UNIT-IV
PAINTS, VARNISHES AND CLEANSING AGENTS

Paint

Paints are viscous, opaque and mechanical dispersion of two or more pigments.

Characteristics of good paints or requisites of good paints:

- It should form uniform film on the metal surface.
- It should posses high covering power.
- It should not crack on drying.
- The film should be stable and corrosion resistance.
- The colour of the paint should be stable.
- It should spread easily on the metal surface.
- It should posses high adhesion capacity.

Constituents and functions of paints

- Pigments
- Drying oil or Vehicle
- Thinner
- Fillers or Extenders
- Dryers
- Plasticizers
- Anti skinning agent.

S.No	Constituents	Functions	Examples
1.	Pigments	1. They provide desired colour and strength to paint. 2. They protect the UV light. 3. It resist to moisture.	White pigment(White Lead) Red pigment (Indian Red) Blue pigment (Prussian blue) Black pigment