene sulphonic acid (acid slurry). Its hydrochloride can be used as an activator for sodium chlorite in bleaching.

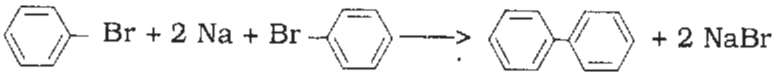
Hydrocarbons

11. Diphenyl **Mol. wt. 154**



This is also called biphenyl and occurs in coal tar. It is manufactured by passing benzene vapours through a hot iron tube packed with pumice.

It is also made by heating bromobenzene with sodium, with subsequent distillation.

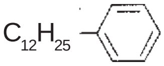


Diphenyl exist in several crystalline forms. It is available as white scales or plates with a pleasant odour, melting at 70ºC and boiling at 256ºC. It is soluble in alcohol and ether but not in water. It is highly toxic. It is a very good carrier for polyester dyeing, for which it is used in an emulsified form. Its carrier efficiency is unaffected by variation in pH.

LD_{50} orally rats:3.28 gm/kg.

Toxicity: central nervous system depression, and paralysis; convulsions have been observed in experimental animals.

12. Dodecyl benzene, DDB — Mol. wt. 246



This is commonly known as alkylbenzene and is a commercial blend of isomeric, mainly monoalkyl, benzenes. The side chains are saturated, linear (soft) or branched (hard), with an average of 12 carbon atoms. It is a combustible liquid. DDB is made by alkylation with isomeric dodecene obtained by tetramerisation of propylene. LAB is made by alkylation of benzene with chloroalkane with 12 carbon atoms, in the presence of anhydrous aluminium chloride. This is moderately toxic by ingestion. Its main use is in the manufacture of anionic detergent, made by sulphonation, followed by neutralisation; sulphonated alkyl benzene is known as acid slurry.

13. Paraffin wax — C_nH_{2n+2}

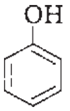
This is class of hydrocarbons, characterised by a straight or branched carbon chain and is a white transluscent, tasteless, odourless solid, containing a mixture of solid hydrocarbons of high molecular weight. It is soluble in benzene, chloroform, turpentine and olive oil. It is insoluble in water and in acids. It melts in the region of 47º-65ºC. It is combustible but is non-toxic. Paraffin wax is used in the form of an emulsion with or without aluminium stearate to produce softening or water-repellency.

14. Polyethylene (low molecular weight)

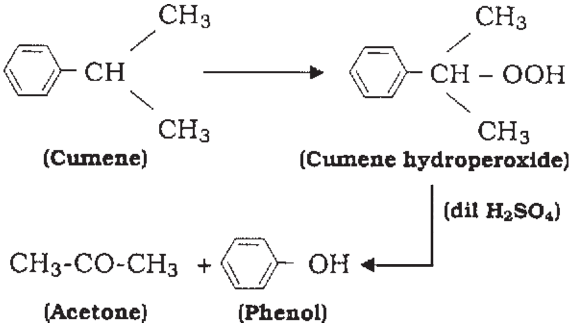
This is a polymer of ethylene, has molecular weight of 2,000-5,000, and is available as white transluscent solids, with excellent abrasion resistance. It is resistant to water and to most of the chemicals. It has a specific gravity of 0.92 and is slightly soluble in turpentine, petroleum naphtha, xylene and toluene at 27ºC and is soluble in xylene, toluene, trichloroethylene and mineral oils at 80ºC, but is practically insoluble in water. It is used in the form of an emulsion for producing softening effect, especially in resin pre-condensate baths.

Phenolic compounds

15. Phenol **Mol. wt. 94**



Phenol is also known as carbolic acid, phenylic acid, hydroxybenzene etc. It is made by the oxidation of cumene (isopropyl benzene) , giving acetone as a byproduct. The first step in the reaction (oxidation of a solution or emulsion of cumene with air at 130ºC) is the formation of cumene hydroperoxide, which is decomposed by dilute sulphuric acid to phenol and acetone.



Phenol forms large deliquescent prisms, with a strong characteristic odour. It melts at 42ºC and boils at 181ºC.

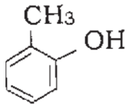
Oral LD_{50} value in rats is 530 mg/kg.

Human toxicity

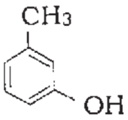
Ingestion of even small amounts may cause nausea, vomiting, circulatory collapse, paralysis, convulsions, coma green-coloured urine, necrosis of mouth and gastro-intestinal tract, death from respiratory failure and from cardiac arrest.

Phenol is used in the manufacture of pentachloro-phenol, which is used as a preservative in the textile industry (sizing and finishing, where starch is used).

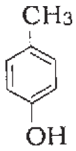
16. Cresols **Mol. wt. 108**



o-Cresol



m-Cresol



p-Cresol

These occur in the middle-oil fraction of coal tar and are usually not separated from each other for technical purposes. By repeated fractionation, o-cresol (boiling point, 191ºC; melting point, 30ºC) may be distilled from the crude product, m-cresol (boiling point, 203ºC; melting point, 40ºC) and p-cresol (boiling point, 202ºC; melting point, 36ºC) are separated by means of their sulphonic acids.

Cresols are available as a colourless, yellowish or pink liquid, with phenolic odour. The liquid is miscible with ethanol, glycol and aqueous alkali, but not with water.

Human toxicity

Cresols – Orally 8 gm or more produces rapid circulatory collapse and death. Chronic poisoning from oral or skin absorption may produce digestive disturbances, nervous disorders with faintness, vertigo, mental changes, skin eruptions and jaundice. This is a general protoplasmic poison.

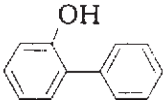
Oral LD$_{50}$ values in rats of 0-, m-, and p-cresols are 1.35 gm/kg, 2.02 gm/kg, and 1.8 gm/kg respectively. It is used in the manufacture of cresylic type of mercerizing wetting agents.

17. Nonyl phenol **Mol. wt. 220**

Commercially, this is a mixture of isomeric monoalkyl (nonyl) phenols, mainly the p-isomer. It is made by the catalytic alkylation of phenol with suitable olefin. It is a pale yellow viscous liquid, with a slight phenolic odour. It is immiscible with water, butmiscible with most organic solvents.

It boils at 293°C and is combustible. When reacted with ethylene oxide (average of 9-10 ethylene oxide moles per mole of nonyl phenol) it gives one of the most important nonionic detergents and lubricating oil additive (as an emulsifier). When added to an anionic detergent, it boosts the detergency of the latter. It is also used in the manufacture of silicone emulsions.

18. o-Phenyl phenol **Mol. wt. 170**

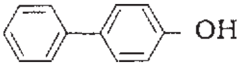


This is made by reacting chlorobenzene with sodium hydroxide solution at elevated temperatures under pressure.

o-Phenyl phenol is available as nearly white crystals with a melting point of 56ºC-58ºC and a boiling point of 280º-284ºC. It is soluble in alcohol but not in water. It forms the sodium salt, which is soluble in water. It is a combustible substance and is moderately toxic by ingestion.

This is used as a carrier in polyester dyeing and is sensitive to pH variation. Thus, it loses its carrier efficiency under alkaline conditions. Hence, it is used under acidic conditions (pH 4 to 4.5) in the form of an emulsion. When the dyeing is scoured, the addition of an alkali to the detergent bath helps the removal of the carrier as its sodium salt, which does not strip the dye from the dyeing.

19. p-Phenyl Phenol **Mol. wt. 170**



This is made by reacting chlorobenzene with sodium hydroxide solution at elevated temperature under pressure. This is available as nearly white crystals, melting at 164º-165ºC and boiling at 308ºC. It is soluble in alcohol and many other organic solvents, but not in water.

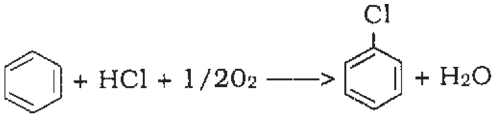
LD_{50} orally in rats: 2.48 gm/kg. Toxic symptoms are similar to those of phenol.

p-Phenyl phenol is used as a carrier in polyester dyeing and is sensitive to pH. It loses its carrier efficiency under alkaline conditions. This property is advantageously used in scouring the dyeing under alkaline conditions, when the scouring bath does not strip the already dyed dye from the fibre material.

Aromatic chloro compounds

20. o-Dichlorobenzene (ODCB) Mol. wt. 147

In the manufacture of ODCB, benzene is first chlorinated in the vapour phase with a mixture of hydrogen chloride and air under pressure a 230ºC in the presence of Cu/Fe catalyst. The required chlorine is obtained from the decomposition of HCl by the atmospheric oxygen and cupric chloride.

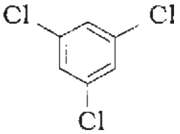


(Chlorobenzene)

Chlorobenzene, on further chlorination, gives a mixture of o-, and p-dichlorobenzene. Some amount of m-dichlorobenzene is also formed.

ODCB is a colourless, volatile, heavy liquid with a pleasant odour. Generally, it is a mixture containing at least 85% ortho isomer and varying percentages of the meta-,and paraisomers. ODCB is a combustible liquid with a flash point of 65.5ºC. It boils in the range 172º-179ºC. It is miscible with common organic solvents, but immiscible with water. can cause injury to liver and kidneys. High concentrations cause central nervous system depression. When suitably emulsified in water in the presence of dodecyl benzene sulphonic acid (either sodium salt or triethanolamine salt), it acts as an effective carrier in dyeing disperse dyes on polyester fibres at the boil at atmospheric pressure. The carrier efficiency of the emulsion is insensitive to pH variation and it retains the carrier efficiency over a wide range or pH. While removing the carrier from the dyed polyester material by the scouring operation, it carries with it some amount of the dye from the dyed material, thereby colouring the scouring bath. This results in a slight loss of colour value of the dyeing.

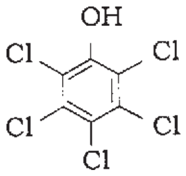
21. Trichlorobenzene Mol. wt. 181.5



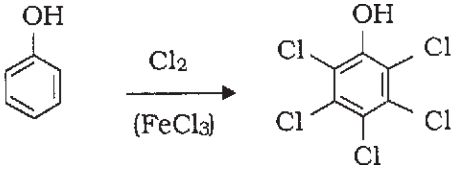
This is made by the further chlorination of chloro-benzene. Trichlorobenzene is a colourless liquid with pleasant odour, similar to that of ODCB and is miscible with most of the organic solvents, but not with water. Usually, it is a mixture of 1,2,4- trichlorobenzene and 1,2,3- trichlorobenzene, boiling in the range of 213°-219ºC. When suitably emulsified in water in the presence of dodecyl benzene sulphonic acid (as sodium salt or tri-ethanolamine salt) as the emulsifying agent, it acts as a carrier in polyester dyeing. This has a slightly higher carrier efficiency than ODCB. The emulsion is insensitive to pH variation and retains its carrier efficiency over a wide pH range. While removing the carrier from the dyed polyester material by scouring operation, it carries with it some amount of the dye from the dyed material, thereby colouring the scouring bath. This results in a slight loss of colour value of the dyeing. Its is moderately toxic when inhaled.

22. Pentachlorophenol

Mol. wt. 266.5
(Sodium salt) 288.5



This is made by the chlorination of phenol in the presence of catalyst such as ferric chloride.



Pentachlorophenol is available as white powder or crystals, melting a 190ºC and boiling at 310ºC with decomposition. It is very sparingly soluble in water (2 mg/100 ml), but is freely soluble in alcohol, ether, and dilute alkalies. The sodium salt (sodium pentachlorophenate) is soluble in water.

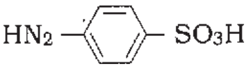
LD_{50} orally in male and female rats: 146 and 175 mg/kg respectively.

Human toxicity

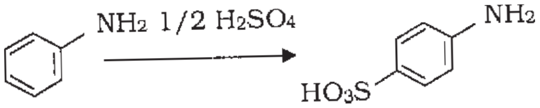
Ingestion causes increase and then decrease of respiration, blood pressure, urinary output, fever, increased bowel action, motor weakness, collapse with convulsions and death. Causes lung, liver and kidney damage, contact dermatitis. May be absorbed through skin. More toxic in organic solvents. Dust causes sneezing. It is a fungicide, bactericide, algicide and herbicide. It dust produces sneezing. It is used as preservative in sizing and finishing formulations containing starch, gums, glue, vegetable and muttom tallows, etc.

Sulphonic acids

23. Sulphanilic acid **Mol. wt. 173**



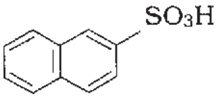
Sulphanilic acid (p-aminobenzene sulphonic acid) is made by heating aniline sulphate with fuming sulphuric acid at 200ºC for 5 hours and pouring the reaction mass in water.



This is available as greyish white, flat crystals, which are soluble in concentrated hydrochloric acid, and slightly soluble in water, alcohol and ether. It melts with charring at 280º-300ºC. It is combustible and has low toxicity.

Sulphanilic acid is used in the manufacture of solution aids (benzyl sulphanilic acid) in textile printing.

24. -Naphthalene sulphonic acid **Mol. wt. 208**

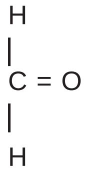


It is made by the high temperature sulphonation of naphthalene, when it is accompanied by a smaller amount of the alpha-isomer. It is available as non-deliquescent white plates, melting at 124º125ºC and is soluble in water, alcohol and ether. It is a combustible substance. It is used in the manufacture of dye-dispersing agent after condensing with formaldehyde. The sodium salt of the condensation product has strong protective colloid property and is especially useful as vat acid-dispersing agent and is also useful in dyeing synthetic fibrs with disperse dyes.

Aldehyde

25. Formaldehyde

Mol.wt. 30



$$\begin{array}{l} H \\ | \\ C = O \\ | \\ H \end{array}$$

Formaldehyde is made by the oxidation of synthetic methanol or propane or butane in the presence of silver, copper or iron/molybdenum oxide.

Formaldehyde is readily polymerizable gas and is available as a 37-40% solution in water, which is called formalin. This solution may contain up to 15% methanol, used to inhibit its polymerisation. The gas has a strong and pungent odour and is soluble in water and alcohol. It has moderate fire risk. Intensely irritating to mucous membranes and high concentrations are intolerable. This substance may reasonably be anticipated to be a carcinogen. Oral LD_{50} value in rats, 0.80 gm/kg (as formalin, which is about 37% solution of formaldehyde in water),

Formaldehyde is extensively used in the manufacture of resin precondensates and crosslinking agents (DMU, DMEU, DMPU, DMDHEU, etc.), cationic dye-fixing agent, dye-dispersing agent and methylol stearamide-based reactive softener. It is also used as a preservative for starch and gum pastes.

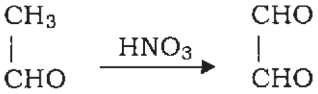
26. Glyoxal

Mol. wt. 58

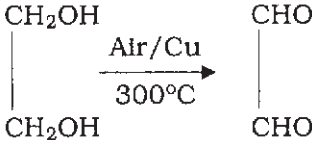
$$\begin{array}{l} CHO \\ | \\ CHO \end{array}$$

Glyoxal is made by the oxidation of acetaldehyde with nitric acid or by passing glycol vapours and excess air over copper at 300ºC.

It is available as yellow crystals or light yellow liquid, with a mild odour. It melts a 19ºC and boils a 51ºC. Its vapour is greenish in colour and burns with a violet flame. It is the simplest coloured compound containing carbon, hydrogen and oxygen only. It undergoes many addition and condensation reactions with amines and amides.



$$\begin{matrix} CH_3 \\ | \\ CHO \end{matrix} \xrightarrow{HNO_3} \begin{matrix} CHO \\ | \\ CHO \end{matrix}$$



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \xrightarrow[300^\circ C]{Air/Cu} \begin{matrix} CHO \\ | \\ CHO \end{matrix}$$

LD_{50} orally in rats and guinea pigs: 2,020 mg/kg and 760 mg/kg. This is moderately irritating to skin and mucous membranes.

Glyoxal is principally used in the manufacture of DMDHEU, the crosslinking, agent, for use in permanent press finishing of cotton and polyester/cotton blend fabrics.

Acids and their derivatives

27. Acetic acid **Mol. wt. 60**

$CH_3–COOH$

Dry distillation of wood produces acetic acid, which is neutralised with lime, the crude calcium acetate separated and decomposed into calcium sulphate and acetic acid by treatment with sulphuric acid.

Acetic acid is also made from acetylene, which is converted into acetaldehyde by the addition of water in the presence of mercury salts and the acetaldehyde in oxidized with atmospheric oxygen in the presence of metal oxides.

$CH = CH + H_2 O \longrightarrow CH_3 – CHO$

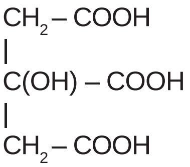
$2CH_3 – CHO + O_2 \qquad 2CH_3 – COOH$

Pure acetic acid has a pungent smell and is corrosive. Anhydrous acid freezes a 16ºC into ice-like crystals, which have given it the name “glacial acetic” acid. It boils a 118ºC.

LD_{50} orally in rats: 3.53 gm/kg. *Human toxicity*: Ingestion may cause severe corrosion of mouth and gastro –intestinal tract with vomiting, hematemesis, diarrhea, circulatory callapse and death. Chronic exposure may cause erosion of dental enamel, bronchitis and eye irritation.

Glacial acetic acid is used in dyeing cotton materials with vat dyes by vat acid method. It is also used solubilize (by salt formation) substituted fatty amines and in the manufacture of cationic dye-fixing agents.

28. Citric acid **Mol. wt. 192**



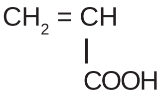
$$\begin{array}{l} CH_2-COOH \\ | \\ C(OH)-COOH \\ | \\ CH_2-COOH \end{array}$$

This acid is widely spread plant acid. It was discovered in lemon juice (which is the chief source of citric acid) . Glucose, maltose and dextrins are converted into citric acid by certain moulds (citromycates).

The acid is available as the monohydrate as well as the anhydrous acid. It melts at 153ºC (the hydrate melts below 100ºC). It is very readily soluble in water. Its i.p. LD_{50} value in rats is 975 mg/kg.

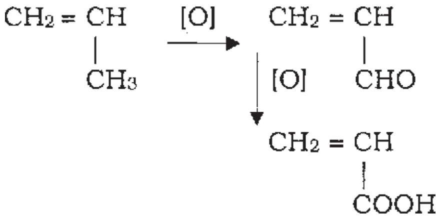
Citric acid is used along with magnesium chloride as the mixed catalyst in durable press finishing using DMDHEU.

29. Acrylic acid **Mol. wt. 72**



$$\begin{array}{ll} CH_2 = & CH \\ & | \\ & COOH \end{array}$$

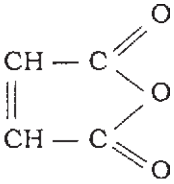
This is also called propenonic acid and acroleic acid. Acrylic acid is made by condensing hydrocyanic acid with ethylene oxide, followed by reaction with sulphuric acid. It is also made from acetylene, carbon monoxide and water in the presence of nickel catalyst. In another method, propylene is vapour-oxidized to acrolein, which is oxidized to acrylic acid at 300ºC with molybdenum – vanadium catalyst.



This is a colourless liquid with an acid odour. It polymerizes readily to poly (acrylic acid). It is miscible with water, alcohol and ether. It melts at 12ºC and boils at 141ºC. It is combustible and is an irritant and corrosive to skin and toxic by inhalation. LD_{50} value orally in rats is 2.59 gm/kg. Acrylic acid is used in the manufacture of poly (acrylic acid) and poly (methacrylic acid) and other acrylic polymers.

30. Maleic anhydride **Mol. wt. 98**

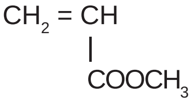
This is also know as 3,5-furandione. It is made by passing a mixture of benzene vapour and air over vanadium oxides catalyst at 450ºC or by the catalytic oxidation of butylene.



Powerful irritant, causes burns. Avoid contact with skin, eyes, and clothing. Inhalation can cause pulmonary edema. Avoid exposure to concentrated vapours. In case of contact, immediately flush skin and eyes with plenty of water for at least 15 min.

Maleic anhydride is available as colourless needles, melting at 53ºC and boiling at 200ºC. It is soluble in acetone, hydrocarbons, ether, chloroform and petroleum ether. It is slowly hydrolyzed by water. It is highly toxic and a strong irritant. After converting it into its dioctyl ester and sulphonating with sodium bisulphite, it gives dioctyl sulphosuccinate, the rapid wetting and rewetting agent.

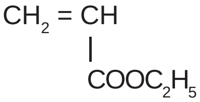
31. Methyl acrylate **Mol. wt. 86**



$$CH_2 = \underset{\displaystyle COOCH_3}{\underset{|}{CH}}$$

This is made form ethylene chlorohydrin, methanol and dilute sulphuric acid. It is also made by the oxo reaction of acetylene, carbon monoxide and methanol in the presence of nickel or cobalt catalyst. It is a colourless volatile liquid, with a boiling point of 80ºC. It is slightly soluble in water and is readily polymerized. Oral LD_{50} value in rats in 0.3 gm/kg. The monomer is highly irritating to eyes, skin and mucous membranes. Lethargy and convulsions may occur if monomer vapours are inhaled in high concentrations. It is used in the manufacture of poly (methyl acrylate).

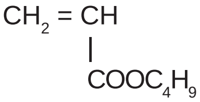
32. Ethyl acrylate **Mol. wt. 100**



$$\underset{\displaystyle COOC_2H_5}{\overset{\displaystyle CH_2 = CH}{|}}$$

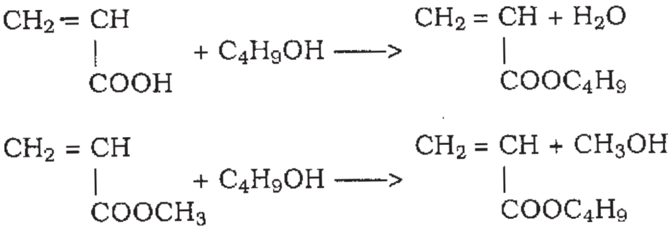
This made from ethylene chlorohydrin, ethyl alcohol and dilute sulphuric acid. It is also made by the oxo reaction of acetylene, carbon monoxide and ethyl alcohol in the presence of nickel or cobalt catalyst. It is a colourless liquid, boiling at 99ºC. It is miscible with alcohol and ether and is readily polymerised. The monomer is highly irritating to the eyes, skin and mucuous membranes. Lethargy and convulsions may occur if monomer vapours are inhaled in high concentrations. It is used in the manufacture of acrylic resins.

33. Butyl acrylate **Mol. wt. 128**



$$\underset{\displaystyle COOC_4H_9}{\overset{\displaystyle CH_2 = CH}{|}}$$

This is made by the reaction of acrylic acid or methyl acrylate with butyl alcohol.



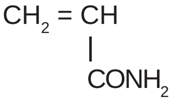
$$\underset{\displaystyle COOH}{\overset{\displaystyle CH_2 = CH}{|}} + C_4H_9OH \longrightarrow \underset{\displaystyle COOC_4H_9}{\overset{\displaystyle CH_2 = CH}{|}} + H_2O$$

$$\underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_2 = CH}{|}} + C_4H_9OH \longrightarrow \underset{\displaystyle COOC_4H_9}{\overset{\displaystyle CH_2 = CH}{|}} + CH_3OH$$

This is a colourless liquid, which polymerizes readily on heating. It boils in the range of 145º-148ºC. It is immiscible with water. It is moderately toxic and irritant.

Butyl acrylate is used as one of the monomers for producing binders used in pigment printing. Acrylic resins are thermoplastic polymers, co-polymers or terpolymers of acrylic acid, methacrylic acid, esters of these acids, acrylonitrile, butadiene and/or styrene.

34. Acrylamide **Mol. wt. 71**



$$\underset{\displaystyle CONH_2}{\overset{\displaystyle CH_2 = CH}{|}}$$

It is made by reacting acrylonitrile with 84.5% sulphuric acid, followed neutralisation.

$$CH_2=CH{-}CN \longrightarrow CH_2=CH{-}CONH_2$$

It is available as colourless, odourless crystals, melting at 84.5ºC. It is soluble in water, alcohol, and acetone but insoluble in benzene. LD_{50} i.p. in mice: 170 mg/kg. Highly toxic and irritant, causes central nervous system paralysis. Can be absorbed through unbroken skin. It is used in the manufacture of poly (acrylamide), which is a textile finishing agent as well as a sizing agent.

35. Stearamide **Mol. wt. 283**

$C_{17}H_{35}CONH_2$

This is made by heating stearic acid with urea:

$$C_{17}H_{35}COOH + H_2NCONH_2$$
$$\downarrow$$
$$C_{17}H_{35}CONH_2 + NH_3 + CO_2$$

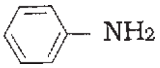
It may also be made by reacting gaseous ammonia with stearic acid at 150º-200ºC under pressure (100 psi):

$$C_{17}H_{35}COOH + NH_3 \longrightarrow C_{17}H_{35}CONH_2 + H_20$$

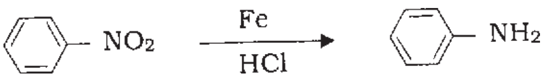
Stearamide is available in the form of colourless leaflets, melting at 109ºC and boiling at 251ºC. It is insoluble in water but is easily soluble in alcohol and ether. Stearamide is used for making reactive softener after reacting with formaldehyde under alkaline conditions. It is also used as a non-reactive softener after emulsifying in water using a suitable emulsifying agent.

Amines and proteins

36. Aniline **Mol. wt. 93**



This is made by reducing nitrobenzene with iron fillings and hydrochloric acid.



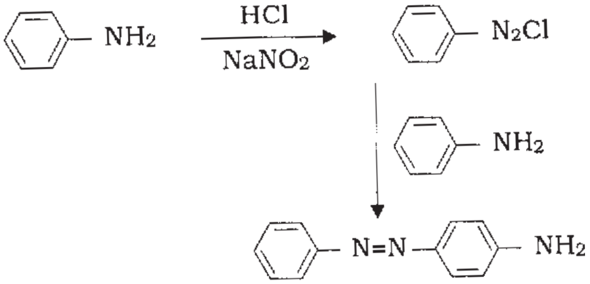
Freshly distilled aniline is a colourless, oily liquid with a boiling point of 183ºC. In light and air, it slowly turns brown. It is slightly soluble in water, but easily soluble in alcohol, ether and benzene.

LD_{50} orally in rats, 440 mg/kg.

Human toxicity

In-todication may occur from inhalation, ingestion or skin absorption. Acute toxicity: Cyanosis, methemoglobinemia, vertigo, headache, mental confusion. Chronic toxicity: anemai, weight loss, and cutaneous lesions.

Aniline is toxic, but the toxicity falls on sulphonation. Aniline is used in the dyeing and printing of aniline black. When it is diazotized and coupled with itself, it produces p-aminoazobenzene, which can be used as a catalyst in dyeing and printing of aniline black:



(p-aminoazobenzene)

37. Casein

This belongs to the most complex group of nitrogenous organic compounds (proteins) and occurs in the milk of all animals to the extent of approximately 3%. It is present in milk in a colloidally dispersed form as a phosphenoprotein (0.85% P and 0.76% S) containing fifteen amino acids and a molecular weight of 75,000 to 375, 000.

Casein is available as a white or light straw coloured, tasteless, odourless, non-toxic amorphous solid, with a moisture content of 8-10%. It is stable when dry, but deteriorates in a damp atmosphere by the absorption of moisture. It is soluble in dilute or concentrated alkalies but almost insoluble in water and gets precipitated from weak acidic solutions. It is used in the manufacture of wax emulsions and as a component of size mixture.

38. Glue

This is a colloidal suspension of various proteinaceous materials in water. The most common ones are made by boiling animal hides, tendons or bones which have high collagen content. The chief sources of glue are slaughter house wastes, blood and milk.

Glue is a typical colloid. It readily absorbs a considerable amount of water and swells, giving jellies. It has powerful protective colloid properties.

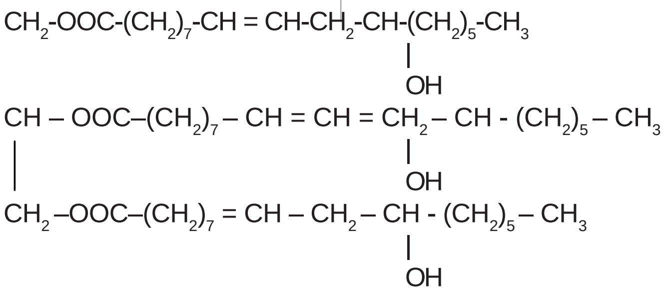
Its solution in water is thickened by alum, formaldehyde and tannins precipitated by chromium compounds (potassium dichromate) when exposed to light. This property is used in the photochemical method of making screens for use in screen printing. Glue is also used in water-proofing formulations, where the property of insolubilisation of metal salts is used.

Gelatine is similar to glue except that it is made form purified raw materials. Both glue and gelatine are used in sizing.

Miscellaneous compounds

39. Castor oil

Chemically, castor oil is the glyceride of ricinoleic acid.



$$\begin{array}{l}
CH_2\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}(CH_2)_5\text{-}CH_3 \\
CH - OOC-(CH_2)_7 - CH = CH = CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - (CH_2)_5 - CH_3 \\
\,| \\
CH_2 - OOC-(CH_2)_7 = CH - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - (CH_2)_5 - CH_3
\end{array}$$

This occurs in the seeds of castor beans. The beans are cold-pressed to get the medicinal grade, while they are hot pressed for other purposes (about 40% of the oil content is obtained by this method). The residual oil form the oil cake is recovered by solvent extraction.

Castor oil is a colourless to pale yellow, transparent viscous liquid with a faint milky odour and a nauseating taste. It is combustible and has low toxicity. It is miscible with alcohol, benzene, chloroform, etc.

Castor oil is extensively used in the manufacture of Turkey Red Oil (TRO), which is used as a wetting agnet, softener, dyeing assistant, etc.

40. Animal and vegetable waxes

These are low melting mixtures of organic compounds of high molecular weight, generally similar in composition to oils an fats, but are not glycerides. Some are hydrocarbons, others are esters of higher fatty acids and higher fatty alcohols. They are combustible and are soluble in most of the organic solvents, but not in water. Water repellency, smooth texture, non-toxicity, freedom from objectionable odour and colour are their common properties.

Beeswax, spermaceti, lanolin (wool wax) and shellac wax are obtained from animal sources, while carnauba, sugarcane, etc. provide vegetable waxes.

41. Starch

This is widely distributed throughout the vegetable kingdom and occurs in the form of granules in the seeds of cereals, in bulbs and tubers or plans and bark and pith of many trees. Starch is obtained mainly from wheat, maize, potato etc. Chemically, starch is a carbohydrate consisting of polyalpha-glucopyranose, in which straight chain (amylose) and branched chain (amylopectin) polymers are present. In amylose, the adjacent alpha-glucose molecules are linked through C_1-C_4 carbon atoms, while in amylopecting, in addition to the straight chain polymer, the branching takes place at the end glucose unit through C_1C_6 positions. Both the components are insoluble in water and alcohol.

When starch is boiled with water, the starch granules swell and break up forming a smooth and homogeneous, gelatinous mass. If starch is treated with water under pressure at about 150ºC, it dissolves and on cooling, a substance, called soluble starch, separates. Soluble starch is sparingly soluble in water at temperatures of less than 70ºC, but completely soluble above this temperature. When starch is boiled with dilute mineral acid, it undergoes hydrolysis with the breakdown of starch molecules, partly losing its thickening property.

Starch is used in sizing, printing and finishing processes.

42. Dextrins/British gums

These are starch degradation product. Whereas starch gives a viscous thickening with low solid content (8 to 10%), dextrin pastes need higher solid content (up to 40 to 50%) to get the required viscosity (in printing). Dextrin is made by calcining dry starch at 200ºC or calcining a paste of starch at 200ºC in the presence of a small amount of nitric acid. During the heat treatment, in the presence or absence of an acid, the starch gets hydrolysed, resulting in the lowering of the degree of polymerisation (starch molecular chains break and the molecular weight decreases). In the case of dextrin (dark British Gum) roasting is continued till the whole of starch is dissolved, while in the case of yellow dextrin (light British Gum), the roasting process is arrested (stopped) before complete solubilisation takes place. The unaltered starch forms the insoluble portion of British Gum, so that when it is boiled with water, it gives a mixture of dextrin and starch paste. The more starch a British gum contains, the more will it have the qualities of starch and less gummy will it be. British gums may be mixed with starch in any proportion and thus it is possible to vary the consistancy and quality of the thickening as desired.

43. Guar gum

This is produced from the endosperms of guar seed. The gum is a nonionic natural polysaccharide and is polygalactomannan. Sodium silicofluoride or sodium pentachlorophenate may be added to it as a preservative. Pure guar gum contains 36% D-galactose and 64% mannose with a molecular weight of about 220,000. This is available as a free flowing powder. It forms viscous, colloidal dispersions when soaked in water. The paste is stable over the pH range 1-10.5 and is insensitive to electrolytes (which do not salt it out). The capacity of giving high viscosity pasts is a unique property of guar gum. Borax is a gelling agent for gum paste. Guar gum paste is stable for many days. Formaldehyde and chlorophenols (0.1%) act as preservatives for guar gum pastes. By chemical reaction, the nonionic natural of guar gum can be changed to anionic. For examples, the hydroxy group can be carboxymethylated by reaction with chloroacetic acid. It may be hydroxyethylated by reacting it with ethylene chlorohydin.

44. Carbon tetrachloride CCl_4 Mol. wt. 154

This is manufactured from carbon disulphide and chlorine at 40º-60ºC in the presence of iron filings and manganese chloride.

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

$$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$$

It is also made by chlorinating methane of natural gas at 250º-400ºC.

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$$

Carbon tetrachloride boils at 76ºC and has a specific gravity of 1.589. This is a colourless, clear, non-inflammable heavy liquid with a characteristic odour. It is immiscible with water, but miscible with alcohol, benzene, chloroform, ether and carbon disulphide. LD_{50} value for mice: 9.528 gm/kg.

Human toxicity: Poisoning by inhalation, ingestion or skin absorption. Acute toxicity: nausea, vomiting, diarrhea, headache, kidney damage, liver injury, and death. Chronic toxicity: primarily, liver damage but kidney injury and visual disturbances also occur. Skin contact can lead to dermatitis through defatting action. This substances may reasonably be anticipated to be a carcinogen. It is used as a fire extinguisher and is a component of stain removers.

45. Chloroform $CHCl_3$ Mol. wt. 119.5

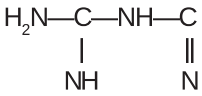
Chloroform is manufactured by the partial reduction of carbon tetrachloride with nascent hydrogen from steam and iron filings. Methylene chloride is a by-product.

$$CCl_4 + 2H \longrightarrow CHCl_3 + HCl$$

$$CCl_4 + 4H \longrightarrow CH2Cl_2 + 2HCl$$

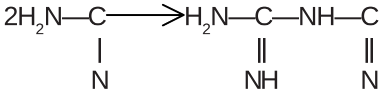
Chloroform is a colourless heavy liquid (sp. gr. 1.4984) which is non-inflammable. It boils at 62ºC and has a sweet, sickly smell. It is practically immiscible with water, but is readily miscible with alcohol, ether, acetone, benzene and carbon disulphide. Chloroform is a solvent for oils and fats and is a component of stain removing systems. It has anaesthetic properties. LD_{50} orally in rats: 2.18 ml/kg. *Human toxicity*: Inhalation of large doses may cause hypotension, respiratory and myocardial depression and death. This substance may reasonably be anticipated to be a carcinogen.

46. Dicyandiamide **Mol. wt. 84**



$H_2N-\underset{\underset{NH}{|}}{C}-NH-\underset{\underset{N}{\|}}{C}$

This is also known as cyanoguanidine and is made by the controlled dimerisation of cyanamide in the presence of a base catalyst, such as ammonia, alkaline earth metal hydroxide, etc.



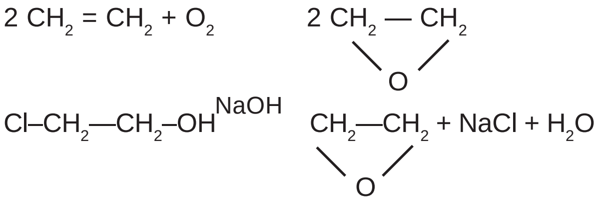
$2H_2N-\underset{\underset{N}{|}}{C} \longrightarrow H_2N-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{N}{\|}}{C}$

This is available as pure white crystals. It is stable when dry and melts in the range of 207º-209ºC. It is non-inflammable, and is soluble in water and alcohol, but is sparingly soluble in ether. Aqueous solution decomposes slowly above 80ºC, giving ammonia.

Dicyandiamide is extensively used in the manufacture of cationic dye-fixing agent.

47. Ethylene oxide **Mol. wt. 44**

This is made by the oxidation of ethylene in the air or oxygen with silver catalyst or by the action of an alkali on ethylene chlorohydrin:



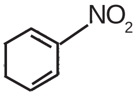
This is a highly inflammable gas with high fire and explosive risk. Workers exposed to ethylene oxide got leukemia. Highly irritating to eyes and mucous membranes. High concentrations can cause pulmonary edema. Exposure should not exceed 50 ppm on an 8-hour time-weighted average. This substance may reasonably be anti-cipated to be a carcinogen. It is extensively used in the manufacture of nonionic surfactants by reaction with nonyl phenol, cetyl alcohol, oleic acid, stearic acid, stearyl amine, castor oil, etc. These give detergents, softeners, antistatic agnets, emulsifiers, etc.

48. Ethylene diamine Mol. wt. 60

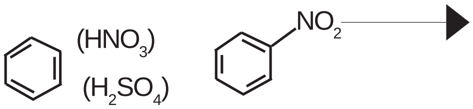
$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$

This is made by heating ethylene dichloride with ammonia, followed by distillation. It is a colourless alkaline liquid with the odour of ammonia. It is a strong base and is miscible with water. It boils at 116ºC and is a strong skin and eye irritant. It is highly toxic by inhalation and skin absorption. Oral LD_{50} value in rats is 1.16 gm/kg. Care must be taken in handling, because of its caustic nature and the irritating properties of its vapour. It is used in the manufacture of the sequestering agent, EDTA.

49. Nitrobenzene Mol. wt. 123



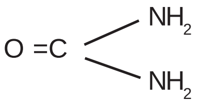
Nitration of benzene is carried out in the presence of concentrated sulphuric acid produces nitrobenzene.



Nitrobenzene is a pale yellow, oily liquid, with a boiling point of 209ºC. It smells like oil of bitter almonds (it is also known as oil of mirbane or essence of mirbane). It is a highly toxic chemical, readily absorbed through the skin, by ingestion and by inhalation. LD_{50} orally in rats: 640 mg/kg. Rapidly absorbed through skin and its vapours are hazardous. Do not get in eyes, on skin and on clothing. Avoid breathing vapour. Use only with adequate ventilation. May cause headaches, drowsiness, nausea, vomiting, methemoglobinemia with cyanosis. It is miscible with benzene, alcohol and ether and is slightly miscible with water.

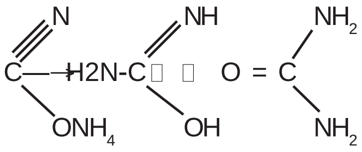
When sulphonated, it gives m-nitrobenzene sulphonic acid, the sodium salt of which is a mild oxidising agent. This mild oxidising agent is used in scouring cotton fabrics, containing coloured effect threads. It oxidises the reducing impurities and protects the dye from getting reduced. It is also used in printing pastes containing reactive and/or disperse dyes to protect the dye from any reducing influences.

50. Urea **Mol. wt. 60**



Urea is made by evaporating an aqueous solution of potassium cyanate and ammonium sulphate. The resulting urea is extracted with ethyl alcohol and crystallised.

$2KOCN + (NH_4)_2\ SO_2 \longrightarrow K_2SO_4 + 2NH_4OCN$

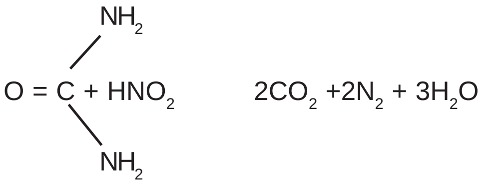


In another method, ammonia is reacted with carbon dioxide to give ammonium carbamate, which is heated under pressure to give urea and water.

$2NH_3 + CO_2 \longrightarrow H_2N - COONH_4$

$H_2N - COONH_4 \longrightarrow H_2NCONH_2 + H_2O$

Urea crystallises in prisms, can be sublimed in vacuum, and is readily soluble in water and alcohol. It melts at 133ºC. Nitrous acid reacts with urea to give carbon dioxide, water and nitrogen (this reaction is used to destroy nitrous acid).



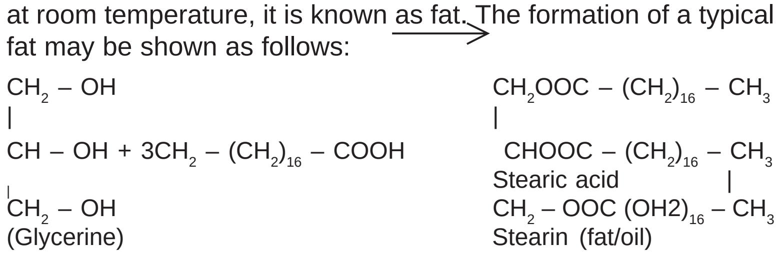
Urea is widely used in the manufacture of urea-formaldehyde precondensate (DMU). It is also used as a clarifying agent while preparing aqueous solutions of dodecyl benzene sulphonate detergents (liquid brands). Urea is used while preparing the printing pastes for printing reactive dyes on cellulosic fibre fabrics.

7

Anionic Surfactants

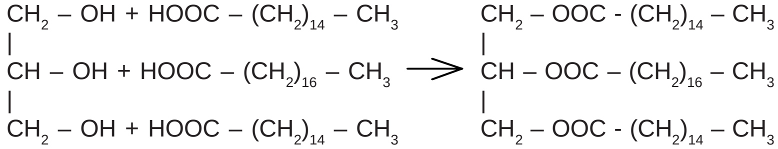
SOAP

Vegetable and animal oils like coconut oil, palm oil, olive oil, castor oil, butter fat, lard, cotton seed oil, soya bean oil, linseed oil etc. are esters of long chain saturated or unsaturated acids. Since these acids are obtained by splitting these oil and fats (hydrolysing), they are known as fatty acids. When the oil is solid at room temperature, it is known as fat. The formation of a typical fat may be shown as follows:

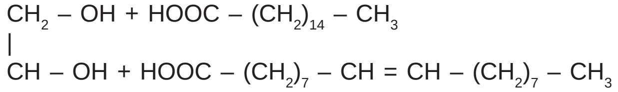


$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH + 3CH_2-(CH_2)_{16}-COOH \\ | \\ CH_2-OH \\ \text{(Glycerine)} \end{array} \longrightarrow \begin{array}{l} CH_2OOC-(CH_2)_{16}-CH_3 \\ | \\ CHOOC-(CH_2)_{16}-CH_3 \\ \text{Stearic acid} \qquad | \\ CH_2-OOC\ (OH2)_{16}-CH_3 \\ \text{Stearin (fat/oil)} \end{array}$$

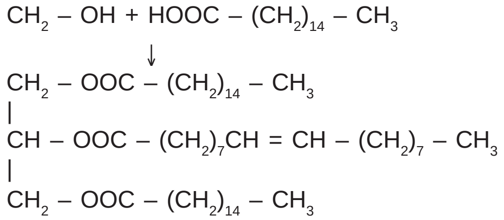
Sometimes mixed glycerides are formed. Thus palmitic and stearic acids combine with glycerine or palmitic and oleic acids combine with glycerine:



$$\begin{array}{l} CH_2-OH + HOOC-(CH_2)_{14}-CH_3 \\ | \\ CH-OH + HOOC-(CH_2)_{16}-CH_3 \\ | \\ CH_2-OH + HOOC-(CH_2)_{14}-CH_3 \end{array} \longrightarrow \begin{array}{l} CH_2-OOC-(CH_2)_{14}-CH_3 \\ | \\ CH-OOC-(CH_2)_{16}-CH_3 \\ | \\ CH_2-OOC-(CH_2)_{14}-CH_3 \end{array}$$

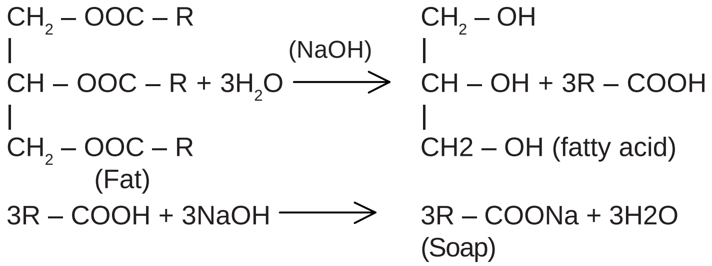


$$\begin{array}{l} CH_2-OH + HOOC-(CH_2)_{14}-CH_3 \\ | \\ CH-OH + HOOC-(CH_2)_7-CH=CH-(CH_2)_7-CH_3 \end{array}$$



$$\begin{array}{l} CH_2 - OH + HOOC - (CH_2)_{14} - CH_3 \\ \qquad\qquad\downarrow \\ CH_2 - OOC - (CH_2)_{14} - CH_3 \\ | \\ CH - OOC - (CH_2)_7CH = CH - (CH_2)_7 - CH_3 \\ | \\ CH_2 - OOC - (CH_2)_{14} - CH_3 \end{array}$$

When fats get split up (hydrolysed) in the presence of an alkali like sodium hydroxide, the original fatty acid and glycerine are first produced; the fatty acid then reacts with sodium hydroxide to form the sodium salt of the fatty acid, also known as soap. Because soap is one of the products of hydrolysis out under alkaline conditions, the splitting reaction is known as saponification.



$$\begin{array}{lcl} CH_2 - OOC - R & & CH_2 - OH \\ | & (NaOH) & | \\ CH - OOC - R + 3H_2O & \longrightarrow & CH - OH + 3R - COOH \\ | & & | \\ CH_2 - OOC - R & & CH2 - OH\ \text{(fatty acid)} \\ \qquad\text{(Fat)} & & \\ 3R - COOH + 3NaOH & \longrightarrow & 3R - COONa + 3H2O \\ & & \text{(Soap)} \end{array}$$

Specifically the following soaps are formed either individually or in mixtures with each other during saponification of oils and fats:

1. Sodium stearte (sodium salt of C_{18} saturated acid or octadecanoic acid, i.e. stearic acid)

   $CH_3 - (CH_2)_{16} - COONa$.

2. Sodium palmitate (sodium salt of C_{16} saturated acid or hexadecanoic acid i.e., palmitic act.

   $CH_3 - (CH_2)_{14} - COONa$

2. Sodium oleate (sodium salt of C_{18} unsaturated acid or 9, 10 – octadecenoic acid i.e., oleic acid).

   $CH_3(CH_2)_7 - CH = CH - (CH_2)_7 - COONa$

3. Sodium myristate (Sodium salt of C_{14} saturated acid or tetradecanoic acid i.e., myristic acid).

   $CH_3 - (CH_2)_{12} - COONa$

4. Sodium laurate (sodium salt of C_{12} saturated acid or dodecanoic acid, i.e., lauric acid).

   $CH_3 - (CH_2)_{10} - COONa$

Soap has been in use as a cleansing/laundering agent from ancient times. This is an anionic surface active agent (with the right degree of hydrophilic-lyophilic balance, HLB). It has tremendous dirt or soil suspending power. During washing of soiled clothes with soap solution, soap facilitates the desoiling process (removal of soil) and then keeps the released soil in a suspension or dispersed form, thereby preventing its redeposition on other portions of the clothes. This property of soil removal and keeping it in suspension (anti-soil redeposition) is called detergency and a compound having the property of detergency is called a detergent. Soap is a good detergent, and an anionic surface active agent.

The alkali metal (sodium, potassium etc.)salts of fatty acids are soluble in water but alkaline earth metal (calcium and magnesium) and some other metal (aluminium) salts of these acids are insoluble in water and are sticky in nature. When hard water (especially of permanent hardness, which is due to the presence of chlorides and sulphates of calcium and magnesium) is used for dissolving sodium soaps, calcium and magnesium chlorides and sulphates present in the water precipitate calcium and magnesium soaps.

$$2R - COONa + CaCl_2 \longrightarrow (R - COO)_2Ca + 2NaCl$$

$$2R - COONa + MgCl_2 \longrightarrow (R - COO)_2MG + 2NaCl$$

If this is used in washing soiled clothes, the soap not only loses the property of detergency but also is converted into sticky calcium and magnesium soaps which firmly adhere to the clothes. Since sodium soap is removed from the solution, the detergency and the wetting power of the solution are removed and the solution fails to produce lather when vigorously shaken (lather formation or foaming is a criterion). However, when more sodium soap is used in washing the calcium and magnesium soaps (also called lime soaps) are dispersed in water and then the excess soap will be useful in cleaning the solid clothes. In other words the soap consumption increases in washing soiled clothes if hard water is used for the purpose.

The other disadvantage of soap is that it is unstable to acidic solution. When a solution of sodium soap is acidified with dilute hydrochloric and or sulphuric acid, the free fatty acid is formed, which being insoluble in water, is precipitated. This is also a sticky mass and the solution loses surface activity and also detergency. It does not lather any more:

$$R - COONa + HCl \xrightarrow{\quad} R - COOH + NaCl$$

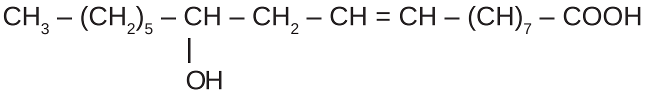
$$2R - COONa + H_2SO_4 \xrightarrow{\quad} 2R - COOH + Na_2SO_4$$

TURKEY RED OIL (TRO)

In order to overcome the defects of soaps, certain attempts were made. The first attempt concerns the reaction of concentrated sulphuric acid with olive oil and almond oil to get sulphated oils. Later (in 1834) the sulphated oils (especially olive oil) were neutralised with potassium hydroxide to obtain an oily, water-dispersible substance. This was first used in the dyeing of Turkey Red. Sulphated oleic acid and other oils were also found to have similar properties. These were known as Turkey Red Oils. Castor oil was sulphated for the first time in 1875 and was found to be more useful than others in the dyeing of Turkey Red. Later ir was found that it had other applications too. Textile finishing and leather industries found sulphated castor oil very useful and large quantities of this product known as Turkey Red Oil (TRO) were manufactured. This product was surpassed all other sulphated oils.

Turkey Red Oil is made by treating castor oil with concentrated sulphuric acid with constant stirring over a prolonged period, followed by neutralising with sodium hydroxide.

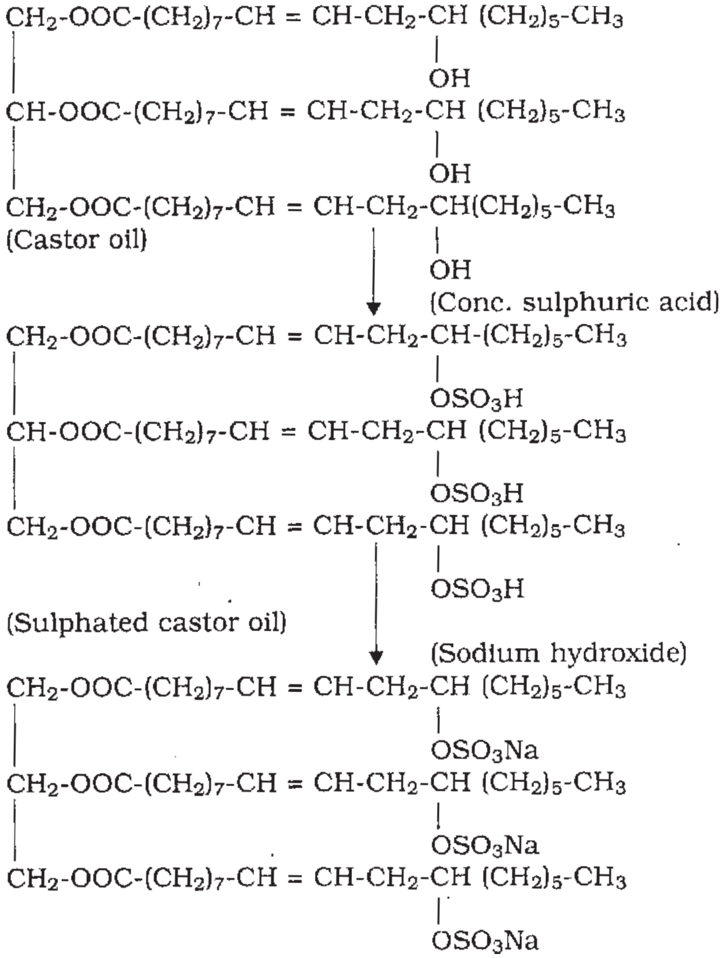
Castor oil is the glyceride of ricinoleic acid (which has a hydroxy group and double bond in its molecule):



$$CH_3 - (CH_2)_5 - \underset{\substack{|\\ OH}}{CH} - CH_2 - CH = CH - (CH)_7 - COOH$$

(Ricinoleic acid or 12-hydroxy-9, 10-octadecenoic acid)

Generally sulphuric acid can react with both the hydroxy group and the double bond, but under controlled conditions of temperature, the reaction may be predominantly restricted to the sulphation of hydroxy group. The different reactions taking place are shown in the following page:



$$\begin{array}{l}
CH_2\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\ (CH_2)_5\text{-}CH_3 \\
| \\
CH\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\ (CH_2)_5\text{-}CH_3 \\
| \\
CH_2\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}(CH_2)_5\text{-}CH_3
\end{array}$$

(Castor oil)

$$\Big\downarrow \text{(Conc. sulphuric acid)}$$

$$\begin{array}{l}
CH_2\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\displaystyle OSO_3H}{\underset{|}{CH}}\text{-}(CH_2)_5\text{-}CH_3 \\
| \\
CH\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\displaystyle OSO_3H}{\underset{|}{CH}}\ (CH_2)_5\text{-}CH_3 \\
| \\
CH_2\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\displaystyle OSO_3H}{\underset{|}{CH}}\ (CH_2)_5\text{-}CH_3
\end{array}$$

(Sulphated castor oil)

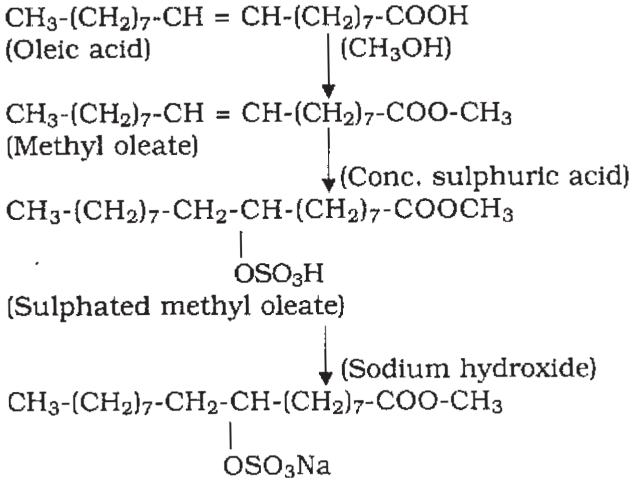
$$\Big\downarrow \text{(Sodium hydroxide)}$$

$$\begin{array}{l}
CH_2\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\displaystyle OSO_3Na}{\underset{|}{CH}}\ (CH_2)_5\text{-}CH_3 \\
| \\
CH_2\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\displaystyle OSO_3Na}{\underset{|}{CH}}\ (CH_2)_5\text{-}CH_3 \\
| \\
CH_2\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\displaystyle OSO_3Na}{\underset{|}{CH}}\ (CH_2)_5\text{-}CH_3
\end{array}$$

(Sodium salt of sulphated castor oil or turkey red oil)

Sodium salts of sulphated vegetable and animal oils (sulphation taking place at alcoholic group and/or the double bond) are reasonably stable; they get dispersed in water usually to give clear solutions, are not completely precipitated by calcium and magnesium salts present in hard water and have limited stability to acidic solutions; (they are more stable to acids than soaps).

Another similar product, but having better wetting power and greater stability is made by esterifying oleic acid with methanol and sulphating the resulting ester with sulphuric acid, followed by neutralising;



$$\underset{\text{(Oleic acid)}}{CH_3\text{-}(CH_2)_7\text{-}CH = CH\text{-}(CH_2)_7\text{-}COOH} \xrightarrow{(CH_3OH)} \underset{\text{(Methyl oleate)}}{CH_3\text{-}(CH_2)_7\text{-}CH = CH\text{-}(CH_2)_7\text{-}COO\text{-}CH_3}$$

$$\xrightarrow{\text{(Conc. sulphuric acid)}} \underset{\text{(Sulphated methyl oleate)}}{CH_3\text{-}(CH_2)_7\text{-}CH_2\text{-}\underset{\displaystyle OSO_3H}{\underset{|}{CH}}\text{-}(CH_2)_7\text{-}COOCH_3}$$

$$\xrightarrow{\text{(Sodium hydroxide)}} CH_3\text{-}(CH_2)_7\text{-}CH_2\text{-}\underset{\displaystyle OSO_3Na}{\underset{|}{CH}}\text{-}(CH_2)_7\text{-}COO\text{-}CH_3$$

(Sodium salt of sulphated methyl oleate)

In products like Turkey Red Oils and sulphated methyl oleate, the solubilising group (Sulphate group) is at the centre of, or inside, the aliphatic chain, unlike in soap where the solubilsing group – carboxylate group – is at the end of the chain.

Generally, sulphuric acid can react both with the hydroxy group and at the double bond, but under controlled conditions the reaction may be predominantly restricted to the hydroxy group, which is sulphated.

Turkey Red Oil is made by sulphating castor oil, followed by neutralising with sodium hydroxide. Under these conditions, the following products are likely to be formed – fatty acid (ricinoleic acid), soap (sodium ricinoleate), glycerol, triglyceride (unreacted castor oil), mono and diglycerides, lactones, lactides, sulphated fatty acid, monoglyceride sulophate, diglyceride sulphate, sulphated triglyceride, corresponding sulphonates and sulphato sulphonates, hydroxy sulphates or sulphonates, hydroxy fatty acid and hydroxy glycerides.

During the preparation of sulphated oils, certain precautions are necessary, including proper temperature control. Sulphation is carried out in a corrosion-resistant vessel, provided with an agitator and cooling coils. The oil is first taken in the reaction vessel and cold concentrated sulphuric acid (20-25% on the weight of the oil) is slowly run in with constant stirring. Cooling is started by circulating cold water. the reaction between sulphuric acid and the oil is an exothermic reaction. Therefore sulphuric acid should be added slowly and the temperature should not be allowed to rise above 30º-35ºC. Above 35ºC hydrolysis of the glyceride into ricinoleic acid and glycerine, as well as desulphation of the already sulphated hydroxy group may take place, thereby reducing the yield, and forming undesirable byproducts.

After all the acid is added, agitation and cooling are continued for some time. Sulphuric acid is taken in slight excess, which is either neutralised with dilute sodium hydroxide solution or washed with sodium chloride solution. Exact temperature control is necessary during this critical step of neutralisation or salt washing. High temperature and higher concentrations of sodium hydroxide lead to desulphation and hydrolysis of the glyceride. As a result, the combined sulphur content (due to $-OSO_3H$) is reduced and free fatty acid content of the final products is increased. In order to avoid or minimise these difficulties, neutralising and washing processes should be done at low temperatures in a short time.

In one method, a batch of 30 kg. sulphuric acid (66ºBe) is slowly run into 100 kg. castor oil. The temperature is not allowed to rise above 350ºC, which requires the use of cooling coils and the addition of acid in not less than 2 hours. Agitation is continued for 2 hours more and the mixture allowed to stand overnight. It is then washed with 1½ times its volume of 15% sodium sulphate solution at 50º-60ºC (not more then 60ºC). Again it is allowed to stand overnight and the acid liquor is drawn off. The washed sulphated product is neutralised and diluted to the required concentration. Alternatively the wshing may first be done by using cold water and then by using 15% sodium sulphate solution at 40ºC to get a light coloured and more fluid product.

In another method, castor oil is agitated at a high speed and sulphuric acid (22.5% on the weight of the oil) is added in 1 hour. The temperature rises to 40º-45ºC. When all the acid is added, the mixture is poured into 10ºBe solution of sodium sulphate (twice the volume of the oil). The mixture is agitated for 5-10 min. and allowed to settle for 30-60 min. and the liquors separated. The sulphated oil is neutralised with caustic soda until it is slightly acidic. After standing overnight, a new separation takes place. When the separation is complete, more caustic soda is added until lit becomes neutral.

SULPHATED DERIVATIVES OF FATTY ACID ESTERS OF MONOVALENT ALCOHOLS

These are made by the esterification of oils with monovalent alcohols (ester exchange) and subsequent or simultaneous sulphonation. The resulting products are better then TRO since in the former the carboxyl group is blocked by esterification. Six methods of making these products are as follows:

(1) Esterification of sulphated oils with monovalent alcohols.

(2) Sulphation of mixture of alcohol and oil in the presence of a dehydrating agent.

(3) Preparation of the alkyl sulphuric acid and reacting it with the fatty acid.

(4) Action of the alcohols on alkaline salts of the fatty acids in the presence of acid catalysts.

(5) Preparation of the ester, followed by sulphation.

(6) Sulphation of the oils, followed by washing and reacting with alcohols.

The fifth method is most frequently used for industrial production. The process is carried out in three stages alcoholysis of castor oil (or olein), sulphation, washing and neutralisation.

Castor oil is mixed with ¼th of its weight of butyl alcohol and the mixture is heated in an enamel-lined autoclave to 90ºC. Then 0.5% (on the weight of oil) sulphuric acid (66ºBe) is added, followed by heating the mixture to 100-130ºC for 3 hours to complete the esterificaton. After cooling, the acid-glycerine liquor is drawn off. The butyl ester of ricinoleic acid is then treated with four times its weight of 98% sulphuric acid in an enamelled sulphonator at –15ºC, and the temperature is not allowed to exceed 5ºC. After sulphation, the product is washed with a mixture of ice and water, the temperature being maintained at –5º to –10ºC. The contents are allowed to settle for 2 hours and the acid water is drawn off. It is washed with a salt solution containing a little amount of caustic soda of aid in setting. It is kept overnight, separated again and neutralised with cold caustic soda solution.

Other alcohols such as propyl, isopropyl, isobutyl, amyl or methyl alcohol may be used instead of butyl alcohol.

Sulphated butyl ricinolate with a little amount of butanol is a good wetting agent, used in all cases where rapid penetration of the material is required. In sizing, 100-1000 g/100 litres of the product gives improved penetration of the size into the fibres. It may be used in enzyme desizing (0.3-1 g/l) continuously; where the cloth is impregnated with the enzyme solution and piled. 0.5-1 g/l of the product may be used in desizing liquor. In wetting, 0.5-1.0 g/l may be used at 20º-30ºC, while in kier boiling 0.5-1 g/l at the high temperature of operation may be added. This may be used (0.5 g/l) in the hypochlorite bleach baths (0.5-2 g active chlorine per litre, 1-2 g/l soda ash).

SIZING SOFTENERS

The materials generally used for sizing include adhesives, softeners, lubricants, penetrating agents, hygroscopic agents, preservatives, anti-foaming agents, fillers etc. In each class there are many materials which can be used with varying efficiency. Thus adhesives, starches, dextrine, gums, glue gelatine, synthetic adhesives etc. may be used. Starches and gums play an important part in giving surface binding properties combined with penetration in the yarn. Thin films of starch impart strength and gums keep the size mixture uniform. Use of proper proportions of starch, thin boiling starch and gums give a size mixture with sufficient penetration, adhesion and transparency to the yarn without stickiness.

The use of a softener in the size mixture is essential to help retention of the size mixture on the yarn by way of penetration as a result of slowing down of drying of starch film on the yarn, reducing dropping, increasing the elasticity which is partly lost due to starching and increasing the flexibility due to plasticising action. Another effect of the softener of the facilitation of the separation of the yarns at the lease rods and the decrease of the amount of the pull on the fibres from the yarn surface at these points and thus resulting in the reduction of percentage breakage of yarns and hence increasing the weaving efficiency.

A number of products including tallow fats, waxes, blends of mineral oil, soap and sulphated or sulphonated oils are available as sizing softeners. The softener is usually used at 5-10% (based on the weight of starch) concentration level.

Melting point and viscosity are the most important properties of sizing softeners. Softeners having high melting points do not have sufficient flow property to produce the desired lubricating effect. Those with low viscosity also do not provide the necessary lubrication to the sized yarn.

The lubricating property is important from the point of view of weaving efficiency, as it reduces the friction between yarns and reeds, healds, drop wires and shuttles and thus increases the resistance to abrasion. Proper lubrication also helps to prevent sticking of slasher to drying cylinders. The reduction in the stiffness of the starch film helps to decrease the friction between the yarns.

Mutton tallow, vegetable tallow, mineral oil-based products, sulphated fats and castor oil-based products are used as the sizing softeners in India. Mutton tallow is considered one of the best sizing softeners. It is free from moisture and hence is very stable towards rancidity on storage. It has low unsaturation and hence is stable towards oxidation.

Mineral oil-based softeners are made in large quantities in India. Their tendency of staining, producing yellowing effect on the yarn and difficulty in the complete removal from the cloth etc. are some of the disadvantages of such softeners.

Castor oil-based softeners, which impart very good lubricating effect and are cheap too, found ready acceptance as sizing softeners. However, they develop rancidity very fast on storage because of the presence of a double bond in the oil molecule. Since they are liquids at the room temperature, the starch on the yarn becomes too soft and lacks considerably in strength.

Vegetable tallow, consisting of lime soaps of vegetable oils also found ready acceptance in sizing as softeners. They contain 10.15% of water in them. These cannot be washed completely form the cloth. Due to the presence of large proportion of water, they develop rancidity very fast and hence their storage stability is poor.

Sulphated products have excellent softening and emulsifying properties with some wetting properties, though their lubricating properties are poor. Many of them cause foaming in the sizing mixture.

A suitable sizing softener should have the following characteristics: (1) low moisture content, (2) very low free fatty acid, (3) neutral pH, (4) low iodine value, (5) melting point in the range 40ºC-50ºC, (6) low ash content and (7) freedom from alkali metal or alkaline earth metal soaps.

Various vegetable and synthetic tallow products are available as mutton tallow substitutes. One of them is described as a combination of an oxidising agent with fatty acids as well as an emulsifying agent and a catalyst. Another is described as that containing mixed esters of certain fatty acids with a small quantity of certain additives and is completely free form mineral oil and waxes.

They resemble hard wax in consistency and act as hydrolysing and softening agents for starch. Hence they bring down the viscosity of starch enabling a better and more homogenous coating of the size to be obtained on yarn. They are available in the form of insoluble slabs, which have to be crushed and added to the starch, pasted with water and boiled with stirring. They are readily dispersible in cold and hot water and are insoluble in water.

FATTY ALCOHOL SULPHATES

History

In fact the knowledge of half esters of primary aliphatic alcohols with sulphuric acid dates back to the first half of the 19th century. As early as 1936 Dumas prepared sodium cetyl sulphate $C_{16}H_{13}OSO_3Na$ for the first time in history in Germany. Soon after the 1st World War detergents were developed by sulphating fatty alcohols obtained from oils like coconut oil. They were classed as Gardinol type of detergents. Typical surface activity is found amongst the alkyl sulphates containing 8 to 18 carbon toms. Those with low molecular weights exhibit maximum activity at room temperature. As molecular weight rises, higher temperatures are required to obtain highest detergency and maximum wetting powder. Alkyl sulfates are rated as one of the most important groups of commercially useful surface active agents. Probably there has been a more thorough scientific study of their properties when compared to that of any other class of synthetic detergents. Their production on commercial scale started around 1930. Form this time onwards there had been an intense activity in the entire filed of synthetic detergents. Alkyl sulphates are among the most widely used synthetic detergents. They find much utility in specialty market where they are quite well established. Even the coming in of the more economical alkene sulphoacids and alkyl aromatic sulphoacids which can be manufactured on a large scale could not disturb their popularity. This may be partly due to the development of more economical and synthetic methods for manufacturing the aliphatic alcohols required as raw materials for the manufacture of their sulphates. Again since 1965 there has been an inclination towards more biodegradable products in detergent industry. This inclination initiated a trend towards ethoxylated and sulphated aliphatic alcohols and away from ethoxylated and sulphated alkyl phenols. This factor also contributes to the popularity of alkyl sulphates in detergent industry.

As such, history of alkyl sulphates is closely linked with the history and progress in the production of detergent range alcohols, more and more economically. Now, in nature, as compared to the long chain aliphatic hydrocarbons and fatty acids the corresponding alcohols occur in more or less limited amounts either as free alcohols or in a combined state. Their procurement on a commercial scale at economical price and in sufficient amount therefore posed a major problem in the detergent industry. In the beginning, in Germany these fatty alcohols were manufactured by high pressure hydrogenation of the simple esters of fatty acids. Even unsaturated alcohols like oleyl alcohol could be made by this process. Next I.G. directly reduced fatty glycerides or esters of fatty acids by employing metallic sodium xylol and isobutanol. To produce oleyl alcohol for example oleic acid was first made into its isobutyl ester which was then reduced to xylol by finely divided sodium at a temperature of 110º-115ºC. Sperm oil alcohols were prepared form moisture free sperm oil by this sodium xylol/isobutanol process. (Sperm oil is obtained form the head of the sperm whale). Sources of sperm oil, coconut oil and oleyl alcohol dwindled down fast in Germany with the progress of the 2nd World War. Fatty alcohols were then made by I.G. by oxidising paraffins to synthetic fatty acids and by converting certain fractions of these fatty acids into fatty alcohols, which corresponded to natural fatty alcohols like lauryl, cetyl etc. In the oxo process $C_{11} – C_{17}$ olefines obtained by

Fischer-Tropsch process were converted into alcohols via aldehydes using appropriate catalyst and proper temperature. The synthetic processes were thus developed to furnish fatty alcohols of right chain-length at economic prices. These synthetic processes have substantially contributed in bringing down the cost of sulphated alcohols. At the same time they have solved the problem of depending upon fats and oils as the only sources of these detergent range alcohols since the source of raw material could be located in petroleum feedstocks also.

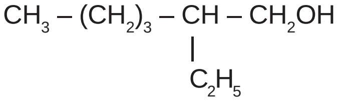
As indicated before sulphates of secondary alcohols can be made by adding sulphuric acid to the corresponding olefine. They also exhibit detergency. However, they were never much popular in U.S.A. But in England at one time they were used even more widely than alkyl benzene sulphonate. They were marketed under the trade name "Teepol" of Shell Oil Company.

Fatty alcohols

Monohydric alcohols from aliphatic series, which contain six or more than six carbon atoms are normally known as higher alcohols. In earlier days of chemistry, higher alcohols. In earlier days of chemistry, higher alcohols were obtained from natural products like oils and fats and sometimes waxes also. These higher alcohols were therefore known as fatty alcohols, being named after their source. With the progress in the chemistry, alcohols similar to fatty alcohols could be made from petroleum feedstocks. This patched up the difference between "natural" and "synthetic" alcohols. In the light of the above situation it appears more plausible to classify alcohols on the basis of their end-used rather than on the basis of their sources.

Form this point of view alcohols containing six to eleven carbon atoms can be classified as plasticizer range alcohols, while alcohols between the range C12 andC18 can be placed in the class of detergent range alcohols. However, there are some alcohols which do not fit in properly in the above classification. Detergent range alcohols are further sub-classified as those belonging to middle cut fraction (C_{12} to C_{15}) and as those that belong to heavy cut fraction (C15 to C18). Middle cut fraction alcohols are in more demand and consequently fetch better price. Hence manufacturers are naturally inclined to augment this fraction by choosing the right feedstock and proper conditions of processing. Heavy cut alcohols are also valued products. As pure materials these detergent range alcohols are sold in small quantities. The important fatty or higher alcohols as we may call them now, which are employed to manufacture useful sulphated products can be enumerated as follows:

1. Octyl alcohol or 2-ethyl hexanol



$$CH_3 - (CH_2)_3 - \underset{\displaystyle C_2H_5}{\underset{|}{CH}} - CH_2OH$$

2. Lauryl alcohol or Dodecanol

   $CH_3 - (CH_2)_{10} - CH_2OH$
3. Cetyl or palmityl alcohol

   $CH_3 - (CH_2)_{14} - CH_2OH$
4. Oleyl alcohol (Octadecenol)

   $CH_3 - (CH_2)_7 - CH = CH - (CH_2)_7 - CH_2OH$
5. Stearyl alcohol $CH_3 - (CH_2)_{16} - CH_2OH$

All the above alcohols are primary alcohols. Octyl alcohol of commerce is 2-ethyl hexanol, a saturated alcohol. It is the only branched alcohol in the above list. The rest are all straight chain saturated alcohols except the oleyl alcohol which carriers a double bond between 9:10 position.

SUPHATION OF ALCOHOLS

Choice of sulphation processes and of sulphating agents

The sulphation of alcohols is carried out either as a continuous process or as a batch process. Similarly there are several sulphating agents that can be put to use commercially. The choice of the batch process or continuous process, as also the choice of the sulphating agents, depends upon the use for which the end-products of sulphation are put to. In the pharmaceutical field, for example, sulphated products with maximum completion of sulphation reactions are needed. Sulphated products containing about 10% of free alcohol are desirable for use in those cases where the requirements of foam volume and stability are optimum. To formulate a relatively highly active liquid product, sulphated alcohol with low salt content is chosen. Where the final formulation is intended to step up detergency, sulphated alcohol having low viscosity and cloud point but with more salt content is preferred. The presence of electrolyte helps in stepping up the detergency.

Several sulphating agents are in use today. These include concentrated sulphuric acid, oleums of different strengths, sulphur trioxide and chlorosulphonic acid. For the sulphation of unsaturated primary alcohols like oleyl alcohol (which has a double bond at 9:10 position) moderate sulphating agents are recommended. Moderate sulphating agents are complexes of usual sulphating agents with different chemicals. They are described later under the topic "Sulphation of unsaturated alcohols".

Sulphation of saturated alcohols with concentrated sulphuric acid is generally incomplete. Dehydration and olefin formation may result. Some alcohols may remain unsulphated. However, the product can be purified by extraction with carbon tetrachloride, gasoline or butanol. Only minor quantities of inorganic salt may remain in the end-product. Since water is formed in the reaction, excess of concentrated sulphuric acid has to be used. The reaction of an aliphatic alcohols with sulphuric acid is already shown earlier. Here it is repeated for the sake of convenience. This we have

$$R - OH + H_2SO_4 \longrightarrow R - O - SO_2OH + H_2O$$

Problems met with by the use of sulphuric acid are avoided by using chlorosulphonic acid in its place. Corrosive hydrochloric acid is evolved but no water is formed and highly active product is obtained by using jut a mole of chlorosulphonic acid. Hence for sulphated products requiring high degree of completion and low salt contents, batch processing with chlorosulphonic acid or sulphur trioxide is preferable. Continuous processes employing oleums and concentrated sulphuric acid are well suited for the production of sulphated products where high salt content is desirable.

Reactions of an aliphatic alcohol with sulphur trioxide and chlorosulphonic acid are shown below.

Batch process and continuous process

$$R - OH + SO_3 \longrightarrow R - O - SO_3H$$

$$R - OH + ClSO_3H \xrightarrow{(0^\circ\text{-}30^\circ C)} R - O - SO_3H + HCl$$

(A) Batch process

In batch process, normally the sulphating agent used is either chlorosulphonic acid or sulphur trioxide. Both have certain benefits as well as certain shortcomings. The choice is made depending upon the end-use of the ultimate product of sulphation. Sulphur trioxide having lower molecular weight is required in lesser amount, weight-wise, than chlorosulphonic acid. Thus to sulphate a mole. Of alcohol 36.6 kgs. of sulphur trioxide is needed as compared to 53.5 kgs. of chlorosulphonic acid. Again a kg. of sulphur trioxide costs less than a kg. of chlorosulphonic acid. However, there is another side to this coin. If dilution system in the process adopted is not proper, local overheating and side reactions may develop. This possibility is comparatively more when sulphur trioxide is used than when chlorosulphonic acid is employed. This decides colour and odour of the final sulphated product which are very important factors and if they are not upto the mark, the product has to be bleached to attain the specified colour. If water is scrupulously removed from the alcohol to be sulphated, sulphur trioxide can give a chloride-free product, if the neutralising base is also free from chloride. If water is not thoroughly removed from the alcohol to be sulphated, sulphur trioxide is more harmful than chlorosulphonic acid. This is because sulphur trioxide forms sulphuric acid with water. The sulphuric acid so formed produces alkyl sulphuric acid – sulphuric acid mixture which ultimately results in giving neutralised alkyl sulphate very high in fatty alcohol and inorganic salt content, and hence highly viscous. On the other hand, when chlorosulphonic acid is used, only a slight excess of it is required to compensate for the small amount of water that may be present in alcohol. Water vapour formed during reaction is carried away along with hydrochloric acid fumes set free in the reaction. Again evolution of hydrochloric acid brings about a cooling effect on the reaction mass and the local heating is thereby avoided. However with the use of chlorosulphonic acid a good ducting system is needed. Nevertheless, hydrochloric acid fumes evolved can be reacted with sulphur trioxide to reform chlorosulphonic acid which can be put to use again. Another defect with sulphur trioxide is, it produces dense troublesome fog even in the presence of little moisture.

(B) Process of continuous sulphation

Here concentrated acid or oleum is the sulphating agent of choice. This process is more economical to manufacture alkyl sulphates on a large scale than the batch process. However, there is no flexibility in this process so far as product formulation is concerned. The final product contains considerable amount of inorganic sulphate. This process therefore, is suitable for manufacturing alkyl sulphate slurries which can be subjected to spray drying to give light dusty powder to about 35% active water content. Such products find use as household detergents. In this process appropriate excess of sulphating agent and its right time of contact, at proper temperature, with a particular alcohol used, are quite rigid to get optimum results, as regards quality and quantity of the final product.

If these conditions are not adhered to properly oversulphation or under-sulphation may result which brings down the yield and quality of the final product. Inspite of all these shortcomings this process is still preferred for manufacturing alkyl sulphates economically when product with medium activity suffices for the purpose. it has certain advantages over batch process. These are: uniformity of the product formed, requirement of lesser space to manufacture large tonnage, lesser ware-house requirements for storing product and product economy on overall basis. Research is underway for using SO_3 as a sulphating agent for continuous processes.

PRECAUTIONS TO BE TAKEN DURING PROCESSING

Both in batch processing as well as in continuous processing it is advisable to maintain the lowest possible reaction temperature. The lower limit of temperature that can be maintained during sulphation is marked as the point at which alcohol tends to collect on heat exchangers. Any departure from maintaining optimum temperature generally results in occurrence of side reactions which impart harmful colour and smell to the finished products. Alkenes, ethers, and aldehydes formation may also occur. All these factors seriously affect the utility of the final product.

Moisture should be scrupulously avoided especially when sulphur trioxide is employed as a sulphating agent. This point has already been discussed earlier. Special attention should be paid to see that any possible leakage of water from the heat exchanging cooling system has been carefully and totally prevented.

NEUTRALISATION

Next the sulphated alcohols are neutralised to yield alkyl sulphate. Here also precautions are necessary. The sulphated fatty alcohols, which can also be looked upon as alkyl sulphuric acid esters, are prone to hydrolysis in acid media especially at an elevated temperature, as per the following reaction, yielding aliphatic alcohol and sulphuric acid.

$$RO\text{-}SO_3H \xrightarrow[(H_2O)]{(100^{\circ}\text{-}110^{\circ}C)} R\text{-}OH + H_2SO_4$$

Hence, during neutralisation of these hydrolytically unstable sulphated fatty alcohol in aqueous medium, well controlled conditions should be maintained to minimize their hydrolysis. Neutralisation is carried out at a temperature a little higher than the freezing point of alkyl sulphuric acid. The latter is fed to the neutralisation chamber at a controlled rate. Efficient agitation is also maintained by using turbine agitator in batch process. Centrifugation in line mixers is recommended for continuous type of processes. pH above 7 is maintained. If all these points are followed properly formation of gel-like lumps is avoided. These gel-like lumps are of congealed alkyl sulphuric acid and contain entrapped water in them. They therefore have a tendency to hydrolyse and spoil the end-product. Except amineneutralised systems that are self-buffering at pH > 7, neutralisation to the end pH is normally succeeded by buffering.

RAW MATERIAL STORAGE

Alcohol to be used for sulphation should be stored under anhydrous conditions. For this a desiccant bed is used which can also be regenerated or replaced periodically. The storage tanks carry desiccant protection in their vents. Sulfan and chlorosulphonic acid also need anhydrous condition for their storage.

Sulfan is a trade name for stabilised sulphuric anhydride which can be procured as colourless liquid which boils at 45ºC. Its melting point is 17ºC. Boron trioxide is generally used as its stabiliser. The stabiliser is sensitive to moisture. Moisture destroys boron trioxide resulting in polymerisation of SO_3 to form $(SO_3)x$. As regards chlorosulphonic acid, attack by moisture produces sulphonic and hydrochloric acid as an outcome of hydrolysis. These attack storage vessels and equipment and corrode them.

RECOVERY OF ALCOHOLS

If on any account it becomes necessary to recover fatty alcohol from an alkyl sulphate, the latter is hydrolysed at pH < 3.0 under boiling. The alcohol obtained after phase separation can be distilled before reprocessing. The hydrolytic reaction is also shown under neutralisation.

SULPHATION OF UNSATURATED ALCOHOLS

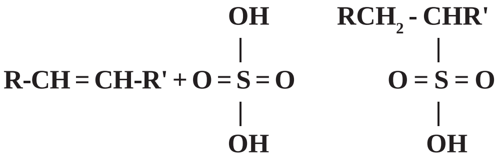
The unsaturated alcohols can be represented by the general formula. $R - CH = CH - CH_2OH$ according to one view, when both, a double bond and an alcoholic hydroxyl group are present in a molecule, the alcoholic group is attacked first and the double bond in attacked only after the free alcoholic hydroxyl groups are blocked by esterification with sulphuric acid. Thus we have:

$$\text{R-CH} = \text{CH-CH}_2\text{OH} + \text{H}_2\text{SO}_4$$
$$\downarrow$$
$$\text{R-CH} = \text{CH-CH}_2\text{-O-SO}_2\text{-OH} + \text{H}_2\text{O}$$

However, it is also reported that the sulphation of an unsaturated alcohol like an oleyl alcohol is complicated process. This is because the sulphating agents generally employed attack the double bond as also the hydroxyl group. Hence, as stated earlier, moderate sulphating agents are recommended. The moderate sulphating agents are complexes of SO_3 with inorganic salts, complexes of $ClSO_3H$ with urea and with inorganic salts, urea complexes with sulphuric acid, dioxane – SO_3 pyridine – SO_3 and sulphonic acid. They partially bring down the possibility of reaction at the double bond position.

FORMATION OF SULPHATED ALCOHOLS FROM OLEFINES

An unsaturated paraffin is attacked by to give sulphuric ester as already described earlier. Thus we have:



$$\text{R-CH} = \text{CH-R}' + \begin{array}{c}\text{OH}\\ |\\ \text{O} = \text{S} = \text{O}\\ |\\ \text{OH}\end{array} \qquad \begin{array}{c}\text{RCH}_2\text{ - CHR}'\\ |\\ \text{O} = \text{S} = \text{O}\\ |\\ \text{OH}\end{array}$$

These sulphuric esters are not stable. Even long standing suffices tham to get hydrolysed to hydroxy fatty acids. This reaction occurs at the time of sulphation as also during the process of washing. The hydroxy fatty acids formed in the process being very active tend to form several complicated esters in the presence of acid.

OLEFINS CAN BE CLASSIFIED AS

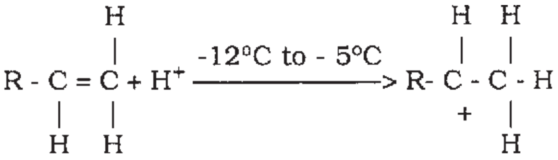
(1) Primary olefins e.g. propylene $CH_3 – CH: CH_2$

(2) Secondary olefins e.g. butene –2 $CH_3CH: CHCH_3$

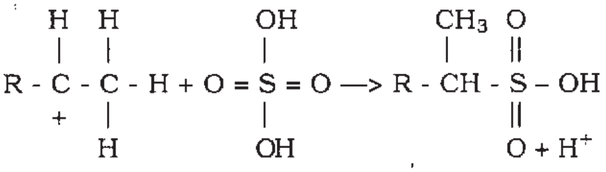
(3) Tertiary olefins e.g. isobutene or isobutylene $(CH_3)_2$ C: CH_2

The third type of olefin need not be considered here as it gives tertiary sulphonate, which being unstable undergoes undesirable side reactions. The first two types of olefins follow Markownikoffs rule while reacting with sulphuric acid to give secondary alkyl sulphate derivative; since surfactants with better foaming power are obtained from alpha-olefins represented by the general formula, the reactions with it are shown. Thus at temperature (-12ºC to –5ºC) carbonium ion is formed by the action of hydrion furnished by sulphuric acid on ionisation. The carbonium ion reacts with a molecule of sulphuric acid of 96% strength to give sulphated product and a hydrion. The hydrion released then touches fresh molecule and the process goes on as a chain reaction.

Thus we have:



$$R-CH=CH_2 + H^+ \xrightarrow{-12^{\circ}C \text{ to } -5^{\circ}C} R-\overset{+}{C}H-CH_2-H$$



$$R-\overset{+}{C}H-CH_2-H + O=S(OH)_2=O \longrightarrow R-CH(CH_3)-SO_2-OH + H^+$$

forms sodium salt with excess caustic soda.

The above reaction needs a very careful control. Thus is the temperature goes upto 0ºC to +5ºC, side reactions occur with the formation of dimers which polymerise subsequently. The strength of sulphuric acid should be not be less than 96%, otherwise side reactions may occur. Acid should be used in excess. The olefin should not be allowed to polymerise itself. This can be achieved by dispersing it rapidly so that is reacts with sulphuric acid only. The product formed should be quickly neutralised. Otherwise, the reactions may be reversed. The amount of excess caustic should be carefully controlled; otherwise harmful side reactions, take place.

Primary olefins with chain-length of C_{14} to C_{20} which can be obtained by the process of cracking from wax can be directly sulphated, rather than first converting them into alcohols by any known method. The product was prepared on a pilot plan scale in Germany. It was reported to be as effective as sulphates of normal alcohols. The general methods of sulphation of alcohols followed by neutralisation of the sulphated products so formed are already dealt with in preceding pages. We have also considered the precautions to be taken in general. The point of sulphating an olefin at double bond position is also dealt with. We shall now consider definite processes of sulphation. Lauryl alcohol we will takes as a representative of saturated alcohols. Unsaturated alcohols will be represented by oleyl alcohol, while sperm oil alcohols will be considered from the point of view of “mixtures of alcohol”. The sulphation of an olefin at double bond position we have already considered.

MERCERIZING WETTING AGENTS

The term mercerisation usually refers to the treatment of cotton yarn or fabric with caustic soda solution to produce increased lustre, dye affinity, strength, stability, moisture regain and general chemical reactivity. In order to achieve these improvements, mercerisation has to be carried out under tension, either during the alkali treatment or after, but before washing the material free from the alkali. During mercerising, the fibres swell, the elliptical cross-section of the fibre changes to circular shape and the convolutions present, in the fibres vanish by untwisting (Fig. 7.1).

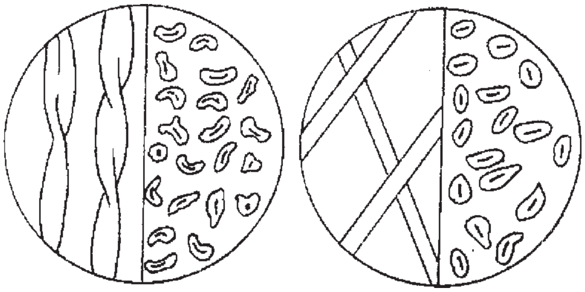


Fig. 7.1: Longitudinal view and cross-sections of cotton (left) and mercerised cotton fibres (right)

Thus the reflection of light incident on the fibres is parallelised and intensified, producing increased lustre. Generally, there is an increase of up to 25% in the tensile strength of the material after mercerisation; the tear strength of the mercerized fabrics is considerably higher than that of the unmercerized one. On the other hand the elongation at break is reduced by 20-30%, due to more homogeneous and uniform nature of the mercerized cotton yarn which can then resist more weight at break without giving prolonged extension before it breaks.

The fibre diameter increases by 25-30% and the length decreases by 5-10% when it is mercerized without tension. Swelling in sodium hydroxide solution reduces the crystallinity of the fibre form 70% of the unmercerized fibre to 50%. This results in the breaking up of hydrogen bonds existing between the hydroxy groups of adjacent macromolecules of cellulose, increasing the accessibility due to these released hydroxy grups, to water molecules, dyes and chemicals. This amount for the increased moisture regain, dyeability and chemical reactivity of mercerized cotton as compared to unmercerized cotton. The dyeability can increase by 30-40%.

The success of the mercerization process depends on the thorough penetration of viscous solutions (about 24% wt/wt) of sodium hydroxide into the individual fibres of yarns or fabrics being mercerized. The fats and waxes present in raw cotton fibres offer considerable resistance to the wetting of the fibres, and the high viscosity as well as high surface tension of sodium hydroxide solution render the penetration of the solution into the fibres difficult. The size (tallow) present on the warp yarn of grey cotton fabric makes it more difficult for the mercerizing solution to penetrate into the fibres.

The use of a suitable wetting agent in the mercerizing liquor overcomes these difficulties. The wetting agent should have high wetting power, should be easily removable after the process is over, should not be preferentially adsorbed by the fibres mercerized and should be stable for a long time over a wide range of sodium hydroxide concentration. Further, it should be soluble in the sodium hydroxide solution, and should not give excessive foaming, turbidity in the solution or deposits on the fibre. The price, the effects on the different parts of the machinery and the interference during the recovery of sodium hydroxide from the spent liquors should also be considered. Uniform penetration of the solution, especially in the mercerization of grey cotton cloth is absolutely necessary for getting even results.

The penetration of the mercerizing solution into cotton yarn is a function of the viscosity of the solution, the degree of swelling of the fibre, the duration of the treatment and the tension the applied during the treatment. the alkali absorption by the cotton fibres depends primarily on the concentration of sodium hydroxide, but the swelling history, fibre maturity and the fibre wall development of the individual fibres also exert influence.

Ordinary wetting agents used in scouring are unsuitable as wetting agents in mercerizing liquors, and special wetting agents, which are effective under these conditions, have been developed. Generally, there are two types – Cresylic and non-cresylic wetting agents. These are not mercerizing agents, but are only wetting agents to be used in mercerizing liquor; sodium hydroxide is the actual mercerizing agent.

Mixtures of ortho-, meta-, and para-cresols (also called cresylic acids) ($CH_3 – C_6H_4 – OH$) are not soluble in water, but dissolve in strong sodium hydroxide solutions. These are found to be stable wetting agents in these solutions. Their wetting power is considerably improved by incorporating certain other additives like methylated spirit, polyhydric alcohols with C_{18} chain, butanol, 2-ethyl hexanol, polyethylene glycol etc. Some of these are not soluble in water, but dissolve in sodium hydroxide solution.

Mixtures of cresol, pine oil and oleic acid; xylenol (95%), methyl cyclohexanol (2%) and carbitol (3%); carvacrol, methyl cyclohexanol, butyl alcohol and cresol; sodium salt of butyl diphenyl sulphonic acid; cresol and terpineol; cresol (93%), benzyl alcohol (4%) and n-octyl alcohol (3%) etc. have been suggested in patents literature as suitable mercerizing wetting agents.

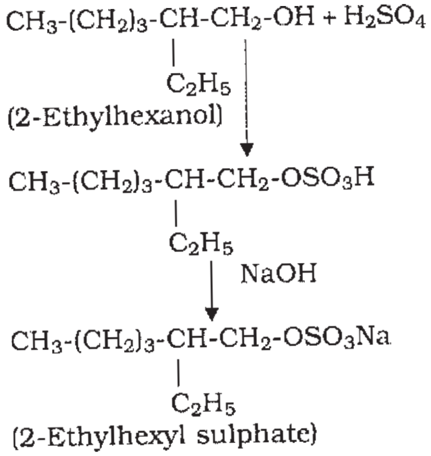
Non-cresylic wetting agents include sulphated lower aliphatic alcohols such as hexyl and octyl alcohols. Alkylated diphenyl oxide sulphate containing 1-1.3 alkyl (C_8-C_{18}) and 1.8-3.3 sulphate radicals per diphenyl oxide nucleus (e.g., sodium dodecyl diphenyloxide disulphanate), along with a water immiscible mono-or polyhydric alcohol is one of the non-cresylic type of mercerizing wetting agents.

Shenai V.A. (Int. Dyer Sept. 2, 1977, p. 246) has reported the synthesis of n-butyl sulphate and 2-ethyl hexyl sulphate and the evaluation of the wetting properties of mercerizing wetting agents in 25 per cent (wt/wt) sodium hydroxide solution.

SYNTHESIS OF 2-ETHYL HEXYL SULPHATE

(a) **Sulphation**: 250 ml of 2-ethyl hexanol was taken in a 1 litre round bottom flask and was cooled to –3ºC using ice-salt-freezing mixture. 96 ml. Of sulphuric acid (sp. gr. 1.84) was added dropwise from a dropping funnel and with constant shaking. The reaction between the alcohol and sulpuric acid being exothermic, the addition of the addition of the acid should be very slow, taking care to see that the temperature of the reaction mixture does not exceed 5ºC. After all the amount of the acid was added, the reaction mixture was allowed to stand for 24 hours with occasional shaking of the flask.

(b) **Neutralisation**: The excess of sulphuric acid present in the reaction mixture was neutralised with sodium hydroxide solution (sp. gr. 1.35) with cooling and stirring and the temperature was not allowed to exceed to 10º-15ºC. The neutralisation was carried out to pH 8. Distilled water was added in limited quantity and the contents filtered to remove the excess sodium sulphate formed during the neutralisation step. The filtrate was the required mercerizing wetting agent. The following reactions took place:



$$CH_3\text{-}(CH_2)_3\text{-}\underset{\substack{|\\ C_2H_5}}{CH}\text{-}CH_2\text{-}OH + H_2SO_4$$

(2-Ethylhexanol)

$$\downarrow$$

$$CH_3\text{-}(CH_2)_3\text{-}\underset{\substack{|\\ C_2H_5}}{CH}\text{-}CH_2\text{-}OSO_3H$$

$$\big\downarrow \text{NaOH}$$

$$CH_3\text{-}(CH_2)_3\text{-}\underset{\substack{|\\ C_2H_5}}{CH}\text{-}CH_2\text{-}OSO_3Na$$

(2-Ethylhexyl sulphate)

SYNTHESIS OF N-BUTYL SULPHATE

n-Butanol (250 ml) was sulphated with concentrated sulphuric acid (160 ml) and neutralised by the method followed in the case of 2-ethylhexanol.

ALKYL NAPHTHALENE SULPHONATES

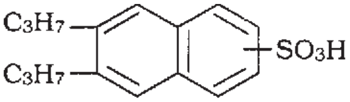
Even though the wetting and penetrating powers of sulphated oils are good, they have no detergent power and hence they do not find use in cleaning/washing operations. Soap is still better than sulphated oils in this respect (detergency) .

During World War I (1914-1918) the shortage of vegetable oils (used in the manufacture of soap) led the Germans to explore alternative sources for producing surface active agents. Alkyl naphthalene suphonates were made and were found to be better than sulphated oils. Propyl and butyl (or dibutyl) naphthalene sulphonic acid are of particular interest.

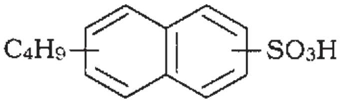
In the products shown alongside the sulphonic acid (or its sodium salt) provides the hydrophilicity, while alkylnaphthalene (with $C_{14} – C_{18}$ alkyl) residue provides the hydrophobicity with the HLB required to produce surface activity in the product.

Alkyl naphthalene sulphonates are anionic products, having pronounced wetting properties. They are stable in the presence of mineral acids like sulphuric acid and hydrochloric acid, and organic acids like acetic and formic acid used in textile processing. They maintain their wetting and penetrating powers in acidic and alkaline solutions.

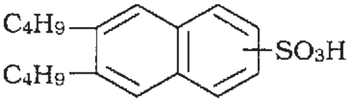
They find use in acid carbonising liquors for wool, in which they assist in rapid wetting and penetration of vegetable fibre contaminations and assist the removal of residual lime soaps and free fatty acid left in wool from previous washing treatments. They may also be added to desizing liquors, when grey cloth is impregnated with acid or enzyme solutions. They may be used in emulsifying vegetable oils and fats to produce oil-in-water emulsions, which are used in textile finishing and for oiling raw wool in spinning operations. Benzyl naphthalene sulphonic acid was found to be a good wool dyeing assistant for producing level shades (retrding or levelling agent) of acid dyes.



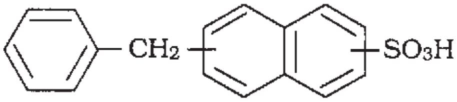
(Dipropyl naphthalene sulphonic acid)



(Butyl naphthalene sulphonic acid)



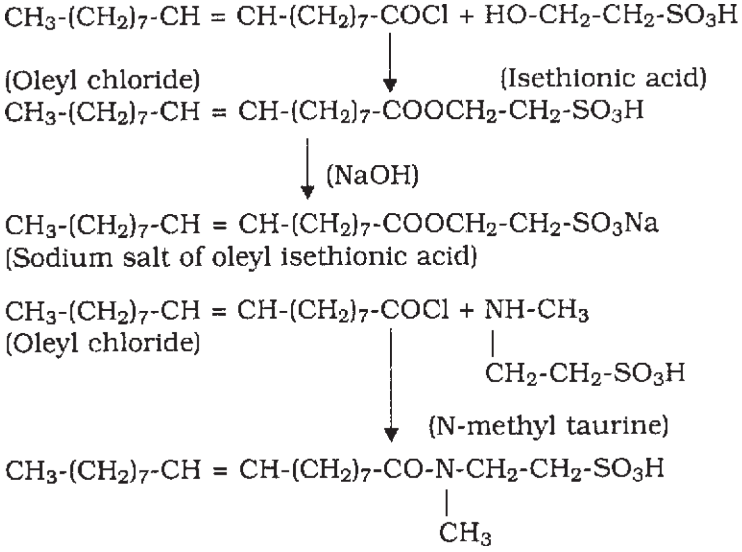
(Dibutyl naphthalene sulphonic acid)



(Benzyl naphthalene sulphonic acid)

FATTY ACID ESTER AND AMIDE SULPHONATES

Alkyl naphthalene sulphonates were lacking in detergency and hence by themselves were inferior to soap as scouring/cleansing agents. Then came fatty acid ester sulphonates and amide sulphonates which are anionic surface active agents. They are prepared by condensing fatty acid chlorides and hydroxy ethyl sulphonic acid:



$$CH_3\text{-}(CH_2)_7\text{-}CH = CH\text{-}(CH_2)_7\text{-}COCl + HO\text{-}CH_2\text{-}CH_2\text{-}SO_3H$$

(Oleyl chloride) (Isethionic acid)

$$\downarrow$$

$$CH_3\text{-}(CH_2)_7\text{-}CH = CH\text{-}(CH_2)_7\text{-}COOCH_2\text{-}CH_2\text{-}SO_3H$$

$$\downarrow \text{(NaOH)}$$

$$CH_3\text{-}(CH_2)_7\text{-}CH = CH\text{-}(CH_2)_7\text{-}COOCH_2\text{-}CH_2\text{-}SO_3Na$$

(Sodium salt of oleyl isethionic acid)

$$CH_3\text{-}(CH_2)_7\text{-}CH = CH\text{-}(CH_2)_7\text{-}COCl + \underset{\displaystyle CH_2\text{-}CH_2\text{-}SO_3H}{\underset{|}{NH\text{-}CH_3}}$$

(Oleyl chloride) (N-methyl taurine)

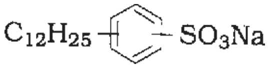
$$\downarrow$$

$$CH_3\text{-}(CH_2)_7\text{-}CH = CH\text{-}(CH_2)_7\text{-}CO\text{-}\underset{\displaystyle CH_3}{\underset{|}{N}}\text{-}CH_2\text{-}CH_2\text{-}SO_3H$$

Both these (ester and amide) have excellent wetting and detergent properties useful in textile processing. The amide product has excellent wetting, dispersant and detergent properties, which make it useful in textile processing especially in scouring of cotton and man-made fibre materials. It is stable in aqueous solutions of acids, alkalies and hypochlorite. It has good lime soap dispersing properties in hard water. the amide link (-CO-N-) CH_3 is more stable to alkaline hydrolysis than the ester-group (-COO-) in the above compounds.

DODECYL BENZENE SULPHONATE

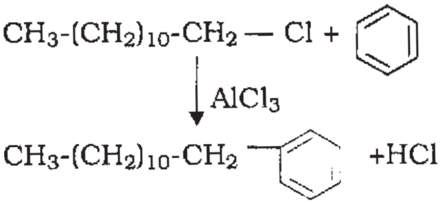
The next products of commercial importance are alkyl aryl sulphonates. As pointed out earlier, if naphthalene is used as the hydrophobic part of the surfactant, dipropyl or dibutyl groups have to be added to it before sulphonation so that there are 16 or18 carbon atoms in it. Similar effect can be produced with benzene attaching C_{12} chain to it to have 18 carbon atoms and then sulphonating it. Thus dodecyl benzene sulphonate:



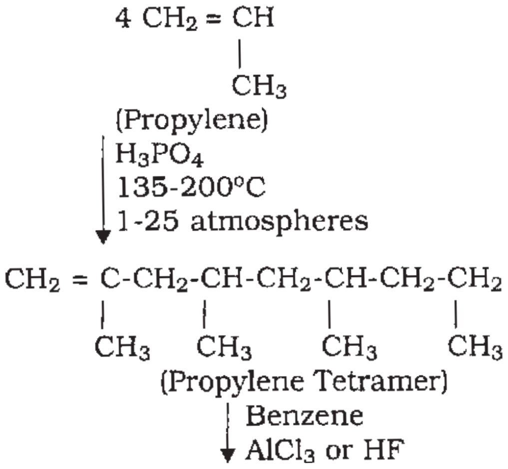
Has the right hydrophilic-lyophilic balance (HLB) to have optimum surface activity (balanced water-solubility insolubility).

Dodecyl benzene may be made by condensing benzene with a monochlorinated aliphatic chain having 12 carbon atoms by the Friedel-Crafts reaction using anhydrous aluminium chloride as the catalyst. The aliphatic chain may be a petroleum fraction or synthetic hydrocarbon obtained by condensing a lower molecular weight aliphatic hydrocarbon (e.g. propylene) to its tetramer state. This does not need prechlorination reactivity with benzene. The main reactions taking place are:

$$CH_3\text{-}(CH_2)_{10}\text{-}CH_3 + Cl_2 \longrightarrow CH_3\text{-}(CH_2)_{10}\text{-}CH_2\text{-}Cl + HCl$$



(Linear alkyl condensate)



$$4\ CH_2 = \underset{\displaystyle CH_3}{\underset{|}{CH}}$$

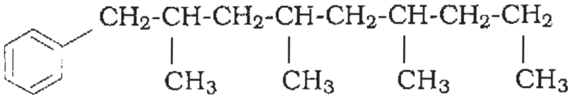
(Propylene)

$$\Big\downarrow\ H_3PO_4,\ 135\text{-}200°C,\ 1\text{-}25 \text{ atmospheres}$$

$$CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}}\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH_2}}\text{-}CH\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH_2}}$$

(Propylene Tetramer)

$$\Big\downarrow\ \text{Benzene},\ AlCl_3 \text{ or } HF$$



(Dodecyl benzene)

Because of the comparatively high cost of chlorine and the resultant production of hydrogen chloride both at the chlorination of the aliphatic hydrocarbon and the condensation of the chloroparaffin with benzene, the second method of condensing tetra propylene with benzene is favoured.

There are three principal means of producing the detergent: (1) sulphonation of dodecyl benzene (requiring high initial expenditure) and then neutralising, (2) neutralising dodecyl benzene sulphonic acid (known as acid slurry) and (3) purchasing sodium dodecyl benzene sulphonate in a cocentrated form of spray-dried or drum-dried powder or flakes and then diluting or making a solution in water with suitable additives.

In another method saturated kerosene (chiefly C_{14} alkane) fraction (d.p. 200º-300ºC) is chlorinated at 60º-70ºC in the presence of iodine or ultraviolet light as the catalyst till there is an increase of 20% in weight (equivalent to 1 mole of chlorine per mole of the hydrocarbon). The resulting product, known as keryl chloride (1 mole) is treated with benzene (5 moles) and aluminium chloride (0.10 mole) at 35º-50ºC. The alkyl benzene thus produced in separated by distillation and sulphonated with sulphuric acid or oleum at less than 60ºC. The product may be neutralised as such when it contains a large amount of salt(sodium sulphate) or a small amount of water is added to the reaction mass when the spent acid separates as a lower layer, which is then drawn off. The upper layer is neutralised to give a product of low salt content.

DODECYL BENZENE SULPHONATE (NA)

Dodecyl benzene is available as a stable, non-corrosive colourless liquid of low viscosity and bright appearance, free of water and sediments. It has a molecular weight of 240-250 and a density of 0.867-0.869 g/cc. It has viscosity of 1.1 and 1.5 cps at 20ºC and 100ºC respectively.

The manufacture of dodecyl benzene sulphonate involves sulphonation, separation of spent acid, neutralisation and bleaching.

SULPHONATION

Corrosion-proof, agitator vessels, allowing through and rapid mixing and quick dissipation of heat may be used for sulphonation. Lead –lined containers or those of austenitic steels (18% Cr and 8% Ni and Mo) and provided with cooling jacket or cooling coil are preferred. Mixing and cooling can be intensified by using a separate heat exchanger through which the sulphonation mixture is pumped. This improves the colour of the final product.

Far carrying out the sulphonation, 98% sulphuric acid or oleum (up to 24% SO_3) can be used. The iron content of the acid should not exceed 10 mg/kg, since iron can affect the colour of the end-product or its storage properties.

The lead-lined iron vessel, equipped with a cooling coil, a cooling jacket and paddle-type stirrer is charged with 1000 kg. (1150 litres) of tetrapropylene benzene (alkyl benzene). The stirring and cooling are started and 1500 kg. of 98% sulphuric acid (817 litres) are added (3.8 moles per mole of alkyl benzene). The excess of the acid is necessary, since with a drop in the acid concentration below 90%, the sulphonation stops. During the addition of the acid, the temperature is maintained at 35ºC or below. By the time all the acid is added, sulphonation proceeds to about 90%.

The remaining alkyl benzene gets sulphonated slowly at low temperatures and, therefore, the temperature of the reaction mixture is raised to 55ºC by circulating hot water through the cooling system and the temperature is maintained there at for 3 hours, when sulphonation proceeds to 98%.

SPEND ACID SEPARATION

It is desirable to separate the excess sulphuric acid as much as possible before neutralisation (the excess acid produces sodium sulphate) in order to increase the ratio of the active matter to sodium sulphate.

The contents of the sulphonator are kept at 55ºC for 2 hours after the agitation it stopped when the spend acid (86% acid) collects at the bottom, from where it is discharged through an outlet valve. The black spent acid can be distinguished from the dark red sulphonic acid. The separation yields 1,700 kg. of sulphonic acid and 800 kg. of the spent acid. A second quantity of spend acid can be removed by adding 8% (130 kg.) of the remainder acid mixture, followed by thorough stirring and standing for 3 hours at 55ºC. Then the second spent acid (76% acid) can be separated.

NEUTRALISATION

This is done in a similar vessel as the sulphonator, provided with a stirrer and a cooling device. Neutralisation is done using aqueous caustic soda solution, the concentration depending upon the desired concentration of the final product. The solution of the proper concentration may be prepared and used, or 50% solution and water simultaneously run in, maintaining the temperature at 35º to 40ºC. Neutralisation at higher temperatures produces a darker product. Further, at 60ºC gelling may take place, impairing the heat transfer process. The course of neutralisation may be followed by using pH paper and the end point may be accurately adjusted. In the above case, 460 kg. of 50% caustic soda is required.

BLEACHING

Sodium hypochlorite is used to brighten the sulphonate solution. The neutralisation output (1,900 kg.) is pumped into a brick-lined agitator vessel where it is mixed with 100 kg. of sodium hypochlorite (13% active chlorine). The excess of sodium hypochlorite is later decomposed by heating to higher temperatures while stirring. The required active content of the detergent is adjusted by adding water. After the spend acid has been removed twice (as described earlier), sodium sulphate content in the end-product amounts to 10% with respect to the active content.

Linear alkyl benzene (soft alkyl benzene) can be readily sulphonated using any of the conventional sulphonating agents such as sulphur trioxide or oleum (containing upto 20% sulphur trioxide). LAB has some advantages over hard dodecyl benzene (branched dodecyl group formed from propylene tetramer). This LAB sulphonated product with lower viscosity results in reduced pumping and reduced energy loads of pumps, stirrers, etc. The yield of sulphonic acid is high (1.45 times the weight of LAB giving an yield of 85% sulphonic acid).

BATCH SULPHONATION WITH 20% OLEUM

A typical reactor for this process has a capacity of 1 tonne and is made of stainless steel which withstands 95% sulphuric acid and is fitted with an anchor type stirrer operating at 150-200 rpm. The reactor is provided with a mild steel jacket for circulation of water at 25º-29ºC. The reaction vessel is charged with 300 kg. of LAB. The stirrer is turned on and cooling water is circulated through the jacket. The 20% oleum is metered slowly in 2-2.5 hr. into the reactor at such a rate as to maintain the temperature of the reaction mass between 40ºC and 45ºC. The total weight of the oleum would be 360 kg. in the hand operated units, the oleum may be added over a period of 4 hours. The temperature of the reaction mixture should not exceed 45ºC, since LAB gets charred at higher temperatures and undesirable by-products like sulphones, disulphonic acids and sulphonic anhydride are likely to be formed. After the addition of oleum is complete, the temperature is maintained at 45ºC for 1 hour. The completion of the reaction (98% conversion of LAB) is checked by shaking 2 drops of the reaction mass with 10 ml 35% ethanol in water. A clear solution indicates 98% conversion. After the completion of this reaction, the reaction mass is transferred to a lead-lined mild steel vessel of 1 tonne capacity with a conical bottom, fitted with a drain valve and used as a separater vessel. The mass is stirred with the addition of crushed ice (79.2 kg. i.e. 12% of the total weight of LAB and oleum). The temperature rises gradually and the addition of ice is controlled, keeping the temperature around 60ºC. When the addition of ice is completed, the mass is stirred for 15 min. more and allowed to settle for 10-12 hours. The separation of the upper sulphonic acid phase and the lower sulphuric acid phase (approximately 78% strength) can be effective only if the temperature during dilution is kept at about 60ºC. After 12 hours settling, the lower acid layer is withdrawn and the upper sulphonic acid is stored either in stainless steel barrels or in high density polyethylene carboys.

SULPHONATION WITH SULPHURIC ACID-OLEUM MIXTURE

For this purpose, 98% sulphuric acid and 20% oleum mixture in the ratio 55:45 (amounting to 4% oleum) is used. The procedure is essentially the same as described for oleum sulphonation. The sulphonating mixture is prepared by gradual addition of 45 parts by weight of 20% oleum to 55 parts by weight of 98% sulphuric acid. The temperature during the mixing is maintained at 45ºC and then the mass is digested at 45ºC for 90 min. If the unit has no provision for cooling jacket, the temperature should be controlled by regulating the metering of the sulphonating mixture. The ratio of LAB to the sulphonating mixture is kept at 1:1.5. If the sulphonation has not gone to completion, the ratio may be kept at 1:1.6, the extra mixture being added subsequently. For dilution, crushed ice (12% by weight of the total charge) is added while maintaining the mass at 60º-65º (IPCL product Bulletin on Linear Alkyl Benzene) .

The sulphonate based on linear alkyl benzene is easily biodegradable (hence it is called soft variety), while propylene tetramer based alkyl benzene is the hard variety being hard (difficult) to biodegrade.

COMMERCIAL ANIONIC DETERGENTS

Wet processing of textiles involves treatment of textile materials like fibres, yarns and fabrics in various forms with dyes and chemicals, usually from an aqueous medium. The success of these processes depends on the uniformity with which the dyes and chemicals are picked up by the textile materials being processed and the ease with which they react (or interact) in a reasonably short time. Since the transfer of the dyes and chemicals into the fabric should take place from an aqueous medium it becomes necessary for the water to quickly and uniformly impregnate or wet out the textile materials. Water has a high surface tension and by virtue of this, it is difficult for the water to wet out the textile materials. This is made more difficult, if the fibre material itself is hydrophobic in nature in the case of synthetic fibres like polyester fibre materials or if the fibre materials (even though they are hydrophilic in nature like cellulose fibres) contain fatty and waxy substances either naturally present in the fibres, or acquired during the preparation for weaving (sizing).

All these difficulties are overcome by lowering the surface tension of water considerably by the use of suitable wetting agents (or surfactants) in appropriate concentrations in the processing solutions (liquors) of dyes and chemicals. They facilitate rapid wetting out of the textile materials with the processing liquors so that the interaction between the fibres and the dissolved dyes and chemicals can take place uniformly and in a reasonably short time.

Detergents of anionic and nonionic types are more important than those of the cationic type. Anionic detergents are mostly based on alkylbenzene sulphonate or fatty alcohol sulphate. The former are available in the form of a liquid (solution), a paste or a powder of varying active content. Fatty alcohol sulphates are generally available in the form of pastes.

Liquid brands are easy to dilute prior to use but they contain the least amount of the active matter (this is generally about 20%). Pastes contain about 28-30% detergent, and powders, about 40% detergent. Dissolution of powder brands in water is more difficult (lump formation may take place during the dissolution, which may produce uneven results in processing) than dilution of liquid brands. Detergent pastes are also difficult to disperse and then dissolve in water.

Anionic detergents are generally used under alkaline (soda ash or caustic soda) conditions. They may be used under neutral conditions also. They find applications in the following processes.

(1) Scouring of cotton fabrics in a kier, in which they are treated with caustic soda, soda ash, sodium silicate etc. During this process, the vegetable fatty matter present in the fabric and caustic soda dissolved in the kier liquor are brought into intimate contact with each other by the wetting agent resulting in the complete conversion into glycerine and the corresponding fatty acids (which then form their soidum salts by reaction with caustic soda and these sodium salt-soaps – also aid the wetting agent in its wetting action). The anionic wetting agents are used in the concentration range of 2-5 g/l (liquid brands or correspondingly less amounts of paste of powder brand).

(2) In the case of azoic and vat dyeing, the final pigments formed in the fabric are insoluble and a certain amount of the pigments deposited on the surface of the fibre, where they are not firmly fixed, but are loosely held, even though the bulk of the pigment is, penetrates the fibre material and is held by substantive forces (affinity). The surface-deposited pigments decrease the rubbing fastness, the dyeings are subjected to a “soaping” treatment at the boil in a bath, which contains an anionic detergent (1-2 g/l) and soda ash (1-2 g/l). The detergent removes the surface-deposited particles and holds them in a finely dispersed form in the “soaping bath” and does not allow them to get deposited on the fabric being “soaped”.

(3) When textile materials are dyed with reactive dyes, a certain amount of the dye reacts with water (gets hydrolysed) and

becomes inactive which then remains in the textile material. Since the hydrolysed dye has low affinity for cellulosic fibres, it reduces the washing fastness of the dyeing (the chemically reacted dye, however, is fast to washing). In order to overcome this problem, the dyeings are soaped with an anionic detergent solution at the boil, when most of the hydrolysed reactive dye is removed form the material and the dyeing attains the maximum washing fastness expected of a reactive dyeing. When chlorotriazine (Procion-type) reactive dyes are being dyed, the soaping bath may contain an anionic or non-ionic detergent in the presence of soda ash. However, when vinyl sulphone (Remazol-type) reactive dyes are dyed, the soaping bath should not contain any soda ash (only a non-ionic detergent is enough), since some amount of the dye already reacted with the fibre is separated form the fibre the rupture of the chemical bond formed between the two during soaping under alkaline conditions (the stability of vinyl sulphone dye-cotton bond to alkali is limited).

(4) Anionic detergents may be used in the soaping baths used in the washing of printed and steamed fabrics, where azoic (naphthol-base, Rapid Fast and Rapidogen), vat and solubilised vat dyes and reactive dyes were used in printing.

In these cases, the loosely held particles or the hydrolysed reactive dyes and the thickeners and the decomposition products of reducing agents and others are removed. For this purpose 1-2 g/l of the anionic detergent with or without 1-2 g/l soda ash may be used.

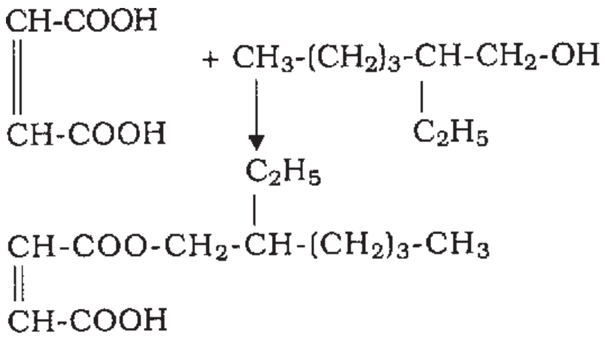
DIALKYL SULPHOSUCCINATE

The preparation of a series of aliphatic sulphodicar boxylic acids has been described in USP 2,028,091 (American Cyanamid and Chemical Corp.), which deals with esters of aliphatic sulpho dicarboxylic acids.

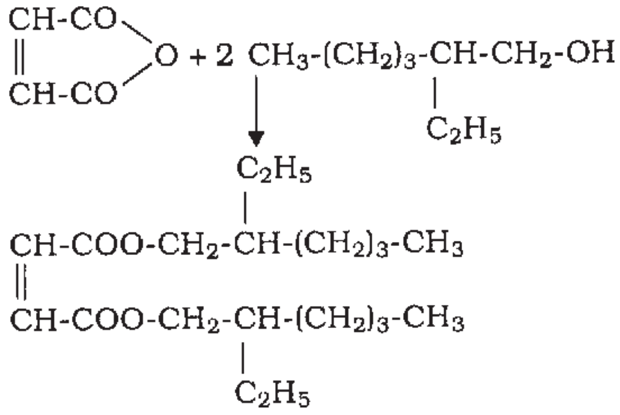
These are prepared by esterifying the sulpho acids (which, in turn, are made by sulphonating saturated acid or by adding a sulphite or bisulphite to the corresponding unsaturated acid or its salt or treating halogenated saturated acid with alkali sulphite under pressure).

Another method involves esterification of the unsaturated acid and then treating the ester with alkali bisulphite. This method is superior to the other one since the unsaturated acid is more easily esterified and the ester can be readily purified.

Thus 2-ethyl hexyl ester of sulphosuccinate, the most powerful wetting agent, may be made by esterifying maleic anhydride with 2-ethyl hexanol in the presence of hydrochloric acid as a catalyst. If maleic acid is used for the esterification, mostly the monoester is formed. While with maleic anhydride, the diester is formed:

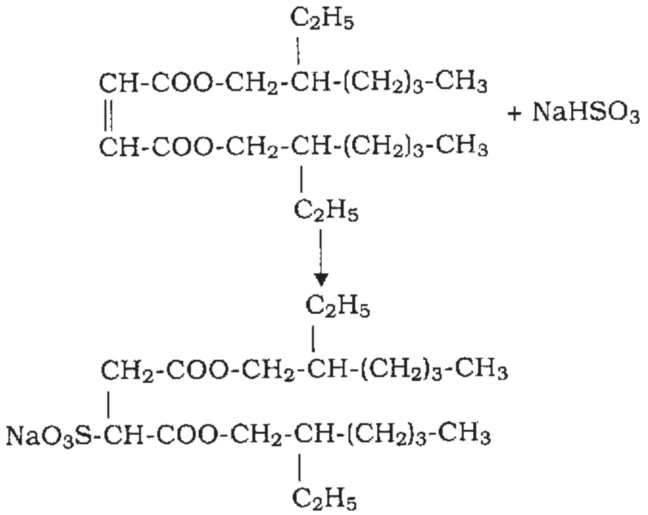


$$\begin{matrix} CH\text{-}COOH \\ \| \\ CH\text{-}COOH \end{matrix} + CH_3\text{-}(CH_2)_3\text{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}\text{-}CH_2\text{-}OH \longrightarrow \begin{matrix} CH\text{-}COO\text{-}CH_2\text{-}\overset{\displaystyle C_2H_5}{\overset{|}{CH}}\text{-}(CH_2)_3\text{-}CH_3 \\ \| \\ CH\text{-}COOH \end{matrix}$$



$$\begin{matrix} CH\text{-}CO \\ \| \\ CH\text{-}CO \end{matrix}\!\!>\!O + 2\ CH_3\text{-}(CH_2)_3\text{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}\text{-}CH_2\text{-}OH \longrightarrow \begin{matrix} CH\text{-}COO\text{-}CH_2\text{-}\overset{\displaystyle C_2H_5}{\overset{|}{CH}}\text{-}(CH_2)_3\text{-}CH_3 \\ \| \\ CH\text{-}COO\text{-}CH_2\text{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}\text{-}(CH_2)_3\text{-}CH_3 \end{matrix}$$

In the second stage, the diester is sulphated by using sodium bisulphite in an aqueous medium

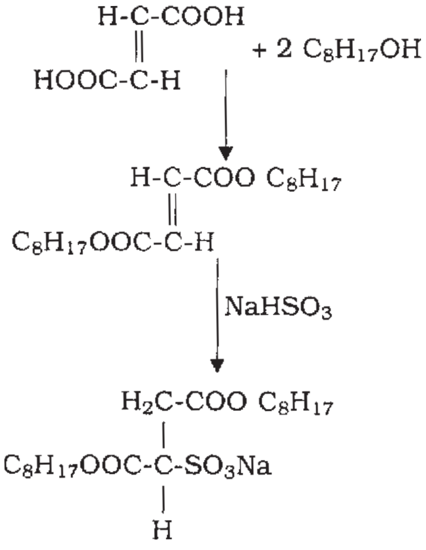


$$\begin{array}{l} C_2H_5 \\ | \\ CH-COO-CH_2-CH-(CH_2)_3-CH_3 \\ \| \hspace{12em} + NaHSO_3 \\ CH-COO-CH_2-CH-(CH_2)_3-CH_3 \\ | \\ C_2H_5 \end{array}$$

$$\downarrow$$

$$\begin{array}{l} C_2H_5 \\ | \\ CH_2-COO-CH_2-CH-(CH_2)_3-CH_3 \\ | \\ NaO_3S-CH-COO-CH_2-CH-(CH_2)_3-CH_3 \\ | \\ C_2H_5 \end{array}$$

Specifically one such product can be made by mixing 340 parts of dioctyl fumarate (prepared by the esterification of fumaric acid with 2-ethyl hexanol) with 109 parats of sodium bisulphite and water to form 50% solution. The contents are agitated at 100ºC till complete solution is achieved. The mixture may be dried and if required, freed from inorganic salts by dissolving in benzene, filtering and evaporating benzene.



$$\begin{array}{l} H-C-COOH \\ \| \hspace{6em} + 2\ C_8H_{17}OH \\ HOOC-C-H \end{array}$$

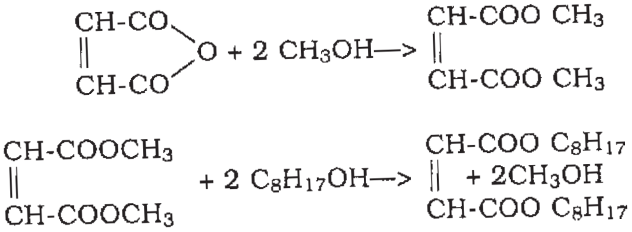
$$\downarrow$$

$$\begin{array}{l} \phantom{C_8H_{17}OOC-}H-C-COO\ C_8H_{17} \\ \phantom{C_8H_{17}OOC-C}\| \\ C_8H_{17}OOC-C-H \end{array}$$

$$\downarrow NaHSO_3$$

$$\begin{array}{l} \phantom{C_8H_{17}OOC-}H_2C-COO\ C_8H_{17} \\ \phantom{C_8H_{17}OOC-C}| \\ C_8H_{17}OOC-C-SO_3Na \\ \phantom{C_8H_{17}OOC-C}| \\ \phantom{C_8H_{17}OOC-}H \end{array}$$

In another method, the diester is made by transesterification. For this purpose dimethyl maleate is made which is then treated with 2-ethyl hexanol



$$\begin{array}{l}\text{CH-CO}\\ \|\\ \text{CH-CO}\end{array}\!\!>\text{O} + 2\ \text{CH}_3\text{OH} \longrightarrow \begin{array}{l}\text{CH-COO CH}_3\\ \|\\ \text{CH-COO CH}_3\end{array}$$

$$\begin{array}{l}\text{CH-COOCH}_3\\ \|\\ \text{CH-COOCH}_3\end{array} + 2\ \text{C}_8\text{H}_{17}\text{OH} \longrightarrow \begin{array}{l}\text{CH-COO C}_8\text{H}_{17}\\ \| \quad + 2\text{CH}_3\text{OH}\\ \text{CH-COO C}_8\text{H}_{17}\end{array}$$

Alternatively, (USP 2,028,091), 92 g glycerine is heated with 282 g of oleic acid at 200ºC for 10 hours and then with 196 g of maleic anhydride at 120ºC for 3 hours and finally with amyl alcohol to give an ester which is further sulphated with sodium bisulphite.

Rapid wetting agents are marketed in the form of a semisolid, pale yellow glassy material, resembling water glass (sodium silicate) or in the form of a pale yellow clear liquid or a gelatinous opaque dispersion (paste). The glassy material is nearly 100% pure product, while the other forms are aqueous solutions/paste of lower concentrations. This is an anionic wetting agent. Being ester, its stability to alkali (above pH 10.7) is limited. When it gets hydrolysed under alkaline conditions, it loses its wetting power. In aqueous solution (1% of the 100% pure product) has a pH of 6.5-7.5. The product is soluble in water and has solubilities of 1.5% and 6% at 28º and 70ºC respectively. It has excellent stability to hard water.

These products are stable over the pH range 1-10 at room temperature. They are more stable in the acidic region than in the alkaline. Their wetting efficiency is not adversely affected by a rise in temperature, provided neutral conditions are maintained. They are compatible with anionic and nonionic auxiliaries as well as with starch, glue, dextrin, polyvinyl alcohol, CMC and casein. They are stable to hard water of up to 300 ppm hardness (as $CaCO_3$).

The rapid wetting agent finds use in many textile processes where problems of wetting are faced, particularly in bleaching and dyeing. For example in size baths for polyester and nylon to achieve better penetration 0.5-1 g/l (of the 100% product may be selected. The same concentration may be used in enzymatic desizing baths to increase the penetration of the enzyme liquor during padding. It also finds use in grey chemicking of cotton fabrics such as hosiery material.

When added (0.9-1.2 g/l) to hypochlorite bleach baths, it ensures thorough wetting of the cloth with the bleaching solution to achieve thorough and uniform bleaching. It is also useful in bleaching under acidic conditions, as in the case of chlorite bleaching of synthetic fibre materials.

In grey yarn dyeing, the yarn is wetted out in water containing Turkey Red Oil or other wetting agents and kept overnight before dyeing. If the rapid wetting agent is used instead of Turkey Red Oil in the operation, lower concentrations and shorter treatment times are sufficient to bring about the required wetting. Thus the grey yarn may be steeped in water containing the rapid wetting agent (0.6-1.2 g/l) at the room temperature for 2 hours.

When cotton yarn packages like cheeses, cones, beams etc. are boiled out before dyeing in a liquor circulating machine, alkali is generally not used to prevent swelling of the yarn, for this purpose, 0.5-1 g/l of the rapid wetting agent solution may be used with advantage.

The rapid wetting agent may be used in dyeing processes such as the following:

(1) As a penetrating agent in the pigment pad-stream processes of dyeing vat dyes.

(2) As a penetrating agent in the dyeing of cotton felts with direct dyes.

(3) As a penetrating agent in the padding of vat dyes on mineral khaki-dyed cloth (or vice versa),

(4) In the winch dyeing of heavy rayon fabrics to prevent floating of the fabrics, and

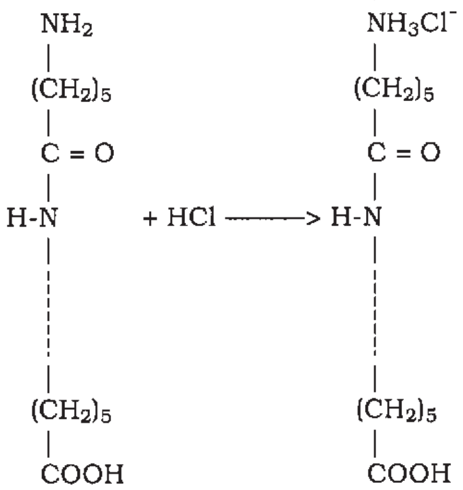
(5) In the dyeing of nylon with acid or metal-complex dyes. Addition of the rapid wetting agent to the final rinse water (0.5 g/l) increase the absorbency of cotton fabrics, which may be have improperly kier-boiled.

In order to improve the absorbency of ducks, tightly woven poplins and twills, they may be padded with 0.25-0.5 g/l of the rapid wetting agent and dried.

In order to produce Sanforised fabrics, the cotton fabric is subjected to compressive shrinkage in a moistened state. For moistening the fabric it is sprayed with water before feeding it to the compressive shrinkage machine. This can be facilitated by adding 0.5-1 g/l of the rapid wetting agent to the water used for spraying.

NYLON DYEING ASSISTANTS

Dyeing of nylon with acid dyes involves the use of an acid in the dyebath. Initially, the amino groups at the molecular chain ends get protonated, creating positive sites in the fibre material and the anion of the acid is attracted and retained in the vicinity of the positive site to maintain electrical neutrality:



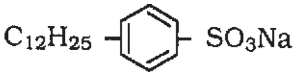
$$\begin{array}{c} NH_2 \\ | \\ (CH_2)_5 \\ | \\ C=O \\ | \\ H\text{-}N \\ | \\ \vdots \\ | \\ (CH_2)_5 \\ | \\ COOH \end{array} + HCl \longrightarrow \begin{array}{c} \overset{+}{N}H_3Cl^- \\ | \\ (CH_2)_5 \\ | \\ C=O \\ | \\ H\text{-}N \\ | \\ \vdots \\ | \\ (CH_2)_5 \\ | \\ COOH \end{array}$$

Nylon molecule

Since the dyebath contains the acid dye anions ($R\text{-}SO_3\text{-}$), these are also attracted by the protonated amino groups in the fibre and in the competition between the chloride and the dye anions for the positive sites in the fibre, chloride ions being comparatively small ions get preference over the dye anions in occupying the positive sites. These ions are held by electrostatic bonds which are fairly strong. However, the binding process is a reversible one and hence the adsorption and desorption of chloride and dye anions go on simultaneously. When the dye anion is bound by the electrostatic bond, it is bound to the fibre molecules by other forces also (including hydrogen bonds, van der Waal's forces, etc.) .As a result, the desorption of the dye anion is more difficult than that of the chloride anion, which is bound only by the electrostatic bond. Thus even though the chloride ions get preference over the dye anions (for adsorption) initially, the desorption of the bound dye anion takes place more slowly than that of the bound chloride ions. The bigger size of the dye anion also slows down the dye desorption process. The overall effect is the initial rapid exhaustion of the dyebath with respect to chloride ions, accompanied by slow exhaustion with respect to the dye anions and gradual replacement of the bound chloride ions in the fibre by the dye anions and a gradual building up of the dye anion in the fibre.

Since the chloride ion slows down the initial dye adsorption, the addition of additional chloride ions (or sulphate ions) by way of common salt (or Glauber's salt) favours initial slow dyeing (retarding). In fact, these salts act as retarding agents in the dyeing of acid dyes on polyamide fibres in the presence of an acid. On the other hand, if the concentration of the acid is increased, more of the hydrogen ions are adsorbed by the fibre, thereby increasing the number of positive sites (protonated amino groups) and more dye can be taken up by the fibre. In other words, acids act as exhausting agents in this dyeing system. Thus in certain cases, the dyeing may be started with little or no acid in the dye bath, in the presence of common salt or Glauber's salt, and after some time acid may be added. The production of level dyeing with maximum dye utilisation is favoured by initially retarding and finally accelerating the dyeing process.

In many of the cases, the retarding action of the salts is not sufficiently effective in preventing uneven dyeing. In these cases other levelling agents have to be used. Such levelling agents should have certain structural features. An anionic surfactant like a fatty alcohol sulphate, sodium dodecyl benzene sulphonate,



Turkey Red Oil, sulphated methyl oleate or butyl oleate, and other compounds have the required properties of a levelling agent. These should be an anionic group (sulphonate or sulphate) and when they are dissolved in water, they ionise into long anions and small sodium cations. By virtue of the presence of the sulphonate or sulphate group, the ionised compound competes with the dye anion for the positive site in the firbe.

The structural features of the levelling agent (linear molecule, absence of hydrogen bond forming groups and the ability to form weak links via van der Waal's forces) can diffuse faster than the dye anions, which are bound to the fibre by electrostatic bonds, hydrogen bonds, van der Waal's forces etc. As a direct consequence of the different strengths of the bonds formed between the levelling agent and the fibre on the one hand and between the dye and the fibre on the other, the desorption of the bound levelling agent takes place faster than that of the adsorbed dye. Even though the levelling agent anions are adsorbed faster than the dye anions and occupy the cationic sites in the fibre, the dye gradually builds up in the fibre.

This creates the desired conditions of initial slow dyeing to prevent the production of uneven dyeing results. Alternatively, the fibre material may be worked in a bath containing the anionic levelling agent and the acid (in the absence of the dye) for some time, when the anionic agent is picked up and retained by the anionic sites in the fibre and when the dye is added subsequently, the number of cationic sites available for the dye anions is reduced, because some of them are already occupied by the anions of the levelling agent. As the dyeing proceeds they are gradually replaced by the dye anions. This procedure also prevents the production of uneven dyeing results.

There is another principle of retarding the dyeing process to get even dyeing effects. Since the acid dye is attracted and held in the fibre mainly by the cationic sites in the fibre, the rate of dyeing could be decreased by neutralising the charge on the dye anion temporarily. This is usually done by using a cationic surfactant which ionises into a long cation and small anion (chloride, bromide, acetate etc.). The surfactant cations forms a complex with the dye anion by mutually neutralising the negative and positive charges of the different ions. By controlled addition of the cationic surfactant most of the dye anions can be complexed and the small amount of the free dye anions are taken up by the fibre. Thus the dyeing rate is decreased (or the dyeing process is retarded).

This method of levelling poses two problems. Firstly, neutralisation of the negative charge of the dye anion by the positive charge of the cation of the levelling agent added decreases the solubility of the dye to such an extent that the complex may get precipitated in the dyebath itself. In order to prevent this precipitation of the dye-levelling agent complex in the dyebath, a nonionic surfactant (fatty alcohol-ethylene oxide condensation product) is also incorporated in the system, so that the insoluble complex formed is held in a fine state of dispersion in the dyebath.

As the dyeing continuous, the complex gradually breaks up into the component ions (dye anions and levelling agent cations) and the released dye anions are adsorbed by the fibre gradually. The splitting up of the complex into the component ions is facilitated by raising the temperature. However, the entire amount of the complex does not break up at the maximum temperature of dyeing, so that at the end of the dyeing some amount of the dye anions (this amount varies with the dye) is bound with the cations of the levelling agent, entailing a loss of colour value, which is not the case when anionic levelling agents are used.

Therefore, cationic levelling agents should be used only when the dye produces thoroughly uneven dyeins in the absence of any levelling agent. Since even dyeing results have to be obtained, the colour value may have to be sacrificed to some extent. The exhaustion of the dyebath containing a typical acid dye, Benzyly Fast Red 2BL, wile dyeing, on nylon tricot at 100ºC in the presence and absence of anionic and cationic levelling agents is shown in Fig. 7.2.

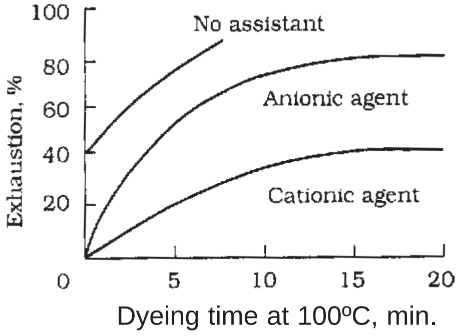
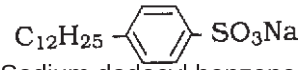
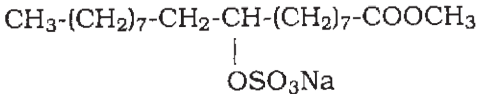
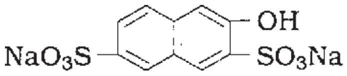
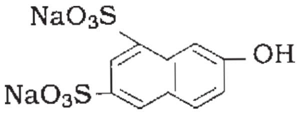
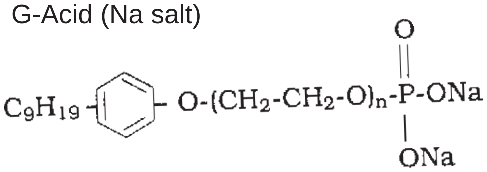


Fig. 7.2: Effect of different levelling agents on the rate of dyeing of nylon with 0.5% Benzyl Fast 2BL at 100ºC

It is seen that in the absence of any levelling agent, a fairly large amount of the dye (about 40%) is taken up by the fibre in a very short time of dyeing and that the exhaustion reaches a value of about 90% in 6-7 min. When an anionic levelling agent is present, the dyeing rate is decreased considerably (70% exhaustion in 10 min.). When the cationic levelling agent is present, the dyeing rate is decreased still further.

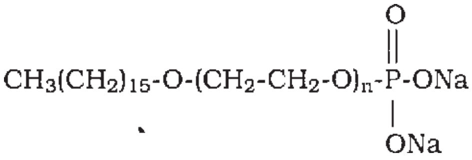
It is significant to note that the exhaustion is about 40% in 20 min. of dyeing entailing a loss of colour value. This indicates that the cation forms a fairly strong complex with the dye anion and that a considerable portion of the complex does not split up into the component ions.

Some suitable anionic retarding agent in nylon dyeing are sown below:-

1. $CH_3 – (CH_2)_{11} – OSO_3Na$
   Sodium laurly sulphate
2. $CH_3 – (CH_2)_{15(17)} – OSO_3Na$
   Sodium cetyl stearyl sulphate
3. 
   Sodium dodecyl benzene sulphonate
4. 
   $CH_3\text{-}(CH_2)_7\text{-}CH_2\text{-}\underset{\displaystyle OSO_3Na}{\underset{|}{CH}}\text{-}(CH_2)_7\text{-}COOCH_3$
   Sulphated methyl oleate
5. 
   R-Acid (Na salt)
6. 
   G-Acid (Na salt)
7. 

Phosphate ester of nonyl phenol ethylene oxide adduct

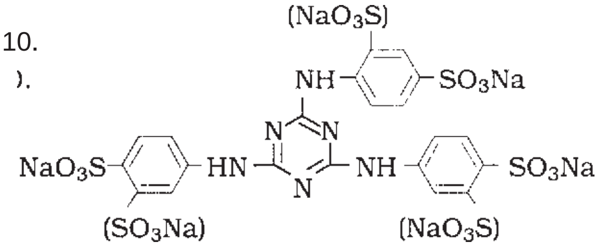
8.



$$CH_3(CH_2)_{15}\text{-O-}(CH_2\text{-}CH_2\text{-O})_n\text{-}\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{P}}\text{-ONa}$$

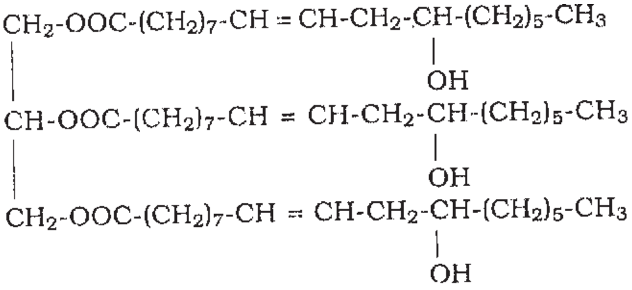
Phosphate ester of cetyl alcohol ethylene oxide adduct

9., 10.



Cyanuric chloride-sulphanilic acid/
metanilic acid condensate

11.



$$\begin{array}{l} CH_2\text{-OOC-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}(CH_2)_5\text{-}CH_3 \\ | \\ CH\text{-OOC-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}(CH_2)_5\text{-}CH_3 \\ | \\ CH_2\text{-OOC-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}(CH_2)_5\text{-}CH_3 \end{array}$$

Castor oil (to be sulphated)

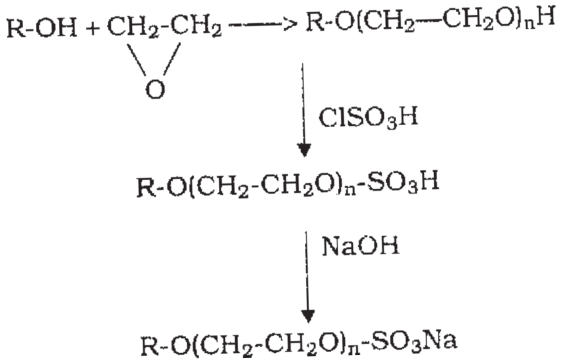
Commercial anionic levelling agents are available in the form of clear brown (solutions), which promote levelling, migration (from deeper dyed areas to lighter dyed ones) and penetration of acid dyes. Usually, they are used in the concentration of 2-4 per cent (owf). Using a selected range of acid dyes, even barre nylon fabrics can be satisfactorily dyed with the aid of the levelling agents. Where the dye has high affinity and where deeper shades are dyed, 3-4 per cent (owf) of the levelling agents should be used. At the end of the dyeing, they can be easily removed form the dyed material by washing.

SULPHATED ETHERS

When a certain number of ethylene oxide moles are condensed with a fatty alcohol, fatty acid, fatty acid amide or a fatty amine, a surfactant is produced (these will be discussed latter). Some of them are excellent detergents, emulsifiers, softeners, dyeing assistants etc. These are nonionic in character.

The non-ionic detergents produce weak foams and though soluble in water, they produce turbidity at higher temperatures and are likely to form separate layers over water. fatty alcohol sulphates, the anionic surfactants, on the other hand are high foam formers but do not produce clear solutions of sufficiently higher concentrations.

Fatty alcohol-ethylene oxide condensate has an end hydroxy group, which can be sulphated to overcome the difficulty of turbidity appearing in the solutions on heating.



These sodium salts of sulphated ethers are made form fatty alcohols ethoxylated not to form detergents by themselves. They are in fact made by condensing 2-4 ethylene oxide moles per fatty alcohol (the resulting product is still water insoluble) and then sulphated and neutralised. The aqueous solutions of the final products do get turbid at fairly low temperatures and their wetting properties are lower than those of other anionic detergents. However their foaming properties are considerably higher. They increase the detergency of alkyl aryl sulphonate detergents. They can be added up 20% on the total weight of the alkyl aryl sulphonate.

Since the ethoxylation of the fatty alcohol is carried out to a low degree considerable amount of the fatty alcohol remains unreacted. Thus 25% and 18% of the fatty alcohol remain unreacted when 2 and 3 moles respectively of ethylene oxide are added per mole of the fatty alcohol. Hence, during the subsequent sulphation of the ethoxylated product, the free alcohol is also sulphated so that the final product contains a substantial amount of the fatty alcohol sulphate as well. Usually chlorosulphonic acid is used as the sulphating agent. Hence this requires special corrosion-proof equipment, either glass-lined steel or glass.

ALKYL SULPHONATES

Linear alkyl sulphonates of the type

$CH_3 – (CH_2)_6 – CH_2 – SO_3Na$

are typical anionic surface active agents. Hexadecyl (C_{16}) and octadecyl (C_{18}) members of the series are relatively insoluble in water, especially in the cold and their detergency is inferior to the corresponding sulphates.

In one method of making alkyl sulphonates, Reed's reaction is used. Aliphatic hydrocarbons from the petroleum industry are used as the raw materials. In this reaction, the hydrocarbon is heated with a mixture of sulphur dioxide and chlorine to 40º-100ºC when alkyl sulphonyl chloride is formed –

$$R – H + SO_2 + Cl_2 \longrightarrow R – SO_3Cl + HCl$$

This on treatment with dilute aqueous solutions of sodium hydroxide gives alkyl sulphonate:

$$R – SO_2Cl + NaOH \longrightarrow R\text{-}SO_3Na + HCl$$

The sulphonation is activated by ultraviolet light or visible light of short wave-length.

In a modification of Reed's reaction ssulphuryl chloride (SO_2Cl_2) is used instead of the mixture of sulphur dioxide and chlorine for sulphonating the hydrocarbon. When benzoyl peroxide is used as a catalyst, the sulphonation may be carried out in the dark. In another modification, a mixture of sulphur dioxide and oxygen ozone is used as the sulphonating agent in the presence of organic peroxide or ultraviolet light as the catalyst.

Straight chain alkane fractions have been sulphonated using a mixture of air and sulphur dioxide by ESSO using gamma-rays from Co-60 source. These products are biodegradable and are good detergents and are very similar to those produced by sulphochlorination. However, they are available as a neutralised salt in a semi-concentrated form. In yet another method n-paraffin sulphonates are produced by the production of peroxy sulphonic acid, which is then reacted with sulphur dioxide and water alkyl sulphonate.

Alkyl sulphonates are available as liquid detergents (aqueous solution) and since they are heat sensitive, powders have not been prepared from them. They give a sticky product on dyeing.

Alkyl sulphates with 8-12 carbon atoms are good dispersing agents and also good wetting agents in the mercerising bath.

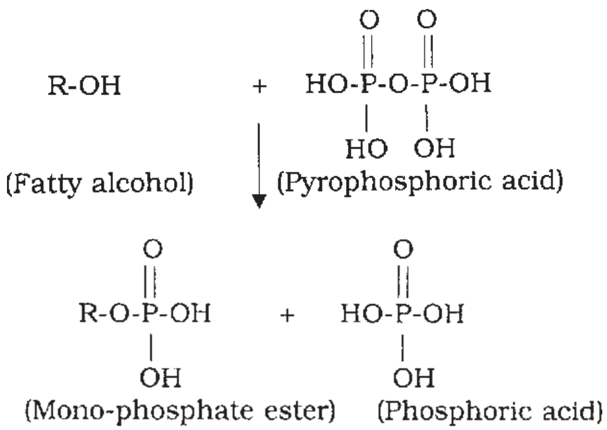
Fatty alcohol sulphates ($R – OSO_3Na$) are readily distinguishable from alkyl sulphonate ($R – SO_3Na$) in that they are readily hydrolysed by hot dilute mineral acids and the hydrolysed product (fatty alcohol) is insoluble in water. the sulphonates on the other hand are not affected at all. Alkali fusion (with molten sodium hydroxide) or boiling with very concentrated sodium hydroxide solution is needed to separate the sulphonate group from the alkyl sulphonate.

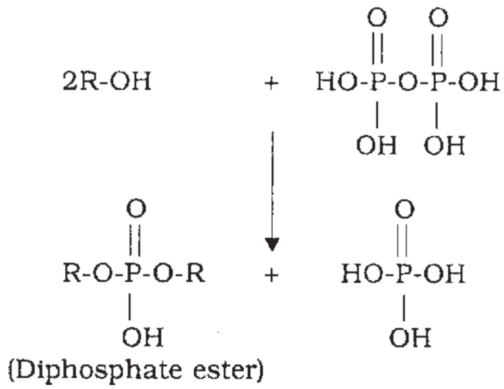
In the refining of petroleum by sulphuric acid, alkyl sulphonates are produced as by-products. These find use as emulsifying agents for cutting oils, textile spinning oils, sludge dispersing agents in lubricating oils etc.

PHOSPHATE ESTERS AND ALKYL PHOSPHATES

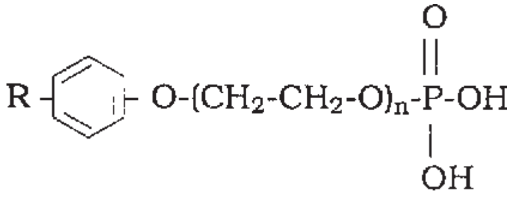
When fatty alcohols, fatty alcohol-ethylene oxide condensates or alkyl phenol-ethylene oxide condensates are treated with pyrophosphoric acid, the corresponding phosphate esters, which are mixtures of mono-and diphosphate esters are formed.

In practice, the products formed contain about two-thirds monoester and one-third, diester. One mole of phosphoric acid formed, as shown in these reactions is normally not separated form the final product. The partially of fully neutralised phosphate esters are good detergents especially on hard surfaces. They have good stability to acids and alkalies and have low foaming properties. They are biodegradable. They are very soluble in organic solvents and are used as drycleaning detergents in combination with solvents.





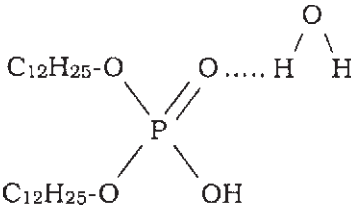
Non-volatile phosphate esters of alkyl phenol ethylene oxide condensates are found to be antistatic agents and in combination with volatile fatty acid-ethylene oxide condensate can be used as lubricant-cum-antistat for synthetic fibres (Text. Res. J., 1973, p. 198).



$R\text{-}COO(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$

The mixture has been found to have highly effective antistatic properties and the optimum concentration of the phosphate ester has been found to be 10-15%. The antistatic properties have been found to be better on polyester than on polyamide fibres. The phosphate ester is thermally stable. For example, when the thermal property was determined by measuring volatiles on 2 g draft oven at 200ºC for 1 hour and expressing as weight loss, the phosphate ester lost only 2.4%, compared to 70.62% in the case of the fatty acid condensate. The 75/25,50/50 and 25/75 mixtures of the lubricant/antistat composition lost 14.3%, 9.87% and 5.5% respectively.

It has been postulated (Amer. Dyest. Reptr., 1954, p. 368) that the alkyl phosphate associates with water at moderate humidities as shown below:



In some cases more than one water molecule may be bound to a single functional group. Thus the system antistatic agent – water on the fibre surface consists of polar centres, each holding several water molecules. It is known that an antistat which is very effective on one fibre, may be moderately active on another. This indicates that besides the ability of the compound to associate with water molecules, an important factor in imparting antistatic properties is the mode of association of the agent with the fibre.

Another use has been found by Shenai, V.A. and Parameshwaran (unpublished work) for fatty alcohol-ethylene oxide condensate and nonylphenol-ethylene oxide condensate both esterified with phosphoric acid followed by neutralising with sodium hydroxide. These have been found to be effective retarding agents in the dyeing of acid dyes on nylon since they produce long anions when dissolved in water, which can compete with the dye anions for the cationic sites present in the polyamide fibre.

8

Cationic Surfactants

QUATERNARY AMMONIUM SALTS

There are various methods of improving the washing fastness of direct dyes on cellulosic fibre fabrics. The most widely used method involves the application of a cationic dye fixing agent subsequent to dyeing in a separate bath. The earlier types of dye fixing agents were based on alkyl pyridinium halides. When dissolved in water, they ionise into long cations and small anions. On the other hand, when a direct dye is dissolved in water, it ionises into long coloured anions and small sodium ions. When these two solutions are mixed the long ions of opposite ionic charge combine with one another to form an insoluble complex. If the dye fixing agent solution is applied after dyeing with the direct dye, the complex is formed inside the fibre and due to insolubility of the complex the washing fastness is improved.

$R - SO_3Na \ \square \quad R - SO_3^- + Na^+$

(Dye)

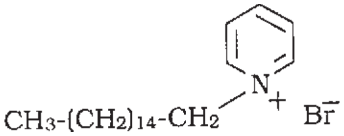
$R_4 - NCl \ \square \quad R_4N^+ + Cl^-$

(Dye fixing agent)

$RSO_3^- + R\ N^+ \qquad RSO_3^-NR_4$

Typical examples of such compounds are Fixanol C, Sandofix WE, Lyofix EW, Lyofix DE, Sapamine A, CH, KW, Solidogen B etc.

Fixnol C of ICI is cetyl pyridinium bromide in the form of a brown paste with an acid reaction.



It dissolves readily in hot water to give solutions stable to electrolytes. In addition to its use in improving the washing fastness of direct dyeing it finds use in softening of cellulosic fibre fabrics, in dispersing sulphur in the production of viscose rayon etc.

Solidogen BS of Casella Farbwerke is a polyamine compound based on methylated polyethylene diamine and it contains the following basic structure.

$-NH - (CH_2 - CH_2 - NH)_n - CH_2 - CH_2 - NH -$

It is a slightly alkaline brownish liquid, which is freely miscible with water and is applied in the form of a cold solution (1-4 ml/litre) to cotton and viscose rayon materials dyed with direct dyes for improving their fastness to water.

A reference to patents literature revels that many amines, quaternary ammonium, phosphonium and tertiary sulphonium compounds can be used as dye fixing agents. These include:

(a) products obtained by heating a mixture of acetone and formaldehyde in the presence of ammonium chloride at 70ºC.

(b) the product of reaction of ammonia with epichlorohydrin, which is subsequently methylated.

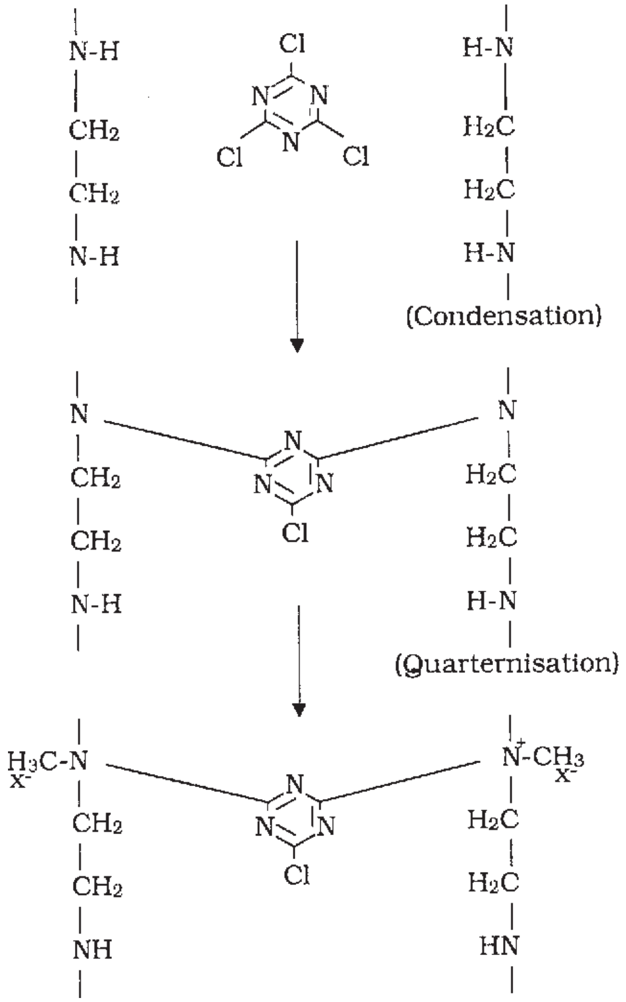
(c) sulphonium salt obtained by heating dichlorohydrin with sodium sulphide and further heating with dimethyl sulphate.

(d) the methylated reaction product obtained by heating triethanolamine with urea.

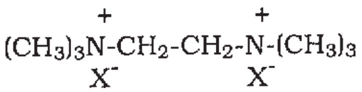
(e) aromatic sulphurised hydroxy compounds obtained by heating phenol with sulphur or sulphuryl chloride in aqueous alkaline solution and further condensed with secondary aliphatic amine and formaldehyde.

(f) condensation product obtained by heating sulphurised phenol, formaldehyde and primary amines, and

(g) dicyandiamide-formaldehyde condensation products prepared under acidic conditions.



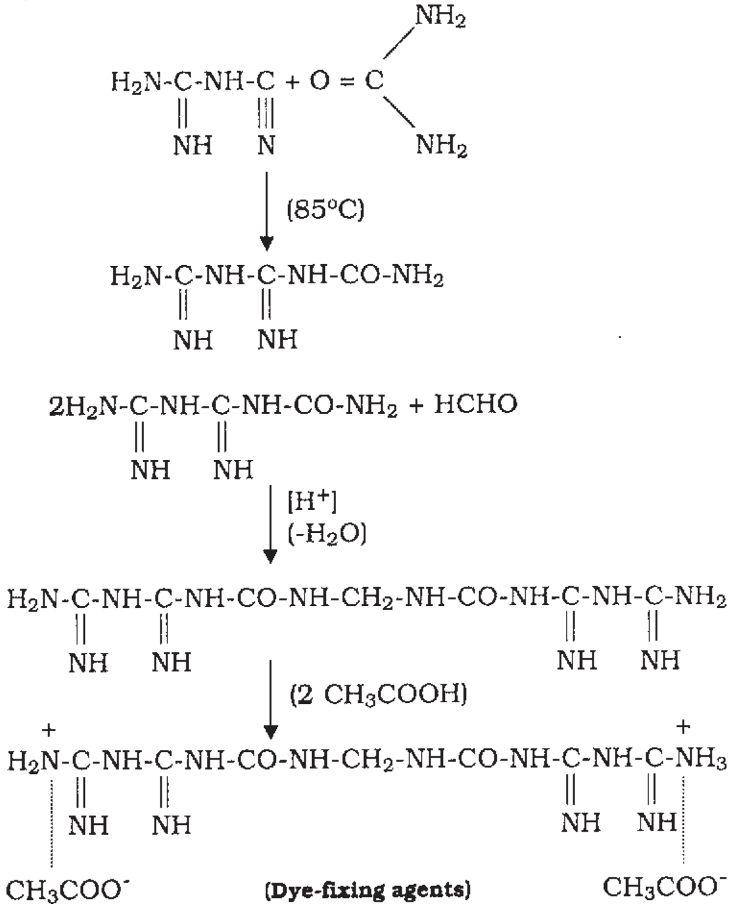
Some other types of dye fixing agents contain two or more quaternary ammonium groups in their molecule with suitable anions. Some of them can be made by condensing polyamides with polyhalides:



$$(CH_3)_3\overset{+}{\underset{X^-}{N}}-CH_2-CH_2-\overset{+}{\underset{X^-}{N}}-(CH_3)_3$$

QUATERNARY AMMONIUM COMPOUND WITH TWO QUARTERNARY ATOMS

The synthesis of at a cationic dye fixing agent, based on dicyandiamide, urea and formaldehyde. (The reactions are shown below):



$$H_2N\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{N}{|||}}{C} + O = C\begin{smallmatrix} \diagup NH_2 \\ \diagdown NH_2 \end{smallmatrix} \xrightarrow{(85^oC)} H_2N\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}CO\text{-}NH_2$$

$$2H_2N\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}CO\text{-}NH_2 + HCHO \xrightarrow[(-H_2O)]{[H^+]}$$

$$H_2N\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}NH\text{-}CO\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH_2 \xrightarrow{(2\ CH_3COOH)}$$

$$\overset{+}{H_2N}\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}NH\text{-}CO\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}\overset{+}{NH_3} \quad CH_3COO^- \quad CH_3COO^-$$

(Dye-fixing agents)

The product was prepared as follows:

To 84 g of dicyandiamide 40 g or urea was added in a 1 litre flat bottomed pyrex flask. In another flask 84 g of dicyandiamide and 20 g ammonium chloride were taken and the contents of both the flasks were heated in a water bath at 85ºC for 3 hours after adding minimum amount of water to dissolve the solids. The contents of the flasks were mixed with one another and heating continued at 85ºC for 1 hour. Subsequently, 54 g formaldehyde (40% solution) was added and heating continued at the same temperature for 2 hours. The reaction was carried out at pH 6-7 by adding 0.2 M acetic acid (9.5 ml.) and 0.2 M sodium acetate (0.5ml).

In another method (BP 594, 791) 1 mole of dicyandiamide is heated with 0.5-2 moles of formaldehyde in a closed vessel in the absence of water until they condense and liberate water, after which heating is continued until a compound with basic properties and soluble in organic acids is obtained. Treatment of direct dyeings with acid solutions of these increase the wet fastness with slight deterioration of light fastness of the dyeings.

In a third method (USP 2,741,535) a mixture of dicyandiamide (1 mole), formaldehyde (1.5-2 moles) and ammonium chloride (0.5 mole) is prepared and the reaction is started at the room temperature. The reaction is exothermic; the temperature is raised to 80º-100ºC and kept threat for 1½-8 hours. The pH is maintained at 6.5. The ammonium salt (instead of ammonium chloride, ammonium sulphate or phosphate may also be used) dissociates and liberates the corresponding acid, which makes the entire solution acidic. A part of the ammonium salt ionises into ammonium and chloride ions and the former reacts with the condensate and forms an integral part of the final condensate. The best effects are produced when treated at pH 7.

Specifically, 84 g dicyandiamide, 54 g formaldehyde (as 38% solution) and 30 g ammonium chloride are mixed, when a pH of 6.55 is obtained. The temperature is raised to 80ºC and the reaction carried out at 95º-98ºC for 8 hours. Running the reaction mixture in salt solution, the condensate precipiates, which is filtered and dried.

This condensate (100 g) is mixed with cupric chloride or acetate (10-100 parts), an aminocarboxylic acid like glycine, alanine, leucine, aspartic acid, glutamic acid etc. (2-50 g) and a buffering agent like ammonium acetate (0-45) to get a pH 7.

A solution of 2% solids contents (above mixture) is applied to dyed or printed fabrics at 140º-160ºF for 20-30 min. when it is completely exhausted. The treated fabrics are dried and no curing is necessary.

The aminocarboxylic acid acts as a coordinating compound to form a soluble complex of the copper salts, thus preventing the precipitation of cupric hydroxide in the range of about pH 7 and avoiding the precipitation of the resinous condensate.

In a yet another method (BP 576,562) acid soluble condensation products are obtained from dicyandiamide, urea, an inorganic ammonium salt and formaldehyde by heating 1 mole of dicyandiamide with urea and the ammonium salt in molar proportions and condensing the reaction product with at least two moles of formaldehyde. In one example, a mixture of 17 g dicyandiamide, 12 g urea and 30 g hydrochloric acid (30%) is refluxed for 6 hours. Then it is treated at 30ºC with 50 g of formaldehyde solution (30%) and the whole stirred for 6 hours at 75º-85ºC. Finally, it is treated with 10 g of glacial acetic acid. The solution may be directly added to the after-treating baths of improving the washing fastness of direct dyeings.

Cationic dye fixing agents are marketed in the form of a clear and colourless to faintly yellow liquid, which is miscible with water in all proportions, to form clear and transparent solutions. Being cationic in nature, it is compatible with other cationic and nonionic products, but not with anionic detergents and auxiliaries. Whereas it is stable to acids, it is not so to alkalies.

In the actual application, the dyed material is treated with a solution containing 1-3 g/l of the dye fixing agent at room temperature for 10-15 min. followed by rinsing and drying. Since the dye fixing agent loses its efficiency in alkaline solutions, it is preferable to keep the treating solution slightly acidic by adding acetic acid.

Cationic dye fixing agents, which have been predominantly used for improving the washing fastness of direct dyeings, have also found another use with dyeings and prints produced from reactive dyes on cellulosic fibre materials. The dyeing of reactive dye involves a final thorough soaping treating to remove the hydrolysed reactive dye from the dyed material. Since the hydrolysed reactive dye has very low affinity for cellulosic fibres. It has to be removed to achieve the excellent washing fastness expected of the reactive dyeing. This results in an inevitable loss of dyestuff. This assumes great importance in printing reactive dyes where the hydrolysed dye has to be removed from the printed portion along with the thickener and other chemicals. This dye, striped in the after-treating (soaping) bath stains the unprinted (white) ground and it is very difficult to remove this tinting. It remains there with the slight affinity it has for the fibre. As a result it is not possible to obtain absolutely white ground. If any mild oxidative or reductive treatment is given to the printed cloth to destroy the tint of the ground a part of the dye at the printed portion also is destroyed. In order to overcome this problem, cationic dye fixing agent may be used. In this case, the hydrolysed reactive dye, being anionic in nature, is fixed with the cationic dye fixing agent, like a direct dye. However, the dye is not fixed like a reactive dye with a covalent bond between the dye and the fibre. If, prior to the rinsing stage at which the thickener is removed, the printed and (and steamed) cloth is given a treatment with the dye fixing agent the hydrolysed dye is fixed like a direct dye, and when it is subsequently rinsed, less of hydrolysed dye is removed with the consequent production of white ground. Additionally, increased colour value at the printed portion is also achieved.

The mechanism of mixing direct dye or hydrolysed reactive dye may be explained as follows. When the cationic dye fixing agent is dissolved in water, it ionises into long cations and small anions. On the other hand, when a direct dye (or a hydrolysed reactive dye) is dissolved in water, it ionises into long, coloured anions and small sodium cations. If these two solutions are mixed, the long ions of opposite ionic charge combine with one another to form an insoluble complex. If dye fixing agent solution is applied after dyeing with direct dyes, the insoluble complex is formed inside the fibre and due to its insolubility in water, the washing fastness is improved.

$$\underset{\text{(Dye)}}{\text{R-SO}_3\text{Na}} \rightleftharpoons \text{R-SO}_3 + \text{Na}^+$$

$$\underset{\text{(Dye fixing agent)}}{\text{R'}_4\text{NCl}} \rightleftharpoons \text{R'}_4\text{N}^+ + \text{Cl}^-$$

$$\text{R-SO}_3 + \text{R'}_4\text{N}^+ \longrightarrow \text{RSO}_3\text{........R'}_4\text{N}\downarrow$$

SOFTENERS

Cationic surfactants have been defined as materials which dissolve or disperse in water, concentrate and orient at interfaces and ionise in such a way that the cation includes a hydrocarbon chain, which is hydrophobic and contains from 8 to 25 carbon atoms.

Softening agents are applied to textiles to improve their hand, drape, cutting and sewing qualities. An effective softener must be readily dispersible in rinse water and rapidly absorbed so that uniform deposition on the fabric can occur within a relatively short treatment time and generally, exhaustion should take place in about 5 min. for the softener to be effective and economically usable. It must impart softness, fluffiness and lubricity to the treated cloth and reduce static build-up, especially in the case of hydrophobic fabres like cellulose acetate, nylon, polyester and acrylic fibres. These effects should be obtained without the loss of fabric whiteness or brightness, and then, the treated fabric should retain its ability to absorb water in subsequent use for drying the body (bath towels) or other surfaces.

THE ORIGIN OF CATIONIC SOFTENERS

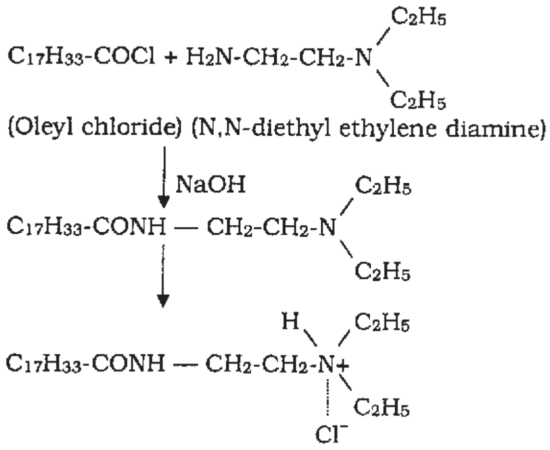
The origin of cationic softeners may be traced to the attempts made during the early 1930s in improving the washing fastness of direct and acid dyeing by complex formation between the dye anions and the quaternary ammonium cation of the dye fixing agent on the fibre. While short chain cationics were ineffective, long chain compounds were found to be better in both aspects of softening and dye fixing. Some of these compounds are shown in Fig. 8.1.

In the preparation of the Sapamines (Ciba) asymmetric diethyl ethylene diamine was used instead of ethylene diamine, because of the ease with which the former could be quaternised to give a cationic compound. Thus, treatment of the reaction product of oleyl chloride and asymmetric diethyl ethylene diamine with dimethyl sulphate gives the corresponding metho-sulphate (Sapamine MS), a quaternary compound having high substantivity for textile fibres.

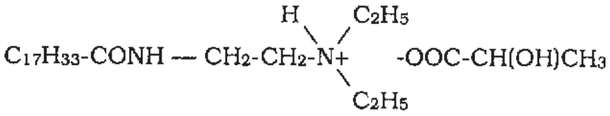
Fabric softeners are used to modify the hand and to restore the lost physical properties to the laundered fabrics. These mainly belong to cationic type and are made from quaternary ammonium salts, imidazolinium salts and amido salts. The hydrophobic portion of quaternary ammonium salts is usually a fatty hydrocarbon which causes the cationic softener to lubricate the fibres in the fabric. The principal effect of lubrication is believed to have a bearing on the wear life or abrasion-resistance of the fabric.

INTERESTING ADVANTAGES

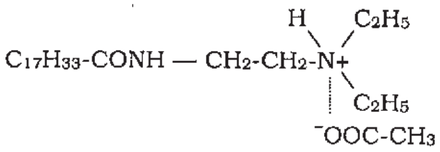
Cationic compounds present some interesting advantages are textile softeners. Because of their substantivity to textile fibres they



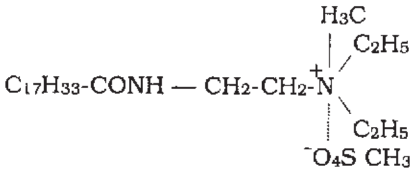
Sapamine CH (Chloride)



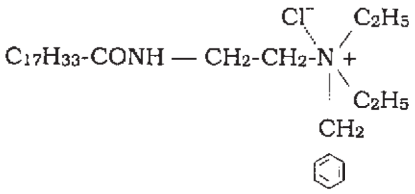
Sapamine L (Lactate)



Sapamine A (Acetate)



Sapamine MS (Methosulphate)



Sapamine BCH (benzyl chloride)

Fig. 8.1 Structures of some Sapamines

produce a more permanent softening effect than either anionic or nonionic compound. Further, they are more effective as well, since they are effective at much lower concentration.

The alkyl chain found to be the most satisfactory in softening is the saturated C_{18} chain (stearyl). Since it is a saturated molecule there is minimum tendency of yellowing. The compounds containing this chain are more likely to produce colloidal dispersions than compounds prepared with lauryl (C_{12}) chain or with unsaturated (oleyl) carbon chain. Dialkyl chain produces a greater total softening effect and greater efficiency per mole than the same type of compound containing only one long chain.

Most of the cationic softeners shown strong germicidal properties. According to bacteriologists, those cationic compounds with shorter alkyl chains or those having unsaturation are better bactericides than those which are usually preferred as textile softeners. The long, saturated alkyl groups ($C_{16}H_{33}$ – $C_{18}H_{37}$ -) are preferred for softening, but they reduce water solubility. However, when the amine is quaternised, increased solubility and greater pH stability results. The anion may be chloride, acetate, bromide, methosulphate, phosphate, lactate, etc. in general, the structure and composition of the cation determines the overall effect of the molecule and the anion effects certain physical properties.

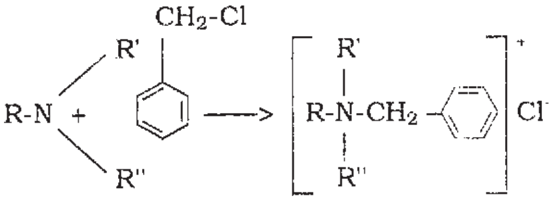
HYDROPHILICITY AND HYDROPHOBICITY

The cationics, like anionics, are usually molecules with balanced hydrophilicity and hydrophobicity. When the cationic product is held on the fabric, the primary effect is one of lubrication, of increased yarn-to-yarn or filament slippage. Anionics and nonionics exhibit no substantivity (direct surface attachment) and operate by mere deposition after the evaporation of the solvent (water). This results in loose covering of the fibre with an oily film. The effect is one of poor lubricity – only pliability. However, incorporation of fats or oils will help.

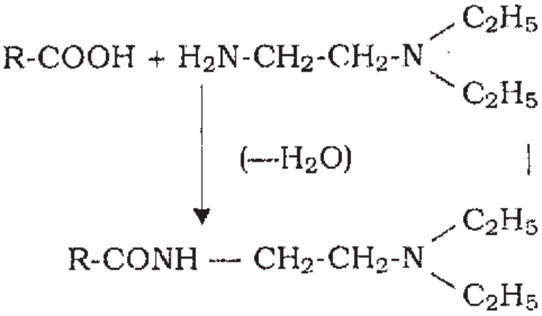
The substantivity of cationics for synthetic hydrophobic fibres is limited, the order of increasing adsorption being acrylic, polyester, polyamide, acetate, cotton, viscose rayon and wool. Softening, however, is a function not only of the softener, but also of the fabric used, method of application, softener concentration, pH, subsequent treatment, etc.

CHEMISTRY OF CATIONIC SOFTENERS

The simplest cationics are the primary, secondary and tertiary mono-amines and their salts, formed by neutralisation of the amines, usually with acetic acid. The primary and secondary amines have little importance in the textile field, since the free hydrogen on the nitrogen atom leads to fabric yellowing. But, they serve as raw materials for making quaternary ammonium compounds. Reaction with alkylating agents like methyl chloride, benzyl chloride, dimethyl sulphate, etc., converts the insoluble amines into water-soluble salts, which are more active then the original amines. These quaternary compounds have excellent thermal stability, especially on the acidic side. Stearyl or distearyl ethyl ammonium chloride or mrthosulphate, cetyl dimethyl benzyl ammonium chloride or methosulphate etc., belong to this group.

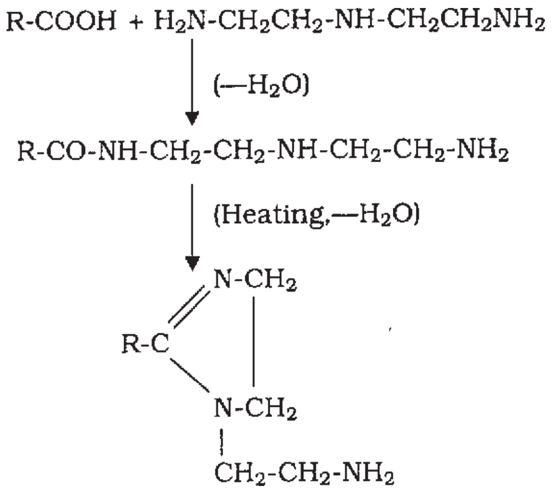


The next group of commercial importance are amido-amines, which are formed by the reaction of a fatty acid or a glyceride (fat) and a substituted or unsubstituted shortchain polyamine. Generally, the reaction occurs at only one of the amine functions, giving an amide leveling one or more unreacted amino functional groups. The amine may be diethylene triamine, N,N-diethylethylene diamine, etc. Derivatives of ethylene diamine have high melting points and exhibit poor solubility:-



This amide is quaternised either with glacial acetic acid or hydrochloric acid to give cationic fabric softeners. They are good, especially for chlorinated wool, which is quite harsh. All the members of this group are quite stable to hydrolysis.

Imidazolines are the next group of cationic softeners. These are formed fatty acids and polyethylene polyamine:



$$\text{R-COOH} + \text{H}_2\text{N-CH}_2\text{CH}_2\text{-NH-CH}_2\text{CH}_2\text{NH}_2 \xrightarrow{(-\text{H}_2\text{O})} \text{R-CO-NH-CH}_2\text{-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2 \xrightarrow{(\text{Heating}, -\text{H}_2\text{O})}$$

The cyclic compound (imidazoline) has a lower melting point and higher solubility than the parent amidoamine. These cyclic products may, subsequently, be acetylated, neutralised or reacted with ethylene oxide.

A fourth group of cationics include aminoesters, prepared by reaction of fatty acid or acid chloride with amino-alcohols like diethanolamine or hydroxyethyl ethylene diamine.

$$\text{R-COOH} + \text{HOCH}_2\text{-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-OH}$$
$$\downarrow$$
$$\text{RCOOCH}_2\text{-CH}_2\text{NH-CH}_2\text{-CH}_2\text{-OH}$$
$$\text{R-COOH} + \text{HO-CH}_2\text{CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2$$
$$\downarrow$$
$$\text{R-COO-CH}_2\text{-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2$$

These are quite water soluble, give good softening properties and are easy to make, but being esters, have a definite disadvantage of being easily hydrolysed. After quaternisation also, the ease of hydrolysis is retained by them.

Cationic softeners belonging to the fifth group may be prepared from dicyandiamide and stearyl amine followed by reaction with ethylene oxide and quaternisation. The treatment with ethylene oxide to obtain the adduct is done to impart water solubility to the compound (Fig. 8.2)

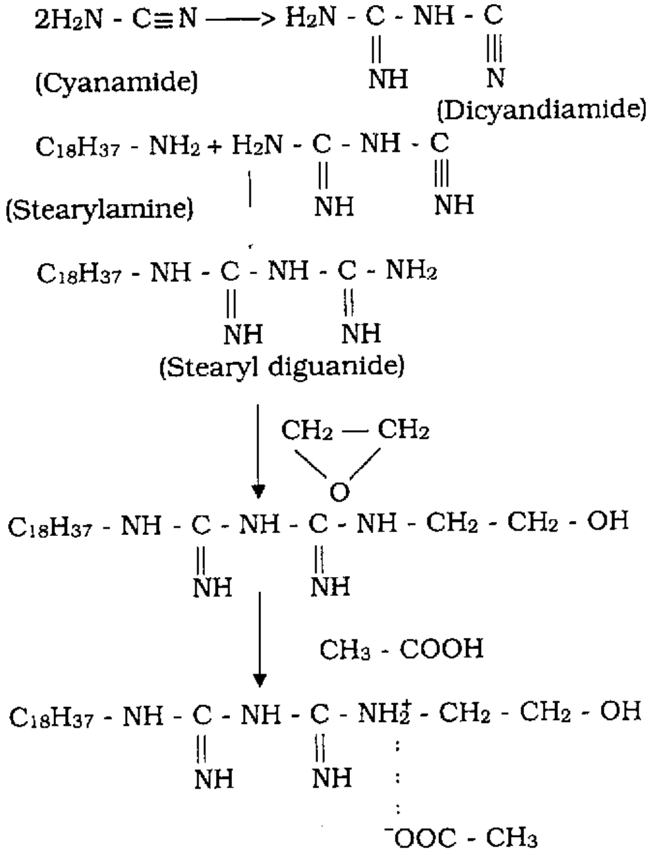


Fig 8.2 Method of preparation of quaternary stearyl diguanide

MODE OF ACTION

When a quaternary ammonium softener is dissolved in water, it ionises into a hydrophilic head with a negative charge and a hydrophobic tail carrying a positive charge.

On the other hand, when textile fibres are entered into water they acquire a negative charge (zeta potential). When a textile fibre is entered into an aqueous solution of a cationic softener, the system may be represented as in Fig. 8.3.

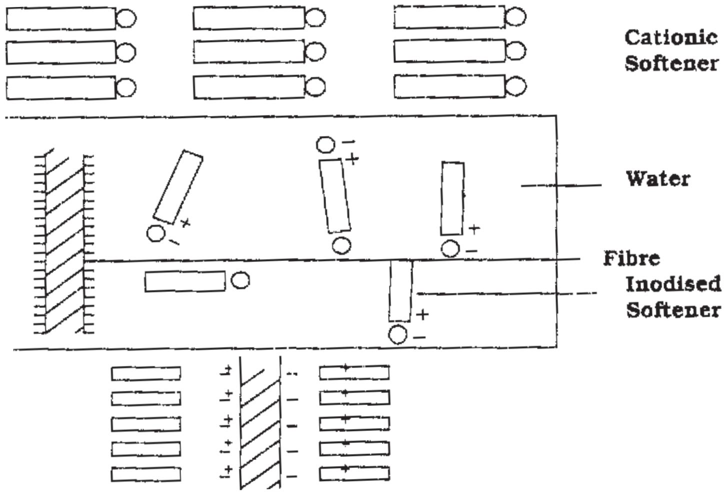


Fig. 8.3: Diagramatic representation of softening treatment

During the softening treatment the negative charge on the fibre surface attracts the positive tail of the cationic softener. This results in firm anchoring of the softener residue on the fibre substance, somewhat similar to sheathing the fibre with an oily film. This is responsible for obtaining a soft handle and pliable, well lubricated fibre surface.

ADVANTAGES

Substantivity of cationic softeners to textile fibres involves complete exhaustion from application baths as well as firm bonding of the softener to the fabrics. High degree of softening is one of the advantages of cationic softeners.

Cationics impart other useful textile properties. For example, they improve the fibre tear strength due to increased internal lubrication which reduces the effect of abrasion. Better sewability and reduced needle cutting are the effects of softener treatment. in these cases, lubrication allows highspeed needles to push the fibre aside without cutting the thread. For example, on a particular wool/ nylon shirt, at 4,500 stitches/min, only one or two yards could be sewn; when the softeners is applied to the fabric, a minimum of 52 yards can be sewn.

DISADVANTAGES

Lack of general compatibility with certain textile processing chemicals is the foremost disadvantage of cationics. Thus anionic detergents and soaps react with cationic softeners and form precipitates of an insoluble, unionised complex.

$$\begin{array}{c} \text{R-COO}^- \text{Na}^+ + [\text{R'N}(\text{CH}_3)_3]^+ \text{Cl}^- \\ \downarrow \\ \text{R-COO} [\text{R'N}(\text{CH}_3)_3] + \text{Na}^+ + \text{Cl}^- \end{array}$$

This precipitation reaction eliminates their use in anionic detergent processing solutions and on insufficiently washed fabrics pre-treated with anionic detergents. When the precipitation takes place, the softening property is reduced. This precipitation makes it necessary to incorporate cationic softeners as after-rinses for fabrics (after the complete removal of anionic detergents). There is a yellowing effect, particularly on ageing of bleached cotton fabrics. However, this may be minimised by a proper choice of the softener.

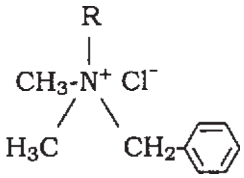
APPLICATION

There are two principal methods of application of cationic softeners – (1) exhaustion from dilute baths, and (2) padding from relatively concentrated solutions.

The long-bath (exhaustion) process is especially suitable because of the natural substantivity of the softeners and is usually adopted for knitted goods, not requiring resin treatment. with thermosetting resin (urea-formaldehyde resin), cationic lubrications/ softeners are a valuable adjunct to the treatment; since, they are not appreciably removed in the subsequent washing operation and serve to reduce needle cutting during garment manufacture and generally impart improved tear and abrasion resistance.

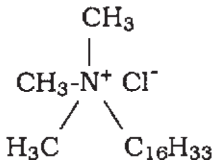
SOME PRODUCTS

Ammonyx BC of Onyx International is cation active alkyl dimethyl benzyl-ammonium chloride.

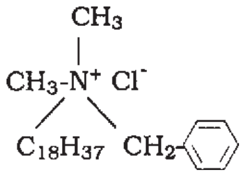


Where R is a mixture of C_{12-18}. This softens textile materials and also makes direct dyeings faster to washing.

Cirrasol OD (ICI) is a neutral pale, amber-coloured gel readily soluble in water and consists of cetyl trimethyl ammonium chloride–



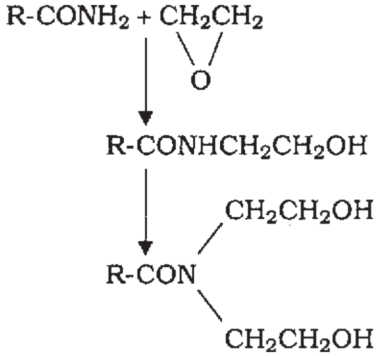
This is recommended for softening chlorinated wool for which is has a high substantivity.



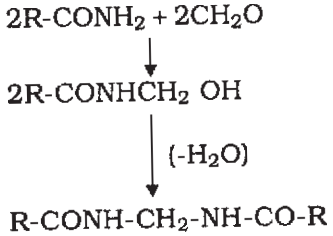
Triton of K of Rohm and Haas Co., is a 25% aqueous dispersion of stearyl dimethyl benzyl ammonium chloride and; is a powerful permanent softening agent for textile materials, for which it has substantivity. It is useful for softening textile materials treated with urea-formaldehyde and other resins for imparting crease resistance. It is not precipitated by aluminium salts or water-proofing agents containing such salts. High molecular weight amides like stearamide, $C_{17}H_{35}$ $CONH_2$ are high melting, wax-like materials. Chemically pure amides are water-insoluble and neutral. Commercial varieties contain some free fatty acids from they are made.

Stearamide is a soft paste. The colour of saturated amides is lighter than that of unsaturated amides. They are soluble in ketones, esters, alcohols, fats and fatty acids. Their solubility increases with temperature. In the saturated series, the longer the chain, the lower is the solubility. In the case of solvents, the higher the molecular weight of the solvent, the higher is the solubility of an amide.

Unsubstituted amides react with ethylene oxide to give mixtures of mono-and disubstituted amides, which are dispersible solids to soluble waxes.



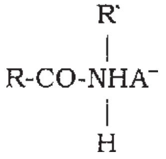
Reactions of amides with formaldehyde may give methylol stearamide or methylene bis-stearamide, depending on the conditions:



Methylol stearamide undergoes a number of reactions leading to the production of textile water-proofing agents, surface-active agents and high melting waxes. It serves as a raw material for cationic and nonionic softeners.

A mixture of acetic acid and stearamide (CH_3COOH + $C_{17}H_{35}CONH_2$) acts as a cation-active, slightly, acid water-soluble softening agent for cotton materials.

High molecular weight fatty amide compounds having basic properties may be used as such or after quaternising to make them water-soluble. Thus, the following compound is soluble in water:



$$\begin{array}{c} R' \\ | \\ R\text{-}CO\text{-}NHA^{-} \\ | \\ H \end{array}$$

where R is a fatty hydrocarbon residue and R’ is short alkyl chain and HA, the quaternising acid.

Sapamine KW (Ciba) is another quaternary ammonium compound, the trimethyl ammonium methyl sulphate of monostearyl m-phenylene diamine, obtained by heating stearic acid with m-amino dimethylaniline, followed by the addition of dimethyl sulphate to the product.

ZWITTERION

Alkyl amino acids, which exhibit zwitterion characteristics, are cationic in nature in solutions of low pH and anionic in nature in alkaline solutions. Their fatty alkyl amino acids have softening, lubricating and antistatic properties. Disodium N-tallow-Beta-imino dipropionate, $C_{18}N_{37}N(CH_2 – CH_2 - COONa)_2$, which is strongly adsorbed from acidic solutions also exhibits higher wetting, solubility and foaming properties. They are strongly substantive to cotton and wool at low pH values.

The effect of pH on the absorption of the long-chain acid on wool and cotton is shown in Fig. 8.4.

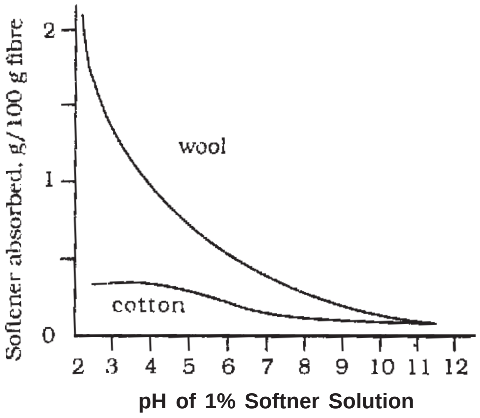
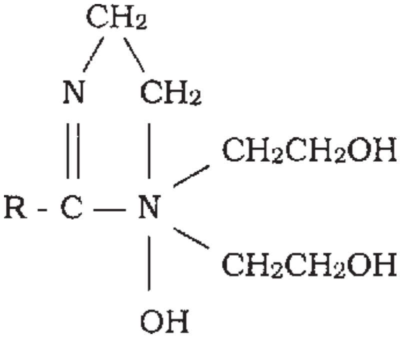


Fig. 8.4: Absorption of dodecylaminopropionic acid on wool & cotton with respect to pH variation

Marked adsorption effects at low pH values are seen especially on wool. As the pH increases, there is a progressive drop in softener absorption until it reaches a very small value at pH 9 and is undetectable at pH 10. The absorption on cotton (less polar fibre than wool) is not so pronounced. The flattening of the curve (over the pH range 2-5) shows that cotton is saturated with the cationic product at a much lower concentration that for wool.

Cyclic amphoteric imidazolinium compounds of the following structure have fabric softening properties.



It imparts a full smooth handle to all textiles made of animal, cellulosic or synthetic fibres. It becomes cationic in acidic solutions; and, hence absorption by the fibres is enhanced by the addition of acids to the treating solution. When used along with a thermosetting resin (urea-formaldehyde resin), an almost permanent softening effect is obtained.

An advantage claimed by the makers of the stearic acid substituted imidazole is its compatibility with soap and detergents. Thus is may be added to the soap or detergent in the washing machine; though, for best results, it has to be added to the last rinse. In contrast to the long-chain cationic softeners which build up on the fabric due to their higher substantivity and cause a hydrophobic effect on the fabrics, the amphoteric imidazole is said to be free of this defect. This is due to the fact that in the soap bath (pH 9) or in the last rinse (pH 8), the anionic nature of amphoteric compound pre-dominates and comparatively less amount of the softener is picked up by the fabric. This is further confirmed by the increased absorption which takes place when phosphoric acid is added to the rinse bath to lower the pH to 4.5.

DYEING ASSISTANTS

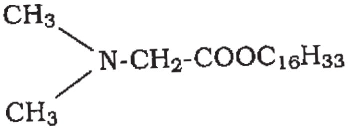
Cetyl trimethyl ammonium bromide is available as Lissolamine A and V (ICI) (powder and paste respectively) and is soluble in water. They are used in the presence of sodium hydrosulphite to assist stripping of azoic and vat dyeings by complexing the stripped dye and making it difficult for it to be reabsorbed during striping. Lissolamine A is for stripping azoic dyeing under alkaline conditions and Lissolamine V is for stripping vat dyes under alkaline conditions. They may also be used in the presence of oxidising agents (hydrogen peroxide or hypochlorite).

Solidegal K of Cassella Farbwerke is a brown viscous oily compound, freely miscible with water and consists of a polyamide derivative of polyethylene diamine further reacted with ethylene chloride to give a quaternary ammonium compound:

$-NH - (CH_2 - CH_2 - NH)_n - CH_2 - CH_2 - NH -$

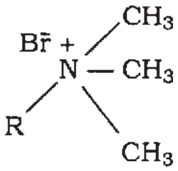
It is intended for adding to vat dyebaths to promote levelling. It does not form undue foaming and is resistant to hard water.

Du Pont Product BC is an alkaline clear brown liquid miscible with water. It is cation-active in acid solutions and anion-active in neutral and alkaline solutions. It is based on cetyl betaine:



This product has wetting, dye-levelling, dye-dispersing, softening and detergent properties over a wide range of pH. Its principal use is as a dye-levelling agent (in vat dyeing) and promoting rubbing fastness of azoic dyeings (this is added to the developing bath). When used along with sodium hydroxide and sodium hydrosulphite, it promotes partial stripping of faulty vat dyeing.

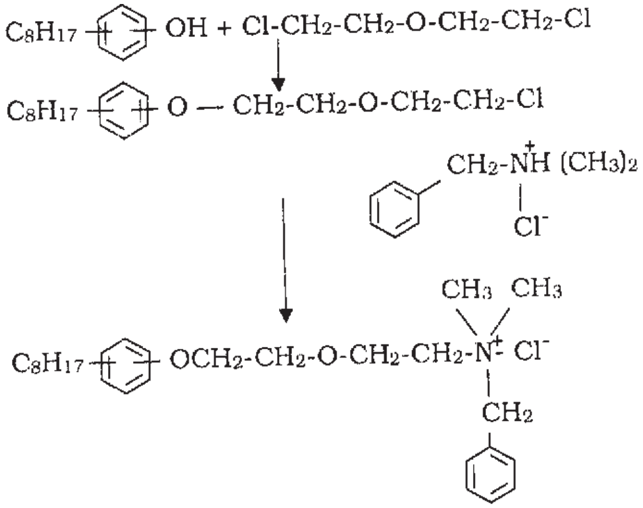
Du Pont Retarder LAN and LV is a slightly acid, light brown liquid containing higher alkyl trimethyl ammonium bromides:



where R is a higher fatty alkyl group. The product is freely miscible with water to give solutions which are stable to acids, alkalies and hard water, as commonly used in textile processing. Du Pont Retarder LAN assists in the stripping of azoic colours from cellulosic fibre substances when used in the presence of sodium hydrosulphite and sodium hydroxide. Du Pont Retarder LV is suitable for use in the stripping of vat dyes.

GERMICIDES

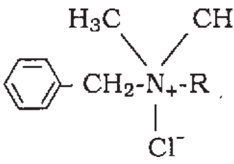
A product made by condensing p-tert. Octyl phenol with dichloro diethyl ether and then converting the resulting monochloro-compound into a quaternary ammonium compound by further reacting with benzyl dimethyl ammonium aniline chloride has been introduced by Rohm and Haas Co. under the denomination Hyamine 1622:



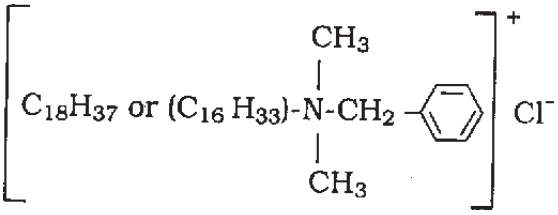
This is a colourless, non-irritating crystalline substance, which is stable on exposure to light and air. It has strong fungicidal properties, which are not adversely affected by wide temperature variations during prolonged storage. However, its effects are not fast to washing. This cation-active substance is substantive to many textile fibres and hence is readily absorbed form aqueous solutions by many fabrics to protect them from bacterial attack.

PRODUCT OF THE GENERAL FORMULA:

where R is an alkyl group with 6-18 carbon atoms have distinct affinity for wool. When these are mixed with nonionic detergents



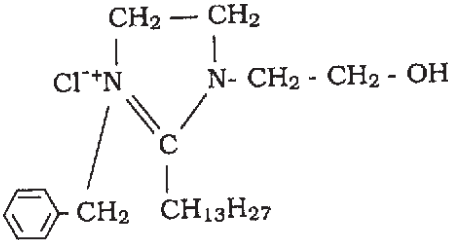
(nonylphenyl-ethylene oxide condensate) moth-proofing detergent compositions are obtained. For example, Leda stearyl dimethyl benzyl ammonium chloride of Leda Chemicals Ltd., is 25% aqueous solution of an 85/15 mixture of stearyl and cetyl dimethyl benzyl ammonium chloride of the type:



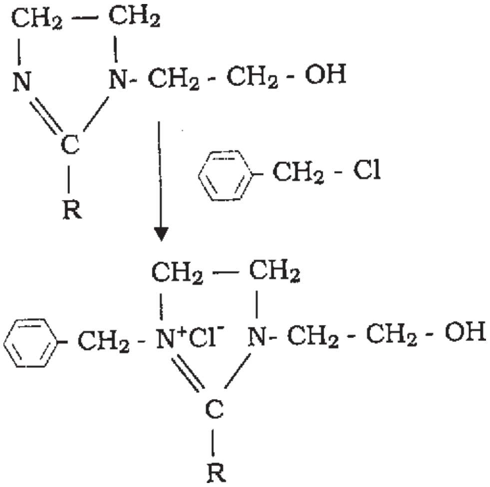
It has a characteristic odour and bitter taste. It is cation-active, soluble in water, alcohols, acetone, amyl and ethyl acetates and carbon tetrachloride. Aqueous solutions have excellent foaming and wetting properties as well as powerful germicidal properties and hence are useful in sizing and finishing. It has substantivity towards wool, viscose rayon. It has also direct dye-fixing property. In addition, it has detergent, softening and emulsifying properties.

Leda Chemicals Ltd. have introduced Leda Cetyl Dimethyl Benzyl Ammonium Chloride, which is a yellowish brown 25% aqueous solution of cetyl dimethyl benzyl ammonium chloride containing 4% of a mixture of the corresponding myristyl and stearyl derivatives. This is soluble in water and most of the organic solvents. A 5% solution does not turn turbid on standing. It has excellent foaming and fat emulsifying properties. It is a powerful germicide and fungicide capable of preventing mildew in textile materials and the growth of algae and moulds in water supplies. Aqueous solutions of the product are not stable to alkalies. It has substantivity towards textile fibres and improves the washing fastness of direct dyes, in addition to conferring softness on the dyeings. It is useful for pretreating textile materials printed with direct dyes to prevent colour bleeding in the subsequent washing of the prints. It is also useful in sizing and finishing because of its germicidal and fat-emulsifying properties.

Alrosept MBC-50 of Alrose Chemical Co. is another cationic germicide and is a 50% aqueous solution of tridecyl benzyl hydroxyethyl imidazolinium chloride.

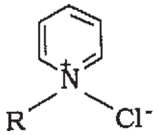


Such compounds are made by condensing a fatty acid with 2-amino ethyl ethanolamine and then quaternising with alkyl or aryl halide like benzyl chloride:



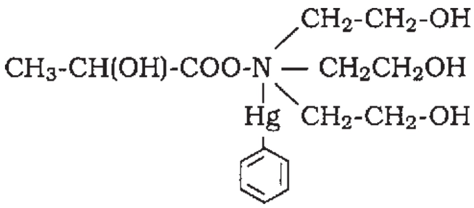
It is effective as a germicide over the pH range 3-10 and acts as a softener for textile materials.

Leda Lauryl Pyridinium Chloride of Leda Chemicals Ltd. is a cream coloured waxy solid. It consists of a mixture of alkyl pyridinium chlorides of the type: where R is largely lauryl ($C_{12}H_{25}$). This is also available as a mixture with R having octyl, lauryl, myristyl and cetyl groups. The product is soluble in water as well as in organic solvents. It has powerful bactericidal and germicidal properties

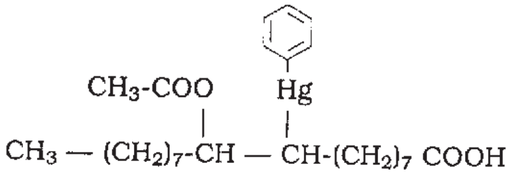


and is able to emulsify fats. In addition, it has substantivity to textile fibres on which it confers softening effect and it improves the washing fastness of direct dyes. It has antistatic properties as well and hence can be used in the processing of man-made fibres. It main use is as an additive to viscose rayon spinning solutions and to coagulation baths so that clogging or incrustation of the spinneretes with insoluble by-products is prevented.

Puratized Process Products of Gallowhur Chemical Corporation are a series of products for making various types of antiseptic, bacteriostatic and fungistatic compounds. Some of these are used as mildew proofing agents for textiles. The treated materials are non-toxic. Puratized N$_5$DS contains phenyl mercuric tri-ethanol ammonium lactate which is applied on a fabric form an aqueous emulsion of the product, (0.22-0.45% on the weight of the fabric). During the subsequent drying the product gets insolubulised as mercuric diphenyl in the fibre.



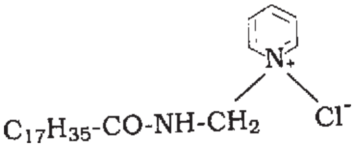
Puratized LN contains 9-phenyl- mercuric-10-acetoxy octadecanoic acid in an organic solvent-



When 0.1-0.25% of this product is deposited on fabrics, it provides full protection against bacteria and other microorganisms.

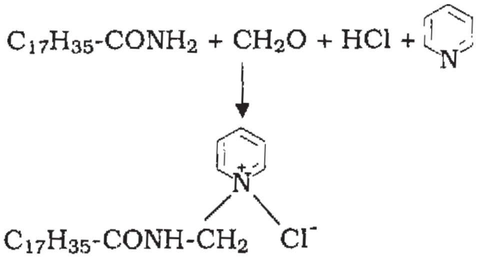
WATER-REPELLENT FINISHES

Some of the cation-active compounds are effective water-repellents. Thus Velan PF (ICI) is a cream coloured powder containing about 60% of stearamidomethyl pyridinium chloride, which partyl dissolves in water to give slightly acid, opalescent solution having fair stability in the cold, but is precipitated by alkalies (sodium hydroxide, soda ash, borax etc.):

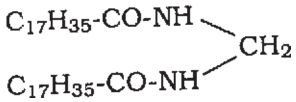


This can be used to produce soft or soft-water-repellent finishes on cotton, wool, viscose rayon etc. by padding them with its solution (1 g/litre for softness and 10 g/litre for water-repellency), drying at 105ºC and baking at 120ºC for 10 min., followed by washing and drying. (Soda ash should be added to the pad liquor to neutralise any free acid formed during baking and which might tender cellulose).

A similar compound is introduced by Du Pont Co. under the name Zelan AP. This is made by heating stearamide with formaldehyde in the presence of hydrogen chloride and pyridine.



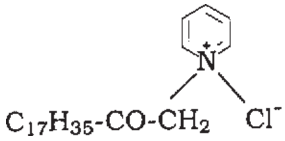
When applied to textile fibres by the pad-dry-cure process it imparts permanent water-repellency. During the curing stage the product undergoes chemical change to form a complex substance on the fabric (e.g. methylene bisstearamide):



This repels water and is very resistant to removal by laundering. Pyridine and pyridine compounds are formed simultaneously.

Norane R of Warwick Chemicals Co. is a water-soluble pyridinium salt stated to be stearyl methyl pyridinium chloride:

This imparts permanent water repellency to textiles when applied by pad-bake technique.



CATIONIC RETARDERS IN ACRYLIC DYEING

Dying of acrylic fibres with cationic dyes (Maxilon, Astrazon, Basacryl, Sevron, Sandocryl, Remacryl, Sumicryl etc.) may be divided into three steps:

(1) The coloured cations of the ionised dye are adsorbed on the acrylic fibre surface, the rate of adsorption depending on the concentration of the external dyebath.

(2) The adsorbed dye cations diffuse in the interior of the fibre, the rate of diffusion being determined by the temperature.

(3) The cations are attracted and retained by the anionic sites in the fibre substances by strong electrostatic attraction forces, thereby imparting very good wash-fastness to the resulting dyeing.

Since the anionic sites are distributed in the entire fibre material, the initially adsorbed cations on the fibre surface are also held there by strong electrostatic bonds, which resist the diffusion of the bound dye cations into the interior of the firbe. Any significant diffusion is possible only by the rupture of these bonds which may be effected by a rise in temperature. Even then all the bonds may not get broken and hence if uneven dyeing results initially, it is very difficult to correct the faulty dyeing. In any case, the diffusion is the slowest of the three processors (absorption, diffusion and electrostatic binding) and this process governs the overall rate of dyeing.

There are two ways of obtaining perfectly even distribution of the dyestuff in a fibre:

(1) The migration properties of the dyestuff can be utilised to get the desired effect, provided the dyestuff is not immediately fixed during adsorption of the dye on the firbe surface, itself, and the fibre sites having affinity for the dyestuffs are distributed evenly in the fibre. In this case any initial poor migration and unevenness can be corrected

subsequently by inducing the dyestuff molecules to migrate. However, in the case of dyeing of cationic dyes on acrylic fibres, the conditions are not conducive at 100ºC or below, since the dye-fibre bond (electrostatic bond) is very stable from the moment it is formed.

(2) The build-up of the dyestuff during the first phase of dying (adsorption) can be controlled when the migration subsequent to adsorption is not possible. Dyeing of acrylic fibres with cationic dyes falls in this category.

The regulation of the dyeing process can be done by adding either a cationic auxiliary or an anionic auxiliary to the dye-bath. When the former is used, its cations compete with the dye cations for the anionic sites presents in the fibre, thereby reducing the effective dye concentration in the dyebath. At a later stage of dyeing, especially at a higher temperature, some of the bound cations of the added auxiliary get separated form the fibre, thereby making those sites available for the occupation of the dye cations. However, some cations permanently block the fibre sites and the build-up of the shade may create a problem. The cationic product (auxiliary) acts as a retarding agent to produce level dyeing results. Commercial cationic retarders include Tinegal CRA, Basacryl Salt G, Levegal PAN, Lyogen BPN/AN, DU Pont Retarder LAN etc.

Anionic auxiliaries may also be used as the retarding agents. The anions of the auxiliaries form electrically neutral complexes with the dye cations. These complexes have to be formed in a finely dispersed form (in the presence of a non-ionic dispersing agent). During dyeing, the complex is taken up by the fibre on its surface from where if diffuses into the fibre. Since there is no electrical charge, there is no affinity for the fibre. As the temperature rises, the complexes break into the component ions, the dye cation gets fixed at the fibre anionic sites and the anions of the auxiliary leave the fibre substance.

An ideal retarder for acrylic dyeing should have the following properties:

(1) it should provide level uniform dyeing,

(2) it should allow dyes of different diffusion characters istics to be used in combination shades,

(3) it should allow full saturation of dyeing,

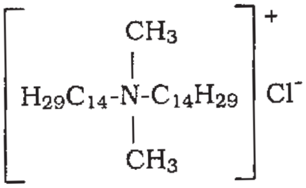
(4) it should allow full bulking of bi-component fibres,

(5) it should be usable with softeners, and

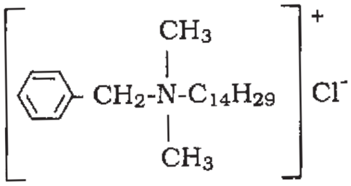
(6) it should slow the overall exhaust rate sufficiently to overcome the thermal and mechanical inconsistency of the dyeing machine, etc.

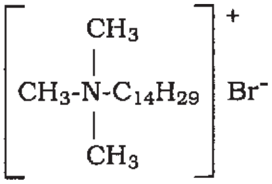
An exhaustive study of the use of various cationic retarders in the dyeing of acrylic fibres with a anionic dye (Sevron Green B – CI Basic Green 3) has been reported by Cohen and Endler. The retarders studied included long-chain amine hydrochlorides (C_{10}-C_{16}), as well as long chain quaternary ammonium compounds like alkyl trimethyl ammonium chloride, where the alkyl chain is lauryl, cetyl, stearyl and those derived from tallow and coconut oil. They concluded that any long-chain amino compound is likely to have a retarding effect in the dyeing of acrylic fibres with cationic dyes. Solubility at higher pH values and resistance to discolouration are some factors which determine the suitability of the retarders. Further, they established on optimum of C_{12} chain length (lauryl)for alkyl trimethyl ammonium chloride to get steady dyeing rates up to high saturation value. Cetyl and stearyl compounds show an induction period of very slow dyeing rate followed by high rate of exhaustion after the dyeing begins. Lauryl (90%) product shows a steady retarding action and a much lower dyeing rate than the other compounds. The cocoamine quarternary compound with an average chain length of C_{12}, but actually containing about 50% lauryl, gives a lower dyeing rate than cetyl and stearyl compounds, but without the induction period. Despite the average chain length of C_{12}, the cocoamine quaternary compound is much less effective than the 90% C_{12} compound. They concluded that in practice C_{16} or C_{18} might be preferable, since the induction period in the dyeing prevents uneven strike of the dye and a high level exhaustion is reached more quickly than with C_{12} compound. If higher concentrations of retarders are used the retarding is more efficient; but this is accompanied by a loss of colour value, more so with acetates than with chlorides.

In one of the most information research papers, the Metropolitan Section of the American Association of Textile Chemists and Colorists with a team of research workers from a group of American companies presented a paper on the compatibility of cationic retarders used in acrylic dyeing. They selected five commercial cationic retarders and elucidated their structures by proton nuclear magnetic resonance (NMR) studies and by infrared spectroscopy. The structures of these retarders are as follows:

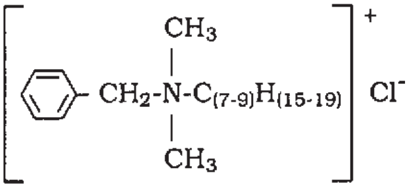


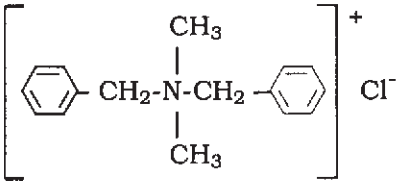
$$\left[\begin{array}{c} CH_3 \\ | \\ H_{29}C_{14}\text{-}N\text{-}C_{14}H_{29} \\ | \\ CH_3 \end{array}\right]^+ Cl^-$$





$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3\text{-}N\text{-}C_{14}H_{29} \\ | \\ CH_3 \end{array}\right]^+ Br^-$$





A close examination of the above structures reveals that Leucotrope O (benzyl phenyl dimethyl ammonium chloride), which is used in discharge printing of vat dyes, has an almost identical structure as the last retarder mentioned above. Thus Leucotrope O should also work as a good cationic retarder in acrylic dyeing.

Quaternary ammonium compounds of the type RN $(CH_3)_3 - Cl$, where R is a long chain alkyl group can be made by two routes:

(a) Exhaustive alkylation of a primary or a secondary fatty amine, as in the case of cetylamine:

$$C_{16}H_{33}NH_2 + 2CH_3Cl \longrightarrow C_{16}H_{33}N(CH_3)_2 + 2HCl$$

$$C_{16}H_{33}N(CH_3)_2 + CH_3Cl \longrightarrow C_{16}H_{33}N(CH_3)_3Cl$$

In this case hydrogen chloride is formed as a byproduct and hence the reaction does not go to completion in an acidic medium. In order to counteract this a scavenger for the acid should be used. Industrially sodium carbonate or potassium carbonate is used for the purpose in a polar solvent like methanol or water at 60º-95ºC under slight pressure.

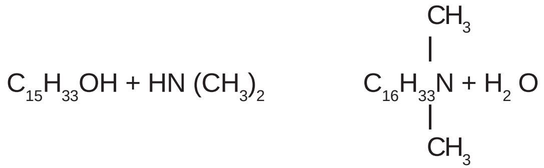
(b) Alkylation of low molecular weight tertiary amine with an alkyl chloride:

$$C_{16}H_{33}Cl + N\,(CH_3)_3 \longrightarrow C_{16}\,H_{33}N(CH_3)_3Cl$$

The alkyl chloride may be made by converting a fatty alcohol by reaction with hydrogen chloride in the presence of zinc chloride catalyst. Alternatively other chlorinating agents like thionyl chloride, phosphorus trichloride or pentachloride may be used. The resulting alkyl halide may be reacted with dimethylamine in in the presence of an alkali at 140ºC for 10 hours.

$$\begin{array}{l} C_{16}H_{33}Cl + NH(CH_3)_2 + NaOH \\ \qquad\qquad\quad \downarrow \\ C_{16}H_{33}N(CH_3)_2 + NaCl + H_2O \end{array}$$

In a modification, the fatty alcohol may be directly reacted with dimethylamine in a reducing atmosphere at 250º-300ºC under high pressure (3000-4000 psi) in the presence of copper chromite:



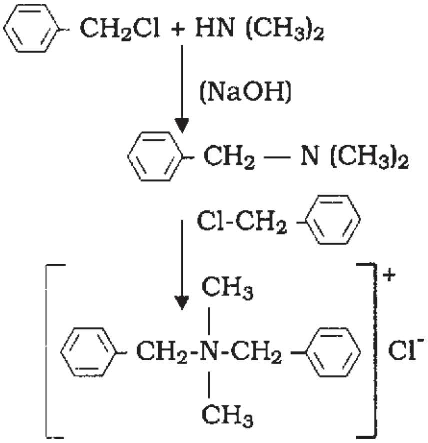
$$C_{15}H_{33}OH + HN\,(CH_3)_2 \qquad C_{16}H_{33}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}} + H_2\,O$$

The tertiary amine thus formed further be quaternised using methyl chloride or dimethyl sulphate:

$$C_{16}H_{33}N\ (CH_3)_2 + CH_3Cl$$
$$\downarrow$$
$$C_{16}H_{33}\overset{+}{N}\ (CH_3)_3Cl^-$$

$$C_{16}H_{33}N\ (CH_3)_2 + (CH_3)_2SO_4$$
$$\downarrow$$
$$C_{16}H_{33}\overset{+}{N}\ (CH_3)_3\ \overset{-}{SO_4CH_3}$$

Dibenzyl dimethyl ammonium chloride can be made by condensing dimethylamine with benzyl chloride, followed by quaternisation with benzyl chloride:



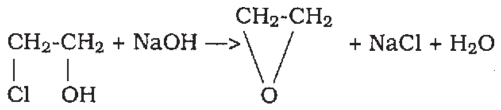
9

Nonionic Surfactants

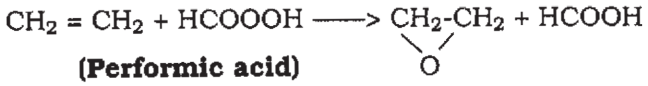
It has already been pointed out that in order to impart surface activity to a compound, it must have tow portions having balanced water solubility and insolubility (the right type of hydrophilic-lyophilic balance). In the earlier cases of the anionic type, water solubility is imparted by ionisable groups like carboxyl, sulphonate, sulphate, phosphate ester etc. and the hydrophobic part was provided by aliphatic and/or aromatic residues. The sodium salts of these compounds after ionisation produce the required water solubility. Thus their water solubility is based on the ionisation of the sodium of salts. However, when their solutions are treted with solutions of salts of other metals like calcium, copper, aluminium etc., insoluble compounds of these metals are formed with greater or lesser ease and in such a case, the solutions lose their detergent and other properties; in addition, the precipitates get deposited on the fabric or machine parts.

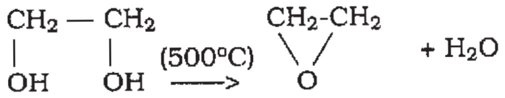
In another approach, solubility due to ionisation is replaced by nonionic compounds having “centres of hydration”. In this field, ethylene oxide and/or propylene oxide adducts with suitable compounds containing active hydrogen occupy a prominent place.

Ethylene oxide is formed when ethylene chlorohydrin is distilled with a solution of sodium hydroxide in water or when ethylene is oxidised by performic acid. In another method ethylene glycol is heated at 500ºC when it gets dehydrated and forms ethylene oxide. The reactions taking place are shown below:



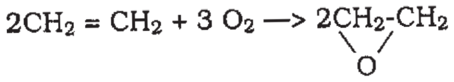
(Ethylene chlorohydrin) **(ethylene oxide)**





(ethylene glycol)

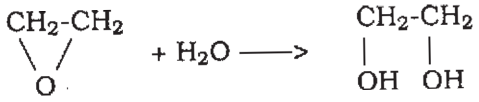
Ethylene oxide is manufactured by passing a mixture of ethylene and air (1:10) under pressure over silver catalyst at 300ºC. A part of ethylene is simultaneously oxidised to water and carbon dioxide. The contribution of this reaction increase with increasing temperature.



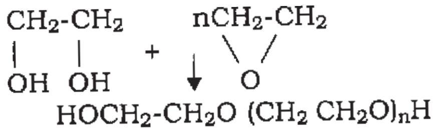
$$CH_2 = CH_2 + 3\ O_2 \longrightarrow 2CO_2 + 2\ H_2O$$

Ethylene oxide is an inflammable and explosive gas which condenses to a liquid with a pleasant smell and boils at 10.7ºC at atmospheric pressure.

It reacts with water to form ethylene glycol

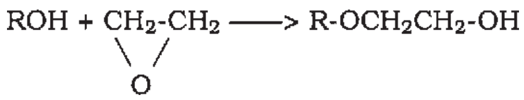


Further molecules of ethylene oxide can then be added to ethylene glycol to form polyethylene glycols (PEG).



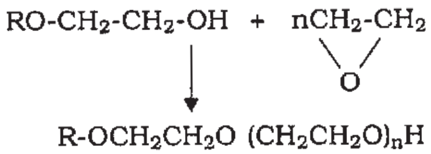
(polyethylene glycol)

Ethylene oxide reacts with an alcohol to form an ether.



$$ROH + \underset{\diagdown\ O\ \diagup}{CH_2\text{-}CH_2} \longrightarrow R\text{-}OCH_2CH_2\text{-}OH$$

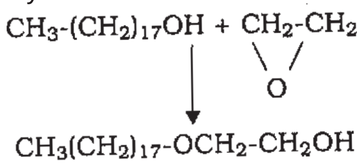
Any number of ethylene oxide molecules can then be added to the above ether to give polyoxyethylene compound of the ether. This is also known as alcohol-ethylene oxide adduct:



$$RO\text{-}CH_2\text{-}CH_2\text{-}OH + n\underset{\diagdown\ O\ \diagup}{CH_2\text{-}CH_2} \longrightarrow R\text{-}OCH_2CH_2O\ (CH_2CH_2O)_nH$$

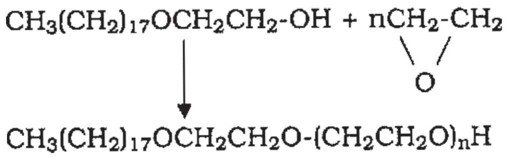
This reaction is called polyoxyethylation and the product is called alcohol-ethylene oxide condensate.

Fatty alcohols like lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, etc. have long chain hydrophobic pats and their hydrophilic group (hydroxy group) is not powerful enough to impart the balanced water solubility-water insolubility. When one molecule of ethylene oxide is added to a fatty alcohol, say stearyl alcohol, the oxygen atoms (now there are two) provide weak hydrophilicity:



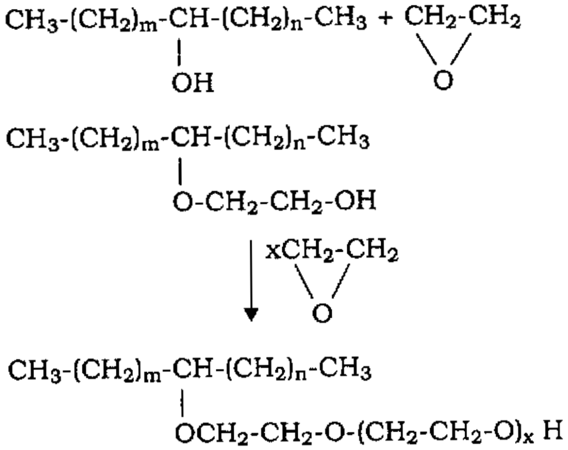
$$CH_3\text{-}(CH_2)_{17}OH + \underset{\diagdown\ O\ \diagup}{CH_2\text{-}CH_2} \longrightarrow CH_3(CH_2)_{17}\text{-}OCH_2\text{-}CH_2OH$$

However, the product is not soluble in water. The reaction with ethylene oxide has to be continued and various ethylene oxide molecules have to be added:



$$CH_3(CH_2)_{17}OCH_2CH_2\text{-}OH + n\underset{\diagdown\ O\ \diagup}{CH_2\text{-}CH_2} \longrightarrow CH_3(CH_2)_{17}OCH_2CH_2O\text{-}(CH_2CH_2O)_nH$$

This product has a number of ether linkages, which are basically strong and are not broken by dilute acid or alkalies (or even acids and alkalies of moderate concentrations). The oxygen atoms present in the chain can get hydrated (hydrogen bonded with water molecules) due to their hydrophilicity and hence can dissolve in water. Optimum HLB is obtained with 10-15 molecules of ethylene oxide is reacted with one mole of fatty alcohol. In practice various alcohols are condensed with upto 50 moles of ethylene oxide. When secondary alcohols are used (prepared by the oxidation of n-paraffins) they are first condensed with one mole of ethylene oxide in the presence of an acid catalyst like boron tri-fluoride (BF_3). The catalyst and the unreacted alcohol are then removed from the reaction mixture and further ethoxylation is carried out with more moles of ethylene oxide.



Nonionic detergents of oleyl alcohol-ethylene oxide condensates (15 moles of ethylene oxide) are very effective in scouring wool and cotton. Their lack of substantivity for wool is in advantage (ionic detergents are firmly held by the fibre) in that they can be completely washed off from the fibre after scouring. They are poor foam formers when compared to ionic detergents of similar effectiveness.

The number of ethylene oxide molecules needed to impart water solubility depends on the molecular weight and the structure of the fatty alcohol. Thus when hexanol is ethoxylated fewer moles of ethylene oxide are enough to effect solubilisation than in the case of stearyl alcohol. Also with a given alcohol the solubility of the final product varies with the number of ethylene oxides moles reacted.

A fatty alcohol-ethylene oxide condensate (Cirrasol SF) is a nonionic product which confers scroop effect on textile fibres, especially of cellulosic type. It is dispersible in water but the presence of electrolytes depresses the degree of dispersion. It is also an antistatic agent.

A yellowish liquid containing a condensation product of lauryl or stearyl alcohol and several moles of ethylene oxide (Leucaphor O of Doittau-Produits Chimiques) has strong wetting, dispersing and emulsifying properties and readily dissolves in water to give solutions stable to moderate concentration of acids and alkalies, hard water etc. When used in small amounts, it can be used in stripping vat dyes.

Another fatty alcohol-ethylene oxide condensate (Dispersol VL of ICI) is a pale yellow neutral liquid which is freely miscible with water an is stable to dilute acids, alkalies and electrolytes. This is most useful an addition to vat dyebaths as a levelling agent. It retards the dyeing of many vat dyes on cellulosic fibre materials. In can also be used as a mild stripping agent when it is only necessary to reduce the depth of shade.

Dispersal (Royce Chemical Co.) is a neutral colourless viscous liquid containing fatty alcohol-ethylene oxide condensate and is miscible with water. this is used as a retarding or levelling agent in dyeing of cellulosic fibres with vat dyes and also a stripping agent for faultily dyed vat dyes. It is also used in the developing bath in azoic dyeing.

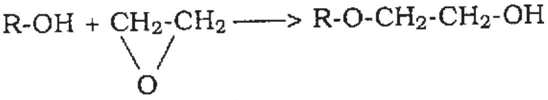
Azopol A (ICI) is a neutral yellow transparent liquid containing a nonionic product obtained by condensing several moles of ethylene oxide with fatty alcohol. It is miscible with water to give solutions which are stable to acids, alkalies, electrolytes and hard water. it is added to developing baths containing diazotised bases while applying azoic dyes to improves the stability of the developing bath and rubbing fastness of the final dyeing.

Avcoluble 100 and 104 (Atlas Powder Co.) are light tan coloured waxy solids containing fatty alcohol-ethylene oxide condensates, which are applicable as lubricating and antistatic agents for synthetic fibres. They are self-emulsifying and give stable emulsions in warm water. Both are insoluble in water and slightly soluble in most organic solvents. These are recommended for application to the fibres before carding and spinning (especially if they are dyed in the loose form).

Berol EGA-07 Conc. (Aktiebolaget Berol-Produketer) is a nonionic semi-solid, which dissolves readily in water to give neutral to slightly alkaline solutions. Its main use is as a levelling agent in vat and azoic dyeing. It is also useful for addition to the developing bath in azoic dyeing to stabilise the diazotised bath and to improve the rubbing fastness of the final dyeings. It is reasonably stable to acids and alkalies and to many metal salts including oxidising agents. If is not an effective wetting agent at low temperatures but in warm to hot solutions it has wetting and detergent properties. Berol EMU-60 of the same company is a neutral or slightly alkaline light amber coloured paste, which freely dissolves in water to give clear solutions, stable to hard water. It is an ethylene oxide condesnate of a fatty alcohol. It has excellent wetting, dispersing and fat-emulsifying properties. One of its uses is in producing viscose rayon, for which it is added to the alkali cellulose during shredding or in the xanthaion mixture and to the viscose spinning solution to improve its filterability. Another product, Berol EMU-75, is a mixture of mineral oil and fatty alcohol-ethylene oxide condensate. Its main use is an emulsifying agent for mineral oils for use in lubricating textile fibres to prepare them for spinning. A good emulsion is produced by mixing one part of the product with three parts of mineral oil and then diluting with water. Yarns containing these emulsions can be scoured free from the oil easily since the emulsifying agent assists in its remove. Berol TVM-09 Conc. is also a fatty alcohol-ethylene oxide condensate, which is a yellowish brown, neutral to slightly alkaline liquid and is readily miscible with water. It has good wetting and detergent properties. It has little affinity for textile fibres and hence may be readily washed out of them. Common salt or Glauber's salts (5-8/ litre) improves the scouring action of the product. It is recommended as a detergent and a wetting agent for use in scouring cotton and woollen materials and in soaping of vat and azoic dyeings and prints. Berol VMA-09 is an yellowish brown oil, easily miscible with cold or hot water to give neutral to slightly alkaline solutions. It is also a fatty alcohol-ethylene oxide condensate. It is recommended for use as wetting agents in warp sizing, in wool carbonising, kier boiling, bleaching, wool crabbing and dyeing. It also assists in producing level dyeings with vat dyes.

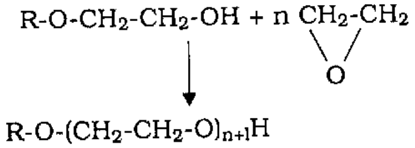
Emullant CO 10, CO 18 and CO 25 (of Union Chemique Belge) are anionic yellow to brown pastes, which are miscible with water to give solutions stable to dilute acids and alkalies and to hard water. They are made by condensing fatty alcohols with several moles of ethylene oxide. Emullant CO 10 is an emulsifying agent and has good mineral oil dispersing power. The other two products are wetting agents and dye dispersing agents and retarding agents in dyeing direct, acid and vat dyes. They have good olein-emulsifying properties as well. Emullant CO 25 is also useful as an additive to the kier liquor used in scouring cotton materials. Emullant R 40 of the same company is a brownish liquid, miscible with water and is based on condensation product of ethylene oxide-vegetable oil (having a hydroxy group).

Ethylene oxide can be condensed with an organic compound containing an active hydrogen. Thus it may be reacted with a fatty alcohol to give a primary reaction product:



$$R\text{-}OH + \underset{\diagdown\;/\atop O}{CH_2\text{-}CH_2} \longrightarrow R\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH$$

The product formed contains a newly formed active hydrogen that can react with another mole of ethylene oxide. This process may be repeated to build long hydrophilic polyoxyethylene chains (as many as 100 oxyethylene units has been added). The principal nonionics contain 6-20 oxyethylene units.



$$R\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH + n\,\underset{\diagdown\;/\atop O}{CH_2\text{-}CH_2} \longrightarrow R\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_{n+1}H$$

However, these are not single compounds but are very complex mixtures. The number of ethylene oxide moles reacted and shown in the formula of a particular nonionic surfactant is the average number.

The formation of nonionic surfactants involves the formation of long polyoxyethylene chains by the gradual and stepwise addition of ethylene oxide. The hydrophobic compound (fatty alcohol, fatty acid, amide, alkyl, phenol etc.) and the catalyst are heated to the desired reaction temperature and ethylene oxide gas bubbled gradually, no faster than it reacts until the required ethylene oxide-hydrophobic ratio is obtained. The condensation reaction is a highly exothermic one (the heat liberated being 20 kcal/mole reacted). Hence adequate cooling has to be provided and large amounts of unreacted ethylene oxide should not be allowed to accumulate in the reactor.

The temperature of the reaction depends on the reaction variables and on the nature of the starting material. Initially the reaction is very slow, unless higher temperatures are maintained. In the presence of alkaline catalysts, the temperature range is 120º-180ºC. In the case of acidic catalysts like boron trifluoride, the condensation reaction may be carried out at 50º-75ºC.

The use of catalyst is necessary since the reaction rate is too slow even at 200ºC. Most of the reactions are carried out in the presence of alkaline catalysts like sodium hydroxide, sodium acetate, potassium hydroxide, potassium carbonate, sodium carbonate, sodium methoxide, etc. Usually 0.1-1% (on the weight of the starting material) of the catalyst is sufficient.

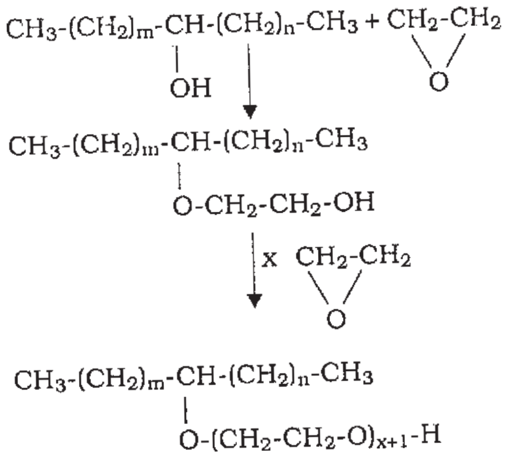
Acidic catalysts like boron trifluoride, acid clays etc. are less frequently used than alkaline catalysts, but lower temperature used. The products formed under acid catalysts are lighter coloured. However, they promote undesirable side products. In fact 10-20% of ethylene oxide introduced may be converted into by-products such as dioxane, dioxolenes etc. Hence acidic catalysts are rarely used.

The condensation reactions are carried out under pressure to maintain a reasonably high ethylene oxide concentration in the hot reaction mixture and to shorten the reaction time. Usually 20-50 psig pressure is selected.

The raw materials (hydrophobes) used include lauryl, cetyl, oleyl, tallow, hydro obietyl and other alcohols. Fatty alcohol-ethylene oxide condensates have excellent stability to acids (the other bond is very stable).

In a laboratory method of the preparation of fatty alcohol-ethylene oxide condensate, 00 g fatty alcohol and 4.5 g potassium hydroxide is taken in a weighed 3-necked flask with gas disperse inlet, thermometer and out-tube. Potassium carbonate has been found to be unsuitable as a catalyst. The mixture is heated in an atmosphere of nitrogen to 160ºC and ethylene oxide gas is passed at such a rate that the temperature lies between 160ºC and 190ºC. The flask and its contents are weighed at intervals until the desired amount of ethylene oxide is added on to the alcohol.

When secondary alcohol (prepared by the oxidation of n-paraffins) are used, they are first condensed with one mole of ethylene oxide in the presence of an acidic catalyst. The catalysts and the unreacted alcohol are then removed from the reaction mixture and further ethoxylation is carried out with more moles of ethylene oxide.



In one method, 800 kg oley alcohol is charged in a glasslined kettle of 3000 litres capacity and 80 kg (0.01%) of powder caustic soda is added. The contents are heated to 160°-180°C and the pressure in the kettle is reduced to 10 mm. Ethylene oxide from a storage tank (2000 kg capacity) is allowed to flow using a nitrogen pressure of 3 atmospheres. The reaction between the alcohol and ethylene oxide is highly exothermic and goes to completion in 12-14 hours. The resulting product is a soft, waxy paste which gives clear solutions in cold water, but becomes cloudy (turbid) at 40°C. This contains about 15 moles of ethylene oxide per mole of oleyl alcohol. They are marketed as 20% or 30% aqueous solutions. These are good detergents for washing wool and scouring cotton. Their lack of affinity for wool is an advantage (ionic detergents are firmly held by the fibre), in that they can be completely washed off from the fibre after scouring. They are poor foam formers compared to ionic detergents of similar effectiveness.

Cetyl alcohol-ethylene oxide condensate (mole ratio, 1:20) is a very useful nonionic surfactant. This is available as 100% active content and 30% active content products.

VAT LEVELLING AGENTS

In class (Aq1) of vat dyes, in their soluble leuco form, have different affinity for cellulosic fibres. These dye the fibres at a high rate and as such the production of even shades becomes difficult, especially when pale shades are dyed. In such cases the dyeing conditions are altered to decrease the rate of dyeing to get even dyeing results. In one of the methods, the rate of dyeing is controlled by incorporating certain auxiliaries or dyeing assistants, which either compete with the dye for the fibre sites, thereby reducing the effective rate of dyeing, or combine with the dye to form a loose complex, which then cannot be adsorbed on the fibre surface. However, this complex has to be broken subsequently, generally by raising the temperature so that the dye is again made available, but gradually, for the dyeing process. Since these dyeing assistants slow down the rate of dyeing and help producing level dyeing, they are called retarding agents or levelling agents. Fatty alcohol-ethylene oxides condensate (mole ratio 1:20) may be used for the purpose.

These products (vat levelling agents) are available in the form of a clear pale yellow solution. They act by forming a complex with the soluble leuco vat dyes in the dyebath. Hence, quantities in excess of the recommended quantities should not be used, otherwise they may lead to greater restraining action and hence to permanent loss of colour value.

The degree of retardation effected by the levelling agent varies form dye to dye and a concentration of the levelling agent that is suitable for one dye may not be so for another. The quantity of the levelling agent should not exceed about 0.5 g/l of the dye liquor and should be added immediately before the material to be dyed is entered. The dye liquor should be as dilute as possible before adding the levelling agent, which should not be added to the stock vat (concentrated solution of the vatted dye). The levelling agent should also be diluted 3-4 times its volume before adding to the dyebath. If too much retarding has taken place and dyebath insufficiently exhausted, Turkey Red Oil may be added to neutralise the effect of the levelling agent to some extent. This neutralising agent also should be added in the form of a dilute solution.

An addition of 0.2-0.5 g/l levelling agent may be made while dyeing in a jigger or a winch. With heavy canvas and other goods which are difficult to dye because of the close weave, the amount of the levelling agent may be increased to 1-1.5 g/l.

AZOIC FASTNESS IMPROVERS

The production of azoic colours on cellulosic fibre materials involves the application of an alkaline solution of a naphthol, followed by developing (coupling) in a separate bath containing a diazotised base. During the first stage, the fibre material holds a part of the naphthol substantively (and firmly) and another, dissolved in the solution is picked up and retained by the material (this is not held firmly). When this wet material enters the developing bath, some amount of the naphthol solution gets drained into the external bath from the material and forms the azoic pigment in the bath. The substantively held naphthol forms the azoic pigment, which is then firmly held in the fibre material. In addition, the loosely held naphthol also forms the azoic pigment, which gets deposited on the fibre material. The azoic pigment formed in the external bath and on the surface of the fibre creates rubbing fastness problems in the final dyeing. The loosely held pigments are generally removed from the fibre subsequently by a soaping treatment at the boil. However, if a dispersing agent, is added to the developing bath, the naphthol which has bled from the fibre material into the developing bath forms the azoic pigment in the form of an extremely fine dispersion, which is retained in the developing bath itself and is prevented from getting deposited on the fibre substance. Thus the rubbing fastness of the final dyeing is improved. Further, the dispersing agent also stabilises the diazotised base (it inhibits the decomposition of the diazotised base coupling with the naphthols), resulting in a better utilisation of the base.

Fatty alcohol-ethylene oxide condensates (especially cetyl alcohol-ethylene oxide, 1:20 mole ratio) are suitable for the purpose. These are available in the form of a pale yellow liquid, active content, (about 30%), which is readily miscible with water. Being nonionic in nature, they are stable to hard water, dilute acids and alkalies and to inorganic salts like aluminium sulphate. They are compatible with anionic and cationic products.

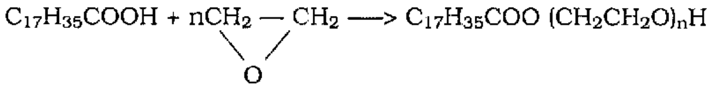
They are recommended in all types of azoic dyeing, but the improvement in the rubbing fastness is the most marked in the case of cops, cheeses and warp beams and loose cotton dyed in package dyeing machines, where bigger particles of azoic pigments are formed and get precipitated in the package itself if the recommended auxiliary is not added to the developing solution.

As far as the stability of the developing baths are concerned, such products (diazo stabilisers) are of particular value such standing baths are used to dye a large number of lots by replenishing the bath each time a new lot is dyed, as in tub liquoring.

The nonionic surfactants may be used to the extent of 2 g/l in the developing bath. Their azoic pigment dispersing ability may be advantageously used in the soaping baths by adding about 0.5 g/l of the product. They may also be added to the printing paste (0.2%) containing diazotised bases or Fast salts intended for printing on naphtholated grounds.

FATTY ACID-ETHYLENE OXIDE CONDENSATES

These are another series of nonionic surfactants. These are either by reacting a number of ethylene oxide molecules with one molecule of a fatty acid or by reacting a polyethylene glycol with the fatty acid:



$$C_{17}H_{35}COOH + nCH_2 - CH_2 \longrightarrow C_{17}H_{35}COO\ (CH_2CH_2O)_nH$$

$$C_{17}H_{35}COOH + HO(CH_2\text{-}CH_2\text{-}O)_nH \longrightarrow C_{17}H_{35}COO(CH_2CH_2O)_nH$$

$$\begin{array}{c} C_{17}H_{35}COO\ (CH_2CH_2O)_nH + C_{17}H_{35}COOH \\ \downarrow \\ C_{17}H_{35}COO\ (CH_2CH_2O)_n\ OC\text{-}C_{17}H_{35} \end{array}$$

These nonionic condensates contain a number of oxyethylene units (ether links) as well as one or two ester groups. Because of the presence of ester groups, they are subject to hydrolysis under strong acid or alkaline conditions. In this respect they re inferior to fatty alcohol-ethylene oxide condensates or alkyl phenol-ethylene oxide condensates. However, like the latter (being non-ionic in nature) they are usually unaffected by electrolytes (hard water slats),dilute acids and alkalies of moderate concentration.

The condensates have good wetting, softening detergent, fat-emulsifying properties. They may be added to vegetable and mineral oils (lubricants), which are applied to textile fibres (cotton, wool, etc.) to improve their spinning performance by helping the lubricant to spread over the yarn. Their presence in these oils makes their subsequent removal (after making the yarn and cloth) easy. These compositions act as self-emulsifying ones in these scouring baths. When present on finished fabrics, they do not discolour the fabrics, nor do they develop rancidity (except those made from oleic acid or other unsaturated fatty acids). They are also stable towards oxidising agents like potassium dichromate, sodium perborate/acetic acid, hydrogen peroxide, sodium hypochlorite etc. and hence may be added to bleach baths. They have good lime soap dispersing power. Their softening power is used to soften cellulosic fibre fabrics, like cotton, viscose rayon etc. The good dye dispersing ability of these nonionic surfactants makes them suitable for use in acetate rayon dyeing as well as in dyeing naphthols and bases, where they stabilise the diazotised bases. The following products are of importance in this respect:

(1) Stearic acid-ethylene oxide condensate.
(2) Oleic acid-ethylene oxide condensate.
(3) Ricinoleic acid-ethylene oxide condensate.

Polyethylene glycol stearates (Kessler Chemical Co.) are nonionic products having strong wetting and emulsifying properties even in hard water. They also disperse calcium and magnesium soaps. They comprise a range of mono-and distearic acid esters of polyethylene glycols, differing in molecular weight (depending on the number of ethylene oxide molecules condensed per molecule of stearic acid). These can be made by condensing ethylene oxide with stearic acid under pressure or by first polymerising ethylene oxide to form the polyethylene glycol, which is then esterified with stearic acid. These are white to cream-coloured wax-like solids, which are soluble or dispersible in hot water to give acidic solutions or dispersions. They are generally soluble in acetone, methanol, isopropanol, toluene, ethyl acetate but are (except distearates) insoluble in mineral and vegetable oils. They have good wetting, penetrating and grease-emulsifying properties and are recommended for adding to sizing compositions, scouring and dyeing liquors and re-wetting liquors used in sanforizing. They are also useful additives to lubricating oil formulations, for application to fibres and yarns at all stages of manufacture.

Renex 48 and 28 (Atlas Powder Co.) are described as oily, neutral, light amber coloured mixture of polyethylene glycol esters of fatty and resin acids. These nonfoaming products have powerful wetting and detergent properties. These are characterised by being effective in the presence of hard water, acids, alkalies and electrolytes. These are soluble in water and many organic solvents but not in mineral oils. Detergent properties can be imparted to them by builders like sodium phosphates, silicates and carbonates and hence they are useful in textile scouring processes. They depress the foaming and increase the detergency of anionic detergents, and increase the solubility and diffusibility of cation-active auxiliaries.

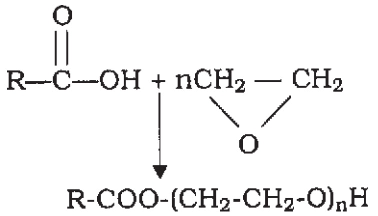
Polyethylene glycol 400 monoesters (Kessler Chemical Co. Inc.) are pale yellow to amber coloured liquids (a few are very soft solids) having wetting, softening, detergent and fat-emulsifying properties making them useful additives to various textile processing liquors (desizing, scouring, dyeing, rinsing and finishing). They are stable to dilute acids and alkalies and are not affected by hard water and electrolytes. These may be added to the lubricating oils applied to textile fibres during spinning as they make the lubricating oils spread and make them self-emulsifying in subsequent scouring. They are also useful in wetting fabrics before they are sanforized. These esters include acetate, propionate, laurate, myristate, palmitate, stearate, oleate, ricinoleate etc.

Synthonon (Synthron Inc.) is a neutral, clear amber-colourd viscous liquid consisting of fatty acid-ethylene oxide condensate, having wetting and detergent properties. It is readily soluble in water and is stable to hard water, acids, alkalies and sea water. It is not salted out by electrolytes. At low temperatures (6ºC) it becomes cloudy and on warming becomes clear and homogeneous. It has a cloud point of 52º-55ºC and is partly or wholly miscible with organic solvents. The strong detergent properties of the product are enhanced by alkaline builders like sodium carbonate and pyrophosphates. They foam less them anionic detergents in aqueous solutions.

Etilon A (Industric Chimiche Sadaf) is a viscous brown liquid with a neutral reaction and consists of oleic acid-ethylene oxide condensation product which is soluble in vegetable and mineral oils. Its oil-emulsifying properties are useful in textile processing.

A saturated fatty acid-ethylene oxide condensate in the form of amber-coloured paste (Berol MTX-10) gives a faintly opalescent solution in warm water and is stable to hard water, acids and alkalies of moderate concentrations. It is a softening agent.

A recent method of making a non-ionic softener involves the reaction of ethylene oxide with a compound containing hydrophobic chains as well an active hydrogen. A fatty acid provides such as example:



(Ethoxylated fatty acid)

Fatty acid esters of this type are used as softeners. For this purpose water-soluble or water-dispersible glycol or polyglycol esters of fatty acids (saturated) like palmitic or stearic acid are most suitable. These have additional properties of a lubricant as well as an antistat. Shenai and Samdadiya synthesised some nonionic softeners by condensing polyglycol with stearic acid and oleic acid under acidic or alkaline conditions under reflux. Stearic acid (60 g) was melted in a one litre Pyrex flask and 100 g of commercial polyethylene glycol (mol. wt. 400) was added. The required catalysts (2 ml. Of concentrated HCI catalysts of 1 g of sodium hydroxide dissolved in 5 ml. Of water) was added and the contents refluxed for 1 hour at 100ºC using a water condenser. Oleic acid-polyethylene glycol condensate was prepared by the same method:

$$R - COOH + HO - (CH_2 - CH_2 - O)_nH$$

$$\downarrow$$

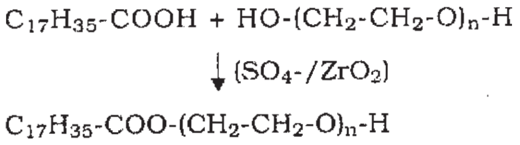
$$R - COO - (CH_2 - CH_2 - O)_n H + H_2O$$

The pH of 0.1% aqueous solutions was found to be nearly 7.0.

After applying these softeners by the pad-dry technique on cotton cloth pieces and comparing them for their softening effect-subjectively it was found that the acid catalysed stearic acid-polyethylene glycol condensate was the most active and the softener produced by condensing the polyethylene glycol with oleic acid under alkaline conditions was the least active.

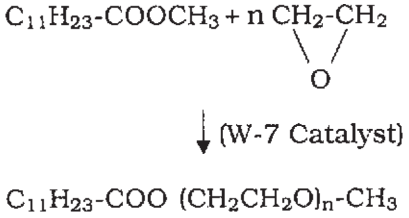
SYNTHESIS AND PROPERTIES

The synthesis of polyethylene glycol (PEG-400) monostearte has been studied by G. Feng et. al. [*Riyong Huaxue Gongye*, 1998 (No. 5), p. 12] from stearic acid and PEG-400 using super acidic catalyst (mixture of sulphate and zirconium – SO_4^-/ZrO_2). The catalyst was prepared by calcination of zirconium oxychloride ($ZrOCl_2 . 8H_2O$) and sulphuric acid. They studied the effects of the dosage of the catalyst, the ratio of stearic acid to PEG-400, the reaction temperature and time on the yield of the condensate. The optimum conditions for the synthesis, as determined by the orthogonal experiment design are: (1) mole ratio of stearic acid to PEG-400, 1:2, (2) dosage of the catalyst, 15 gm. mol of stearic acid; (3) reaction temperature 125ºC; and (4) reaction time 6 hours. Conversion of stearic acid reached 93.2% and the yield of the condensate (monostearate) reached above 90%. The new method was compared with p-toluene sulphonic acid (PTSA)-catalysed esterification method. The results showed that the new catalyst (SO^-_4/ZrO_2) had higher activity and selectivity for direct esterification of stearic acid with PEG-400 to give the monostearate:



$$C_{17}H_{35}\text{-}COOH + HO\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H \xrightarrow{(SO_4\text{-}/ZrO_2)} C_{17}H_{35}\text{-}COO\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$$

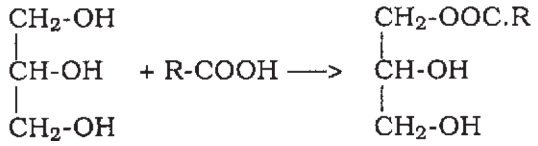
Polyethylene glycol methyl ether dodecanoates (MPD) have been synthesised by Y.-S. Kang et. al. (*Kongop Hwakhah*, 1998 (No. 9), p. 5) by the addition of ethylene oxide (5,7,9, and 12 moles) to methyl dodecanoate (DME) using a solid metal catalysts (W-7):



$$C_{11}H_{23}\text{-}COOCH_3 + n\,CH_2\text{-}CH_2 \ (\text{O}) \xrightarrow{(\text{W-7 Catalyst})} C_{11}H_{23}\text{-}COO\ (CH_2CH_2O)_n\text{-}CH_3$$

Because ethylene oxides does not react directly with DME, which does not have reactive hydrogen, the reaction to add ethylene oxide was carried out using the active solid catalyst. By using IR, HPLC and ^{1}H-NMR analyses, the structural confirmation of MPD showed yields of 93-97%. The ethylene oxide adduct distribution of MPD had a normal distribution curve, like that of polyoxyethylene alkyl ethers (fatty alcohol-ethylene oxide adducts.). In another study W. Hreczuch et. al. (*Comun. Jorn Com. Esp. Deterg*.,1999, p. 351) have compared the synthesis and composition of directly oxyethylated fatty acid methyl esters and oxyethylated alcohols with narrow and broad distribution of homologues. The synthesis of the narrow range of oxyethylated fatty acid methyl esters and fatty alcohols was carried out in the presence of claicum-based catalysts W7. The composition of the products was determined by gas chromatography. The distribution of homologues was used to discuss the kinetics of the subsequent addition steps. There was a distinct difference in the reaction route in each case. At the lower range of average poly addition degree, methyl ester is relatively broad as in the case of conventional alcohol ethoxylates. Afterwards it changes gradually and becomes equivalent to that of narrow distributed alcohols at average oxyethylation degree to 4. A further increase of the average poly addition degree makes the distribution of oxyethylated fatty acid methyl ester even more selective.

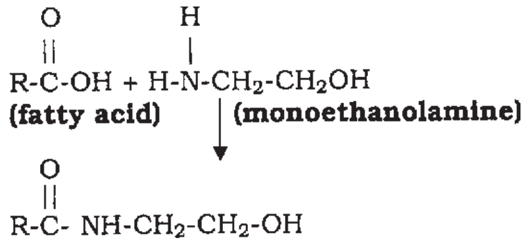
It is clearly reflected by the Natta-Mantica distribution coefficients. Synthesis and properties of several acyl glycerol emulsifiers have been described by H. Szelag (*Zesz. Nauk Politec. Gdansk Chem*., 1998, p. 3). The emulsifiers with programmed HLB values were prepared by esterification of glycerol with fatty acids in the presence of fatty acid soaps, formed *in situ*. The modification of surface activity of the emulsifier was obtained by programming sodium or potassium soap content and hydrocarbon chain length, as well as the length of acyl group in the mono acyl glycerol (C_{12} – C_{18}). The kinetic studies showed that the esterification of glycerol with the fatty acid is a first order consecutive reaction with the monoacyl glycerol, as a stable intermediate product (R is C_{11}, C_{13}, C_{15} and C_{17} alkyl):



$$\begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array} + R\text{-}COOH \longrightarrow \begin{array}{l} CH_2\text{-}OOC.R \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array}$$

The corresponding rate constants and activation energies were calculated. Knowing the reaction rate constants, the maximum concentration of monoacyl glycerols and sodium or potassium carboxylates in the modified acyl glycerol emulsifiers was investigated to find out the influence of the product composition on the interfacial tension in the paraffin oil/water system. The effectiveness of the synthesized emulsifiers was studied in the model emulsion systems. The influence of the phase volume ratio on the emulsion inversion stability and the emulsion droplet size was also studied. It was stated that the reaction product may directly be used as emulsifiers for the preparation of oil-in-water emulsions. Generally, emulsions of hydrophobic liquid in water with the help of an emulsifier, is an unstable system, in which the minute (micro) particles of the hydrophobic liquid are dispersed in water, where they are prevented from coalescing with each other by the emulsifiers.

Fatty acid alkylolamides fall in an important group of nonionic surfactants. These were first discovered by Kritchevsky (USP 2,089,212) and are made by reacting fatty acids after alkylolamines:



$$\begin{array}{l} R\text{-}\overset{\overset{O}{||}}{C}\text{-}OH + H\text{-}\overset{\overset{H}{|}}{N}\text{-}CH_2\text{-}CH_2OH \\ \textbf{(fatty acid)} \quad \big\downarrow \quad \textbf{(monoethanolamine)} \\ R\text{-}\overset{\overset{O}{||}}{C}\text{-}\ NH\text{-}CH_2\text{-}CH_2\text{-}OH \end{array}$$

The resulting alkylolamide is not soluble in water and does not possess detergency since it has very weak hydrophilic properties.

If fatty acids like lauric acid, myristic acid, coconut fatty acids, palm-kernel fatty acids are reacted with diethanolamine, and if the amide is further reacted with diethanolamine, water solubility is imparted and the product becomes a detergent. These are seldom used as detergents by themselves. They are good additives (foam boosters) to anionic detergents like dodecyl benzene sulphonates.

The reaction between the fatty acid and alkaonlamine proceeds at the room temperature producing waxy, non-crystalline materials (mainly emulsifiers). With alkylolamine esters, amide esters, amine diesters and amide diesters are also formed as by-products:

$$\mathrm{RCOOH{+}HOCH_2{-}CH_2{-}NH_2 \qquad RCOOCH_2{-}CH_2{-}NH_2}$$

$$\mathrm{R{-}COOCH_2{-}CH_2{-}NH_2{+}R{-}COOH \longrightarrow RCOO{-}CH_2{-}CH_2{-}NH{-}OC{-}R}$$

$$\mathrm{2R{-}COOH{+}(HOCH_2{-}CH_2)_2NH \longrightarrow (RCOOCH_2{-}CH_2)_2{-}NH}$$

$$\mathrm{(RCOOCH_2CH_2)_2NH{+}R{-}COOH \longrightarrow (RCOOCH_2CH_2)_2N{-}OC{-}R}$$

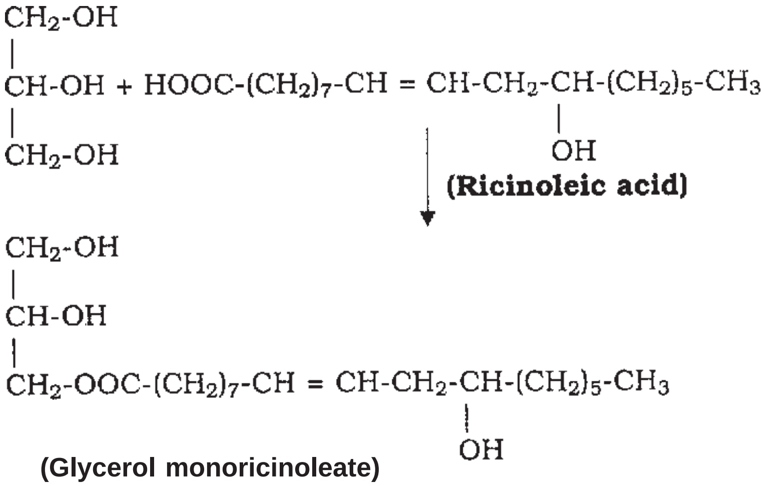
Reaction of diethanolamine with fatty acid (2:1 mole ratio), results in products (containing N-methylamide, amine ester, amine diester and unreacted diethanolamine) which display aqueous solubility. These are useful as detergents and detergent additives.

Fatty acid alkanolamides are softeners as well. Thus Ultramarine Softeners SS of Ultra Chemicals Works Inc. is a slightly alkaline cream-coloured paste containing the reaction product of stearic acid and mon-ethanolamine:

$$\mathrm{C_{17}H_{35}COOH + H_2N{-}CH_2{-}CH_2{-}OH}$$
$$\downarrow$$
$$\mathrm{C_{17}H_{35}{-}CONH{-}CH_2{-}CH_2{-}OH}$$

Under acidic conditions, it acquires cationic properties. It has good wetting properties but its detergency is poor. It is dispersible in water at almost any pH and the resulting dispersions are unaffected by acids, alkalies and low concentrations of electrolytes. It is fairly substantive to textile fibres. It does not discolour white fabric when the treated fabrics are dried a high temperature and does not materially affect either the tone or the light fastness of dyeing and prints.

Another type of nonionic product can be prepared by reacting glycerine with fatty acids. Thus glycerol monoricinoleate may be prepared as shown in the figureon next page.



$$\begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH + HOOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}(CH_2)_5\text{-}CH_3 \\ | \\ CH_2\text{-}OH \end{array}$$

(Ricinoleic acid)

$$\downarrow$$

$$\begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OOC\text{-}(CH_2)_7\text{-}CH = CH\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}(CH_2)_5\text{-}CH_3 \end{array}$$

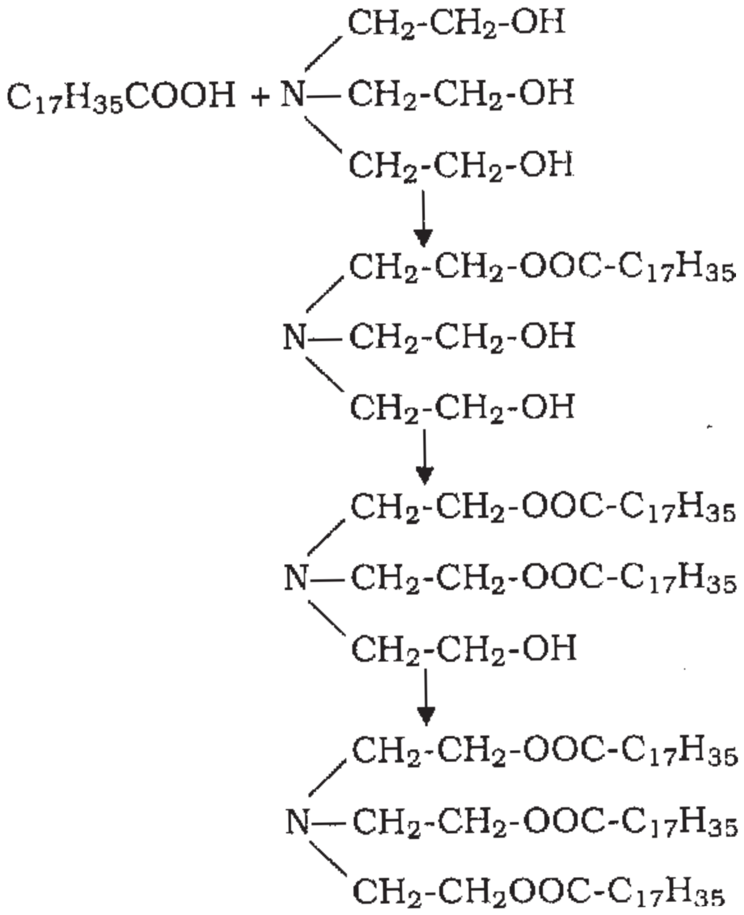
(Glycerol monoricinoleate)

Softolo of Societa An, per L' Industria Chemica Italiana is a white paste, which is slightly acidic in nature. It is easily dispersible in water and is made by reacting stearic acid with triethanolamine. This final product is mixture of mono, di, and tri-stearyl ethanolamine.

This is useful as an additive to pigment pastes (used in pigment printing), which contain polymers or copolymers including, vinyl, styrene and acrylate products, where it improves pigment dispersion without thickening.

A number of oily liquid to waxy solid products are marketed as Span (Atlas Powder Co.) which are fatty acid esters of anhydrosorbitol compounds. Sorbitol (hexahydric alcohol) is heated with fatty acids like lauric, palmitic, stearic and oleic acid when two reactions take place:

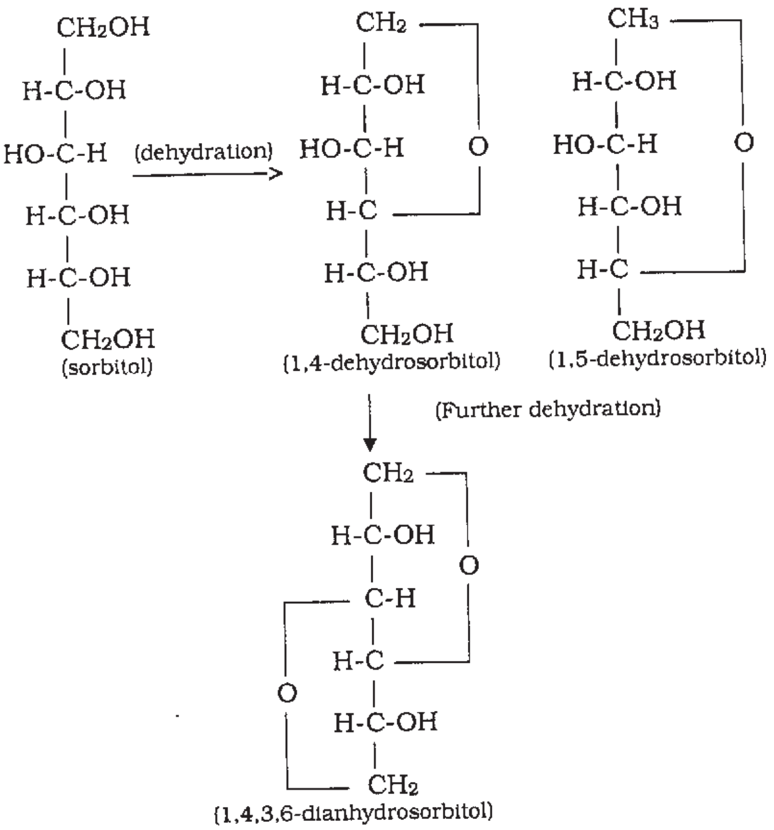
Sorbitan mono-laurate, sorbitan mono-palmitate, sorbitan mono-stearate, sorbitan-tri stearate, sorbitan mono-oleate, sorbitan trioleate etc. are chief commercial products in the Span series. Since commercial fatty acids themselves are mixtures of different acids and since it is difficult to form mono-esters (di-and tri ester are always formed to different extents) the final products are complex mixtures. They are excellent softeners and lubricants for textile fibres and are water-dispersible (if liquids) or dispersible in the presence of emulsifiers (if waxy solids). They may also be used as emulsifiers for preparing water-in-oil emulsions of vegetable and mineral oils. They are moderately soluble in organic solvents.



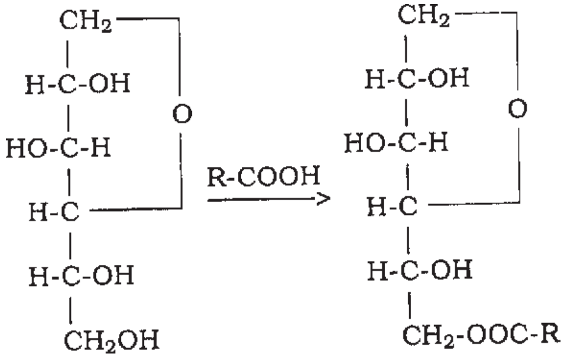
- **i) Dehydration** (see page 361)
- **ii) Esterification** (see page 361)

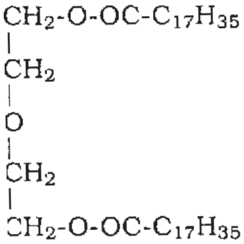
Fatty acid esters and made by reacting a fatty acid (lauric, oleic, ricinoleic and stearic acids) with a glycol (ethylene glycol, propylene glycol and diethylene glycol) in equimolar proportion. Commercial products may be a mixture of mono-and diesters of various fatty acids.

i) Dehydration



ii) Esterification



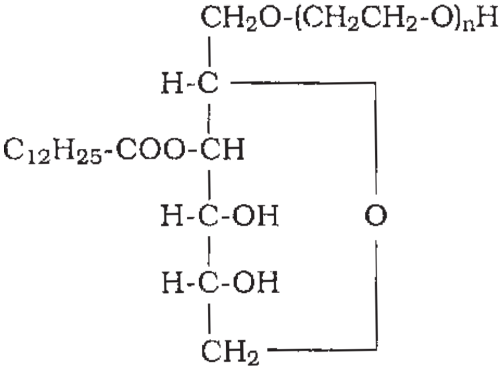


$$\begin{array}{l} CH_2\text{-}O\text{-}OC\text{-}C_{17}H_{35}\\ | \\ CH_2 \\ | \\ O \\ | \\ CH_2 \\ | \\ CH_2\text{-}O\text{-}OC\text{-}C_{17}H_{35}\end{array}$$

(Diethylene glycol distearate)

These are nonionic surfactants which have wetting, emulsifying, detergent, softening and lubricating properties. They are in varying degree soluble in organic solvents including methanol, ethanol, acetone, toluene and mineral and vegetable oils.

Polyethylene glycol sorbitan fatty acid esters are nonionic lemon-orange coloured oily liquids, which are miscible with water to give solutions, stable to acids, alkalies and electrolytes and are soluble in organic solvents. Poly-oxyethylene sorbitan mono-laurate is a typical compound of the group. This made by dehydrating (by heating) sorbitan, etherifying with several moles ethylene glycol and finally esterifying with lauric acid. Water solubility is imparted by the oxyethylene units, the hydrophilicity of which more than balances the hydrophobicity of the lauric acid group.



This has strong wetting, detergent and emulsifying properties and can be used in scouring raw wool, wool yarn and fabrics. The scouring properties of the product are improved by the addition of tetrasodium pyrophosphate. It enhances the detergency of alkyl aryl sulphonates.

Nonionic surfactants can be classified into three groups, depending on their behaviour towards water-non-dispersible, dispersible, and soluble.

Non-dispersible nonionic surfactants comprise fatty acid ester and of polyhydric alcohols (glycol, glycerol, sorbitol etc.). They are emulsifying agents, which augment the action of soaps, fatty alcohols and alkyl aryl sulphonates and have certain interest as softeners.

Water-dispersible nonionics are used for producing water-in-oil and oil-in-water emulsions and are recommended for use in compounds for oiling textile fibres, for spinning and sizing additions to foaming agents, softeners and detergents. Esters of sorbitol, sorbitan, mannitan and esters of polyethylene glycol contain 4-5 oxyethylene groups. They are softeners and emulsifiers.

Water soluble nonionics give opalescent or clear solutions and have softening and penetrating properties, particularly in aqueous solutions containing electrolytes and metallic ions.

Nonionic surfactants have the following advantages:

(1) They are available mostly in liquid form and hence their solutions can be made easily. Their lack of affinity for textile fibres makes them easily rinsable from textile materials.

(2) Being nonionic in nature, they are compatible with many surfactants and may be used in many formulations.

(3) Nonyl phenol-ethylene oxide condensates of proper HLB have good wetting, emulsifying, detergent, lime soap dispersing properties and stability to acids, alkalies and oxidising agents and find use in many textile processings.

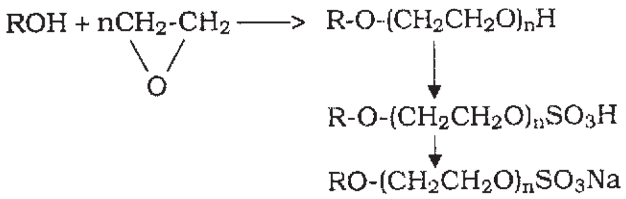
(4) Tailor-made products can be by varying HLB. The disadvantages of nonionics are:

    (1) Most versatile products are sparingly soluble in hot water (more than 70º-80ºC) and in many concentrated electrolyte solutions.

    (2) Quick rinsing and lack of affinity to fibres make the nonionic softeners purely of a temporary nature.

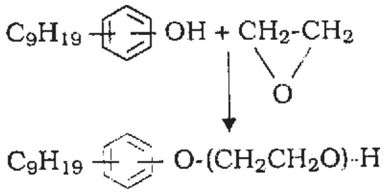
    (3) They cause too much foaming.

The solubility in water of nonionic surfactants made by condensing ethylene oxide with fatty alcohols can be increased by sulphating (and neutralising) the terminal hydroxy groups of the nonionic surfactants:

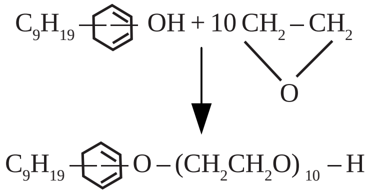


The hydrophilicity of one – OSO_3Na group is equivalent to four oxyethylene units. By replacing ethylene oxide by – OSO_3Na group foaming properties and solubility at high temperatures can be improved.

The alkyl phenols are chemically different from fatty alcohols, but they behave towards ethylene oxide in a similar manner. There is a wide choice of the alkyl group, but generally nonyl (C_9H_{19}-) or octyl (C_8H_{17}) is used as the alkyl group. Thus when nonyl phenol is polyethoxylated using 4 moles of ethylene oxide per mole of nonyl phenol, the product is still insoluble in water.

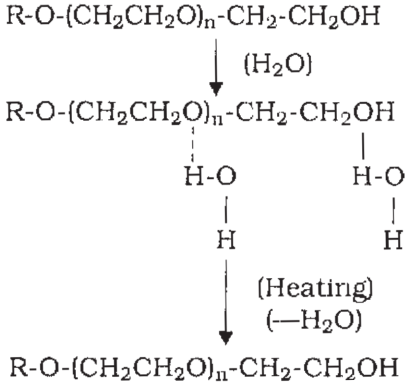


If the number of ethylene oxide molecules condensed is increased to 6-7, the resulting product is soluble in cold water. excellent detergency is obtained when 8-12 moles of ethylene oxide are condensed with one mole of nonyl phenol.



The product, known as nonyl phenol-ethylene oxide condensation product is the most widely used non-ionic detergent alkyl phenol-ethylene oxide condensate.

Ethylene oxide condensates are more soluble in cold water than in hot water. When their cold solutions are heated, they become turbid and when the temperature is sufficiently high, two phases separated. This has been attributed to the breaking up of the hydrogen bonds existing between ethoxylate oxygen and water molecules, when the water solubility of the product is decreased.



$$R\text{-}O\text{-}(CH_2CH_2O)_n\text{-}CH_2\text{-}CH_2OH \xrightarrow{(H_2O)} R\text{-}O\text{-}(CH_2CH_2\underset{\underset{H}{|}}{\underset{\vdots}{O}}\!\!\!\!\!\!)_n\text{-}CH_2\text{-}CH_2OH$$

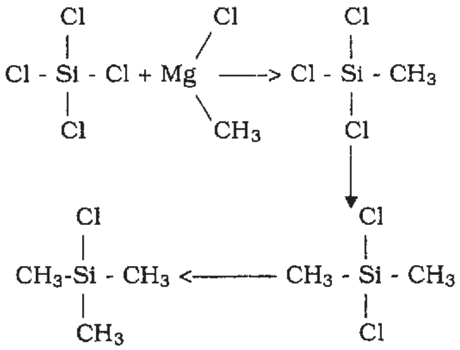
$$R\text{-}O\text{-}(CH_2CH_2\underset{\substack{\vdots\\ H\text{-}O\\ |\\ H}}{O})_n\text{-}CH_2\text{-}CH_2\underset{\substack{|\\ H\text{-}O\\ |\\ H}}{OH} \xrightarrow[(-H_2O)]{(Heating)} R\text{-}O\text{-}(CH_2CH_2O)_n\text{-}CH_2\text{-}CH_2OH$$

10

Miscellaneous Important Compounds

SILICONES

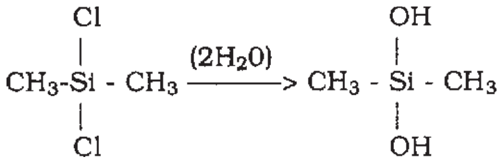
When silicon tetrachloride, which is made by heating silicon dioxide (SiO_2) with coke in a current of gaseous chlorine, is reacted with a suitable Grignard reagent, several alkyl chlorosilanes are obtained:



$$Cl-\underset{Cl}{\overset{Cl}{Si}}-Cl + Mg\begin{smallmatrix}Cl\\CH_3\end{smallmatrix} \longrightarrow Cl-\underset{Cl}{\overset{Cl}{Si}}-CH_3$$

$$CH_3-\underset{CH_3}{\overset{Cl}{Si}}-CH_3 \longleftarrow CH_3-\underset{Cl}{\overset{Cl}{Si}}-CH_3$$

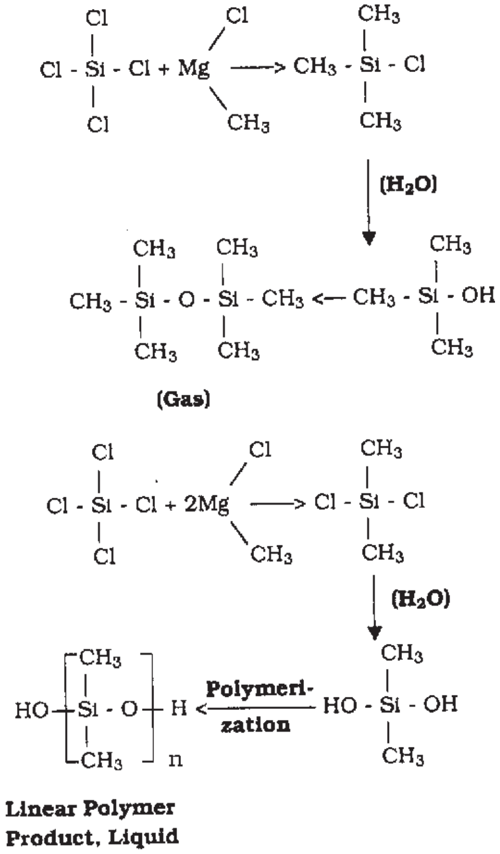
The alkyl chlorosilanes get easily hydrolyzed in the presence of water to give the corresponding alkyl hydroxy silanes. Thus, when dimethyl dichlorosilane is hydrolysed, dimethyl dihydroxysilane is obtained.

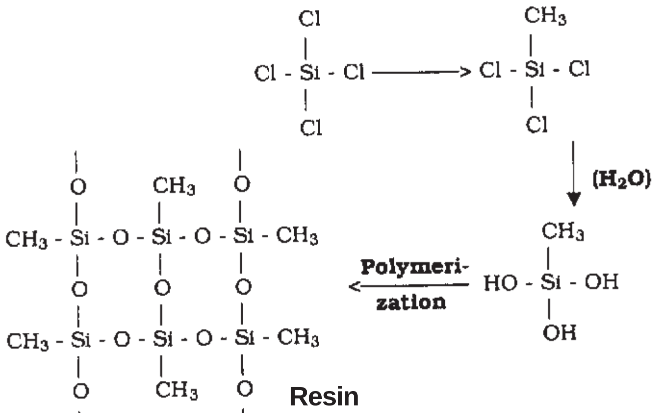


$$CH_3\text{-}\overset{Cl}{\underset{Cl}{Si}}\text{-}CH_3 \xrightarrow{(2H_2O)} CH_3\text{-}\overset{OH}{\underset{OH}{Si}}\text{-}CH_3$$

The dihydroxy compound can polymerize with the elimination of water to give polyorganosiloxanes.

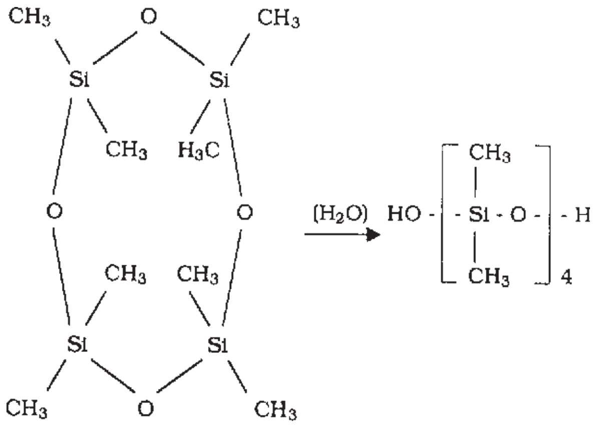
When three or four chloro groups of silicone tetrachloride are replaced by the methyl groups, the final product of condensation is a fluid. A linear or cyclic product is obtained when two chloro groups replaced by methyl groups and when only one chloro group is replaced by methyl group, the final product is a resin.



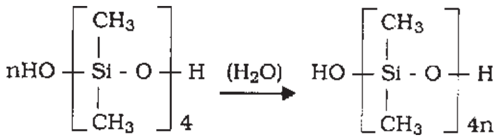


Resin

In another method, anionic emulsion polymerisation is carried out in the presence of dodecylbenzene sulphonic acid, involving (1) opening up of cyclosiloxane and (2) polymer growth via silanol condensation:



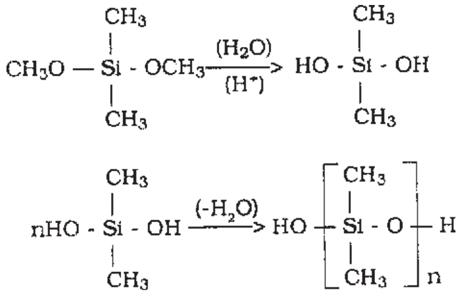
Octamethyl cyclo terasiloxane



$$n\,HO-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_4-H \xrightarrow{(H_2O)} HO-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_{4n}-H$$

When these reaction are carried out at 50º-100ºC, a stable, linear poly (dimethyl siloxane) emulsion with terminal silanol (hydroxy) groups is obtained. 1.5 to 4 parts of dodecylbenzene sulphonic acid per 100 parts of the cyclosiloxane give emulsions of excellent stability. The molecular weight and the viscosity of the polymer can be easily controlled by controlling the temperature of polymerisation. Thus, a polymer with a molecular weight of 49,000 and viscosity of 5,200 cPs is obtained at 90ºC, while a polymer with a molecular weight of 172,000 and viscosity of 1,260,000 cPs results at 25ºC. Polymers of commercial importance have viscosity higher than 100,000 cPs.

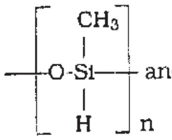
In a yet another method alkoxy silanes such as dimethyl dimethoxy silane, which hydrolyze rapidly in aqueous acidic medium can also be used as the monomer in this reaction.



$$CH_3O-\underset{CH_3}{\overset{CH_3}{Si}}-OCH_3 \xrightarrow[(H^+)]{(H_2O)} HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH$$

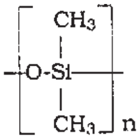
$$nHO-\underset{CH_3}{\overset{CH_3}{Si}}-OH \xrightarrow{(-H_2O)} HO\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n H$$

Two of the most important polysiloxanes having textile application are the methyl hydrogen and dimethyl derivatives having the formulae.



$$\left[-O-\underset{H}{\overset{CH_3}{Si}}-\right]_n$$

and



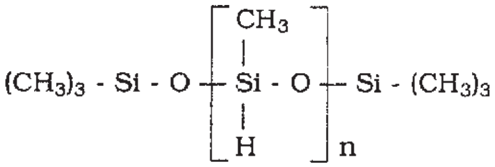
$$\left[-O-\underset{CH_3}{\overset{CH_3}{Si}}-\right]_n$$

methyl hydrogen polysiloxane

dimethyl polysiloxane

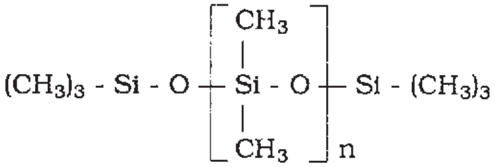
Polysiloxanes of low molecular weight are liable to undergo further polymerization by a lengthening of the Si-O-chain and also by cross-linking of adjacent Si-O-chain. If, in a textile application, this is considered to be undesirable, then in can be prevented by previously replacing the end hydrogen atoms by more inert substituents, say, methyl groups. Then such polysiloxanes are said to be end blocked. A commercial polysiloxane product, which has found considerable use for making textile materials water repellent, consists of about 60% by weight of trimethyl siloxy end blocked methyl-hydrogen polysiloxane and 40% dimethyl polysiloxane which has a viscosity of 12,500 cPs at 25ºC.

Each of these fluids fulfils a particular function in the softener structure. The dimethyl polysiloxane is generally credited with the lubricity characteristics by virtue of its many organic groups, while the methyl hydrogen polysiloxanes contribute durability.



$$(CH_3)_3 - Si - O \left[\begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ H \end{array} \right]_n Si - (CH_3)_3$$

where n = 500 - 600

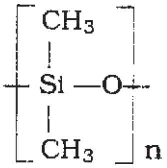


$$(CH_3)_3 - Si - O \left[\begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ CH_3 \end{array} \right]_n Si - (CH_3)_3$$

where n = 40 - 60

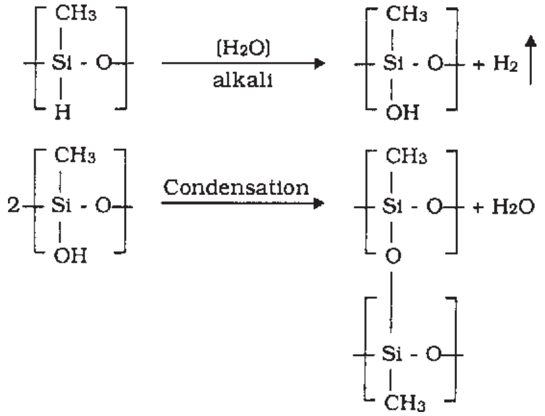
Both these polysiloxanes are water-insoluble, but are soluble in a number of organic solvents. Thus, they can be applied to textile materials from solution in an organic solvent or from an aqueous emulsion. It is much more convenient and economical to use an aqueous emulsion, but it is generally found that the most permanent water-repellent finish is obtained by the use of organic solvent solution of polysiloxane.

In treatment with a solvent solution or aqueous emulsion of a polymer containing a large proportion of reactive hydrogen-atoms, built up from methyldichlorosilane the repeating unit in the polymer is:



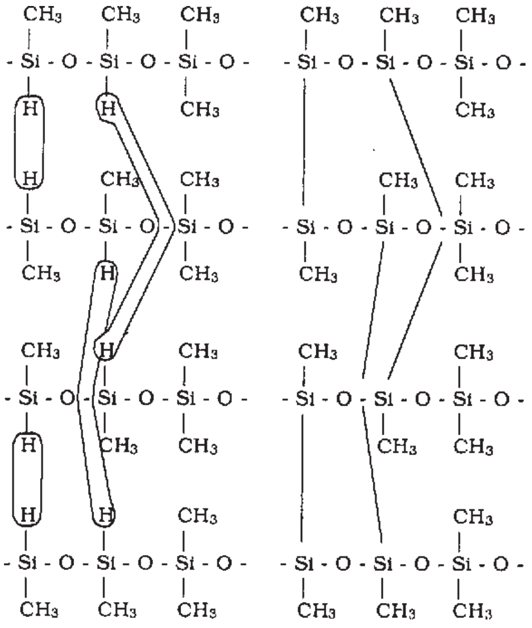
$$\left[\begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ CH_3 \end{array} \right]_n$$

This process takes place in the presence of mildly alkaline catalyst such as an organic tin compound or a zinc salt of an organic acid. On curing at 100º-150ºC for about 5 min. hydrolysis of some of the active H-atoms occur, leading to intermolecular condensation with the formation of new siloxane bonds so that each fibre becomes surrounded with a rubbery envelope.

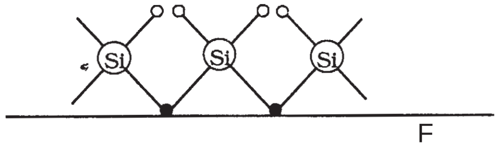


Thus, after a linear polymer component and a crosslinking polymer component are mixed with appropriate catalysts and applied to fibrous substrates from organic solvents or aqueous media, high temperatures are used to begin hydrolysis and condensation reactions necessary to cure the silicone-structures.

Silicone curing with liberation of hydrogen can be illustrated as follows.



The water-repellent finish is produced by the methyl groups facing away from the surface of the fibre.

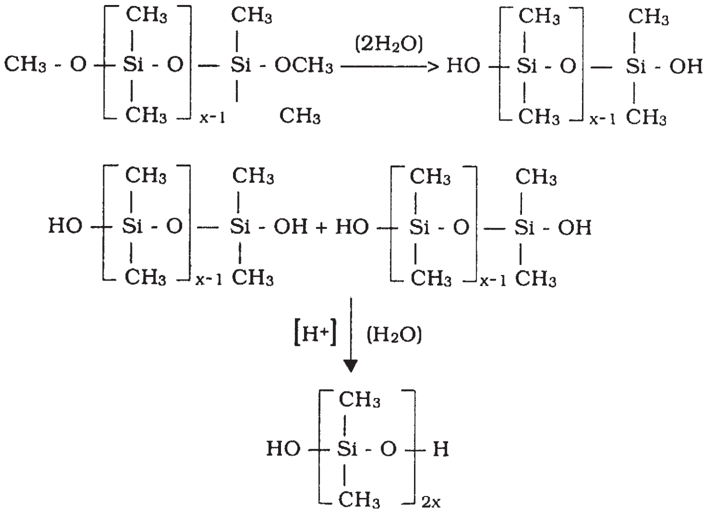


○—Methyl; ●—Oxygen; F—Fibre surface

Polysiloxanes of low molecular weight can undergo further polymerisation (chain extension) by lengthening of –Si-O-chain. Usually the terminal groups in polysiloxanes are hydroxy or methoxy groups, by virtue of which the compound can react with itself or with the hydroxy groups of cellulose under acidic catalytic conditions at elevated temperatures. Aqueous solutions of sodium hydroxide react with poly (methyl hydrogen siloxane), thereby producing poly (methyl hydroxy siloxane), and gaseous hydrogen. The hydrogen derivative can react with cellulose via the hydroxy form at elevated temperature under mildly alkaline conditions produced by tin or zinc salts or organic acids in the presence of moisture.

Some of these reactions are shown below:

(a) Chain extension of low molecular weight polyorgano siloxanes



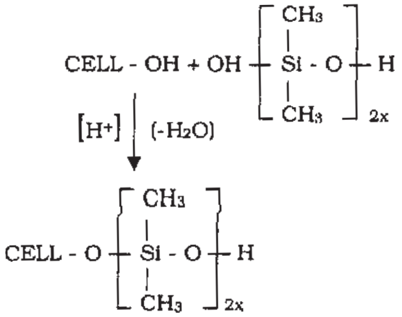
$$\mathrm{CH_3-O}\left[\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{Si-O}\\|\\\mathrm{CH_3}\end{array}\right]_{x-1}-\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{Si-OCH_3}\\|\\\mathrm{CH_3}\end{array}\xrightarrow{(2\mathrm{H_2O})}\mathrm{HO}\left[\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{Si-O}\\|\\\mathrm{CH_3}\end{array}\right]_{x-1}-\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{Si-OH}\\|\\\mathrm{CH_3}\end{array}$$

$$\mathrm{HO}\left[\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{Si-O}\\|\\\mathrm{CH_3}\end{array}\right]_{x-1}-\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{Si-OH}\\|\\\mathrm{CH_3}\end{array}+\mathrm{HO}\left[\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{Si-O}\\|\\\mathrm{CH_3}\end{array}\right]_{x-1}-\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{Si-OH}\\|\\\mathrm{CH_3}\end{array}$$

$$\Big\downarrow\,[\mathrm{H^+}]\ (\mathrm{H_2O})$$

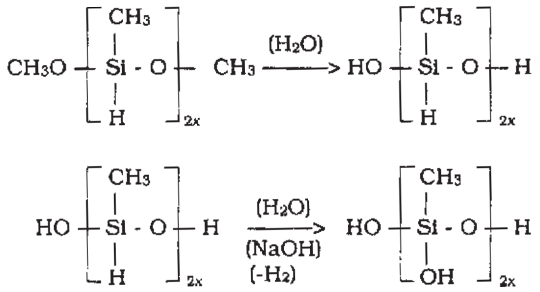
$$\mathrm{HO}\left[\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{Si-O}\\|\\\mathrm{CH_3}\end{array}\right]_{2x}\mathrm{H}$$

(b) Reaction with cellulosic hydroxyl under acidic conditions:



$$\text{CELL-OH} + \text{HO}\left[\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O\right]_{2x}H \xrightarrow[(-H_2O)]{[H^+]} \text{CELL-O}\left[\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O\right]_{2x}H$$

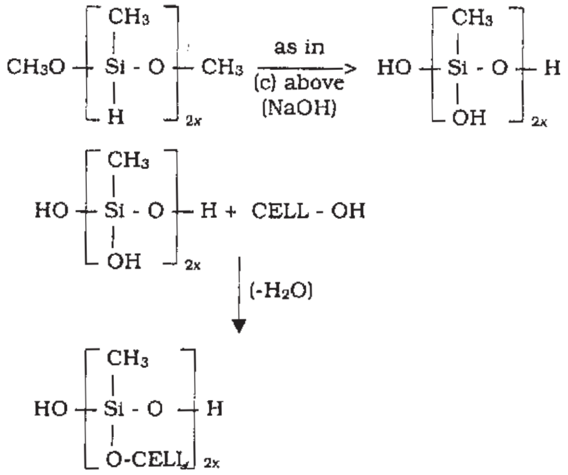
(c) Reaction with alkaline solutions:



$$CH_3O\left[\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}-O\right]_{2x}CH_3 \xrightarrow{(H_2O)} HO\left[\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}-O\right]_{2x}H$$

$$HO\left[\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}-O\right]_{2x}H \xrightarrow[\substack{(NaOH)\\(-H_2)}]{(H_2O)} HO\left[\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{Si}}-O\right]_{2x}H$$

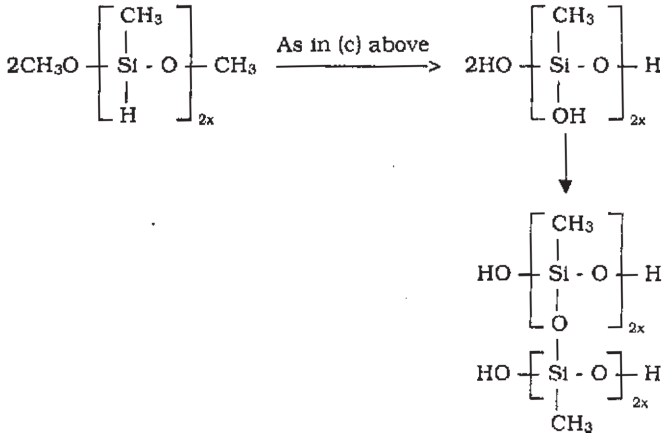
(d) Reaction with cellulose under mildly alkaline solutions:



$$CH_3O\left[\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}-O\right]_{2x}CH_3 \xrightarrow[\substack{\text{(c) above}\\(NaOH)}]{\text{as in}} HO\left[\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{Si}}-O\right]_{2x}H$$

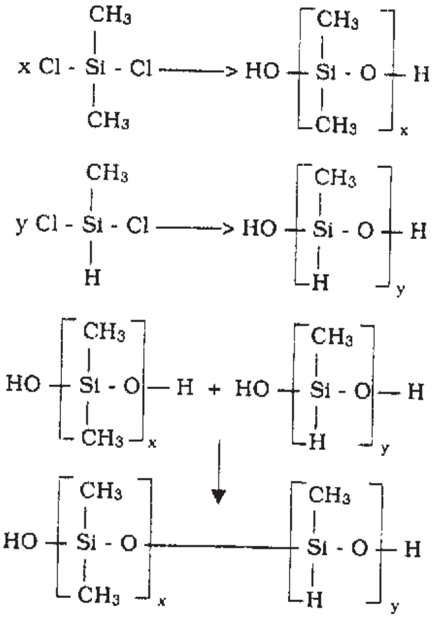
$$HO\left[\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{Si}}-O\right]_{2x}H + \text{CELL-OH} \xrightarrow{(-H_2O)} HO\left[\overset{\overset{CH_3}{|}}{\underset{\underset{\text{O-CELL}}{|}}{Si}}-O\right]_{2x}H$$

(e) Self-crosslinking reaction

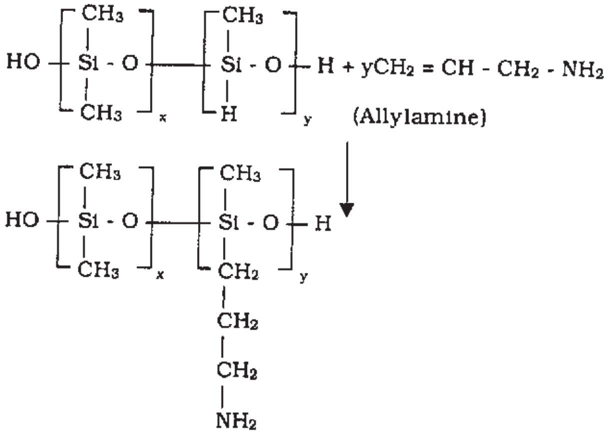


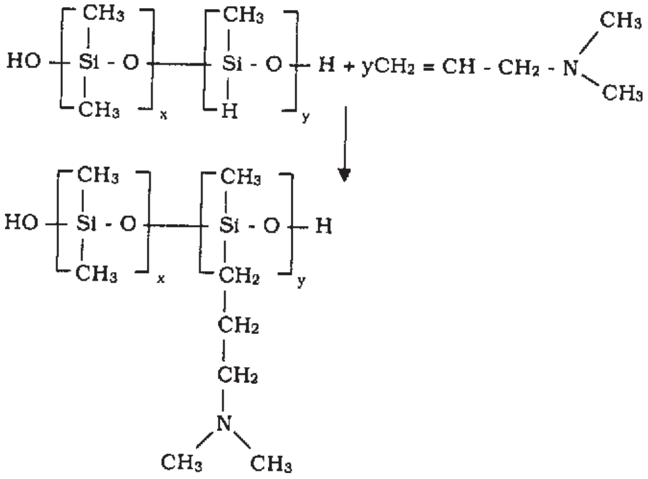
CHEMICALLY MODIFIED POLYORGANO-SILOXANES

Apart from poly (dimethyl siloxane) and poly (methyl hydrogen siloxane), mixed poly organo siloxanes are also made. The basic reaction (methyl chlorosilanes hydrolysed to hydroxy silane followed by condensation) is the same as in the case of other polyorganosiloxanes. However low molecular weight polymers are first made and then condensed:



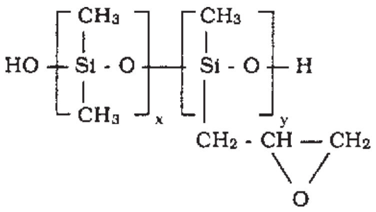
This mixed polymer forms the basic material for further modification. Essentially, an allyl compound is reacted with the mixed poly (organo siloxane), when addition reaction takes place at the ethylenic part of the allyl compound and the reactive silane hydrogen of the siloxane compound. Thus, amino functional poly (organosiloxane) can be made by reacting poly (organosiloxane) with either allylamine or N-substituted allylamine:



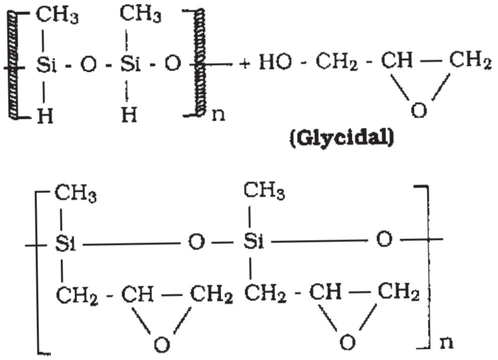


These are known as aminosilicones.

Epoxy-modified silicones have been successfully commercialised abroad:

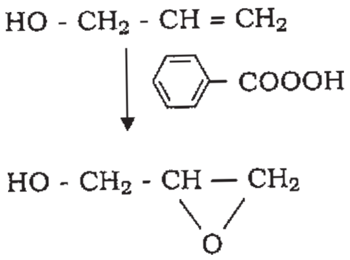


These are made by reacting poly (methyl hydrogen siloxane) with glycidol:



(Glycidal)

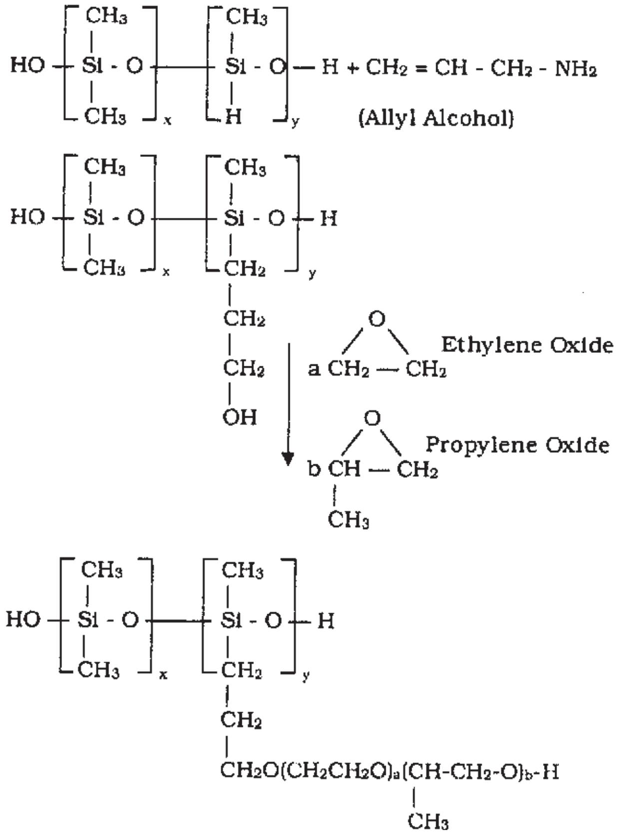
Glycidol may be from allyl alcohol and benzoyl hydroperoxide:



These modified silicones are reactive products and can react with cellulosic fibres. The amino silicone reacts by virtue of the presence of silanol end group and the epoxy silicone by virtue of both the silanol end group and the reactive epoxy group.

Interesting products, like nonionic surfactants with considerable water solubility, have been made from the mixed type of poly (organo-siloxanes). Thus, it is first reacted with allyl alcohol and then reacted with ethylene oxide and/or propylene oxide.

A very useful property of such nonionic condensates is that unlike other silicone and modified silicones, which require an emulsifying agent prior to their application to textile materials in the form of an emulsion, they are soluble in water and hence do not require an emulsifying agent.



APPLICATION OF SILICONE EMULSIONS

Since most silicones are oily in nature and are not miscible with water, emulsion techniques are employed to prepare a suitable aqueous system.

(An emulsion is a heterogeneous system consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameters, in general, exceed 0.1 µm.). This is readily accomplished by use of emulsifying agents together with mechanical processing in colloid mills or homogenizes. In selecting a suitable emulsifier, it must be kept in mind that any compound having high wetting and/or rewetting properties, must be avoided since such an agent will tend to nullify the water-repellent characteristics of the finish. The ideal emulsifying agent is the one which is des-troyed or rendered inert during the processing of the fabric. The key factors in emulsion stability are proper choice of emulsifier, size and size distribution of the emulsified particles, the presence of impurities and temperature.

Emulsifiers are classified as anionic, cationic and nonionic. Nonionic emulsifiers from the largest and fastest growing group of emulsifying agent (an example is polyoxyethylene alcohols). Silicones form normal oil-in-water and water-in-oil emulsions.

Instead of a single surface-active agent, mixtures of emulsifiers are often used to give more efficient surface activity and greater emulsion stability.

Generally, silicone oil, which is available in the form of 30% emulsion is used extensively in textile processing. These emulsions should be suitably diluted depending on the original concentration before using in the padding mangle. The expression of the mangle should also be considered in culating the final deposit of silicone on the fabric.

The important factors in the application of silicones are as follows:

(1) Fabric to be processed must be thoroughly cleaned and should contain no residual agents from the scouring or dyeing operations. The pH of the cloth to be treated is preferably in the range of 6-7.

(2) The fabric must be processed in such a way as to obtain thorough and uniform impregnation in order to pick up the required amount of silicone from the treating bath. This is usually done on conventional mill equipment such as a padder.

(3) Following impregnation, the fabric is dried and then subjected to high temperature curing. Under the influence of curing temperature, some of the silicone-to-hydrogen bonds are replaced by the very stable silicon-oxygen-silicon linkages. The silicon ‘skin’ thus formed then becomes insoluble in both water and the common dry-cleaning solvents.

In order to develop satisfactory durability, it is essential to introduce a catalyst in the silicone emulsion system, the catalyst providing the means of promoting the crosslinking of the methyl hydrogen silicon units. Generally, organometallic salts of zinc, tin and zirconium are used as catalysts. These catalysts are preferably packaged separately and then are added to the silicone emulsion immediately prior to sue, as the mixture of the two products can give rise to polymerization of silicone even at room temperature.

To obtain the best properties, usually between 1% to 2% increase in the dry weight of the fabric is required to encase the fibres with a silicone film only a few molecules in thickness.

To determine the necessary the polymerizing temperature, various factors must be taken into account: weight of the fabric, mode of wearing, nature of fabric, higher or lower reactivity of the silicone and of the catalyst.

The generally recommended temperature are as follows:

8 to 10min. at 130ºC.

or 2 to 5 min. at 150ºC.

or 1 to 2 min. at 170ºC.

Properties imparted to textiles

(a) The property, which is primarily associated with the application of silicones to textiles, is water-repellency. While this factor is outstanding, there are several other factors which are of considerable importance, particularly when associated with water-repellency. Among these are stain-and-spot resistance, which is actually a part of the property of water-repellency.

(b) Improvement in abrasion or wear resistance, tear strength and sewing qualities.

(c) Improvement of hand or feel of the goods. A soft hand flexibility is imparted and the fabric appears to be smoother than that obtained by the use of any other softener.

(d) Silicone film has good resistance to solvents (drycleaning) and a fairly good resistance to household washing.

(e) The treated fabric does not wrinkle or shrink badly.

(f) Silicone polymers are incorporated in the melt stage of synthetic fibre manufacturing to improve spinerette performance.

(g) When used with thermosetting resins, the silicone water-repellents provide improved crease-resistance and abrasion resistance compared with the resin treatment alone.

Their use in shrink-resisting wool has been described in patents. They give soft handle and improved wrinkle recovery on wool.

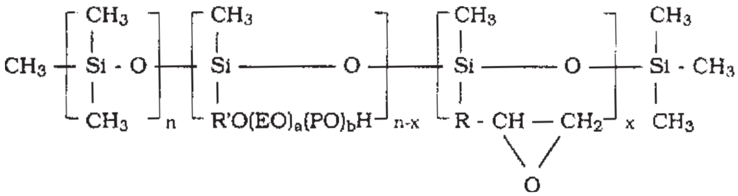
(h) A series of silicone copolymers have been developed to satisfy two major requirements in fibre processing operations: low machine-to-thread friction and control of static electricity.

Amino functional silicone emulsions have a disadvantage over the conventional non-reactive (dimethyl siloxane type) or reactive (silanol-ended, methoxy-ended or methyl hydrogen siloxane type) silicone emulsions. Thus, when applied to while fabrics or those dyed with pastel, shades and presence of amino functional silicone may cause yellowing after prolonged exposure to light and heat. In the case of fabrics dyed in deep shades, the discolouration is not visible, and hence this is not a serious disadvantage.

Further, the cationic nature of the amino or alkyl substituted amino group attached to the siloxane chain precludes the use of anionic emulsifier in the preparation of emulsion. Mixtures of nonionic emulsifiers made from lauryl alcohol ethylene oxide adduct mole ratio, (1:6 and 1:8) can be conveniently used to prepare stable emulsions of amino functional silicones.

Amino functional silicones have been applied on cotton fabrics as softening agents. These and other organo-functional silicones contain groups such as amino, substituted amino, epoxide or alcohol groups attached to the polymer backbone. They offer durable, soft and lively hand and a slight increase in wrinkle recovery and flat appearance. In a hand evaluation study or reactive silicones and other organic textile softeners (polyethylene softener and fatty acid amide-type softener), amino functional silicones have shown softening ability. Increased tear strength, greater abrasion resistance and improved wrinkle recovery were seen on polyester/cotton blends and 100% cotton woven fabrics treated with amino functional silicones along with a durable press resin. Cotton knit fabrics showed improved durable press ratings and an increase in stretch and recovery when softened with amino functional silicone. All these fabric property improvements exhibited durability to repeated launderings. In addition, the ability to blend these amino functional silicones with organic softeners and retain performance properties allows the reaction of softeners blend with optimum cost-performance parameters. Thus, a polyester/cotton blend fabric showed improvement in durable press rating, wrinkle recovery and tear strength, even when half the amino functional silicone softener was replaced by an organic softener, which, however, caused a loss in stretch/recovery performance of cotton knit fabric after five washes.

Zhang Liang et. al. Has studied the effect of modified silicone on the finishing of cotton fabrics with DMDHEU. For this purpose, they used CGE-343 silicone of the following formula –



As can be seen from the formula a large number of ethylene oxide and propylene oxide units impart water solubility to the silicone, which then need not be emulsified like poly (dimethyl siloxane), and poly (methyl hydrogen siloxane). The epoxy groups makes the modified silicone reactive towards cellulosic fibres. When this silicone id added to DMDHEU crosslinking agent, the demands of high grade finishing are met with and the properties of DMDHEU are improved. Further, the quantity of DMDHEU used can be reduced to 30-50% with the addition of CGF-343 silicone (3-5 g/litre).

In addition, formaldehyde release can also be restricted to 70-80%. Fabrics treated with CGF-343 silicone and DMDHEU have good washability, permanent soft handle and improved tear strength.

J.D. Turner has reported the means of improving the durable press (DP) appearance of cotton fabrics with certain additives and aminosilicones. He found that aminosilicones can improved the DP appearance of cotton fabrics without using a celulosic crosslinking agent. The improvement is usually 1.0-1.5 DP rating units, depending on the fabrics. The mechanism of this action appears to be a superior fibre-to-fibre and yarnto-yarn lubrication that results in potential wrinkles dropping from the fabric. Another advantage is that there is no loss in fabric toughness; abrasion resistance is better for the treated than for the untreated cotton fabric. When aminosilicones are combined with cellulose crosslinking agents no improvement in DP was seen for 100% cotton fibre fabrics over that obtained with the crosslinking agent and polyethylene softener. Synergistic effects have been found on polyester/cotton blends.

The amino silicones must be durable on cotton fabrics when no crosslinking agent is used. This may be achieved by applying amino silicone with a silicone crosslinking or a reactive polysiloxane such as poly (methyl hydrogen siloxane) or that having silanol groups. Internally modified reactive amino silicones (perhaps epoxy modified) are available. All these vary slightly in the hand, durability, DP properties and tendency towards discoloration. The amino silicones can be applied by pad-dry-cure technique. Curing may be done either at 150ºC for 3 min. or at the room temperature for 24 hours. It has been shown that, when a crosslinking agent such as etherified DMDHEU (catalyzed by magnesium chloride) is used on 100% cotton fabric, diethylene glycol (5% owf) and coco diethanolamide (3% owf) along with the usual polyethylene emulsion, better retention of strength and abrasion resistance can be achieved.

CARRIERS

Dyeing of synthetic fibres, like polyester fibres, which are essentially of hydrophobic nature, is difficult at 100ºC at atmospheric pressure, because of the very compact structure, pronounced lengthwise orientation of the molecular chains, dense packing and high degree of orientation. In order to achieve practical dyeing of polyester fibre materials with disperse dyes at 100ºC at atmospheric pressure in conventional dyeing machines, certain chemicals, called carriers have to be used. The carriers alter the dispersing properties of the dyes and the physical characteristics of the fibre, so that more of the dyestuff can be transferred from the dyebath to the fibre than in the absence of the carriers.

It had been established that certain hydrocarbons, phenols, amino acids, amides, alcohols, esters, ketones, nitriles etc. accelerate the dyeing of polyester fibres with dispersing dyes from anaqueous medium at 100ºC.

While selecting a carrier for use in dyeing polyester fibres, the following points should be considered – (1) high carrier efficiency, (2) availability at low cost, (3) little or no effect on the light fastness of the final dyeing, (4) absence of unpleasant odour, (5) non-toxicity, (6) no degradation or discolouration of the fibre, (7) ease of removal after dyeing, (8) high stability under the dying condition, (9) compatibility with the dyestuffs, (10) ease of dispersion in the dyebath, (11) low volability and (12) uniform adsorption by the fibre.

Commercial carriers are mainly based on phenyl phenols (ortho and para) and di-trichlorobenzene. Orthophenyl phenol may be used in the concentration range of 3-6 g/1. The free phenol is insoluble in water and difficult to disperse in water. it melts at 56ºC and forms oily stains on the fabrics being dyed. To overcome this defect, its sodium salt is used, which is soluble in water, but has no carrier action (it is only the free phenol that is the actual carrier). Therefore, after dissolving the sodium salt in the dyebath, the free phenol should be liberated in the dyebath by the addition to an acid-liberating agent such as diammonium hydrogen phosphate. This carrier adversely affects the light fastness of the final dyeing, if not completely removed from the dyeing. A heat treatment at about 195ºC removes the residual carrier. Alternatively, scouring under alkaline conditions (when the carrier is converted into the soluble form with no carrier action) can be given to remove it completely. During this removal, the dye does not come out of the fibre into the scouring bath.

Di-and trichloro benzenes are good carriers, which promote dye absorption by the fibre and the residual carriers do not affect the light fastness of the final dyeing. The carrier action is unaffected by changes in pH of the dyebath (phenyl phenols lose their carrier action under alkaline conditions). These water-immiscible (water-insoluble) carriers have to be emulsified in the dyebath, using an emulsifying agent, such as an anionic detergent (dodecyl benzene sulphonate, either the sodium salt or triethanolamine salt). These carriers are toxic in nature and hence their use involves the use of enclosed dyeing machines. An emulsifying agent should be added to the scouring bath after dyeing to remove the carrier from the dyed material. During this process, some amount of the dye comes out from the dyed fibre into the scouring bath, since the carrier retains its carrier action; the carrier which carried the dye into the fibre during dyeing, now takes in out of the fibre during scouring.

Carriers based on chlorinated benzene are available in the form of self-emulsifiable, light yellow brown liquids, which give neutral, milky emulsions on diluting with water. They may be added in the concentration range 3-5 g/l (5-20% on the weight of the material) in closed dyeing machines. Alternatively, the material may be treated with first bath containing the carrier (5 g/l) at not more than 80ºC for 30 min. The material may then be rinsed and dyed in a separate bath, containing the dye (without further additions of the carrier). After dyeing by either of the methods, the dyed material should be scoured in the presence of a nonionic detergent at 70ºc, rinsed and dried.

Ortho-phenyl phenol-based are marketed as their sodium salts as a dark brown liquid (about 45% solution in water) with an alkaline reaction. These can be easily diluted with water. in order to release the actual carrier (the free phenol) in the dyebath, equal amounts of diammonium hydrogen phosphate or 30% acetic acid and an anionic dispersing agent should be used. The carrier (solution form) may be used in the concentration range of 6-10 g/l, depending on the depth of shade. A pretreatment with the carrier may be given at 70ºC for 15 min., followed by the addition of the disperse dye, raising the temperature to 100ºC and dyeing continued for 60-90 min. at the boil. After the dyeing, scouring of the dyed material may be done in bath containing an anionic/nonionic detergent and sodium hydroxide at 70ºC for 20-30 min. Heat setting at 190º-195ºC for 1min. is an alternative method of removing the residual carrier from the dyed material.

Another carrier, which has attained commercial success in the United States is based on butyl benzoate which has high carrier efficiency and is free from toxicity. It is stable over a wide pH range. According to the swelling phenomenon, which is supposed to be one of the mechanisms, based on which carrier dyeing is explained, a polyester swelling agent opens up the compact fibre structure, thereby widening the micropores present in the fibre material, thereby increasing the diffusion rate of the dye molecules. Butyl benzoate has a structure, which is almost identical with a part of the polyester molecule (Fig. 10.1).

The reaction product of ethylene glycol and benzoyl chloride or benzoic acid in the molar ratio of 1:2 should be a better carrier, since its molecular similarity to the polyester molecule is more striking (Fig. 10.1).

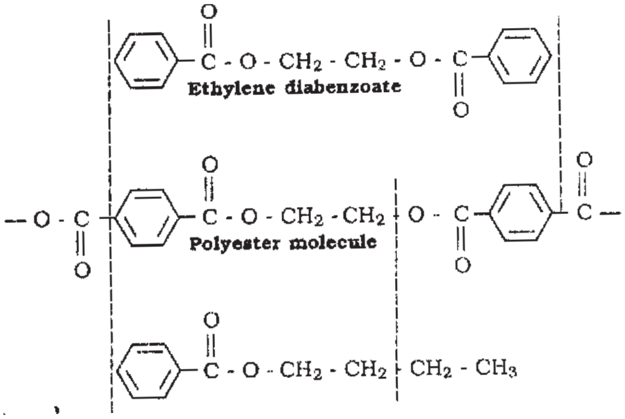


Fig. 10.1 Structural similarity between polyester molecule and carriers

Shenai and Patil (unpublished work) synthesised butyl benzoate and ethylene dibenzoate and used them in the dyeing of polyester fibres with a few disperse dyes.

One mole of benzoic acid (122 g) and 2 moles of butanol (148 g), which is a solvent for benzoic acid are taken in a 1 litre round bottom flask, to which 5 ml. Of concentrated hydrochloric acid is added. The mixture is heated under reflux (at 120ºC) using a water condensor for 1 hour. The contents are cooled.

Ethylene dibenzoate was prepared by condensing 2 moles of benzoic acid with 1 mole of ethylene glycol in the presence of hydrochloric acid by the reflux method.

Polyester fibres were dyed with a few disperse dyes in the absence and presence of various amounts (5, 8 and 10 g/l) of the carrier, keeping a liquor ratio of 50:1. The dyeing was started at 40ºC, the temperature raised to 100ºC and the dyeing continued at this temperature for 60 min. At the end of the dyeing, the dyebath and the dyed fibres (after rinsing, scouring, washing and drying) were visually examined for exhaustion of the dyebath and depth of shade. The results obtained with ethylene dibenzoate and butyl benzoate are given in Table 10.1.

Table 10.1
Dyeing of Polyester Fibres at 100ºC in the Presence of Carriers

Dye	Carrier Conc., g/l	Exhaustion characteristics	
		Ethylene dibenzoate	Butyl benzoate
1. Foron Scarlet E-2 GFL	5	Good	Good
	8	Nearly Complete	Nearly Complete
	10	Complete	Complete
2. Setaron Blue RFL	5	Good	Good
	8	Nearly Complete	Nearly Complete
	10	Complete	Complete
3. Setaron Yellow T-3GL	5	Good	Good
	8	Nearly Complete	Nearly Complete
	10	Nearly Complete	Nearly Complete
4. Setaron Golden Yellow RL	5	Good	Good
	8	Nearly Complete	Nearly Complete
	10	Nearly Complete	Nearly Complete
5. Setaron Red BL	5	Good	Good
	8	Nearly Complete	Nearly Complete
	10	Nearly Complete	Nearly Complete
		Complete	Complete

Thus, it is seen that, as expected, both butyl benzoate and ethylene dibenzoate are good carriers in the dyeing of polyester fibres, when used as a concentration of about 8 g/l.

The carrier efficiency may be quantitatively determined by dyeing polyester fibres in the presence and absence of the carrier and estimating the dye present on the fibre after stripping.

Polyester yarn (2 g) in the form of a hank is dyed with a liquor ratio of 20:1, staring in a blank bath (waer, dispersing agent and a carrier,(say 5 g/l), raising the temperature to 60ºC, adding the dye (2% disperse blue dye), raising the temperature to 100ºC and dyeing at the boil for 45-60 min. The hank is taken out, rinsed with cold water, scoured in a bath containing 2 g/l nonionic detergent at the boil for 15-20 min. the dyeing may be carried out at a given concentration of series of carriers of different manufactures. A dyeing is also carried out in the absence of any carrier. The dyed hanks may be compared visually. A good carrier should produce deep dyeings.

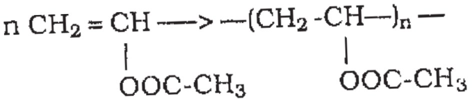
Alternatively, small samples of the dyed hank (20 mg) may be treated with hot chlorobenzene or diemethyl formamide twice, the extracts collected, diluted to a known volume with the corresponding solvent and the absorbance (optical density) of the solution determined at the wavelength of maximum absorption using a suitable spectrophomoter. The absorbance values for carrier dyeings may be compared among themselves for grading a series of carriers under test.

POLYVINYL ACETATE EMULSION

Plasticized polyvinyl acetate dispersions find many applications in the finishing of fabrics made from natural and man-made fibres. They impart body, weight, stiffness, dimensional stability and other desirable properties to the treated fabrics. Thus, they impart drape to the fabrics, which become transparent, resistant to sunlight, abrasion, mildew attack etc. Dilute acids and alkalies do not affect the treated fabrics and the finish does not exhibit chlorine retention property. Addition of thermosetting resin precondensates and crosslinking agents (DMU, DMEU, DMDHEU etc.) to the polyvinyl acetate application baths, followed by padding, drying and curing produce washfast effects. They are compatible with other finishing agents like starch, dextrin, wax emulsion, water-repellents, cationic and anionic softeners, fluorescent brighteners, etc.

MANUFACTURE OF POLYVINYL ACETATE DISPERSION

Polyvinyl acetate is made by emulsion polymerisation (BIOS 1166). In this process, a solution of 52 kg. of polyvinyl alcohol in 1000 kg. of water is heated to 85º-95ºC and pumped to a jacketed enamelled reaction kettle. To this 1.5-2.5 kg. formic acid and 3 kg. 40 vol hydrogen peroxide were added. Then, 100 kg. of vinyl acetate is charged in 5-10 min. The addition is made to give a controlled foaming. When the temperature drops to 72ºC, additional vinyl acetate (950 kg.) is added over 90-120 min. giving a final temperature of 85ºC. No heating is done during the polymerization. When the addition of vinyl acetate is completed, the temperature is raised to 95ºC by circulating water and steam in the jacket and the residual monomer (1-1.5%) is removed under vacuum for 1 hour (final monomer content in the emulsion is less then 0.5%). The charge is cooled to 50ºC and dumped into a mixing and adjusting vessel. Several batches are dumped together in this vessel. The viscosity is adjusted, if necessary by adding small amounts of water. Plasticizers are also added, if necessary, at this stage. The finished product is run through a pressure filter into containers.



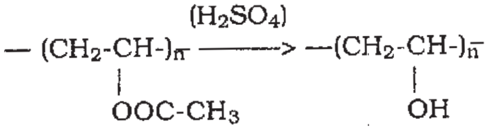
$$n\,CH_2{=}\underset{\substack{|\\ OOC\text{-}CH_3}}{CH} \longrightarrow \text{—}(CH_2\text{-}\underset{\substack{|\\ OOC\text{-}CH_3}}{CH}\text{—})_n\text{—}$$

(Vinyl acetate) (Polyvinyl acetate)

NOTES

(1) Polyvinyl alcohol

This is used as the emulsifying agent for the final polymer. For this purpose fully hydrolysed (98.5%) grade of polyvinyl alcohol should be used. This is made by dissolving 100 moles of polyvinyl acetate (mol. wt. 40,000) in methanol/methyl acetate (60/40) mixture to form a 15% solution. With sulphuric acid as the catalyst, the mixture is heated under reflux for 24 hours, when polyvinyl acetate is hydrolysed to polyvinyl alcohol –



$$\text{—}(CH_2\text{-}\underset{\substack{|\\ OOC\text{-}CH_3}}{CH}\text{-})_n\text{—} \xrightarrow{(H_2SO_4)} \text{—}(CH_2\text{-}\underset{\substack{|\\ OH}}{CH}\text{-})_n\text{—}$$

(Polyvinyl acetate) (Polyvinyl alcohol)

The reaction mixture is cooled, when the polyvinyl alcohol crystallizes out, which is centrifuged, washed with methanol, neutralised with dilute sodium carbonate solution, washed and vacuum-dried.

(2) Formic acid

Vinyl acetate has the highest stability at pH 5.0. If it rises above 7.0 hydrolysis occurs and the polymerization slows down and does not go to completion. If the pH drops below 2, hydrolysis takes place. Therefore, formic acid is used to get the required pH. The volatility of this acid makes it easy to remove by evaporation.

Proper pH is important to control the particle size and the viscosity of the final dispersion.

(3) Vinyl acetate

This monomer must be of high purity. Variation in the particle size of the final polymer is due to the impurities present in the starting monomer.

(4) Material of construction

Enamel is better than stainless steel for the reaction kettle, since is must be free from iron. Bacterial reduce sulphuric acid to hydrogen sulphide, which with iron produces blackish discolouration.

(5) Temperature control

The polymerization reaction is carried out without external cooling. The heat of reaction is removed by evaporation of vinyl acetate ad water, which condense in the reflux condenser and return to the kettle. External cooling by jacked is found to be unnecessary. Internal cooling is preferable, since there is no temperature gradient from the cold wall to the warm interior with the resulting differences in the reaction conditions. The reflux is running counter-current to the rising vapour and is heated to near kettle temperature before hitting the reaction mixture.

(6) Agitation

The speed of the agitator is 64 rpm.

(7) Cleaning of the kettle

After each run, the kettle is inspected and cleaned of any crusts at the liquid-vapour line.

The final product must have a solid content 48-52% with an acid number of not more than 2 (pH-5-6). The dispersion is stable even over a period of years. The particle size varies between 0.02 mm and 0.002 mm.

Polyvinyl acetate dispersions (these are wrongly called emulsions) are marketed in the form of white pastes, with a specific gravity of 1-1.1 and can be diluted with water in all proportions. The dispersion thus produced are stable, since they contain a protective colloid. The marketed dispersions themselves are stable over a period of several months. They may be stored in milk steel containers, lined with polyethylene and should be protected from excessive heat as well as from freezing.

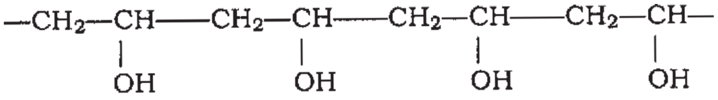
They are usually applied by the pad-dry technique and do not need any curing step. The fabric may be padded with a suitable diluted dispersion at 25º-30ºC with 60-70% expression. They may also be applied by the exhaustion method in a jigger or winch.

After padding or exhaustion, the fabrics may be dried at a temperature higher than 80ºC on a stenter or a cylinder dryer. In the latter case, it is preferable to wrap the first few drying cylinders with cloth to lower the temperature of initial drying. If the dried fabrics are subsequently calendered, this operation has to be carried out at high temperatures to avoid sticking of polyvinyl acetate to the rollers. Some typical recipes for semi-permanent and durable finishes are given in Table 10.2.

When DMU/DMEU are used, the fabrics have to be cured at 140º-150ºC for 5-3 min. and when the polyvinyl acetate dispersion is used in the absence of the resin precondensates or crosslinking agents, a sample pad-dry technique may be followed.

Polyvinyl alcohol

Polyvinyl alcohol can be described as a polyhydric alcohol, having secondary alcohol groups on alternate carbon atoms of an aliphatic macromolecule:-



$$-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-$$

(Polyvinyl alcohol)

It is made by polymerizing vinyl acetate into polyvinyl acetate and then hydrolyzing the polyvinyl acetate.

The properties of polyvinyl alcohol depend on the degree of polymerization and the degree on hydrolysis.

The hydrolysis may be carried out in alcoholic medium in the presence of an alkali or acid.

In one method powdered polyvinyl acetate (80 kg.) is treated with a solution containing 45 kg. of caustic potash in 500 kg. ethanol at the room temperature, when solid polyvinyl alcohol separates in 1 hour. Complete (100%) hydrolysis is supposed to occur in this reaction.

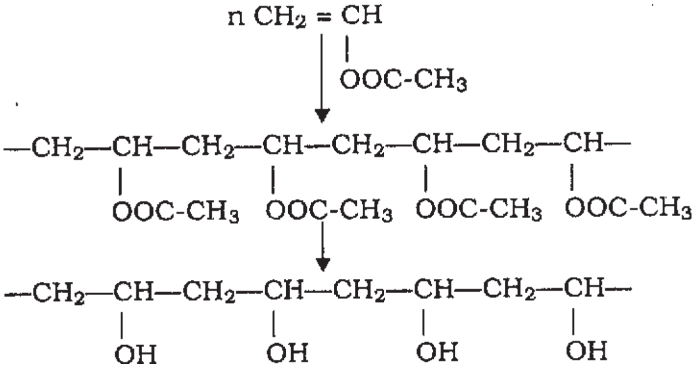


Table 10.2
Finishing Recipes With Polyvinyl Acetate Dispersion

Compound	Pad liquid composition, g/l Stiff finish on cotton voile	Light finish on cotton poplin	Multiple finish on cotton poplin	Buckram finish on cotton
1. Polyvinyl acetate dispersion	5-10	2-5	5-20	200-400
2. Cationic softener	-	2	-	-
3. Wax emulsion	-	-	5-10	-
4. Starch/dextrin	-	-	5-10	-

	Durable finishes Viscose Rayon	Cotton poplin	Nylon	Nylon georgette
1. Polyvinyl acetate dispersion	5-10	5-10	20	30
2. DMU (U-F pre condensate)	100-150	-	60	-
3. Catalyst	6*	20**	10***	-
4. Cationic	10-20	20	-	-
5. DMEU	-	100-150	-	-

*Diammonium phosphate, **Magnesium chloride hexahydrate and ***Ammonium chloride.

In another method (FIAT 860), the polyvinyl acetate is first prepared by charging 5.4 kg. of benzoyl peroxide and 100 kg. of vinyl acetate into an aluminium vessel (40 gallon capacity) provided with a water jacked and an anchor-type agitator, and dissolved by stirring at 20º-25ºC. Benzoyl peroxide is available as a 70% solution and the water separates as a layer while dissolving, as lower layer, carrying with it the coloured impurities. After separating the water layer, the solution is filtered under nitrogen pressure into another vessel (200 gallon capacity) provided with aluminium cooling coil and a paddle agitator, where is mixed with 500 kg. vinyl acetate and 3 kg. ethyl acetate. The temperature of contents should not be more then 28ºC. Then 800 1 of distilled water and 1.2 kg. of styrene-maleic acid copolymer (1:1 mole ratio) as ammonium salt are charged into a steam-jacketed, enamel-lined iron vessel (3 cu.m. capacity) with an anchor type agitator (the arms of which extend almost to the top of the pan and rotating at 40 rpm) and heated to 80ºC. The monomer solution is added to this vessel at the rate of 400 1/hour until about 1/3rd of it has been charged and then the rate is reduced to 300 1/hour. The temperature of the mixture falls to 65ºC, but when nearly half of the monomer has been added polymerization starts and the temperature rises to 85ºC. The reaction is controlled by variation in the rate of monomer addition to keep the temperature at 85ºC without the reflux.

Polymerization is carried out in a nitrogen atmosphere. When all the monomer has been added and the rate of reflux begins to slow down, heating is started and the temperature raised to 93ºC where it is held for 15 min. The reaction mixture is blown under nitrogen pressure into an iron vessel (3 cu.m. capacity) coated on the inside with Bakelite resin and jacketed for cooling with brine. The contents are cooled to 0º-5ºC. first by cold water in the jacket and then by brine. The polymer beads are separated by centrifuging in a basket-type of centrifuge, where they are washed thoroughly with distilled water at 10ºC.

The beads are transferred to racks of aluminium trays in a dryer (forced circulation of warm air). For the first 30 hours, the drying is done at 20º-25ºC, the temperature is then raised to 35ºC and held until the moisture content is 1% (estimated by the oven method – 2 hours at 105ºC). The total drying time is 36-48 hours, during which the polymer beads sinter together and the sintered mass is broken and turned over by hand once or twice during the drying process. They are discharged from the drying trays through a disintegrator and are thoroughly mixed up in a batch blender (stainless steel).

In the second stage (hydrolysis), 1200 kg. of a mixture of methanol and methyl acetate (40-50% methanol) and 12 kg. of 98% sulphuric acid are charged into an enamelled iron vessel (3 cu.m. capacity), jacketed for steam heating and fitted with anchor-type agitator, having a shaft 80 mm diameter driven at 40 rpm by 9.4 KW motor. 300 kg. of the polyvinyl acetate beads from the blender (describe above) are added to the iron vessel containing the methanol-methyl acetate mixture, which is then heated to reflux under nitrogen atmosphere (to avoid fire and explosion hazards) for 48 hours. Initially a clear solution is obtained, but after 10-16 hours, it becomes cloudy and precipitation of polyvinyl alcohol starts. During the early stage of precipitation, the viscosity of the reaction mixture rises considerably and the power consumption on the agitator motor rises from 8 amp. To 20 amp. The end point is determined by withdrawing a sample of the liquor and testing whether any precipitation occurs on addition of an equal volume of either water or ether.

When the test sample shows hydrolysis to be complete, the reaction mixture is blown under nitrogen pressure to a Buna-lined vessel (3 cu.m.) jacketed for cooling with water and fitted with Buna-covered agitator. The bottom run-off valve to a Buna-covered centrifuge is operated by means of water under 40 atm. pressure. The mixture is cooled in the jacketed vessel to 20ºC. Polyvinyl alcohol is separated from the mother liquor by running to the centrifuge. Polyvinyl alcohol cake is washed on the centrifuge with 300 kg. of methanol. Polyvinyl alcohol cake is discharged from the centrifuge into trolleys-sufficient soda ash added to neutralise the product to pH 7-7.3 (the amount of soda ash required being calculated from the pH of a solution of 1 g of the product in 40 ml. of water).

Drying of polyvinyl alcohol is done in a rotary dryer for 12-14 hours at 100-200 mm pressure at 40º-50ºC, 400 kg. being dried at a time. The methanol-methyl acetate vapours from the dryer are recovered by passing them through condensers on both the suction and the compression sides of the vacuum pumps, the condensers being cooled to –12º to –15ºC by calcium chloride solution.

After drying, the polyvinyl alcohol falls from the bottom of the dryer into a storage bunker, from where it can be sieved through mechanical sieve into sales packages.

Polyvinyl alcohol has a unique combination of useful properties such as water solubility, film, forming capacity, solvent resistance, adhesive binding properties, gas impermeability of its films, emulsifying ability etc. and because of this, it finds extensive use in sizing and finishing.

Polyvinyl acetate is insoluble in water, but when the acetate groups are converted into hydroxy groups the polymer dissolves in water. However, it is not necessary to effect 100% conversion of the acetate groups to confer water solubility on the polymer. Commercially, a product with 87-89% conversion is available as a partially hydrolyzed grade (PH grade) of polyvinyl alcohol. Another product, fully hydrolyzed grade (FH grade) with 98-99% conversion is also available. Depending on the degree of polymerization of polyvinyl acetate, from which polyvinyl alcohol is made, these products (PH and FH grades) have different viscosities (high, medium and low viscosity).

In the fully hydrolyzed grade, with plenty of hydroxy groups, a large number of hydrogen bonds are formed between the adjacent molecules of polyvinyl alcohol. During the actual dissolution in water, the hydrogen bonds should be broken and reformation of these bonds prevented. Water molecules are capable of breaking these bonds and of forming hydrogen bonds with the hydroxy groups of polyvinyl alcohol. In the partially hydrolyzed grade, there are less hydrogen bonds (11-13% acetate groups are still present) and therefore cold water is able to break them. Hence this grade is soluble in cold water (this is called cold water soluble grade). On the other hand, cold water is not able to break all the hydrogen bonds present in the fully hydrolyzed grade. However, if heat is applied (i.e., when hot water is used), hot water is able to break the hydrogen bonds and dissolve it (this is called hot water soluble grade). Therefore, FH grade needs hot or boiling water to dissolve but PH grade dissolves in cold water, but in dissolves in hot or boiling more easily.

Polyvinyl alcohol is characterised by the viscosity of its solution in water. Generally, polyvinyl alcohols are marketed in three molecule weight ranges (high viscosity, medium viscosity and low viscosity polyvinyl alcohols). The average molecular weight of these types are as follows –

High viscosity	170,000-220,000
Medium viscosity	120,000-135,000
Low viscosity	30,000-35,000

High viscosity polyvinyl alcohol exhibits minimum water sensitivity; lower the degree of polymerisation, greater is the water sensitivity. Similarly, tensile strength, tear strength, elongation and flexibility of polyvinyl alcohol films are better in high and medium viscosity ranges than in low viscosity ranges.

Typical samples of polyvinyl alcohol are available as white-to-cream coloured powder, with a density of 1.27-1.31 g/cc and a refractive index of 1.49-1.53. Its specific heat is 0.4 cal/g/deg. C. Polyvinyl alcohol film is flammable. The viscosity of polyvinyl alcohol solution is reduced by treatment with potassium permanganate, potassium dichromate or hydrogen peroxide.

For the preparation of solution of polyvinyl alcohol in water, a high speed stirrer is needed. A suitable vessel is filled with the required volume of water and stirring started. Polyvinyl alcohol powder is directly added into the vortex, when it gets wetted out and is dispersed rapidly to produce a slurry. The contents are stirred for 10 min. more and then heated to 90ºC or higher, while continuing the stirring. The mixture is stirred till complete solution is obtained. A solution of polyvinyl alcohol can be prepared at 10-15% concentration. Higher than 15% concentration is not possible at atmospheric pressure.

Water is the only practical solvent for polyvinyl alcohol. Substantial amounts of lower aliphatic alcohols (methyl, ethyl, isopropyl etc.) can be added to aqueous solutions of polyvinyl alcohol without the danger of precipitation. The extent of toleration for organic solvent which could be safely added increases as the per cent hydrolysis of polyvinyl acetate decrease. When the amount of the organic solvent added exceeds the toleration limit, a part of the dissolved polyvinyl alcohol gets precipitated. A number of inorganic and organic compounds such as sodium chloride, sulphate, nitrate, potassium chloride, b-naphthol, resorcinol etc. cause gelling or precipitation of polyvinyl alcohol from aqueous solution, even when added in low concentrations. Sodium carbonate is a very effective precipitating agent and borax causes gelling instead of precipitation.

IDENTIFICATION OF POLYVINYL ALCOHOL

When polyvinyl alcohol solution is treated with boric acid and concentrated sulphuric acid in a test tube, a green colour is produced.

In another test, the blue colour produced when polyvinyl alcohol reacts with iodine in the presence of boric acid is used to identify polyvinyl alcohol when present on a fabric. For conducting this test, several drops of distilled water are placed on the cloth. A drop of N/100 iodine solution and one or two crystals of boric acid are placed on the wetted portion of the cloth. A pastel blue that first appears at the boric acid crystal and grows from it indicates the presence of polyvinyl alcohol. A dull blue colour over the wet area indicates the presence of starch and strong reddish brown colour indicates the presence of polyvinyl acetate.

POLYVINYL ALCOHOL IN SIZING

Because of its high tensile strength, abrasion resistance, adhesion and flexibility, coupled with water-solubility, polyvinyl alcohol is an ideal sizing material for warp yarns of cotton and synthetic fibres and their blends. The size is readily applied by the conventional methods (slashing, skein and single thread) to the filament and spun yarn, including synthetic fibres such as polyamide, polyester etc. In warp sizing, polyvinyl alcohol produces a colourless flexible film and penetrates thev yarn and imparts reduced resiliency and other physical properties needed during the weaving and knitting operations. Fully hydrolyzed, high viscosity polyvinyl alcohol is very effective as a size for cotton, polyester and their blends.

Fully hydrolyzed grade of polyvinyl alcohol is an effective size for cotton. It is much superior to starch as it has a very low biochemical oxygen demand (BOD), can be incorporated readily in size formulations and does not require enzyme desizing. This grade of polyvinyl alcohol gives a superior performance at a relatively low size pick-up.

Sizing problems encountered in the hardening of polyester spun yarn differ somewhat from those met with in the weaving of cotton. Polyester fibre is hydrophobic in nature and the staple yarn prepared with this fibre has a fuzzy appearance. Such yarn has a pronounced tendency to shed fibres readily and also to felt during weaving.

Fully hydrolyzed polyvinyl alcohol along with glycerine is very useful as a warp size for polyester/cotton (67/33) blend, also for polyester/viscose rayon and for nylon yarn used in knitting.

Polyvinyl alcohol in textile finishing

Polyvinyl alcohol finds use in textile finishing process. Fully hydrolyzed grade can be used in conjunction with resin pre-condensates and crosslinking agents on cellulosic fibre fabrics. The resins require the addition of 5-15% polyvinyl alcohol on the weight of the resin to improve the handle and drape. The finish produced is permanent and becomes fast to washing as polyvinyl alcohol is fixed by chemical reaction with the resin.

WAX EMULSIONS

Vegetable for animal waxes are mixtures of esters of fatty acids and fatty alcohols. When waxes, like paraffin wax, bees wax, carnauba wax, etc., are applied from an emulsion form on textile materials, they impart a soft and supple handle to the materials. They also impart gloss to the objects treated with them.

Stabilized paraffin wax emulsions, having softening and finishing properties for cotton and rayon fabrics, are available. They are marketed as smooth, uniform and white emulsions, which give stable emulsion on dilution with water. The diluted emulsions are stable to alkali and hard water salts. The emulsion is anionic in character. They are compatible with starches, CMC, glue, gelatine, gums etc. When applied alone, the wax emulsions impart a soft and supple handle to the fabrics. The material to be treated may be steeped or padded with 1-5 g/l of the wax emulsion and dried without washing. If the fabric is calendered subsequently, it acquires lustre.

In the actual preparation of the pad liquor, the wax emulsion is diluted with 3-4 times its weight of water at 40º-50ºC with stirring. The smooth cream, thus produced, may be diluted to the desired concentration with cold water.

When cotton or rayon fabrics are finished with starch and other stiffening agents, the wax emulsions may be used as softening agents to counteract the brittleness of the film of the stiffening agent. For this purpose, 5-15% (on the weight of the material) of the wax emulsion may be used.

When wax emulsions are used in sizing mixtures, the diluted emulsions should be added to the size mix after the latter has been boiled. Generally 10-20% (on the weight of the adhesive used) of the wax emulsion is recommended.

Wax emulsions can be used as binding agents for China clay in combined dulling and weighting of rayon. The following recipe may be used for the purpose.

China clay	30 g
Wax emulsion	20 g
Glycerine	5 g
Water	945 g
Total	1 kg

The China clay is first boiled with 200 g water. Glycerine is mixed with 30 g water. Both these are mixed, stirred for 30 min. and finally the wax emulsion diluted with 30 g water at 50º-60ºC added and the whole stirred for 1 hour. The mixture may then be diluted to the required concentration and applied to the fabric by padding at about 50ºC and dried.

In order to produce water-proofing effects on cotton, linen, wool, silk and other fabrics, the wax emulsion may be used in conjunction with aluminium acetate. Two baths are prepared separately as follows:-

First bath

Wax emulsion	1-3 kg.
Water	50 litre

Second bath

Aluminium acetate (12º Tw)	1-3 litres
Water	50 litres

The fabric is impregnated with the first bath and after squeezing, it is entered in the wet state in the second bath. The fabric is squeezed and dried at 100º-120ºC (on a stenter or a drying cylinder).

The two-bath method of making fabrics water-repellent involving the use of wax emulsion and aluminium acetate is along procedure. In order to shorten the process, a single bath process has been developed, in which an emulsion of wax and aluminium stearate (aluminium soap) is used to obtain the desired effect. These emulsions are available in the form of a thin cream, which may gel on prolonged storage. However, the gel can be readily dispersed in water without decreasing its efficiency.

The emulsions are readily dispersible in water. the resulting dispersions are stable to hard water, dilute acids and dilute solutions of acidic salts. The emulsions break under alkaline conditions. Hence, the fabrics to be treated with these emulsions should be properly washed free of any alkali; the final rinse may even contain dilute acetic acid. The emulsion is not compatible with anionic products like detergents, wetting agents etc.

The emulsions may be diluted by thoroughly mixing them with equal quantity of water at 50º-70ºC and then adding not water with stirring. The diluted emulsion may be applied by padding or in a jigger. In the former, the cloth is padded with the diluted emulsions and dried on cylinder dryer or a stenter. The temperature of drying should be at least 100ºC. In the jigger application, the cloth is given 6-8 ends in the jigger in the open width and dried on a cylinder dryer or a stenter. A concentration of 5-8% (owf) may be sufficient to get good results.

A typical recipe for the application of the emulsion is given below:-

> The emulsion (5-10 kg.) is added to 20 litres of water at 50º-70ºC with stirring and poured into 80 litres of water a 80ºC.

For 50 kg. of the cloth 150-200 litres of the diluted emulsion may be used in a jigger, giving 6-8 ends, followed by squeezing and drying on a cylinder dryer cylinder dryer. the dried cloth may again be passed around the drying cylinder and plaincalendered to close up the interstices of the cloth and thus improve the penetration of water through the cloth.

In water-repellent finishing, the individual fibres present in the fabric are coated with a continuous water-impermeable film, without at the same time binding the fibres to each other or blocking the interstices of the fabric. The chemicals must be tough, pliable and elastic and must adhere to the fibres firmly. These hydrophobic film-forming substances include acetate and soaps of aluminium and zirconium, ammonium zirconyl carbonate, paraffin wax, microcrystalline waxes, methylol stearamide, stearamidoethyl pyridinium chloride etc.

Water-repellent finishes are produced usually by the pad-dry technique. Where the finishing agent is cation-active, exhaustion processes (jigger application or winch application) are employed, since the positively charged ions of the water-repellent are easily attracted and held by the negatively charged fibre surface in an aqueous medium. In either case, the penetration of the solution into the fabric is important, since the main objective is to coat the individual fibres present in the fabric.

Certain reactive softeners and curing on fabrics in the presence of magnesium chloride or ammonium dihydrogen phosphate impart water-repellency to cellulosic fibre fabrics, in addition to softness and lubrication. However, strength losses to occur during curing at elevated temperatures in the presence of acidic catalyst. However, these strength losses may be minimized, when the reactive softener is applied along with resin precondensates, which also need curing at elevated temperatures in the presence of acidic catalyst. Thus, softness, lubrication, water-repellency and crease resistance can be given to the fabrics from a single bath.

Even though many man-made fibres are essentially hydrophobic in nature, they do need a treatment with suitable water-repellent compounds. A compound which works well on natural fibres may not work on synthetic fibres. Other types of water-repellent finishes have been found to be successful on synthetic fibre fabrics. These withstand several mild washings. These include zirconium-type pyridinium compounds, melamine amide compounds, urea-amide compounds, melamine-hydrophobe condensates, silicones and fluorocarbons. They produce excellent results on man-made fibres. Silicone compounds have certain advantages such as durability to several launderings and drycleanings, increased abrasion resistance, no loss of strength, ease of application by conventional methods (pad-dry-cure), compatibility with resin precondensates, etc. Organo-metallic catalysts like lead octoate, zinc acetate etc. are used in the padding liquors, along with diluted silicone emulsions. The catalysts operate during the curing step.

CARBOHYDRATES

Polysaccharides (glycans) are an important group of natural polymers, finding varied uses in textile processing. They are condensation polymers of sugars ($C_{12}H_{22}O_{11}$) produced in nature through the agency of enzymes and hence are specific polymers. These are divided into two groups- (a) homoglycans, formed from one sugar only, and (b) heteroglycans, formed from more than one sugar. Thus, cellulose (cellobiose), amylose and amylopectin components of starch (maltose), etc., are homoglycans, whereas guar rum (mannose and galactose), gum arabic (galactose, rhamnose, glucose and arabinose), gum karaya (galactose and rhamnose), gum tragacanth (galactose, fructose, xylose, and arabinose), alginic acid (mannose and glucose) etc. are heteroglycans.

A typical aldohexose (*b*-glucose) contains four secondary hydroxy groups, one primary hydroxy group and one aldehyde group (Fig. 10.2). The end aldehyde group reacts with the hydroxy group attached to the 5-carbon atom forming a hemiacetal group and giving a ring structure. The hydroxy group at the hemiacetal group and the hydroxy group at the 4-carbon atom of another molecule of b–glucose undergo condensation in the presence of an enzyme, linking two b–glucose molecules with the elimination of one molecule of water.

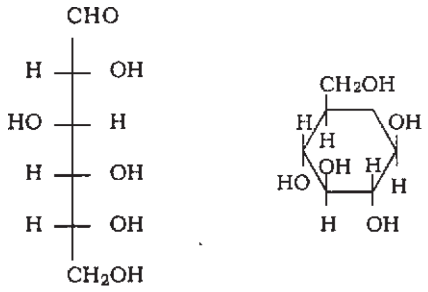


Fig. 10. 2 Glucose (open structure and ring structure)

The resulting product is cellobiose. This further under-goes self-condensation, ultimately forming cellulose. Natural polymers like starches and gums are thus formed from various hexoses. Glucose first forms maltose and then starch. In the case of guar gum, there is a polymannose chain, with galactose attached to every alternate mannose unit through C_6-C_1 linkage. Locust bean gum is also made from polymannose with galactose added to every fourth mannose unit. Thus, both are galactomannan.

All these polyhexoses have an abundance of hydroxy group (primary or secondary hydroxy group), some of which are hydrogen-bonded (inter-molecular hydrogen bonding), whereas others are free, due to which these compounds have great affinity for water (water molecules can get hydrogen-bonded with these free hydroxy groups). When polysaccharides are added to water, they initially swell and finally produce colloidal solutions and not true solutions, since they have high molecular weight. (Some of the gums have a molecular weight of about 10,000,000). They can bind large quantities of water and can produce viscous solutions even when present in low concentrations.

Generally, polysaccharides of high molecular weight and linear molecules produce colloidal solutions of high viscosity. On the other hand, completely linear structures (cellulose) tend to get hydrogen-bonded with the production of crystalline regions of varying degrees. Such polymers are insoluble in water and need chemical modification to dissolve them in water. Polysaccharides with highly branched chains produce mobile solutions, in spite of their high molecular weight. The presence of the branches moves the adjacent polymer molecules apart and since hydrogen bonding is a short-distance-acting force, the hydroxy groups of the adjacent macromolecules do not get hydrogen-bonded and remain free. When such polymers are added to water, these free hydroxy groups get hydrogen-bonded easily with water. In the case of cellulose, which is insoluble in water, when it is carboxymethylated by treatment with monochloroacetate under alkaline conditions, the resulting product has a bulky side chain (carboxymethyl) attached to the cellulose molecule (Fig. 10.3). The very presence of this side chain pushes the adjacent molecules apart preventing hydrogen-bond-formation in the vicinity of the carboxymethyl group. Secondly, carboxymethyl group is a water solubilizing group. Both these factors make carboxymethyl cellulose (CMC) soluble in water, producing viscose solutions, which find use in sizing, printing and finishing.

These are available in low, medium and high viscosity grades. Generally, 2% aqueous solutions of these grades have viscosities of 25 to 50,300 to 600 and 1,300 to 32,000 cPs respectively.

Generally, CMC contains 0.75 carboxymethyl group per anhydro-glucose unit of cellulose. It scorches at 226ºC to 228ºC and chars at 252ºC.

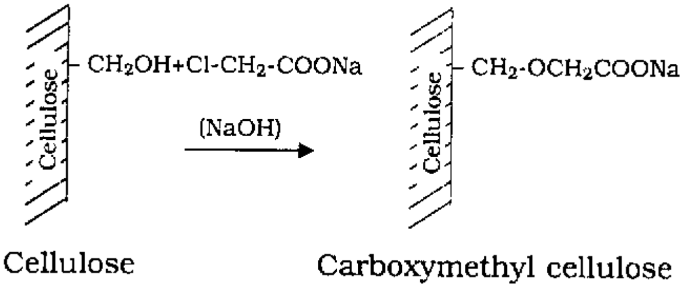


Fig. 10.3: Carboxymethylation of cellulose

CMC (sodium salt) gives clear viscous solutions, which have marked suspending, stabilizing and film-forming properties. Ultraviolet light has no appreciable embrittling or discolouring effect on CMC. Aqueous solutions of CMC become less viscose on heating, but regain their viscosity on cooling. Some electrolytes like barium nitrate, calcium chloride and manganous sulphate do not precipitate CMC from its solutions, but others such as aluminium sulphate, barium chloride, ferric chloride and ferrous sulphate cause precipitation. Carboxymethyl cellulose is a weak acid is precipitated from its sodium salt solutions by strong acids like hydrochloric acid but not by weak acids like citric, tartaric, acetic and tannic acids.

CMC is compatible with other water-soluble gums, like gum arabic, gum tragacanth, locust bean gum, starch, sodium alginate etc. It can be used with a wide range of dyes. It produces sharp prints at high machine speeds. It may be used in printing vat, solubilized vat and azoic colours. It is easily washed off from the fabric after fixing the dye.

METHYL CELLULOSE

Cellulose ethers (methyl, ethyl etc.) can be prepared by first reacting cellulose with concentrated sodium hydroxide solution and then with alkyl halide. Methyl cellulose is prepared as follows:

Methylation should be carried out to 25% methoxy content equivalent to 1.5 OCH_3 groups per glucose unit of cellulose in order to impart water solubility to the final product. If the degree of methylation is high, alkali is needed to dissolve it. Very highly methylated cellulose is insoluble in water, but soluble in organic solvents.

$$\begin{array}{l} \text{Cell-OH} \\ \text{(cellulose)} \\ \quad\big\downarrow \text{(NaOH)} \\ \text{Cell-ONa} \\ \quad\big\downarrow (CH_3Cl) \\ \text{Cell-}OCH_3 \\ \text{(Methyl cellulose)} \end{array}$$

Methyl cellulose is marketed in the loose fibrous state under various trade names such as Methocel, Celacol, Cellofas etc.

In order to protect it from degradation by microorganism, some preservatives may be added. Methyl cellulose is soluble in cold water, but not in hot water (above 50ºC). At higher temperature, the solution gels. Addition of thiocyanate and iodides raise the gelling temperature of solutions of methyl cellulose.

Methyl cellulose is not soluble in organic solvents, like acetone, benzene, alcohol etc., but is compatible with diethylene glycol, glycerine, sorbitol, casein and water, dispersible natural gums. Addition of these gums increases the viscosity and raises and gelling temperature.

Aqueous solutions of methyl cellulose on drying give tough, clear, non-hygroscopic and elastic films, which can be made water-resistant by treatment with urea-formaldehyde, glyoxal or tannins.

In screen or roller printing azoic colours, it does not dull the prints and its film does not crack.

Methyl cellulose is dissolved by first mixing with 20 to 25% of the required quantity of water, heated to 80º to 90ºC and allowed to swell for a short time. Then, the rest of the water (cold) is added and the whole mass stirred till a smooth and homogeneous paste is obtained. Usually 60% methyl cellulose gives a workable paste.

Being nonionic in nature, it is not salted out by the addition of electrolytes. It is stable under alkaline conditions in the absence of oxygen, but loses its viscosity in the presence of alkali and oxygen. Methyl cellulose can be used along with starch in printing vat, azoic, Rapid Fast, Rapidogen and direct dyes.

Solubility in cold water makes methyl cellulose an ideal thickener in textile printing from the point of view of ease of removal from the fabric after the fixation of the dye.

Hydroxyethyl cellulose

When soda cellulose (made by treating cellulose with concentrated sodium hydroxide solution) is reacted with ethylene chlorohydrin, hydroxyethyl cellulose (also called glycol cellulose) is formed.

$$\begin{array}{l}\text{Cell-OH} \\ \text{(cellulose)} \\ \quad\downarrow \text{(NaOH)} \\ \text{Cell-ONa} \\ \quad\downarrow (\text{Cl-CH}_2\text{-CH}_2\text{-OH}) \\ \text{Cell-O-CH}_2\text{-CH}_2\text{-OH} \\ \text{Hydroxyethyl Cellulose}\end{array}$$

This product is soluble in water to give transluscent solutions, which on drying on textile material, give clear transparent films and find use in sizing, dyeing, printing and finishing. It is compatible with solutions of other ingredients like starches, gelatine, gum arabic, gum tragacanth, dextrin, CMC etc. It is partly compatible with methyl cellulose and polyvinyl alcohol. Aqueous solutions of hydroxyethyl cellulose tolerate 105 to 15% of methyl, ethyl and propyl alcohols and acetone and up to 20% methyl acetate. The thickening power (viscosity) of aqueous solutions of hydroxyethyl cellulose is compared with that of some other thickening agents.

Solutions of hydroxyethyl cellulose on drying give films, which are stable to heat and light and are soluble in water, but not in organic solvents. Low molecular weight polyhydroxy compounds and acetic and formic acids dissolve the film with difficulty. The film flexibility increases with moisture content. The film does not become tacky, neither does it dust off and does not build static charges.

The films of hydroxyethyl cellulose can be made partially water-resistant by adding 6% of 30% aqueous glyoxal solution to is before drying at 105ºC. Urea-formaldehyde or melamine-formaldehyde pre-condensates may be used to make it water-resistant by adding a plasticizer (10 to 50%) such as polyhydric alcohol (ethylene glycol, diethylene glycol, polyethylene glycol, glycerine etc.) and sulphated castor oil.

In printing it performs better than gum tragacanth or gum arabic by way of facilitating good penetration and promoting the production of sharply outlined patterns. The printed fabrics acquire a soft hand.

GUAR GUM

In guar gum (Polygalactomannan), the galactose units on the every alternate mannose unit of polymannose acts as the pendent group, leaving many hydroxy groups free. When added to water, guar gum forms a colloidal solution. However, hydration of the free hydroxy groups takes time and solution properties can be improved considerably by adding further pendent groups. So guar gum is chemically modified by carboxymethylation, carboxyethy-lation, hydroxyethylation (Fig. 10.4) hydroxypropylation (Fig. 10.5) etc. the first two modifications give ionic polymers, while the other two produce nonionic polymers. Both are extensively used in printing as thickeners, especially in polyester and nylon printing.

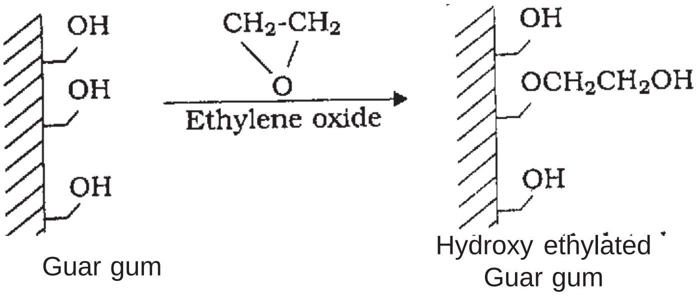


Fig. 10.4: Production of hydroxy ethylated guar gum

PRINTING THICKENERS

Thickeners used in textile printing are high molecular weight compounds giving viscous pastes in water. These impart stickiness and plasticity to the printing paste so that it can be applied to a fabric surface without spreading and be capable of maintaining the design outlines even under high pressure. Their main function is to hold or adhere the dye particles in the desired place on the fabric until the transfer of the dye into the fabric and its fixation are complete. As the printing paste is printed either by roller or screen by the squeegee pressure, the viscosity of the printing paste should be sufficiently high to prevent rapid diffusion or flushing of the colour through the fabric, which would result in poor print definition or mark. Further, the thickener should give a stable paste viscosity, which would allow an even and measured flow through the screen. If the viscosity changes during the run, the shade (depth) changes in the printed cloth. The viscosity stability must not only be durable in terms of the time, during which the printed cloth on the machine, but it must also hold during storage times in terms of weeks/months. Generally it is necessary to have a large volume of stock paste of the thickener of such viscosity (higher than that of the printing paste) that on dilution with the proper amount of the dye, chemicals and water, that will bring it to the desired printing viscosity. The viscosity should not change extra-ordinarily by the addition of dyes and chemicals. Thus, the thickeners should perform its function over a wide range of physical and chemical conditions.

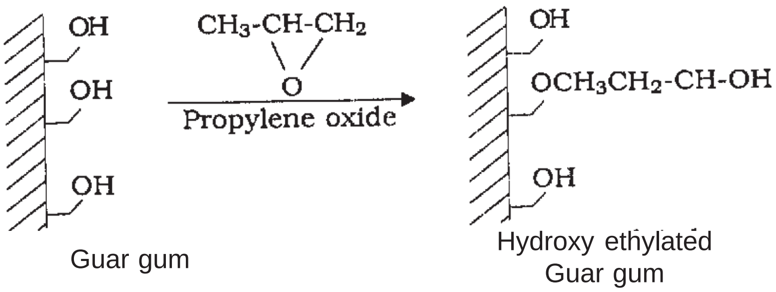


Fig. 10.5: Production of hydroxy propylated guar gum

In rotary screen printing especially in carpet printing where relatively low viscosities are used to get good penetration in the fibre substances, a pseudo-plastic printing paste is particularly effective. Due to this, the viscosity drops as the shearing action of the squeegee is applied and a rise in viscosity after the shearing stress is released takes place.

Before the fixation of the dye by steaming, the thickener film deposited on the fabric surface should not be dried quickly with too much heat as this causes excessive surface colour mark off. One of the functions of the thickener is to prevent the migration of this colour to the surface through viscosity and the adhesive nature of the thickener solid present. The thickener film must not be brittle or flake off during drying and subsequent handling; otherwise, scattered flakes of the thickeners film cause coloured speeks all over the cloth during steaming. In addition, it must not react or precipitate by the action of various dyes and chemicals which are added to the printing paste.

The total solids content of the printing paste is important for producing good prints under different conditions in the limited period of time, especially while printing lightweight materials. In such cases, thickeners of high solids content should be used to safeguard against bleeding and to retain the sharpness of the print.

The thickener must maintain the print sharpness (prevent spreading of the colour beyond the boundaries of the design till steaming or curing is completed to effect dye fixation). During steaming, the adhesive nature of the thickener holds the dye particles, while the fabric becomes saturated with steam and the chemical reactions take place, giving the dye its fastness properties, while the whole system is exposed to the conditions of high temperature, moisture and time. The presence of sufficient amount of the thickener is a necessity, if good mark or definition of a pattern is to be maintained throughout the steaming operation, especially in fine line patterns in deep shades.

Another requirement of the thickener is the ease of removal after steaming by an afterwash. The residual dye and products of decomposition of dyes and chemicals have to be removed from the fabric without staining the ground or areas printed with other colours.

The essential quantities of a thickener may be summarised as follows:-

(1) Stability to keeping (physico-chemical stability) should be good. Aqueous dispersion/pastes of high molecular weight thickeners (carbohydrates) may undergo fractional crystallization on standing, upsetting the flow property and concentration of the dye in the printing paste, leading to the interference with the regular distribution of the dye.

(2) It should have certain physical and chemical properties such as viscosity, flow property, ability to wet and adhere to the internal surface of etchings of the engraved roller. The flow property must be such that the print paste should remain into the engravings for a short time. It should not

adhere to these engravings too fast, so as to allow transfer of the paste of the fabric.

(3) It must be compatible with the other ingredients of the printing paste, e.g., compounds such as oxidizing and reducing agents, electrolytes, dispersing and wetting agents, solvents, hygroscopic substances, acids and alkalies.

(4) The thickener film should dry properly on the fabric to prevent spreading of the colour by capillary action beyond the boundaries of the design (to ensure print sharpness).

(5) Proper extraction of water from steam during steaming should be ensured to provide free space for the dye molecules to move towards the fabric and the free water to carry it.

(6) The thickener should not have affinity for the dye and should not keep the dye from the fabric.

(7) The thickener molecule should have a control over the free water pickup and should not carry the dye beyond the boundaries of the impression (flushing).

(8) Once the dye is transferred from the thickener film (during steaming), the removal of the exhausted thickener film without fetching water-soluble dye should be easy.

(9) The thickener should be cheap and available in abundance.

Proper selection of the thickener is important in polyester printing. This depends on the whether screen or roller printing is employed and also on the method of fixation of the dye. The kinds of fabric also influence the thickener choice. Suitable thickener should have the following properties:-

The thickener film should adhere well to the fabric, should produce an elastic film to prevent cracking, splintering and dusting off. Level prints with sharp outlines should be produced. The thickener must be easily removable in the after-treatment. thickenings with a high solids content bring less water on to the hydrophobic fabric and produce sharper and more level prints than those with low solids content. The dry film is less elastic, and splinters more easily. Thickenings with low solids content behave better with respect to splintering and in thermosol process better colour yield is obtained with such thickenings, but the sharpness of prints is not as good as with high solids content thickenings. In roller printing the sensitivity of the thickener film to crushing is important. Thickeners with high solids content are less sensitive to crushing.

Natural gums, starch ethers, and modified locust bean gums, Gum Indalca are the commonly used thickeners. Sodium alginate is less suitable, since it impairs the brightness of the print with disperse dyes, especially in the thermosol process.

None of these is ideal for polyester printing, when used alone. A combination of thickeners should be used. With natural thickeners sharp prints are obtained and the dried thickener film is relatively elastic. If blotches are printed using these thickeners, levelness is no satisfactory. Prints with CMC are normally level and sharp and have good yield, clarity and brightness. If carboxymethylation of cellulose (from which CMC is made) is not proper, some insoluble particles may remain, which clog the screen.

Starch ethers have been most successfully used in polyester printing, but their wash off properties are not good. Therefore, starch ethers are mixed with locust bean gum, which produce dull prints with poor colour yield when used alone.

Emulsion thickenings are helpful since mineral spirits (used in emulsion thickenings) are excellent wetting agent for hydrophobic fibres. These thickenings increase levelness and penetration of the dye in the fibres. They minimize the colour transfer in roller printing and reduce screen frame marks in screen printing. With hot air fixation, full emulsions (without conventional types of thickening agents) are of advantage, since complete fixation of the dye can be achieved.

Thickenings of reducing nature (British gum) produce dull prints. Addition of Ludigol (1 to 2%) to the print paste prevents shade changes during fixation. Addition of suitable carriers to the print paste can drastically increase the colour yield, but different dyes behave differently towards carriers. P-Phenyl phenol is the most suitable carrier in ageing processes. In thermosol fixation, Luprintan ATP (BASF) may be used.

When polyester/cellulosic fibre blend is printed with disperse/vat dyes, good colour yield and good overall fastness can be obtained with a proper selection of the dyes.

Cold-water-swelling gums are the preferred thickeners. In flash ageing, a thickeners, which coagulates in contact with alkali, is used to preserve print sharpness and to prevent flushing. In thermosoling, only those dyes having high sublimation fastness should be used. Staining of the cotton component can be removed (by reduction clear) during the fixing of the vat dye if the disperse dye used belongs to the azo class but not to anthraquinonoid class. Selection of vat dyes for the cellulosic component is much simpler than that of disperse dyes.

The thickeners used in vat printing, the cotton component include cooked starches, cold-water-soluble starch derivatives, gum tragacanth, gum karaya, dextrine etc. However, other thickeners can be used with the resultant lower colour yields-e.g., alginate, locust bean gum guar gum, CMC hydroxyethyl cellulose, etc.

The mixture of disperse and vat dyes may be printed by screen or roller printing and the cloth dried. It is then thermosoled for 90 sec., 205º to 220ºC. This fixes the disperse dye on the polyester component. Migration of the disperse dye from cellulosic to polyester fibres also takes place.

Chemical padding, followed by flash ageing are the next steps. The pad liquor may contain

80 g Sodium hydroxide (50% solution)
50 g Sodium carbonate
10 g Flotex 18
50 g Sodium hydrosulphite

---

1 litre

Thickeners used in polyamide printing are numerous. Crystal gums produce prints of good colour value and excellent definition and may be easily washed off. These thickeners have relatively little effect on solvents and fixing agents as far as flocculation, coagulation and gelling are concerned. However, they have the drawback that blotches dried in a hot air chamber, become brittle. They may also cause fibre damage if over-dried. This tendency may be overcome by adding low viscosity sodium alginate, starch ethers, etherified locust bean gums, etc. Alginate thickeners produce soft prints and the thickeners are easy to wash off. Some acid azo dyes give lower colour value with alginate but metal-complex dyes produce prints of full colour value. A few metal-complex dyes coagulate alginate thickening, but because a large number of dyes are available for printing on polyamide fibres, these dyes may be omitted. In general, low viscosity alginates print best on hard fabrics like taffetas, whereas low or high viscosity alginates can be successfully used on spun and knitted materials.

Modified locust bean gums print well and do not become brittle when dried. On some weaves, the colour is likely to spread, which may be overcome by adding another thickener. British gumsproduce prints of good colour value and the pastes are not coagulated by solvents and fixing agents. The prints can become quite crips on drying and even after washing, they may be harsh. Emulsion thickenings produce prints of good sharpness, which wash easily, but often give poor colour value, since penetration is usually very good. The print are soft even before washing thus eliminating ovendrying. Care should be taken in the preparation of the printing paste to ensure stability, electrolytes, used as fixing agents.

SOLUTION AIDS

Cellosolve glycol monoethyl ether, $HO – CH_2 – CH_2 – O – H_2H_5$, is completely miscible with water and has a specific gravity of 0.935 and a boiling point of 135ºC. It is useful in printing vat and azoic colours for increasing the solubility of the dyes, so that deeper and better penetrated prints are obtained.

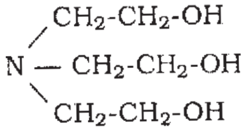
Tetraethanolamine ammonium hydroxide (40% solution in aqueous methanol) is a clear amber coloured, slightly viscous liquid with a specific gravity of 1.71 at 20ºC.

$HO – N – (CH_2\ CH_2\ OH)4$

The pure substance is a crystalline solid, melting at 123ºC. It is a strong base and the aqueous solutions are stable at room temperature but decompose on heating to form weakly basic polyethanolamines. It is an excellent solvent for certain dyes and finds use in screen printing of fabrics with Rapidogen, when the colour yield is increased.

Triethanolamine is a viscous, very hygroscopic liquid with a specific gravity of 1.13 and a boiling point of 277°C at 150 mm pressure. It is miscible with many organic solvents such as alcohol and acetone, but is immisicible with aliphatic hydrocarbons. It is a weak base, comparable to ammonia and may be considered to combine the properties of glycerine and ammonia.

Commercial triethanolamine contains up to 25% diethanolamine and up to 5% monoethanolamine.

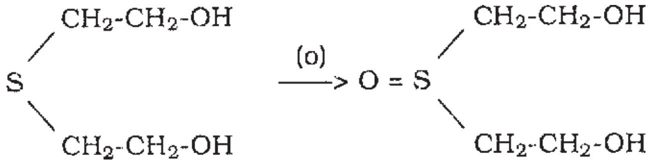


(Triethanolamine)

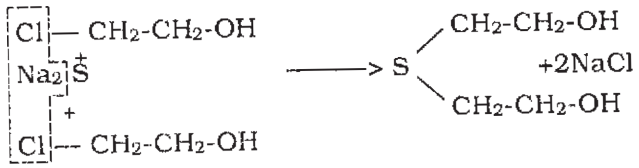
When it is used to neutralise fatty acids (to get soaps), detergents and emulsifying agents are produced.

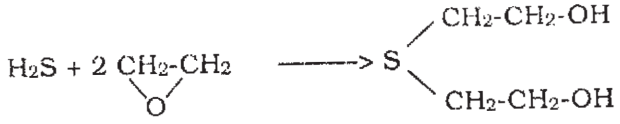
Thiodiethylene glycol is an excellent solvent for basic, direct, acid and disperse dyes and used in textile printing to assist the dissolution of these dyes and promote the production of level and deeper printed pattern. The pure solvent boils at 280ºC. This neutral, clear and colourless liquid is completely miscible with water. It has hygroscopic properties and solvent action for vat dyes in their leuco and solubilised vat forms and also for basic dyes as their fannic acid lakes.

On oxidation, it forms the sulphoxide derivative, which is also useful in assisting the formation of deeper prints in the case of vat dyes.

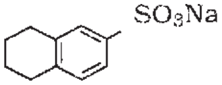


Thiodiethylene glycol is made by the action of sodium sulphide on ethylene chlorohydrin or by reacting hydrogen sulphide with ethylene oxide.





Sodium salt of tetrahydro-naphthalane-2 sulphonic acid is a powder, easily soluble in water and is useful in printing pastes for improving the dispersion of the dyes and promoting the production of deeper prints.



Tetrahydronaphthalene-2 sulphonate (Na)

Sodium lactate, CH_3 CH(OH) COONa, available as a viscous liquid (aqueous solution), freely miscible with water and non-volatile and stable in steam. It is useful as a humectant and can be used in printing pastes, whose prints are subsequently steamed.

A mixture of formamide/urea (40/60 by weight) increases the solubility of dyes in water. When it is present in a printing paste containing chrome mordant dyes, it disperses them and assists their migration in the printing paste so that they become fixed in a textile material more quickly. This implies a shorter steaming time to bring about transfer of the dye from the thickener film into the textile material, ensuring increased colour yield. Similar benefits are realized in the printing of acid dyes, direct dyes and solubilised vat dyes.

Urea is another substance, which is a colourless crystalline solid, very soluble in water and a dye solvent and hygroscopic properties. This is useful as an additive to many types of printing pastes. Urea assists in getting more complete fixation of the dyes so that a deeper print is obtained. It also facilitates the subsequent washing out of the thickener film from the fabric. The beneficial influence of urea can be enhanced by the presence of high boiling phenols or alcohols such as furfuryl alcohol and glycols. The hygroscopic agents are needed to absorb the condensed steam during steaming. It is essential to use the optimum quantities of the hydroscopic agent. When insufficient quantities are employed, all the dye present in the thickener film, may not disslove in the water absorbed by the thickner film resulting in poor colour yields (lighter prints are produced). When larger amounts of the hydroscopic agents (then the optimum amount) are used, more water is supplied to the thickener film, which may result in the spreading of the dye solution beyond the boundaries of the design (print sharpness is lost).

11

DETERGENT PASTE (TEXTILE GRADE)

FORMULATION OF DETERGENT PASTE (TEXTILE GRADE)

1. 40 % Detergent Paste

	Parts/Wt.
Acid slurry (100 %)	40
Caustic soda (45 %)	11.4
Sodium silicate (40 %)	0.6
Sodium hypochlorite solution	0.6
C M C	1.6
Water	45

2. 20 % Detergent Paste

	Parts/Wt.
Acid slurry	20
Caustic soda (45 % solution)	5.8
Sodium silicate (40 % solution)	4.5
Sodium hypochlorite solution	0.6
Oleic acid diethanolamine	1.5
CMC	2.5
Water	2.5

PLANT ECONOMICS OF DETERGENT PASTE (TEXTILE GRADE)

Rated Plant Capacity = 500 Kgs/Day

LAND & BUILDING (Land Area 300 Sq.Mt.) = Rs. 6,15,000.00

PLANT AND MACHINERY

1. Storage tank
2. Mixing
3. Packing machine
4. Other miscellaneous like testing machine, weighing machines, material handling equipments

FIXED CAPITAL

1.	LAND & BUILDING	Rs. 6,15,000.00
2.	PLANT & MACHINERY	Rs. 3,55,000.00
3.	OTHER FIXED ASSETS	Rs. 85,000.00
	TOTAL	Rs. 10,55,000.00

RAW MATERIALS

1. Acid slurry
2. Di-ethanolamine
3. Potassium pyrophosphate
4. Sodium silicate
5. CMC (Carboxy methyl cellulose)
6. Potassium xylene sulphonate
7. Optical brightener
8. Packaging materials & other miscellaneous consumables.

TOTAL WORKING CAPITAL/MONTH

1.	RAW MATERIAL	Rs. 3,39,375.00
2.	SALARY & WAGES	Rs. 57,331.90
3.	UTILITIES & OVERHEADS	Rs. 36,300.00
	TOTAL	Rs. 4,33,006.90

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 10,55,000.00
TOTAL WORKING CAPITAL for 1 MONTH	Rs. 4,33,006.90
TOTAL	Rs. 14,88,006.90

TURN OVER/ANNUM

By sale of detergent paste (textile grade)), 150000 Kgs	Rs. 64,50,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 14%

RATE OF RETURN = Operating profit / T.C.I x 100 = 63%

BREAK EVEN POINT (B.E.P) = 45%

12

DISPERSANT FOR TEXTILES

Dispersants are a class of materials that are capable of bringing fine solid particles into a state of suspensions so as to inhibit or prevent their agglomerating or settling in a fluid medium. Dispersants may break up agglomerates or aggregates of fine particles, bring fine particles into a colloidal solution, or solubilize supersaturated salts to leave a clear solution. In particular, dispersants are useful whenever one wishes to prevent deposition, precipitation, settling, agglomerating, adhering, caking, etc, of solid particles in a fluid medium. This article is concerened only with materials capable of dispersing completely aqueous systems. Dispersants can also refer to the large number of proprietary compositions that facilitate the formulation of paints, inks, dyes, etc, especially by the maintenance of uniform consistency of, eg, inorganic pigments in mixed organic - aqueous media. Often the term is applied to surface active materials that stabilize oil water emulsions in the manufacture of lotions, lubricating oils, resins and latexes. The latter groups of materials are primarily used in systems where a second, nonaqueous liquid phase is present.

Dispersants can be contrasted with flocculants or coagulants which facilitate the aggregation of fine particles in aqueous media to improve separations. Chemically similar materials can often function as either a flocculant or dispersant for the same substrate simply by a change in dosage level or polymer molecular weight. However, dispersants are normally anionic materials of lower molecular weight and higher charge than flocculants.

PROCESS OF MANUFACTURING

Ethoxylation

The reactor in which the ethoxylation is carried out is a pressure kettle of SS 316, with capacities ranging from 500 litres to 4000 litres. They are provided with high speed stirrers, andflame proof motor, steam heating, cooling, nitrogen inlet, Ethylene Oxide sparging, sampling facility, thermowells and charging inlet. A discharge valve is provided for emptying out.

Reactor

The reactor is now charged with requisite quantity of hydrophobes like Alkyl Phenols/ Fatty Alcohols and acids/ Castor oil, containing one or more active hydrogen atoms. Alkaline catalyst is added & heating of the charge is started. When the temperature of 130°C - 140°C is reached, the reactor is flushed with nitrogen gas at least 3/4 times to remove all air and moisture. The presence of air is hazardous because it forms explosive mixtures with Ethylene Oxide. The presence of moisture results in the formation of glycols. After all the preliminaries are over slow addition of Ethylene Oxide is started under nitrogen pressure and combined pressure of Ethylene Oxide and nitrogen is maintained at 2 - 3 Kg/sq.cm. Being exothermic in nature, the temperature is maintained by controlled rate of Ethylene Oxide additon and external coling. When predetermined quantity of Ethylene Oxide is added over a period of 4 - 5 hours, the end point is tested, usually by a cloud point test. After adjustment of cloud point, the system is flushed of all residual Ethylene Oxide by nitrgen and cooling of the charge is started to bring down the temperature to 40°C- 45°C.

TEXTILE DISPERSANT
(FATTY ACID BASED) DISPERSOL) VL (ICI)

Fatty Alcohol Polyethylene Oxide Condensate

R.W. Speke has examined the effect of a single proprietary (Dispersol, VL (ICI), fatty alcohol polyethylene oxide condensate) on the dyeing properties of the leuco compound caustic hydrosulphite vat of some 45 another quinonoid vat dyes.

Textile Dispersants Fatty Alcohol Polyethylene Oxide Condensate

It is produced by the condensation of ethylene oxide with a fatty alcohol (natural or synthetic) such as lauryl, oleyl, tallow, cetyl and tridecyl alcohol.

Formulation

1. Ethylene Oxide = 176 gms (4 mols)
2. Lauryl alcohol = 186 gm (1 mol)
3. Caustic Soda Powder = 0.6 gms.

Formulation

1. Ethylene oxide = 374 to 440 gms\ (8.5 to 10 mols)
2. Trideuyl alcohol = 200 gms. (1.00 mol)
3. Caustic Soda Powder = 0.4 to 0.5 gms.

Procedure (as per Formulation)

186 gm (1.00 mol) of Lauryl alcohol is charged into the flask vessel followed by 0.4 to 0.5 gms of powdered caustic soda. The flask, the thermometer, gas disperser and contents are weighed. A slow stream of nitrogen is passed through the Lauryl alcohol and the tempt o raised to 150°C - 160°C by means of a glass insulated heating mantle. Ethylene oxide gas is admitted to the manifold and allowed to escape momentarily to the atmosphere through the 3-way stop cock. The 3-way stop cock is then turned to vent the nitrogen to the atmosphere and the ethylene oxide is simultaneously introduced into the flask. The operation should be carried out in a well ventillled the hood away from the naked flame.

Absorption takes place immediately with a rise is tempt. The ethylene oxide rate is increased to the point where an accasional bubble of ethylene oxide escapes third white oil. The tempt. is permitted to die to 180 - 220°C and is maintained within this range until the required amount of ethylene oxide has been absorbed (176 gms equivalent to 4 mols). About 2 to 3 hours are required to absorb the above quantity.

In shutting down the ethylene oxide is vented to air and the nitrogen is turned into the flask and a slow stream maintained until all the ethylene oxide has been purge from the system. The flash and contents are weighed to determine the ethylene oxide absorption.

When the desired quantity of ethylene oxide has been obtained, the free alkali is neutralized with either 30% H_2SO_4 or glacial acetic acid to phenol pethalein indicator (external indicator). 10 gms of decoloursing carbon is then added and the mixture stirred and heated to 100°C for 15 minutes. The mixture is then filtered thro a buchner funnel using a small amount of filter aid on the paper as a pre-coat in order to ensure a bright filtrate.

Procedure as per formulation

Ethoxylation of 1 mol of tridecyl alcohol with 8.5 to 10 moles of ethylene oxides proceed as describes for large alcohol ethoxylate is including the same purification method. About 3 to 6 hrs are required to absorb the desired and of ethylene oxide.

PLANT ECONOMICS OF DISPERSANT FOR TEXTILES

Rated Plant Capacity = 500 KGS/Day

LAND & BUILDING(Land Area 750 Sq.Mt.) = Rs. 11,25,000.00

PLANT & MACHINERY

1. Ethylene oxide storage tank
2. Nitrogen cylinder
3. Pressure kettle
4. (3 HP Motor) steam heating, cooling nitrogen inlet, ethylene oxide sparging, thermowells
5. Weighing balance
6. Laboratory equipment
7. Process control equipment.
8. Steam boiler
9. Pipes,fittings, pumps, valves and miscellaneous.
10. Miscellaneous equipment for fire fighting, water sprinkling etc.

FIXED CAPITAL

1. LAND & BUILDING	Rs.	11,25,000.00
2. PLANT & MACHINERY	Rs.	21,35,000.00
3. OTHER FIXED ASSETS	Rs.	7,50,000.00
TOTAL	Rs.	40,10,000.00

RAW MATERIALS

1. Oleyl alcohol
2. Ethylene oxide gas
3. Caustic Soda
4. Laboratory Chemicals

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs.	9,68,750.00
2. SALARY & WAGES	Rs.	63,875.00
3. UTILITIES & OVERHEADS	Rs.	2,05,500.00
TOTAL	Rs.	12,38,125.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs.	40,10,000.00
TOTAL WORKING CAPITAL for 1 MONTH	Rs.	12,38,125.00
TOTAL	Rs.	52,48,125.00

TURN OVER/ANNUM

By sale of 150,000 Kgs of dispersing agent	Rs. 2,10,00,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 23%

RATE OF RETURN = Operating profit / T.C.I x 100 = 93%

BREAK EVEN POINT (B.E.P) = 34%

13

LEVELLING AND DISPERSING AGENT

Processing of textile materials involves the use of diverse types of compounds to perform various functions. The compounds are variously known as textile auxiliaries, textile chemicals, textile process chemicals etc. They may be broadly classified depending on the purpose for which they are used into two groups (1) Those which are used in textile processing to serve some purpose or purposes and after these purposes are served, they have to be removed from the textile material being processed and (2) those which continue to form an integral part of the materials being processed by way of either chemical reaction with the textile substrate or mechanical deposition of water soluble or water insoluble substances in the textile substrate and are expected to remain on the material more or less permanently with standing the subsequent rigorous action of varying degrees exerted on the end products during the use by the consumers. These two classes may be called temporary and permanent textile auxiliaries respectively. Levelling agents used in dyeing acid dyes on wool or nylon as IN class of (normal dyeing) vat dyes on cotton or carriers and dispersing agents used in the dying of disperse dyes on polyester fibres and solution aids used in dissolving sparingly soluble dyes in printing pastes which normally contain a small amount of water are some examples of temporary textile auxiliaries. Their presence in the processing media (dye solution or printing pastes) is absolutely necessary from the print of view of obtaining level shades, good depth and optimum colour value in dyeing and printing. Disperse dyes the only class of dyes suitable for dyeing polyester fibres are essentially water insoluble (sparingly soluble in water) and nud the presence of dispersing agents in the dyebath to prevent any deposition of dyeparticles either on the material being dyed or on the machine parts. The use of the right type of dispersing agents employed in proper concentrations (either of these can upset the dyeing economics whereby a lower colour value as dye-utilization is obtained) has been found to be absolutely necessary to produce the dyeings economically. In the case of dispesre dyes hasing bulity molecules which have poor migration (in the fibre substance) properties and hence produce uneven dyeing levelling agents have to be used to produce even dyeing results. When acid dyes are dyed on polyauide fibre material the retarding of the dyeing process can be achieved either by using an auxiliry of the same ionic nature as the dye (anionic) so that there is a competition for the fibre sites between the dye and the auxiliary molecules thereby reducing the effective concentration of the dye during deyeing or by using an auxiliary of the opposite ionic nature (in this case a catioinc auxiliary) so that a complex (with no ionic charge) between the molecules of the dye and the auxiliary is formd (a suitable dispersing agents has to be used to prevent the precipitation of the complex in the dycloth), the complex being slowly split at the boiling into the dye and auxiliary ions and the dye ions being taken up by the fibers.

PROCESS OF MANUFACTURE OF LEVELLING AND DISPERSING AGENTS

A Superior dispersing agent also helping levelling functions is described in B10S Report - 240 known as Dispersing Agent (B10S-240). It is obtained by the reaction of the condensation product of naphthalene sulphonic acid and formadehyde with Urea formaldehyde sulphite resin. the various steps followed in the manufacture of the above B10S-240 type dispersing agent is described as follows.

i) Naphthalene Sulphonation

1308 kg. crude napthalene (m.p. 78-80°C) is melled in a 2400 litre acid proof bricklined sulphonator and 2190 kg. 100% sulphuric acid (monohydrate) free from iron is run in during 4 hours, keeping the temperature at 80-90°C. The temperature is raised to 110°C in 90 minites compete the reaction. The main reaction product is L-Sulphonic acid.

ii) Formation of Resin Alcohol

25 kg. phenol (m.p. 40°C) 30.4 kg. Phenol oil SHI (Sp.gr. 1.035) and 73.5 kg. 30% aqueous formaldehyde solution are fed to a 3500 litre bricklined kettle equipped with a stream coil and an agitator 0.5 kg. Soda ash is also added and the mixture is heated to 90°C in 1 to 2 hrs. Finally 15.0 kg. common salt is added and the resin is separated at 45°C. The resin should have a sp.gr. of 1.11 -1.12 at 20°C.

iii) Suphite Resin

37.5 kg. of formalin (30%) and 46 kg. of sodium sulphite crystals are fed to a 300 litres iron kettle equipped with a steam jocket and an agitator, and heated to 100°C in 1 hour. The temperature is maintained for 7 hours. The product should be soluble in dilute acetic acid.

iv) Condensation

Sulphonic acid obtained above is fed to 9540 litres bricklined, acid proof brick lined kettle. The alcohol resin obtained above is also added to it folowed by 10 kgs. of 30% formation in one hour at 40°C. The batch should have a litre of 92 to 95 ml. N-NaOH/10 gm. after condensing with alcohol resin and 45 to 46 ml. ofter adding water.

v) Conversion

The above condensation product is fed to a 1500 litre acid-proof bricklined kettle. It is cooked to 40°C, 10.6 kg. Urea dissolved in 20 litres of water is added in 30 min. after stirring for 30 min at 35-40°C 29 kg. 30% formalin diluted with 26 litres of water is added in 30 mm. It is stirred for 30 min more. The litre should now be 40-41 ml. N-NaOH/10 gm. of product. The sulphite resin prepared above is added to it and stirred for 30 min. The titre should now be 29-31 m. N-NaOH/10 gm. Finally 1000 litres of 25% ammonium hydroxide is added with agitation. The finished product should have a titre of 14-15 ml. N-NaOH/10 gm. The yield is 9,900 - 10,000 kgs. Phenol oil used in the second step is a mixture of 50%, phenol, 7% O-Creso, 13% m-Cresol, 9% p-Cresol, 22% Xyenols and 1% neutral oil.

Formulation:

Naphtalene	130.8 kg.
Sulphuric Acid (monohydrate)	219.0 kg.

Phenol	25.0 kg.
Phenol Oil	30.4 kg.
Formaldehyde Solution	
Aqueous (30%)	73.9 kg.
Soda Ash	0.5 kg.
Salt	15.0 kg.
Formalin	76.5 kg.
Ammonium Hydroxide 25%	100.0 litres
For Product	1 M.T.

PLANT ECONOMICS OF DYE LEVELLING AGENT

Rated Plant Capacity = 1 MT/Day

LAND & BUILDING (Land Area 500 sq. mt.) = Rs. 9,87,500.00

PLANT & MACHINERY

1. S.S. lead lined sulphonate
2. S.S. brick lined kettle
3. S.S. Kettle
4. Storage tanks
5. Lab testing equipments
6. Instrumentation & Process control
7. Depoluting equipment
8. Baby boiler steam generating
9. Miscellaneous water supply, pipe - fitting, valves, pumps, motors, etc

FIXED CAPITAL

1. LAND & BUILDING	Rs.	9,87,500.00
2. PLANT & MACHINERY	Rs.	10,10,000.00
3. OTHER FIXED ASSETS	Rs.	2,07,500.00
TOTAL	Rs.	22,05,000.00

RAW MATERIALS

1. Naphthalene
2. Sulphuric acid
3. Phenol
4. Phenol Oil
5. Formaldehyde solution
6. Sodium sulfite
7. Soda Ash
8. Urea
9. Salt
10. Formalen
11. Ammmonium Hydroxide
12. Miscellaneous

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 3,19,761.00
2. SALARY & WAGES	Rs. 1,31,250.00
3. UTILITIES & OVERHEADS	Rs. 1,63,050.00
TOTAL	Rs. 6,14,061.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 22,05,000.00
TOTAL WORKING CAPITAL FOR 1 MONTH	Rs. 6,14,061.00
TOTAL	Rs. 28,19,061.00

TURN OVER/ANNUM

By sale of Dye Levelling Agent 300 M.T.	Rs. 1,05,00,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 23%

RATE OF RETURN = Operating profit / T.C.I x 100 = 87%

BREAK EVEN POINT (B.E.P) = 46%

14

NON-IONIC SURFACTANTS WETTING AGENTS

The basic characteristic of non-ionic surfactants is that by virtue of being non-ionise, they do not ionise, but acquire their hydrophilic character from an oxygenated side chain, usually polyoxyethylene. The oil soluble portion may be derived from fatty acids, alcohols, amides or amines.

The non-ionic surfactants possess valuable properties viz. stability over withe range of pH stability in hard or soft water or in the presence of electrolyte. They exhibit excellent compatibility with other types of surfactants and have no substantivity for textile fibres.

They find application in desizing in continuoes bleaching and as a wax emulsifier in finishing. Two types of non-ionic surfactants are extremely popular viz. (1) Ethylene oxide condensate and (2) Fatty acid alkanolamides.

FORMULATIONS FOR NON-IONIC SURFACTANTS
FORMULATION (A)

1. Berol (Nonyl phenol condensation product (non-ionic surfactant)
   $[C_9H_{19}\ C_6H_4\ (OC_2H_4)\ OH)]$ (As liquid) 25%
2. Octanol (n-octyl alcohol)
   $[CH_3\ (CH_2)_6\ CH_2OH]$
   (Antifoaming agent) (Addtive) (As liquid) 25%
3. Sodium triphosphate or Nitrilo triacetic acid or ethylene

diamine tetraacetic acid or carboxy methyl cellulose (Builders)

(As crystals	65%.
Total	100%.

MANUFACTURE OF NON-IONIC SURFACTANT (As per formulation A)

Builder viz sodium triphosphate is ground to a fine powder in a grinder. It is then mixed with calculated quantities of berol and octanol placed in a mixer for mixing is done for about 1/2 hour. The product i.c. Non-ionic sufactant is then packed suitable containers & marketed.

PLANT ECONOMICS OF NON-IONIC SURFACTANT WETTING AGENT

Rated Plant Capacity = 1000 KGS/Day

LAND & BUILDING (Land Area 500 sq.mt.) = Rs. 13,07,500.00

PLANT & MACHINERY

1. Reaction kettle (Jacketed)
2. Storage tank
3. Filter
4. Lab. testing equipments
5. Packaging Machine
6. Condenser
7. Chilling Roll
8. Grinder
9. Mixer M.S. (Epoxy Lined)
10. Boiler
11. Miscellaneous

FIXED CAPITAL

1. LAND & BUILDING	Rs. 13,07,500.00
2. PLANT & MACHINERY	Rs. 12,60,000.00
3. OTHER FIXED ASSETS	Rs. 2,32,000.00
TOTAL	Rs. 27,99,500.00

RAW MATERIALS

1. Berol
2. Octanol
3. Sodium Teriphosphats
4. Packing Materal

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 12,96,250.00
2. SALARY & WAGES	Rs. 1,05,625.00
3. UTILITIES & OVERHEADS	Rs. 52,200.00
TOTAL	Rs. 14,54,075.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 27,99,500.00
TOTAL WORKING CAPITAL For 3 months	Rs. 43,62,225.00
TOTAL	Rs. 71,61,725.00

TURN OVER/ANNUM

By sale of 300000 kgs of Non-Ionic surfactants wetting Agent	Rs. 2,25,00,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 17%

RATE OF RETURN = Operating profit / T.C.I x 100 = 53%

BREAK EVEN POINT (B.E.P) = 35%

15

PIGMENT EMULSION FOR TEXTILES

MANUFACTURING PROCESS

The preparation of pigment emulsion requires great care & accuracy in the use of colours, thickening agents & other chemicals. To minimise the possibility of errors, all necessary ingredients are prepared in advance. Concentrated solution or paste (emulsion) are prepared, these are called standard & many consist on single chemical or may be mixture of several compounds.

Pigment

The defination of pigment implies general insolubility & almost complete insolubility in water. Further the pigment should be insoluble in dry cleaning solvent like spirit, tetra chloro ethylene, perchloroethylene, carbon tetra chloride, etc.

Pigment suitable for pigment printing should have certain properties. The shade produced by them should exhibit good fastness to light, washing gas fading, chlorine, acid, alkalies, peroxides, perspiration, solvents & especially to abrasion. The emulsion thickening made by using them should give sharp impressions, develop good brilliancy & have good reproducibility. They should be applicable to all fibres. The suitability of pigment in textile industry depend upon their particle size distribution, sp. grade, crystal strictire & stability, hardness, solubility in solvents, purity of intermediates used in manufacture of pigment. Condition of precipitation of pigment etc.

Pigment used in textile colouration may be broadly classified as:

1. Azoic Pigment
2. Vat Pigment
3. Phthalocyanine Pigment
4. Miscellaneous Pigment

Of these classes azoic pigment occupy a minor place in pigment as most of the commercial pigment belong to this category. Yellow, orange, & red pigment are generally selected from this class.

PLANT ECONOMICS OF PIGMENT EMULSION FOR TEXTILES

Rated Plant Capacity = 500 Kgs/Day

LAND & BUILDING (Land Area 500 sq.mt.) = Rs. 11,85,000.00

PLANT & MACHINERY

1. Ball mill
2. Kneader with motor
3. Mixer with heating element glass & agitator
4. Jacketed kettle with stirring arrangement S.S. with M.S. jacket
5. Boiler
6. Miscellaneous

FIXED CAPITAL

1. LAND & BUILDING	Rs. 11,85,000.00
2. PLANT & MACHINERY	Rs. 4,90,000.00
3. OTHER FIXED ASSETS	Rs. 1,80,000.00
TOTAL	Rs. 18,55,000.00

RAW MATERIALS

1. Pigment powder
2. Gums Tragacanth or textile gums
3. Solvent soluble resin emulsions

TOTAL WORKING CAPITAL/MONTH

1.	RAW MATERIAL	Rs. 4,78,125.00
2.	SALARY & WAGES	Rs. 49,200.00
3.	UTILITIES & OVERHEADS	Rs. 1,35,400.00
	TOTAL	Rs. 6,62,725.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 18,55,000.00
TOTAL WORKING CAPITAL for 1 MONTH	Rs. 6,62,725.00
TOTAL	Rs. 25,17,725.00

TURN OVER/ANNUM

By sale of 1,50,000 kgs.	Rs. 1,12,50,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 25%

RATE OF RETURN = Operating profit / T.C.I x 100 = 110%

BREAK EVEN POINT (B.E.P) = 34%

16

PIGMENTS BINDERS FOR TEXTILE PRINTING

MANUFACTURING PROCESS

Emulsion polymerization has become very important industrially, and today large tonnages of lattices and polymers are manufactured by this process. For reasons of cold and non-reactivity water is a much more desirable diluent and heat transfer medium than organic solvents. Two types of polymerization systems that are based on water as the reaction medium are widely used industrially i.e. suspension and emulsion polymerization. In both methods the monomer is dispersed rather than dissolved in the medium, but the two methods differ considerably because of the degree of dispersion attained and because of monomer by which initiation occurs in each.

In emulsion polymerization the loaes of polymerization reaction is a particle of colloidal size (Ca 5 - 150 nm dia) and the initiator radical is formed in aqueous phase. High molecular weights polymers at considerably enhanced polymerization rates are produced. According to classical analysis which may not apply in many practical cases an emulsion polymerization is considered to contain a three phase reaction systems consisting of large droplets of monomer (Ca 1.5 Aim DAI) the GA. water phase containing the dissolved initiation and colloidal particles of monomer swollen polymer particles compared its monomer droplets essentially all the polymerization reaction occurs in former and monomer in droplets gradually transfers to colloidal particles by dissolving in and diffusing through ag. phase. Monomers applicable to emulsion polymerization must have a finite water solubility but not so high as to cause a substantial amount of polymerization to occur in the ag. phase. The monomer droplets and the swollen monomer-polymer particles are stabilized in ag. medium by absorbed surface active agents, which are incorporated into reaction mixture before the start of polymerization. Because the initiation must be present only in ag. phase, generally inorganic peroxides which are highly soluble in water, are used as surface active agents. Hydrogen peroxide and ammonium per oxysulphate are examples of such initiators and their rates of radical formation are often enhanced by addition of inorganic, water soluble reducing agents to the reaction mixture. The combination of peroxide and reducing agent is a redox initiation. Because an inherent characteristic of this method of polymerization is the formation of unusually high m.w polymers, chain transfer agents or modifiers are often added to the reaction mixture to limit the molecular weight without reducing the rate of polymerization reaction.

Emulsion polymerization has certain advantages over other industrial methods such as bulk or solution polymerization as follows:

1. Very high molecular weight polymers may be obtained at fast reaction rates.
2. As invariably an aqueous medium is used there are no problems with heat dissipation.
3. Use of water minimizes cost as no recovery system is required as for an expensive solvent. Also there should be no particular fire or toxicity hazards.
4. Ease of control of each stage of the reaction. i.e. initiation, propagation, chain transfer and termination in conjunction with fairly low polymerisatio temperatures (<100°C).
5. The viscosity of a latex is independent of the polymer molecular weight (c.f. solution polymers) and high concentrations of low viscosity lates can be obtained aiding agitation and heat transfer characteristics, and enabling material to be readily handled (pumped etc.) at ambient temperature.
6. polymer is obtained as a latex and is used as such in many end-use applications.

7. If desired, a solid product may readily be obtained after coagulation, washing and drying.
8. Emulsion processes are easily adaptable to continuous running conditions.

There are a number of disadvantages, but these are of a limited nature.

1. In end-use applications, evaporation of water is a slow process because of in high latent heat.
2. Reactor capacity is not fully utilized as lattices generally only contain up to a maximum of 55 per cent polymer solids as a result of direct polymerization.
3. A solid polymer of high purity cannot be obtained as the isolated material will contain a certain proportion of non-polymer constituents. It must be mentioned, however, that the presence of insoluble soap derivatives is known to be advantageous in many applications.

An emulsion polymerization will contain four basic ingredients, monomer, water, soap (dispersing agent, consulsifier or surfactant) and catalyst (initiator) in the following typical proportions.

	Parts by mass
Monomer(s)	100
Soap(s) Up to	7
Initiator Up to	1
Water Up to	200

The properties of the latex formed and of the polymer or copolymer are very dependent on how the various constituents are put together.

A simplified, somewhat idealized, description of emulsion polymerization is as follows:

1. Emulsifier in aqueous solution above a certain concentration forms micelles (aggregates of molecules).
2. addition of water insoluble monomer, which forms droplets stabilized by emulsifier. Some monomer solubilised in mielles.
3. Free radicals are generated by initiator and cause polymerization inside the micelle.

4. Growing polymer particles obtain further monomer by diffusion from monomer droplets.
5. Monomer droplets used up at about 60 per cent conversion and polymerization continued until remaining monomer in polymer particles is consumed.

PLANT ECONOMICS OF PIGMENTS BINDERS FOR TEXTILE PRINTING

Rated Plant Capacity = 3 TON/Day

LAND & BUILDING (Land Area 500 sq.mt.) = Rs. 11,15,000.00

PLANT & MACHINERY

1. Storage Tanks
2. Jacketed Stirred Reactors
3. Spray drier
4. D.G. Set
5. Miscellaneous (Pump, Motor, Etc.)

FIXED CAPITAL

1. LAND & BUILDING	Rs. 11,15,000.00
2. PLANT & MACHINERY	Rs. 7,00,000.00
3. OTHER FIXED ASSETS	Rs. 1,25,000.00
TOTAL	Rs. 19,40,000.00

RAW MATERIALS

1. Vinyl Chloride Monomer
2. Sodium Lauryl Sulphate
3. t-butyl hydroperoxide
4. Distilled Water
5. Miscellaneous(like chain transfer agent) fugitine alkali solution etc.
6. Packing Material

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 9,03,150.00
2. SALARY & WAGES	Rs. 1,63,500.00
3. UTILITIES & OVERHEADS	Rs. 33,000.00
TOTAL	Rs. 10,99,650.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 19,40,000.00
TOTAL WORKING CAPITAL FOR 3 MONTHS	Rs. 32,98,950.00
TOTAL	Rs. 52,38,950.00

TURN OVER/ANNUM

By sale of 900 T of Pigment binder	Rs. 1,80,00,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 19%

RATE OF RETURN = Operating profit / T.C.I x 100 = 65%

BREAK EVEN POINT (B.E.P) = 41%

17

POLY VINYL ACETATE EMULSION

MANUFACTURING PROCESS

There are two types of emulsions produced today, a fine particle size (0.1-0.24) polyvinyl acetate without a protective colloid but only with anionic or nonionic surfactants and a large particle size (0.5-3.04) emulsion which is only stabilized by the protective colloids.

Protective colloids most often used are polyvinyl alcohol which is 88% hydrolyzed and hydroxy ethyl cellulose.

A typical recipe for a large particle size emulsion is as follows:-

For 100 kg batch

Water	42.75% kg.
Vinyl Acetate	55.00% kg.
Hydroxyethyle cellulose	2.00% kg.
Tergitol NPX	0.05% kg.
Potassium Peroxy disulphate	0.15% kg.
Total	**100.00% kg.**

The starting step for the manufacture of polyvinyl acetate is the mixing and heating of ingredients. The cellosize tergitol NPX and water are mixed in the proper proportion and heated to about 80°C.

The mixing and heating of the above mixture is carried out in same tank. This tank is generally made of mild steel equipped with an agitator and a steam jacket. Agitator is rotated at a speed of 50-80 rpm. For reducing the rpm. of the motor a gear reducer is used. The pressure of the steam is kept around 2 atomosphere.

This heating to 80°C is done for about one to one and half hour. After heating the solution is cooled to about 30°C by flowing cold water into the steam jacket after closing the steam valve and opening the vessel provided at the top of the jacket.

Now about 10% of the total vinyl acetate is added into the above cooled mixture and agitated. Along with vinylacetate, potassium peroxy disulphate and soldium bicarbonate are also added to the above mixture, and mixing is done in a separate vessel. This second vessel is also equipped with a steam jacket for heating purpose. The mixture of all the ingredients is now heated to about 70-75°C by using steam at one atmosphere. At this temperature i.s. 70-75°C, the remaining 90% of the total vinyl acetae is so adjusted that should take about 2 hours. During the addition period of vinyl acetate the temperature of the reaction mixture is kept arround 80°C.

When all the vinyl acetae i.e. monomer is added to the reacter, then the reaction mixture temperature is raised to 90°C. This 90°C temperature is maintained for about half hour. After keeping the mixture at 90°C for about 30 minutes, the solution is cooled to room temperature and filtered through a filter.

One completion of the polymerization of emulsion is either spray-dried or coagulated by adding an electrolyte then filterd and finally flash dried various washing process are necessary for the removal of the soap if polymer of high purity are to be obtained.

PLANT ECONOMICS OF POLYVINYL ACETATE EMULSION

Rated Plant Capacity = 200 KGS/Day

LAND & BUILDING (Land Area 500 sq.mt.) = Rs. 8,60,000.00

PLANT & MACHINERY

1. Mixing tank
2. Polymerisation tank
3. Storage tanks

4. Boiler
5. Filter
6. Weighing machine
7. Miscellaneous.

FIXED CAPITAL

1. LAND & BUILDING	Rs. 8,60,000.00
2. PLANT & MACHINERY	Rs. 4,50,000.00
3. OTHER FIXED ASSETS	Rs. 1,60,000.00
TOTAL	Rs. 14,70,000.00

RAW MATERIALS

1. Vinyl acetate monomer
2. Lergitol NPX
3. Hydroxy ethyl cellulose
4. Potassium peroxydisulphate
5. Sodium bicarbonate

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 1,70,710.00
2. SALARY & WAGES	Rs. 43,125.00
3. UTILITIES & OVERHEADS	Rs. 36,500.00
TOTAL	Rs. 2,50,335.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 14,70,000.00
TOTAL WORKING CAPITAL for 1 MONTH	Rs. 2,50,335.00
TOTAL	Rs. 17,20,335.00

TURN OVER/ANNUM

By sale of 60000 kgs. Polyvinyl Acetate Emulsion	Rs. 42,00,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 19%

RATE OF RETURN = Operating profit / T.C.I x 100 = 46%

BREAK EVEN POINT (B.E.P) = 50%

18

ROSIN SIZING AGENT

Paper sizing agents are chemical compounds, which are used to develop the resistance of paper and paper board that are not pigment coated, to the penetration of liquids, especially waterand aqueous solutions. A sizing agent is a chemical that makescellulose fibre surfaces hydrophobic, so that the contact angleith water or aqueous solutions is high.

The sizing agents must be held on the fibres to resistremoval a liquid. Internal sizing is achieved by the addition ofrepellent chemicals to the aqueous suspension of pulp fibresbefore sheet formation, i.e. at the wet end of aa paper machine.The process is also called beater or Engine sizing. Surface ortub sizing is achieved by the application of repellent chemicals to the surface of the sheet, often before the sheet has been dried.

Internal or surface sizing may also be designed forrepellency against nonaqueous fluids eg. oils, greases, oralcohols.

OUTLINES OF THE MANUFACTURING PROCESS

Rosin-Based: Regular or unmodified rosin size is preparedby the reaction of rosin with aqueous alkali; the degree ofneutralization, i.e. saponification, generally is varied from 75 to 100%, depending on the physical state desired for thecommercial product. Most rosin size is supplied as a viscousaqueous paste containing 60-80 wt% solids. Before use, the pastesize must be converted to a stable, dilute rosin size emulsion bycareful sequential dilution with warm water and then cold waterwith good agitation. Dry size, a completely saponified rosinsize in the form of a dry powder, is readily water-soluble andcan be added directly to a pulp slurry. In addition, protein-stabilized emulsions of partially neutralized rosin may be used.These forms of commercial rosin size perform quite effectively inthe sizing of paper, because they contribute similar physical species in dilute aqueous dispersions.

Rosin sizing involves the separate addition of dilute aqueous dispersions of rosin size and alum to a pulp slurry.Although beater addition of either coreactant is permissible,addition of both before final pulp refining is unwise, becausesubsequently exposed cellulose surfaces may not be properlysized. The size and alum should be added sufficiently early toprovide uniform distribution in the slurry and adequate time forthe formation and retention of aluminium resinates, commonlyreferred to as size precipitate. Size generally is added first,followed by alum; however, reverse addition is more effective incertain systems.

The fortified rosin sizes are based on maleic anhydride or,preferably, fumaric acid adducts of rosin. Usually rosin reactswith less than the theoretical amount of maleic anhydride orfumaric acid. The total product, i.e. adduct, unreacted rosinacids, and neutrals, is converted to a paste soap or emulsion.The paste soaps are sodium or potassium salts whose propertiesare similar to those of ordinary rosin paste sizes.

The same maleic anhydride or fumaric acid adduct of rosin can be converted to high-free-rosin emulsion sizes by usingvarious stabilizers. Typically, these are 35 wt % total solids emulsions and exhibit excellent stability to storage andmechanical action, such as is required in transfer pumps and lines.

The various rosin-based sizes can be used to size all gradesof paper that are made at acid pH. These include bleached board,printing and writing grades, unbleached kraft boxboard, bleachedand unbleached kraft bag paper, and cylinder board. The amountof rosin-based sizing agent which is required varies with thepulp furnish, the required degree of sizing, and the type of rosin-based sizing agent used.

MALEINISATION OF ROSIN

Maleic Anhydride or the more expensive fumaric acid arefrequently used to modify rosins, particularly for use inoleoresinous media.

The anhydrides or acids can readily be converted to thesodium salt by the addition of sodium hydroxide.

ROSIN-MALEIC ADDUCT

Preparation Parts by wt. Rosin 87.5 Maleic Anhydride 12.5

Total 100.00

PLANT ECONOMICS OF FORTIFIED ROSIN SIZE FOR PAPER

Rated Plant Capacity	= 1 TONS/Day
LAND & BUILDING (Land Area Sq.mts.)	**= Rs. 16,50,000.00**

PLANT & MACHINERY

1. Storage Tank
2. Reaction Vessel
3. Sparger
4. Alpha-therm, Dowtherm heater
5. Mixing Tank
6. Condensor for turpentine vapour condensation
7. Sintex water storage tank
8. Laboratory Equipments
9. Pipes, Pumps, Valves, Tanks & Miscellaneous Equipments
10. Electrical Fittings, Switchgears, Cables, Connections
11. Miscellaneous Tools, Jigs, Fixtures and others

FIXED CAPITAL

1. LAND & BUILDING	Rs. 16,50,000.00
2. PLANT & MACHINERY	Rs. 22,95,000.00
3. OTHER FIXED ASSETS	Rs. 11,00,000.00
TOTAL	Rs. 50,45,000.00

RAW MATERIALS

1. Rosin
2. Turpentine Oil

3. Maleic Anhydride
4. Acetone
5. Caustic Soda
6. Packaging Drums

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 11,14,475.00
2. SALARY & WAGES	Rs. 71,998.20
3. UTILITIES & OVERHEADS	Rs. 1,04,000.00
TOTAL	Rs. 12,90,473.20

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 50,45,000.00
TOTAL WORKING CAPITAL for 1 MONTH	Rs. 12,90,473.20
TOTAL	Rs. 63,35,473.21

TURN OVER/ANNUM

1. By sale of paper sizing agent 300 MT	
2. Turpentine Oil 60,000 Lts.	
TOTAL	Rs. 2,47,20,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 31%

RATE OF RETURN = Operating profit / T.C.I x 100 = 123%

BREAK EVEN POINT (B.E.P) = 23%

19

SILICONE EMULSION

FORMULATION OF SILICONE EMULSION

1. Silicon oil	35
Morpholine oleate	7
Water	58
	100

2. Dimethyl silicone	25
Tegnin (515) (Alephnaphylamine condensate)	10
Water	65
	100

In the above two formulations for silicone emulsion, the preference of silicone oil (in formulation No. 1) to Dimethyl silicone (in Formulation No. 2) is based on the fact that the molecular weight of silicone oil is lesser than that of Dimethyl silicone. Besides, the first emulsion is easier o make than the second. In the second formulation, the molecular weigh of the ingredients is more than that of the first one, and dispersability of the colloidal particles takes more time, and besides, higher RPm of the agitator is required for mixing, whereas he first emulsion takes less time, is simpler to make and is quickly well homogenized. That is why the first emulsion is preferred to second.

PLANT ECONOMICS OF SILICONE EMULSIONS

Rated Plant Capacity = 0.50 MT/Day

LAND & BUILDING (LAND AREA 500 SQ.MT.) = RS. 4,55,000.00

PLANT & MACHINERY

1. Storage tank
2. Silicone fluid feed tank
3. Stainless Steel reaction vessel fitted
4. Homogeniser/Colloid mill.
5. Silicone emulsion storage tank
6. Packing Machine
7. Instrumentation,Process control and lab testing equipment.
8. Pipe fittings,pumps,valves and other miscellaneous equipment.

FIXED CAPITAL

1. LAND & BUILDING	Rs. 4,55,000.00
2. PLANT & MACHINERY	Rs. 6,28,000.00
3. OTHER FIXED ASSETS	Rs. 2,45,000.00
TOTAL	Rs. 13,28,000.00

RAW MATERIALS

1. Silicone oil
2. Morphline oleate

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 9,18,750.00
2. SALARY & WAGES	Rs. 1,73,280.00
3. UTILITIES & OVERHEADS	Rs. 43,500.00
TOTAL	Rs. 11,35,530.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 13,28,000.00
TOTAL WORKING CAPITAL for 1 MONTH	Rs. 11,35,530.00
TOTAL	Rs. 24,63,530.00

TURN OVER/ANNUM

By sale of 150 MT silicone emulsion	Rs. 1,95,00,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 28%

RATE OF RETURN = Operating profit / T.C.I x 100 = 218%

BREAK EVEN POINT (B.E.P) = 22%

20

SILK SIZING LIQUID (WATER SOLUBLE)

FORMULATION OF SIZING OF LIQUID

A formulation of silk sizing solution (water soluble) are as follows

Formulation No 1

Ingredients	**Parts by wt.**
Glycerol stearate	16.00
Glycerin	16.00
Pepsin	0.02
Soap	36.00
Glue	40.00
Gum arabic	10.00
Borax	2.40

Formulation No. 2

Ingredients	**Parts by wt.**
Borax	4
Ethylene glycol	12
Soap	60
Gelatin	68

Cauria acid	40
Gum arabic	16
Trypsia	0.10

MANUFACTURING PROCESS

For the manufacturing of silk sizing liquid, making use of the following formulations

Ingredients	Parts by wt.	% age
Pepsin	0.30	0.14
Glyceryl stearate	36	16.34
Soap	64	29.05
Glue	70	31.77
Stearic acid	30	13.62
Borax	4	1.82
Gum arabic	16	7.26
Total	220.30	100.00

Glue in requisite quantity is introduced into the jacketed reaction vessel MS (glass lined) fitted with agitator.

Then, into this vessel, calculated quantities of gum arabic, borax, & soap and well mixed together by means of agitator.

Gradually steam is introduced into the jacket or the reaction vessels and the temperature of the contents is gradually increased.

Meanwhile when the temperature increases to around 40-45°C, glyceryl monostearate and stearic acid in measured quantities are introduced and the contents of the mixture are stirred well, and the temperature is steadily raised till when the temperature reaches 58-59°C, glyceryl monostearate (whose melting point is 58-59°C) meets and goes into solution and the contents of the reaction vessel are well homogenized.

The temperature is gradually raised when stearic acid (m.p. 69.6°C) melts and goes into solution.

As before, the contents are stirred by means of the agitator till a homogenous mass is obtained.

Then, at least, pepsin is added into the reaction mixture and well stirred.

The steam is switched off and the resultant silk sizing viscous liquid, thus formed, is allowed to cool gradually.

Samples are withdrawn & tested for quality assessment. Then the finished product is transferred to a storage tank, from where, it is subsequently withdrawn and subjected to packing operation when the product is packed in suitable desired containers by means of packing machine & then despatched for marketing.

PLANT ECONOMICS OF SILK SIZING LIQUID (WATER SOLUBLE)

Rated Plant Capacity	=	5 MT/Day
LAND & BUILDING (Land Area 600 Sq.Mt.)	**=**	**Rs. 11,77,500.00**

PLANT & MACHINERY

1. Reaction vessel
2. Storage tank
3. Packing machine
4. Mini boiler
5. D.G.set
6. Lab equipments
7. Instrumentation & process control equipments
8. Miscellaneous viz. pipe fittings, pumps, motors, valves, etc.

FIXED CAPITAL

1. LAND & BUILDING	Rs. 11,77,500.00
2. PLANT & MACHINERY	Rs. 15,40,000.00
3. OTHER FIXED ASSETS	Rs. 3,04,000.00
TOTAL	Rs. 30,21,500.00

RAW MATERIALS

1. Pepsin
2. Glyceryl stearate
3. Soap
4. Glue
5. Stearic acid
6. Borax
7. Gum arabic
8. Packing material, plastic bottles

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 57,10,650.00
2. SALARY & WAGES	Rs. 1,34,375.00
3. UTILITIES & OVERHEADS	Rs. 88,500.00
TOTAL	Rs. 59,33,525.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 30,21,500.00
TOTAL WORKING CAPITAL for 1 MONTH	Rs. 59,33,525.00
TOTAL	Rs. 89,55,025.00

TURN OVER/ANNUM

By sale of 1500 MT of silk sizing liquid	Rs. 8,70,00,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 16%

RATE OF RETURN = Operating profit / T.C.I x 100 = 159%

BREAK EVEN POINT (B.E.P) = 16%

21

SOFTENERS (CATIONIC, AN-IONIC AND NON-IONIC)

MANUFACTURING PROCESS

The amine is preheated to 60°C and 35% hydrogen Peroxide is added over one hour per period with good agitation. The reaction mixture is kept at 60-65°C during peroxide addition, as above this temperature the solution become yellow and at lower temperature a longer reaction time is required. During the one hour period of hydrogen peroxide addition the mixture is gel unless water is also added. The water required for dilution is added in portion. Just sufficient to keep the reaction mixture fluid. After all the peroxide has been added. The The remaining water to give the desured final strength is added and the temperature of the reaction mixture is raised to 75°C.

The solution is cooled and the unreacted hydrogen peroxide is destroyed by adding stoichiometric amount of sodium sulphite. While with pure amine the conversion is 100% with commercial amine it is 80% using a 10% molar excess of Hydrogen peroxide.

NON-IONIC SOFTENERS

Formulation - 1.

		%
Tallow Polyglycerol ester	-	21.2
Alkyl phenol condensate (with 20 mol of Ethylene oxide)	-	3.75
Water	-	74.75

Formulation -2.

It is an Emulsion of medialan A. tallow polyglycerol ester, alkyl phenol condensate, 20 molecules ethylene oxide and water.

		%
Medialan - A	-	25
Tallow polyglycerol	-	21.5
Alkyl Phenol Condensate	-	3.75
Water	-	49.75

PROCESS : The tallow polyglycerol is made by heating 66.7 Kgs of tallow with 27.23 Kgs polyglycerol at 200oC and finally raising the temperature to 260°C far 30 minute to complete the reactiuon. Completion of hte reaction is indicated by the solubility of the mixture in alchol. Six grams sodium. hydrosulphite is generally used as a catalyst along with tallow and polyglycerol.

ANIONIC SOFTENERS

The anionic softeners do not possess substantivity to the fabric under not wash fast as most of the textile materials are anionic in nature hence they repel the softeners. Thus anionic softener are mechanically deposited on the fabric by padding.

Formulation :-

		Kgs.
Castor oil	-	30
Mineral oil	-	23
Paraffin Wax	-	15
Stearic Acid	-	10
Olcic Acid	-	10
Sodium Dodecyl benzene Sulphonate	-	12
Water	-	10

The various appropriate ingredeous e.g. Castor Oil, Mineral Oil, paraffin Wax, Stearic Acid, Olecic Acid and surface Acture agent are ingenously blanded in a mixer fited with agitator and motar into the finished product to fulfill the specific and requisite properloies.

CLASSIFICATION OF CATIONIC SOFTENERS

A large number of cationic both non-quaternary and quaternary types have been patented as possible textile softeners but relatively few of these are of any importance in practive. Many of the commercial materials are complex mixtures rather than single compounds, some of the most important ones are given below-

Reaction product of fatty acids or acid chlorides with amino alcohols

Depending on reaction conditions two classes of softeners are obtained from this reaction .

a. Amino Esters -

$RCOO\text{-}N_2N\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}OH$

Hydroxy ethyl ethylenediamine

$RCOO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2$

These esters are finally readily hydrolysed. The quaternary compounds derived from these are also easily hydrolysed.

REACTION PRODUCT OF FATTY ACIDS WITH ETHYLENE TRIAMINES

Another important class of softeners are the imidazolines derived from fatty acids and ethylene triamine. Amide amine are formed first and on raising the temperature, they lose water and cyclise to a ring structure.

Cationic softeners based on fatty amine type and their ethoxylated derivatives used especially for man made fabrics the alcohol amine ester type used for rayons and viscose staple . The compounds with the fatty acid amide bond used for wool and quaternary compounds and their ethoxylated derivatives with improved hydrophilic properties.

PLANT ECONOMICS OF SOFTENERS (CATIONIC, ANIONIC & NON IONIC)

Rated Plant Capacity = 3 TON./Day

LAND & BUILDING (Land Area 2500 sq. mt.) = Rs. 74,70,000.00

PLANT & MACHINERY

1. Reaction vessel
2. Storage Tank.
3. Boiler
4. Distillation Column
5. Laboratory Equipments
6. Miscellaneous pipe
   fitting pump etc.

FIXED CAPITAL

1. LAND & BUILDING	Rs. 74,70,000.00
2. PLANT & MACHINERY	Rs. 26,50,000.00
3. OTHER FIXED ASSETS	Rs. 3,65,000.00
TOTAL	Rs. 1,04,85,000.00

RAW MATERIALS

1. Tallow poly glycerol
2. Alkyl phenol condansate
3. Dimethyldodecyl Amine
4. Hydrogen peroxide
5. Castor Oil
6. Mineral Oil
7. Paraffin Wax
8. Stearic Acid
9. Oleic Acid
10. Sodium dodecyl benzene sulphonate
11. Packaging Materials
12. Miscellaneous

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 23,67,500.00
2. SALARY & WAGES	Rs. 1,13,344.00
3. UTILITIES & OVERHEADS	Rs. 3,15,250.00
TOTAL	Rs. 27,96,094.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 1,04,85,000.00
TOTAL WORKING CAPITAL for 2 MONTHS	Rs. 55,92,188.00
TOTAL	Rs. 1,60,77,188.00

TURN OVER/ANNUM

By sale of Softener (Cationic, Anionic, Non Ionic). 900 MT	Rs. 5,40,00,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 32%

RATE OF RETURN = Operating profit / T.C.I x 100 = 109%

BREAK EVEN POINT (B.E.P) = 22%

22

TEXTILE AND FINISHING AGENTS

MANUFACTURING PROCESS

Dye Fixing Agent

Raw Materials Requirements

The raw materials and their composition required for the production of cationic rearder is as follows:

1. Toluene	24
2. Acetic acid (60%)	12
3. Sodium Sulfate	18
4. Triethylamine	3
5. Ethyl Iodide	0.7

The method of making cationic rearder is very simple but operating conditions must be followed during manufacturing processes. There are only two major steps involved in the manufacturing process viz.

A. Preparation of bath.

B. Final Make up of cationic redarder

A Preparation of bath

In the cationic retarder manufacture no direct mixing is involved. The toluene as a solvent is used in this product. The first step is to prepare bath of toluene.

The following are the components and their amount required for the bath making.

1. Toluene	20%
2. Acetic Acid (60%)	10%
3. Sodium Sulphate	15%
4. Water	55%

The bath is prepared in a mixing tank, made of stainless steel lined on mild steel materials. an agitator is fitted with it for mixing purposes and an jacket is provided with it for steam heating.

First, the tank is charged with acetic acid, diluted with water and followed by addition nof sodium sulphate in the required proportions. The mixture is stireed with agitator and simultaneously it is heated to temp. of 60-65°C & maintained during the whole reaction. After about one hour a homogeneous mixture will be obtained. After the homogeneous mass has been obtained, toluene is run into it with constant agitation. The temperature is maintained at the same range. After about 2 hours, a clear mixture is obtained water is then added to get toluene bath which is ready for the preparation of final products.

B. Cationic Retarder Making:

In the next step, the other ingredients i.e. Triethylamine and Ethyl Iodide are added to the bath prepared in the first step. These chemicals are added in less amount as shown in the raw materials requirements. The agitation is started and the temperature is reduced.

After incorporating the chemicals, and mixing tem properly, the homogeneous products is obtained which is cooled to room temperature, packed and is ready for sale.

WETTING AGENT

	Parts/wt.
Sodium Isopropylnaphthalene Sulphonate	10.0 gm.
Orthophenyl Phenol	2.2 gm.
Water	71.8 gm.
Ethylene Chlorhydrin	6.0 gm.
Alcohol	10.0 gm.
	100.0 gm.

WETTING AGENT FOR YARNS

	Parts/wt
Formaldehyde	7
Sodium Benzoate	3
Sodium Formate	5
Ethylene Glycol	6
Sulfonated Caster Oil	18
Sulfonated wetting Agent (Sulfatate)	8
Water	53
	100

PROCESS:-

Pour all ingredients except sulfonated caster oil into the water stir well to dissolve the use of moderate heat is permitted. All sulfonated caster oil to the clear solution.

For wetting and conserving cotton rayon or wool yarn use a solution containing 0.5-2% of above combination. This material serve double purpose by replacing water in the yarn lost partly at the spinning process and conserving it by preventing the formaton of molds.

If wets the raeyon throughout if properly applied by any custonary spraying system.

Before its use the water content of the Yarn has to be determined and the required amount of the wetting agent - water solution added.

Care shall be taken that the water content of the material after treatment does not exceed the admitted limits of the specific yarn.

PLANT ECONOMICS OF TEXTILE & FINISHING AGENTS

LAND & BUILDING (Land Area 3000 sq.mt.) = Rs. 79,95,000.00

PLANT & MACHINERY

1. (a) FOR DYE FIXING AGENT:- Mixer M.S. (S.S Lined) with agitator for bath preparation
2. Ethyl alcohol Storage Tank
3. Storage Tank
4. Acetic Acid Storage Tank
5. Packing Machine
6. (b) FOR WETTING AGENT:- Mixing kettle with stirrer
7. Storage tank with stirrer
8. Scrubber
9. Filter
10. (c) FOR TEXTILE BINDER:- Storage Tanks
11. Jacketed Stirred Reactors (Glass lined)
12. Spray Drier
13. (d) FOR SOFTNER:-Reaction vessel made of S.S.
14. Distillation Equipment for water
15. (e) FOR WATER PROOFING AGENT:- Mixing kettle with stirrer
16. Dissolving Tank Fitted with stirrer
17. (f) FOR SOFTENING AGENT:- Mixer (Jacketed) with stirrer
18. Boiler
19. DG Set
20. Lab Testing Equipments
21. Instrumentation & Process Control Equipments
22. Misc.Equipments viz pipe fitting, valves, Motors, etc.

FIXED CAPITAL

1. LAND & BUILDING	Rs. 79,95,000.00
2. PLANT & MACHINERY	Rs. 57,29,000.00
3. OTHER FIXED ASSETS	Rs. 9,00,000.00
TOTAL	Rs. 1,46,24,000.00

RAW MATERIALS

1. (a) FOR DYE-FIXING AGENT:- Ethyl Alcohol
2. Acetic Acid
3. Sodium Sulphate
4. Dicyandiamide
5. Ethyl iodide
6. Packaging Material
7. (b) FOR WETTING AGENT:- Formaldehyde
8. Sodium Benzoate
9. Sodium Formate
10. Ethylene Glycol
11. Sulfonated Castor oil
12. Sulfonated wetting Agent (Sulfonate
13. Packing Material
14. (c) FOR TEXTILE BINDER:- Vinyl Chloride Monomer
15. Sodium Lauryl Sulphate
16. T-butyl Hydroperoxide
17. Miscellaneous (like chain tranfer agent) fugitine alkali solution etc.
18. (d) FOR SOFTENERS:- Tallow poly glycerol ester
19. Alkyl Phenol condansate
20. Dimethyldodecyl Amine
21. Hydrogen peroxide
22. Castor oil
23. Mineral oil
24. Paraffin wax
25. Stearic Acid
26. Olcic Acid
27. Linear Alkyl Benzene sulfonated
28. Packaging Material
29. Miscellaneous (Sodium Sulphite,etc)

30. 1(e) FOR WATER PROOFING AGENT:- Paraffin wax
31. Glue
32. Aluminium Oxide
33. Formic Acid
34. Colophony
35. Caustic Potash
36. (f) FOR SOFTENING AGENT:- Oleic Acid
37. Castor oil
38. Paraffin wax
39. Triethanolamine

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 32,75,440.00
2. SALARY & WAGES	Rs. 4,81,460.00
3. UTILITIES & OVERHEADS	Rs. 4,66,200.00
TOTAL	Rs. 42,23,100.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 1,46,24,000.00
TOTAL WORKING CAPITAL for 1 MONTH	Rs. 42,23,100.00
TOTAL	Rs. 1,88,47,100.00

TURN OVER/ANNUM

1. By sale of Dye Fixing Agent (Dicyanimide Based) 1,50,000 kgs,
2. Wetting Agent 3,00,000 Ltrs,
3. By sale of Textile Binder 900 MT.
4. Cationic Softner 30,000 kgs,
5. Anionic Softner 30,000 kgs
6. Non-Ionic Softner 30,000 kgs

7. Water Proofing Agent 3,00,000 kgs
8. Softening Agent 1,50,000 kgs,

TOTAL	Rs. 6,27,00,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 12%

RATE OF RETURN = Operating profit / T.C.I x 100 = 41%

BREAK EVEN POINT (B.E.P) = 53%

23

TEXTILE AUXILLIARIES

DETAILS OF TEXTILE AUXILIARIES CHEMICALS & THEIR MANUFACTURE FOR DIFFERENT PROCESS

STARCH

Milling of corn, zea may provide corn starch. Steeped corn is coarsely ground in an attrition mill to break loose the germ. The mill gap during this step must be adjusted to maximize the amount of germ feeds but minimize rupture of germ. Germ is removed from the aqueous slurry in a cyelone separator. The Germ fraction is processed for corn oil. The cyclone underflow is milled a second time for complete release of the starch grannules. Following the second milling, the kernel suspension contain starch, glutten & fibre. The collected fibre is combined with glutten for feed use.

The starch glutten suspension, is concentrated by centrifugation. The concentrated starch is passed through hydrocyclone to remove the last traces of protein. Strach suspension may be processed dry or marketed as unmodified starch.

GLUE/GELALINE

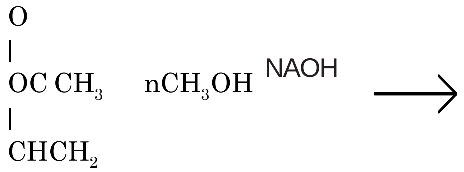
Manufacture of Animal glue is essentially a treatment of a collagen source with heat and water in order to hydrolyziet to a soluble product as rapidly and as efficiently as possible. The resulting solution is filtered, centrifuged to remove fat, concentrated to a suitable solids content, chilled to get the concentrate extruded or cut into particles, dried, grounded and packed.

CASEIN

It is a cheese product derived from milk first milk is processed i.e. cooling homogenization. Paste urization cleaming is done to store milk for long time than cheese is manufactured. Casein is precipitated by acidification which can be accomplished by natural souring of milk.

POLY VINYL ALCOHOL

Polyvinyl alcohol is manufactured by base-catalyzed methanolysis of polyvinyl acetate. Sodium Hydroxide is the usual base. The degree of hydrolysis during alcoholysis is controlled and is independent of molecular weight.



$$\overset{\overset{O}{|}}{\underset{\underset{CHCH_2}{|}}{OC\,CH_3}} \quad nCH_3OH \xrightarrow{NAOH}$$

POLYVINYL ALCOHOL O
|
n CH_3OC CH_3
METHYL ACETATE

SALICYLIC ACID

Salicylic acid is manufactured by the reaction of Alkali phenol & CO_2 by Kolbe-Schmitt reaction. It is obtained as white crystals, fine needles or fluffy white crystalline powder.

BACTERIAL ENZYMES

Bacterial enzymes are excreted by bacteria of germs Bacillus, especially member of the Bacillus sublilis group, a group regarded as harmless saprophytes which has been employed in the production of proleases and amylases.

Fermentation require isolation of the proper strain of bacterium. The most effective nutrient medium and growth conditions are then selected. Culturing is initiated in glass laboratory flask. The medium functions as a source of protein and carbohydrates. A typical medium for enzyme production is 3% potato starch, 2.5% soyabean meal 8% ground barely, 0.4 $CaCO_3$, 0.4% soyabean oil and 85.7% tap water.

The recovery of enzyme begins as soon as the fermentation has terminated. The medium is transported through a cooling stage to a separation process utilizing centrifuge where bacteria & gross insoluble substrate components are removed. The enzyme solution is concentrated by vacuum evaporation or ultra filtration and the enzyme is removed from the filtrate by the addition of a protein precipitation agent. In order to prevent the growth of bacteria during the recovery process, the enzyme precipitate is maintained at the lowest temperature possible.

GELATINE

Gelatine is manufactured by hot water extraction followed by freezing & filtration of Agar. The freezing allows removal of the soluble salts. Manufacture involves the following steps (1) Cleaning or washing of Agar raw materials (b) Bleaching or chemical treatment (3) Extraction (4) Filtration (5) Gelation (6) Freezing (7) Thawing (8) filtration (9) drying (10) bleaching (11) washing & drying.

PALM OIL & TURKEY RED OIL

These oils are manufactured by extraction (solvent) process and further refining of the oil from the oil seed.

CARBON TETRA CHLORIDE

Carbon tetra chloride is produced mainly by chlorinolysis, the chlorination of Hydrocarbon e.g. ethylene. The quantity of carbon tetra chloride produced depends on the nature of Hydrocarbon & condition of chlorination 5:1 mixture of chlorine and methane at 650°C with perchloro ethylene as the by product.

CYCLOHEXANE

Cyclohexane C_6H_{12} is a clear, essentially water soluble, non corrossive liquid. it is easily vaporized, readily flammable, and less loxic than bezene. It is a cycloparaffin. It is manufactured by the hydrogenation of benzene.

NAPHTHELEN SULPHONIC ACID

Generally suphation of napthalene leads to a mixture of products. Sulfonation at less than 100°C is kinetically controlled and produces predominantly 1-napthalene sulfonic acid. Sulfonation at above 150°C provides thermodynamic control of the reaction and 2-napthenelene sulfonic acid is the main product.

TRICHLORO ETHYLENE

Trichloro ethylene is manufactured from ethylene or dichloro ethane. The chlorination of ethylene yields dichloroethane which can be further chlorinated to trichloro ethylene and tetra chlorethylene in an exothemic reaction carried out at 280-450°C using catalyst e.g. potassium chloride, aluminium chloride, graphite or activated carbon. Tetra chloro ethylene conversion is maximized at a chlorine to dichloro ethane ratio of 1.7:1. Tetra chloroethylene conversion is maximized at a feed ratio of 3:1.

GLYCOL MANUFACTURE

Ethylene Glycol is manufactured by direct ehtylene oxidation to ethylene oxide and then hydrolysis of the low to have ethylene glycol.

Ethylene oxide hydrolysis proceeds with either acid or base catalyst or uncatalyzed in neutral medium. In acid catalyzed hydrolysis protonation of oxides activates it for reaction with water. The reaction is conducted in a large excess of water at moderate temperature to obtain 85-90% mono ethylene glycol. The lower poly glycol i.e. diethylene, trielhylene and tetra ethylene glycols, accounts for the remainder the primary bi product being diethylene glycol.

Base catalysis results in considerably lower mono ethylene glycol. The yields of higher glycol products is substantially increased since anions of the first reaction products effectively complete with hydroxide ions for ethylene oxide. Neutral hydrolysis (pH 6-10) conducted in presence a large excess of water at high temperatures and pressures increases mono ethylene glycol.

The water effluent from hydrolysis is removed in a resins of multiple effect evaporators and the ethylene glycol is refined by vaccum distillation.

FORMULATION

Water	150 gal.
Soda Ash	50 oz.
Copper	1%

Sulfate Solution	50 cc.
“Pearl”	
Cornstarch	80 lb .
Hydrogen	35%
Peroxide	135.4 fl. oz.
Tallow	1 lb.

These are filled into the starch kettle in the order given and with constant stirring. The processing temperature of 208°F. is reached in 30 minutes and maintained for another 15 minutes. The paste is used for slasher sizing of 19/1 and 26/1 warp yarns.

Sizing for Backs of Axminster Rugs

U.S. Patent 2,542,344

Sulfite Waste	
Solids	28 - 50.3
Starch	20 - 35.2
Clay	42.3 - 0.0
Ethylene Glycol	
Diabietate	9.7 - 14.5

This is dispersed in water with hheat to give a viscosity of 200 to 2000 cp.

U.S. Patent 2, 576,921

Arrowroot Starch	2 g.
Gelatin	1 oz.
Alum	1/4 oz.
Alcohol	1 fl. oz.
37% Formaldehyde	1 fl. oz.
Water To make	1 qt.

TEXTILE WATERPROOFING

Formula

U.S. Patent 2,455,886

Cetyl Acetamide	17.0
Butyl "Cellosolve"	11.6
Zirconium Stearate	4.2
Zirconium Formate	1.5
Water	65.7

The acetamide is thoroughly mixed and wetted with the water and "Cellosolve" which acts as emulsifier and solvent. The mixture is quickly brought to a boil, then cooled to about 90°F., and dispersed paint mill or similar device. The zirconium salts are dissolved and/or dispersed in water, along with any mineral wax which may be added. Dispersion is facilitated by running the mixture through a colloid mill. The so-prepared two mixtures are now blended and further dispersed by running them together through a cooloid mill.

If desired, 10 to 15% by weight of a high melting mineral wax, such as cerise wax, may be included, preferably by emulsification, with a corresponding reduction in the amount of water.

For the treatment of moderate weight fabrics, for example, it has been found suitable to dilute has been found suitable to dilute the dispersion to 10 to 155 by weightt of its original strength with warm or cold water before application. The dispersion mixture, diluted as required and preferably at about 100°F., may be applied to a fabric by ipregnating in a pad, mangle, quetch, or any similar device and then dried thoroughly at about 280°F., or higher. Drying may be carried out on a tenter frame, drying cans, in a hot chamber or other heating device.

Nonstiffeningg Waterproofing for Cloth

Linseed Oil	1
China Wood Oil	1
Xylol	94
Stearic Acid	2

Mix the two oils with the xylol, and heat them on a hot plate, away from open flames, to 150°F. Wet the stearate and stearic acid with a portion of the solvent and add them to the oils with agitation . Hold at 150°F. until dissolved. Cool to room temperature and strain through cheesecloth.

WATER SOLUBLE FLAMEPROOFING FOR FABRICS

Formula

Borax	9 oz.
Boric Acid	4 oz.
Hot Water	1 gal.
Ammonium Sulfate	21 oz.
Borax	21 oz.
Ammonium Carbonate	6 oz.
Boric Acid	8 oz.
Starch	5 oz.
Warm Water	2 gal.

PLANT ECONOMICS OF TEXTILE AUXILLIARIES & CHEMICALS

Rated Plant Capacity = 2000 KGS/Day

LAND & BUILDING (Land Area 3000 sq.mt.) = Rs. 33,50,000.00

PLANT & MACHINERY

1. Corn Storage Holper
2. Steping tank
3. Attrition mill
4. Cyclone separator
5. Miller
6. Centrifuge separator
7. Hydro cyclone
8. Dryer
9. Agar Storage house

10. Washing tank
11. Bleaching tank
12. Extractor
13. Filter press
14. Freezer
15. Rotary dryer
16. Dryer steam
17. Washing tank with filter
18. Chemical Reactor
19. Tripple effect evaporator
20. Distillation column
21. Absorption lower packed
22. Evaporator
23. Boiling
24. Heat exchanger
25. Rotary drum filter
26. Tripple effect evaporator
27. Boiler
28. Chemical treating tank
29. Automatic packing machine
30. D.G.Set

FIXED CAPITAL

1. LAND & BUILDING	Rs. 33,50,000.00
2. PLANT & MACHINERY	Rs. 47,10,000.00
3. OTHER FIXED ASSETS	Rs. 8,25,000.00
TOTAL	Rs. 88,85,000.00

RAW MATERIALS

1. Corn
2. Agar

3. Ethylene
4. Oxygen
5. Refined oil
6. Alum
7. Activated Carbon
8. Aluminium salts

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 4,87,500.00
2. SALARY & WAGES	Rs. 3,54,750.00
3. UTILITIES & OVERHEADS	Rs. 1,16,000.00
TOTAL	Rs. 9,58,250.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 88,85,000.00
TOTAL WORKING CAPITAL for 1 MONTH	Rs. 9,58,250.00
TOTAL	Rs. 98,43,250.00

TURN OVER/ANNUM

1. By SALE OF 150 MT Corn Starch
2. Glycerol 150 MT
3. Ethylene Glycol
4. Gelatine
5. Bye product fatty acid

TOTAL	Rs. 1,67,40,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 16%

RATE OF RETURN = Operating profit / T.C.I x 100 = 28%

BREAK EVEN POINT (B.E.P) = 64%

24

TEXTILE CHEMICALS

The textile chemicals viz; Turkey red oil, Rayon Lubricating oil, Delustering Rayon, Textile Printing paste, etc. are becoming very demandable products and gaining good eminence now-a-days.

MANUFACTURING PROCESS OF TURKEY RED OIL

The sulphonation process consists of changing the oils into the sulphonator which may be a steel jacketed. lead limed tank with an agitator, or a monel limed tank which is found to be superior. The tank may be a single shell type equipped with a non-corradible cooling coil. The oil is agitated and cooled to room temperature or even lower. Concentrated sulphuric acid 25% of the weight of the oil is added slowly. Experience has shown that oils containing about 4% of combined SO_3 can be used for blending with either vegetable or mineral oil, whereas those that are more highly sulphonated do not blend. The temperature of the mixture is maintained at or below 100°F.

Of a blending oil is to be produced, the entire amount of acid added to the oil within 15 - 30 min. but for higher sulphonation the mixing will require a long period.

Sometimes after the reaction has taken place the mixture is allowed to stand for several hours or overnight. It is then run into the washing tank which may be similar to be sulphonation tank, then it is mixed with an equal volume of water and allowed to stand until the batch has separated into an oily top layer and a bottom layer, consisting of an aqueous acid solution, which is drawn off, one or two washes with brine (1.5 lb of salt to a gallon of water) or glambers salt solution follows. Each time, the brine is thoroughly mixed with the oil and allowed to settle. The object is to wash out as much of the uncombined sulphuric acid as possible.

At this point manufacturers differ as to the mode of procedure. Some neutralize with equammonia while others use 24' B’e solution of caustic soda, which is added with constant stirring, until a clear transparent oil results.

The pH of this oil should be between 5 and 7. The finished oil should be allowed to stand for several days before drawing off, in order to allow any water containing sulphates, to settle out. The finished product usually contains about 35% water.

FORMULA NO. 1:

A German manufacturing process a practiced by M/s. Bohune Felt Chemic is given below. The product was market as “A virol KM”.

MATERIAL REQUIRED:-

Castor Oil 1600 kg

Sulphuric acid (1.84 sp.gr) 380 kg.

Caustic soda (40oBe’) 860 Kg.

PROCESS:

200 kg. of concentrated sulphuric acid are slowly added into castor oil (1600 Kg) with continuous stirring in about four and half hours. The temperature of the mixture is maintained between 25-30°C by circulating water in cooling coils /or jacket. After stirring further, 130 kg. of sulphuric acid is added, slowly with continuous stirring in over 3 hours, without stirring. Finally a further quantity of 50 kgs of sulphuric acid is added in about 1 hour and stirring is continued for another hour. The batch is then neutralized as quickly as possible by stirring with 40°Be’ caustic soda (860 kg). The temperature rises to 90 to 100°C. The batch should now show an acid reaction to phenolphthalein. Lime steam is now passed in for half an hour. After standing over night the aqueous salt layer is run off. The product is settled for 2 weeks, the aqueous layer is run off, and it is then standardized by addition of requisite quantity of water.

Castor oil is charged into a nickel-steel tank fitted with turbine type agitator and cooling coils. Sulphuric acid is added as rapidly as possible without allowing the temperature to go about 95°F. After addition of all the acid the mixture is agitated for 1 hour more. The oil is allowed to lie overnight, the next morning the oil should be brilliantly clear is aqueous solution. The excess acid is neutralized with 30°Be’ caustic soda solution and allowed to settle. The salt water is drawn off and the resulting product will be low in free fatty acid and total alkali. It will be clear, soluble in a 10% solution in both very hot and very cold water. The colour well be lighter and the viscosity, even when cut further with water will be slightly heavier.

Alternatively, the sulphonated oil and mixture is added into a sodium sulphate solution (00 kgs, 10% solution) allowed to settle and the spent acid layer is withdrawn. It is now finished with caustic soda solution. The product will have high free fatty acid and high alkali according to the quantity of alkali added.

FORMULA NO. 2 :-

In this sulphonation of castor oil is carried out in presence of diethyl sulphate.

Castor oil	100 parts
Diethyl sulphate	15 parts
Sulphuric acid 66°Be’	150 parts

Castor oil mixed with diethyl sulphate is treated at 10°C with 150 parts of 66°Be’ sulphuric acid and neutralized with caustic sods solution in the normal manner. The product contains higher percentage of bound sulphur trioxide.

MANUFACTURING PROCESS OF DELUSTERING AGENT FOR RAYON

AS PER FORMULATION NO.1 :-

	% age
Barium chloride	40
Dextrin	3
Starch	16
Anhydrous aluminium Sulphate	36
Anhydrous Sodium Acetate	5
	100

The ingredients viz Barium Chloride, Dextrin, Starch, Anhydrous, Ammonium Sulphate, Acetate are taken in requisite proportions and introduced into a mixer fitted with an agitator. The ingredients are well mixed to form a homogenous mass. It is checked for quality and suitably packed and then stored/despatched for marketing.

PLANT ECONOMICS OF TEXTILE CHEMICALS

LAND & BUILDING (Land Area 3000 sq.mt.)= Rs. 78,95,000.00

PLANT & MACHINERY

1. (a) FOR TURKEY RED OIL:-Sulphonator agitated vessel,made of monel or Lead Lined vessel, equipped with steel jacket
2. Neutralizing tank
3. Intermadiate tanks
4. Settling tanks
5. Soda Ash solution making tank
6. Water adjustment tank
7. Packing Machine (Semi-Automatic)
8. (b) FOR PIGMENT EMULSION FOR TEXTILES: Ball mill
9. Kneader with motor
10. Mixer
11. Jacketed kettle
12. (c) FOR RAYON LUBRICATING OIL:- Jacketed kettle S.S. with M.S.Jac-ket fitted with agitator
13. Storage Tanks
14. (d) DELUSTERING AGENT FOR RAYON:- Mixer with agitator motor and accessories
15. (e) TEXTILE SCOURING AGENT:- Mixer with agitator (S.S)
16. (f) FOR FOAM STABILIZER:- Reaction vessel (S.S) with heating element agitator and accessories
17. Boiler

18. DG Set
19. Lab Testing Equipments
20. Instrumentation & Process Control
21. Miscellaneous viz pipe fitting, valves, Motors, Weighing Balance etc.

FIXED CAPITAL

1. LAND & BUILDING	Rs. 78,95,000.00
2. PLANT & MACHINERY	Rs. 56,60,000.00
3. OTHER FIXED ASSETS	Rs. 9,30,000.00
TOTAL	Rs. 1,44,85,000.00

RAW MATERIALS

1. (a) FOR TURKEY RED OIL:- Castor oil
2. Sulphuric acid concentrated
3. Caustic soda
4. Packing Material
5. (b) FOR PIGMENT EMULSION FOR TEXTILES:- Pigment Powder
6. Gum Tragacanth or textile gums
7. Solvent soluble resin emulsions
8. Packing Material
9. (c) FOR RAYON LUBRICATING OIL:- Sulphonated castor oil
10. Commercial olive oil
11. Acetic Acid
12. Paraffin oil
13. Packing Material
14. (d) FOR DELUSTERING AGENT FOR RAYON Barium chloride

15. Dextrin (white)
16. Starch
17. Anhydrous Aluminium Sulphate
18. Anhydrous Sodium Acetate
19. Packing Materials
20. (e) FOR TEXTILE SCOURING AGENT:-
    Sulfonated castor oil
21. Oleic acid
22. Caustic Potash
23. Packing Material
24. (f) FOR FOAM STABILIZER:- Lauric Acid
25. Diethanolamine
26. Nitrogen
27. Packing Material

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 72,78,115.00
2. SALARY & WAGES	Rs. 5,43,970.00
3. UTILITIES & OVERHEADS	Rs. 3,05,200.00
TOTAL	Rs. 81,27,285.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 1,44,85,000.00
TOTAL WORKING CAPITAL for 1 MONTH	Rs. 81,27,285.00
TOTAL	Rs. 2,26,12,285.00

TURN OVER/ANNUM

1. By sale of Turkey Red oil	3,00,000 kgs
2. Pigment Emulsion for textiles	3,00,000 kgs

3. Rayon Lubricating oil 3,00,000 kgs	
4. Delustering Agent for Rayon	1,50,000 kgs
5. Textile Scouring Agent 3,00,000 kgs	
6. Foam Stabilizer	1,50,000 kgs
TOTAL	Rs.11,32,50,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 10%

RATE OF RETURN = Operating profit / T.C.I x 100 = 49%

BREAK EVEN POINT (B.E.P) = 44%

25

TEXTILE PRINTING PASTE

Textile printing paste plays a vital role in textile industries. Mechanical application methods, including printing by granure roller, flat screen rotary screen, and transfer, were also critically discussed.

The printing of acrylic fabrics and their blends generally consists of two stages-preparatory and printing. Usually the process comprices the following operations.

Preparatory	Printing
Singeling	Printing
Desizing and Scouring	Steaming
Bleaching	Washing
Drying and stentering	Soaping

FORMULATIONS OF PRINTING PASTES

1. Vat Dye Printing Paste (Blue)

Ciba Blue 2 B micro Powder		
(dispersible A.)		4 parts
Glycerol		10 parts
Indian gum-locust bean gum thickner		53 parts
Potassium carbonate		15 parts
Sulfoxylate formaldehyde	A.1	6 parts
A and B is to be mixed		6 parts

2. Soluble Vat Dye Printing Paste :

60	parts soluble vat dye dissolved in
2	parts sodium carbonate and
358	parts warm water, mix with
500	parts neutral starch-locust bean gum thickner
30	parts glycerol, heating to 120oF to mix coal and strain and then add
50	parts of sodium nitrate 33/1/3 solution.

PLANT ECONOMICS OF TEXTILE PRINTING PASTE

Rated Plant Capacity = 300 Kgs/Day

LAND & BUILDING (Land Area 300 sq. mt.) = Rs. 4,50,000.00

PLANT & MACHINERY

1. Tripple Roll Mill
2. Vertical Charge Mixer
3. Storage tanks
4. Filling Machine
5. Balance
6. Lab: Furnace
7. Miscellaneous Lab equipments

FIXED CAPITAL

1. LAND & BUILDING	Rs. 4,50,000.00
2. PLANT & MACHINERY	Rs. 2,94,000.00
3. OTHER FIXED ASSETS	Rs. 1,12,000.00
TOTAL	Rs. 8,56,000.00

RAW MATERIALS

1. Poly Vinyl Alcohol
2. Titanium Dioxide
3. CMC Gwna

4. Glycerine
5. Fixer CCL
6. Calicryl
7. DAP
8. Urea Tech. Grade
9. Tinopal
10. Printing Primer

TOTAL WORKING CAPITAL/MONTH

1. RAW MATERIAL	Rs. 3,90,884.00
2. SALARY & WAGES	Rs. 23,625.00
3. UTILITIES & OVERHEADS	Rs. 29,040.00
TOTAL	Rs. 4,43,549.00

TOTAL CAPITAL INVESTMENT

TOTAL FIXED CAPITAL	Rs. 8,56,000.00
TOTAL WORKING CAPITAL for 1 MONTHS	Rs. 4,43,549.00
TOTAL	Rs. 12,99,549.00

TURN OVER/ANNUM

By sale of 90,000 kgs. of Printing Paste	Rs. 67,50,000.00

PROFIT SALES RATIO = Profit / Sales x 100 = 17%

RATE OF RETURN = Operating profit / T.C.I x 100 = 89%

BREAK EVEN POINT (B.E.P) = 31%

	EIRI PROCESS TECHNOLOGY BOOKS	Price in Rs.	Price in US$
	Chemical/ Dyes/ Petrochemicals/ Lubricant/ Electroplating		
01	Small Medium & Large Chemical Industries	375/-	40/-
02	Industrial Chemicals Technology Hand Book	1100/-	110/-
03	Modern Technology of Organic & Inorganic Chemicals	1400/-	140/-
04	Hand Book of Electroplating Anodizing & Surface Finishing Technology	750/-	75/-
05	Hand Book of Agro Chemical Industries (Insecticides & Pesticides)	900/-	90/-
06	Technology of Synthetic Dyes, Pigments Intermediates	1100/-	110/-
07	Petrochemicals, Lubricants, Greases & Petroleum Refining	900/-	90/-
08	Hand Book of Lubricants, Greases & Petrochemicals Technology	750/-	75/-
	Gums, Adhesives and Sealants		
01	Technology Of Gums, Adhesives & Sealants With Formulations	950/-	125/-
02	Hand Book Of Adhesives With Their Formulae	650/-	100/-
03	Adhesives Technology & Formulations Hand Book	975/-	125/-
	Small Scale Industries/ Stationery/Paper/ Inks/ Candles & Export Business		
01	Start Your Own Export Business (How To Export)	450/-	45/-
02	Start Your Own Small Business And Industry	350/-	35/-
03	Candle Making Processes & Formulations Hand Book	380/-	40/-
04	Stationery, Paper Converting & Packaging Industries	400/-	40/-
05	Modern Inks Formulations & Manufacturing Industries	325/-	35/-
06	Profitable Businesses To Start For Entrepreneurs	400/-	40/-
07	Modern Small & Cottage Scale Industries	650/-	65/-
08	Profitable Small Cottage Tiny & Home Industries	650/-	65/-
	Bio Fuel & Bioprocessing		
01	Technology Of Bio-Fules (Ethanol & Biodiesel)	975/-	100/-
02	Modern Technology Of Bioprocessing	1475/-	150/-
	Printing, Screen Printing & Packaging		
01	Hand Book of Printing Processes Technologies & Industries	375/-	40/-
02	Hand Book Of Printing Technology (Offset, Screen, Flexo, Gravure, Inkjet & Digital)	975/-	100/-
03	Hand Book Of Offset Printing Technology	500/-	50/-
04	Screen Printing With Processes & Tech.	350/-	35/-
05	Hand Book Of Prepress	800/-	80/-
06	Hand Book Of Packaging Technology	900/-	90/-
07	Modern Packaging Technology for Processed Food, Bakery, Snack Foods, Spices and Allied Food Products	900/-	90/-
08	Hand Book Of Food Packaging Technology	900/-	90/-
09	Modern Technology of Printing Inks	1150/-	115/-
	Paint, Varnish, Solvents, Coating & Lacquers		
01	Paint Pigment Varnish & Lacquer Mfg.	450/-	45/-
02	Paint Varnish Solvents & Coating Tech.	750/-	75/-

03	Paint, Pigment, Solvent, Coating Emulsion, Paint Additives & Formulations	900/-	90/-
04	Technology Of Coating, Resins, Pigments & Inks Industries	975/-	100/-
05	Manufacturing Technology & Formulations Hand Book On Thinners, Putty, Wall & Industrial Finishes And Synthetic Resins	900/-	90/-
06	Technology of Synthetic Resins and Emulsion Polymers	975/-	100/-
07	Technology of Paints and Coatings with Formulations	1750/-	175/-
	Plastic/Polymer Process, Compounding, Injection Moulding, Rotational Moulding, Plastic Film, Fibre Glass, Plastic Waste Recycling, Moulds, Pet & Resins Industries		
01	Moulds Design & Processing Hand Book	495/-	50/-
02	Hand Book Of Plastic Materials & Processing Technology	750/-	75/-
03	Injection Moulding Of Plastics	750/-	75/-
04	Plastic Processing and Packaging Industries	975/-	100/-
05	Plastic Waste Recycling Technology	750/-	75/-
06	Technology Of Plastic Films	650/-	65/-
07	Rotational Moulding Technology Hand Book	750/-	75/-
08	Plastic Compounding, Master Batches, Pet & Other Plastics	750/-	75/-
09	Synthetic Resins Technology With Formulations	800/-	80/-
10	Technology Of PVC Compounding And Its Applications	900/-	90/-
11	Hand Book of Polymer And Plastic Technology	950/-	90/-
12	Hand Book Of Fibre Glass Moulding	450/-	45/-
13	Technology of Reinforced Plastics	750/-	75/-
14	Plastic Additives Technology Hand Book	950/-	95/-
15	Technology of Pet Bottles, Preform and Pet Recycling	850/-	85/-
16	Modern Technology of Extrusion & Extruded Products	800/-	80/-
17	Technology of Synthetic Resins & Emulsion Polymers	975/-	100/-
18	Technology of Plastic Additives with Processes and Packaging	900/-	90/-
19	Technology of Disposable Medical Products	1750/-	175/-
	Bakery, Confectionery & Breakfast, Pasta & Cereals		
01	Hand Book Of Bakery Industries	350/-	50/-
02	Hand Book Of Confectionery With Formulations	900/-	90/-
03	Breakfast, Dietary Food, Pasta & Cereal Products Technology	1150/-	120/-
04	Hand Book Of Modern Bakery Products	750/-	75/-
05	Modern Bakery Technology & Fermented Cereal Products With Formulae	1250/-	125/-
06	Technology of Confectionery, Chocolates, Toffee, Candy, Chewing & Bubble Gums, Lollipop and Jelly Products with Formulations	1750/-	175/-
	Agro Cultivation, Animal Farming, Agro Plantation & Agro Chemical/ Pesticides/Floriculture & Bee Keeping		
01	Poultry Farming & Feed Formulations	450/-	45/-
02	Hand Book Of Pig Farming	400/-	40/-
03	Agro Based H.B. Of Plantation, Cultivation & Farming	500/-	75/-

04	Agro Based Plantation Cultivation & Farming	475/-	50/-
05	Agro Chemical Industries (Insecticide & Pesticides)	900/-	90/-
06	Modern Bee Keeping & Honey Processing	375/-	40/-
07	Technology Of Modern Rice Milling And Basmati Rice	600/-	60/-
08	Hand Book Of Goat Farming	450/-	50/-
09	Floriculture Hand Book (Flowers Growing Technology)	1000/-	100/-
10	Aloe Vera Cultivation, Processings, Formulations And Manufacturing Technology	2500/-	250/-
	Dairy Farm, Milk Processing And Ice Cream		
01	Hand Book of Dairy Formulations, Processes & Milk Processing Industries	750/-	75/-
02	Milk Processing And Dairy Products Industries	950/-	95/-
03	Hand Book Of Dairy Farming to Produce Milk with Packaging	450/-	45/-
04	Hand Book Of Ice Cream Technology And Formulae	525/-	75/-
05	Hand Book Of Milk Processing Dairy Products And Packaging Technology	975/-	100/-
06	Dairy Farming for Milk Production Technology	975/-	100/-
07	Commercial Dairy Farming with Project Profiles	750/-	75/-
	Herbs & Medicinal Cultivation		
01	Herbs, Medicinal & Aromatic Plants Cultivation	650/-	65/-
02	Aushidhi And Sungndhit Paudho Ka Vaysayik (Hindi)	800/-	80/-
03	Hand Book Of Aromatic & Medicinal Plants And Biodiesel (Jatropha)	1100/-	110/-
04	Hand Book Of Medicinal & Aromatic Plants (Cultivation, Utilisation & Extraction Processed)	875/-	90/-
	Food & Agro Processing, Preservation, Snack Food, Dehydration, Fruit Beverage, Potato, Maize, Meat Process		
01	Fruits & Vegetables Processing Hand Book	750/-	75/-
02	Fruit Beverage & Processing With Mango	750/-	75/-
03	Food Processing & Agro Based Industries	975/-	100/-
04	Manufacturing Technology of Snacks Food, Namkeen, Pappad & Potato Products	750/-	75/-
05	Preservation & Canning Of Fruits and Vegetables	1200/-	120/-
06	Hand Book of Food Dehydration & Drying	650/-	65/-
07	Meat Processing & Meat Products Hand Book	900/-	90/-
08	Technology of Food Preservation & Processing	950/-	95/-
09	Hand Book of Food Packaging Technology	900/-	90/-
10	Agro Based & Processed Food Products	1100/-	110/-
11	Potato & Potato Processing Technology	850/-	85/-
12	Technology of Maize & Allied Com. Products	650/-	65/-
13	Technology of Food Processing Industries	975/-	100/-
14	Technology of Sweets (Mithai) with Formulae	1050/-	105/-
15	Modern Technology of Frozen Food Products	900/-	90/-
16	Technology of Water and Packaged Drinking water	1100/-	110/-
17	Complete Hand Book on Frozen Food Processing and Freeze Drying Technology	1000/-	100/-
18	Technology of Sweets (Mithai), Namkeen and Snacks food with Formulae	1750/-	175/-

19	Complete Book on Banana Cultivation, Dehydration, Ripening, Processing, Products and Packaging Technology	975/-	100/-
20	Technology of Chicken Meat and poultry Products	1750/-	175/-
21	Agro Food Processing and Packaging Technology	1100/-	110/-
	Soaps & Detergents		
01	Household Soap. Toilet Soap & Other Soap	750/-	75/-
02	Profitable Small Scale Manufacture Of Soaps & Detergents	375/-	40/-
03	Synthetic Detergents With Formulations	900/-	90/-
04	Modern Technology of Acid Slurry, Surfactants, Soap and Detergents with Formulae	850/-	85/-
	Organic Farming And Food		
01	Hand Book Of Organic Farming And Organic Foods With Vermi-Composting And Neem Products	1100/-	110/-
	Fish Farming & Fishery Products		
01	Hand Book Of Fish Farming And Fishery Products	650/-	65/-
	Cosmetic (Synthetic & Herbal)		
01	Cosmetics Processes & Formulations	900/-	90/-
02	Herbal Cosmetics & Beauty Products With Formulations	750/-	75/-
03	Profitable Small Scale Manufacture Of Cosmetics (Synthetic & Herbal)	950/-	95/-
04	Hand Book Of Synthetic & Herbal Cosmetics	575/-	60/-
05	Technology Of Herbal Cosmetics & Toiletries Products With Formulae	1100/-	110/-
	Oil And Fats		
01	Hand Book of Oils, Fats And Derivatives With Refining & Packaging Technology	950/-	95/-
02	Technology of Oilseeds Processing, Oils & Fats and Refining	1400/-	140/-
	Essential Oils & Aromatic		
01	Essential Oils Manufacturing & Aromatic Plants	650/-	65/-
02	Modern Technology Of Essential Oils	850/-	85/-
03	Technology Of Perfumes, Flavours & Essential Oils	1175/-	120/-
04	Essential Oils Processes & Formulations	650/-	65/-
	Perfumes And Flavours		
01	Hand Book Of Flavours & Food Colourants Technology	1400/-	140/-
02	Hand Book Of Perfumes & Flavours	600/-	60/-
03	H.B. Of Perfumes With Formulations	750/-	75/-
04	Technology Of Perfumes, Flavours & Essential Oils	1175/-	120/-
05	Hand Book Of Flavours Technology	750/-	75/-
	Building Materials & Chemicals		
01	Technology Of Building Materials & Chemicals With Processes	950/-	95/-
	Textile, Garments, Dyeing		
01	Modern Technology Of Bleaching, Dyeing, Printing & Finishing Of Textiles	750/-	75/-
02	Technology Of Textiles (Spinning & Weaving, Dyeing, Scouring, Drying, Printing And Bleaching)	900/-	90/-
03	Garments Manufacturing Technology	900/-	90/-

	Spices & Cold Storage		
01	Spices & Packaging With Formulaes	750/-	75/-
02	Start Your Own Cold Storage Unit	750/-	75/-
	Pulp & Paper Technology		
01	Hand Book Of Pulp & Paper, Paper Board & Paper Based Technology	1150/-	120/-
	Textile Auxiliaries & Chemicals		
01	Textile Auxiliaries And Chemicals With Processes And Formulations	950/-	95/-
	Pharmaceuticals & Drugs		
01	Pharmaceuticals And Drugs Technology With Formulations	950/-	95/-
	Leather & Leather Products		
01	Hand Book Of Leather & Leather Products Technology	850/-	85/-
	Biotechnology		
01	Hand Book Of Biotechnology	900/-	90/-
	Ceramics		
01	Hand Book of Ceramics and Ceramics Processing Technology	1975/-	200/-
	Tree Farming		
01	Hand Book Of Tree Farming	800/-	80/-
	Mushroom Cultivation/Process		
01	Hand Book Of Mushroom Cultivation, Processing And Packaging	550/-	55/-
	Biofertilizers & Vermiculture		
01	Hand Book Of Biofertilizers & Vermiculture	900/-	100/-
	Mineral And Minerals		
01	Hand Book Of Minerals And Minerals Based Industries	975/-	100/-
	Rubber Chemicals, Compound & Rubber Industries		
01	Rubber Chemicals & Processing Ind.	400/-	40/-
02	Modern Rubber Chemicals, Compounds & Rubber Goods Technology	1500/-	150/-
03	Technology Of Rubber & Rubber Goods Industries	900/-	90/-
	Ayurvedic Medicines		
01	Ayurvedic & Herbal Medicines With Formulaes	750/-	75/-
02	Hand Book Of Ayurvedic Medicines With Formulations (A Complete Hand Book Of Ayurvedic & Herbal Medicines)	900/-	90/-
	Steel, S.S., Non Ferrous Metals, Rolling Mill		
01	Modern Technology of Non Ferrous Metals and Metal Extraction	1100/-	110/-
02	Processing Technology of Steels and Stainless Steels	1900/-	190/-
03	Modern Technology of Rolling Mill, Billets, Steel Wire, Galvanized Sheet, Forging & Castings	2500/-	250/-
04	Manufacturing Technology of Non-Ferrous Metal Products	1750/-	175/-
	Wood, Veneer, Plywood, Particle, Board, Fibreboard, Bamboo & Forest Products		
01	Modern Technology Of Wood, Veneer, Plywood, Particle Board, Fibreboard, Bamboo & Forest Products	1600/-	160/-
	Waste Based Products Including Industrial, Agriculture,		

	Medical, Municipality, Organic & Biological		
01	Technology Of Products From Wastes Industrial, Agriculture, Medical, Municipality, Organic & Biological	900/-	90/-
	Multiple Project Reports on CD Rom		
01	92 New Lucrative Project Reports In Cd	25000/-	1250/-
02.	45 Infotech/It, Hospitality, Hospital, College, School & Club	16000/-	800/-
03.	23 Profitable Construction Projects	16000/-	800/-
04.	56 Agro Based & Food Processing Projects	16000/-	800/-
05.	52 Food, Dairy, Bakery, Confectionery & Snacks Foods	16000/-	800/-
06.	45 New Chemicals & Allied Project Reports	18000/-	900/-
07.	100 Profitable Plastic, Polymers & Allied Projects	21000/-	1050/-
08.	44 Textile, Garments, Hosiery & Allied Products In Cd	16000/-	800/-
09.	23 Dairy Farming (Buffalo & Jersey Cow, Dairy Products & Other Milk Processing Ind.	16000/-	800/-
10.	42 Paper, Pulp & Paper Converting Products Reports	18000/-	900/-
11.	31 Essential Oils, Perfumes, Flavours & Aromatic Compounds	16000/-	800/-
12.	28 Surgical And Disposable Medical Projects	16000/-	800/-
13.	36 Profitable Printing & Allied Projects Reports	16000/-	800/-
14.	63 Profitable Packaging & Allied Project Reports	16000/-	800/-
15.	99 Profitable Printing & Packaging	21000/-	1050/-
16.	42 Electroplating, Anodizing & Allied Projects	16000/-	800/-
17.	31 Profitable Plantation & Cultivation Projects	16000/-	800/-
18.	55 Profitable Products From Agro And Other Industrial Wastes	18000/-	900/-
19.	35 Profitable Gums, Adhesives, Sealants And Resins Projects	18000/-	900/-
20.	54 Paint, Varnish, Solvents, Lacquers, Resins, Enamel, Pigments, Thinners & Powder (54 Project Reports In Cd)	18000/-	900/-
21	43 Iron, Steel, Casting, Fabrication, Wire Drawing & Rolling Mills Projects	18000/-	900/-
22.	26 New Educational Projects (Schools, Colleges, Training/Management Institute, Hostels Etc.)	16000/-	800/-
23.	12 Mosquitoes Preventive Projects (Coils, Mats, Liquids, Agarbatti, Nets, Spray Etc.)	12000/-	600/-
24.	21 Bakery And Allied Products	12000/-	600/-
25.	67 Rubber And Rubber Goods Industries	18000/-	900/-
26.	37 Aluminium And Aluminium Based Industries	16000/-	800/-
27.	14 Potato And Potato Based Industries	12000/-	600/-
28.	50 Electrical, Electronics And Computer Based Industries	18000/-	900/-
29.	52 Cosmetics (Herbal & Synthetics) Technology Projects (52 Project Reports)	18000/-	900/-
30.	10 Molasses Based Lucrative Projects	16000/-	800/-
31.	24 Fruits/Veg. & Allied Food Dehydration Projects	16000/-	800/-
32.	7 Power Plant Projects (Thermal, Hydro, Solar, Wind Energy And Lignite Coal Based)	16000/-	800/-
33.	35 New Profitable Industries	16000/-	800/-
34.	160 New Export Oriented And Profitable Projects (160 Project Reports In Cd)	30000/-	1500/-

35.	5 Ginger & Ginger Processing Industries	12000/-	600/-
36.	13 Fish Farming And Fishery Products	16000/-	800/-
37.	6 Agarbatti And Allied Projects	15000/-	750/-
38.	28 Fruit Juices, Food Dehydration And Allied Products	16000/-	800/-
39.	9 Tea Plantation And Processing Based Industries	15000/-	750/-
40.	14 Roasted/Salted Cashew Nuts, Almonds, Namkeens, Spices Projects	15000/-	750/-
41.	23 Injection Moulded Plastic Products (23 Project Reports)	15000/-	750/-
42.	38 Biofertilizer, Biofuel, Enzyme, Organic Farming & Manure, Protein And Allied Lucrative Projects	18000/-	900/-
43.	10 Maize & Corn Processing Projects	15000/-	750/-
44.	11 Profitable Solar & Solar Based Products	15000/-	750/-
45.	11 Infotech/It Projects	16000/-	800/-
46.	42 Hospitality, Building Material, Power Steels, Alcohol & Other Food Products	18000/-	900/-
47.	24 Soap & Detergents (Scouring Powder, Toilet Cleaner, Laundry Soap, Detergent Cake & Powder, Toilet Soap, Enzyme Based Detergents, Phenyl & Soap Coated Paper)	18000/-	900/-
48.	10 Coconut And Coconut By Products	16000/-	800/-
49.	22 Alcohol, Beer, Imfl, Country Liquor, Wine & Other Related Projects	22000/-	1100/-
50.	30 Chemicals, Mechanicals, Packaging & Other Profitable Projects	16000/-	800/-
51.	43 Automobile Parts, Gears, Polish, Petrol Pump, Components, Service Station & Other Accessories Projects	18000/-	900/-
52.	23 Canning, Dehydration, Dairy, Jatropha, Fish Other Profitable Projects	16000/-	800/-
53.	83 Export Oriented Units (100% Eou/Eou) Projects	20000/-	1000/-
54.	6 Lucrative Projects On Thinners (In Cd Rom)	12000/-	600/-
55.	10 Leather Tanning Garments, Footwear, Chemicals, Adhesive & Goods Industries	18000/-	900/-
56.	25 Ayurvedic/Herbal Pharmacy & Cosmetic Products	18000/-	900/-
57.	63 Multi Crores Profitable Projects (From 1 Crore To 50 Crores Above Projects)	65000/-	3250/-
58.	28 Multi Crores Profitable Projects (From 10 Crores To 50 Crores Projects)	30000/-	1500/-
59.	16 Multi Crores Profitable Projects (From 50 Crores & Above)	20000/-	1000/-
60.	19 Multi Crores Profitable Projects (From 1 Crore To 10 Crores Projects)	20000/-	1000/-
61.	9 Wheat And Wheat Projects In Cd	16000/-	800/-
62.	24 Lubricating Oils, Greases, Break Oil, Bitumen, Transformer Oil, Reclamation Used Engine Oils, Cutting Oils Projects In Cd	22000/-	1100/-
63.	75 Entertainment, Infotech, Educational, Management, Hospitality & Ware House Projects (75 Project Reports In Cd)	22000/-	1100/-
64.	46 Projects On Infrastructure, Real Estate, Hotels, Hospitals, Hospitality, School, Colleges, Clubs, Resorts &	21000/-	1050/-

	Construction Based Projects In Cd. (24 Project Reports In Cd)		
65.	8 Mango And Mango Based Projects In Cd Rom	16000/-	800/-
66.	29 New Profitable 1.5 Cr. To 3 Cr. Projects In Cd (29 Project Reports In Cd)	27000/-	1350/-
67.	100 Food Processing & Agro Based Profitable Projects	30000/-	1500/-
68.	212 Highly Demandable Profitable Projects in Cd	60000/-	3000/-
69.	20 Copper and Copper Based Industries	25000/-	1250/-
70.	52 Small Scale 25 To 50 Lakh Investment Projects	20000/-	1000/-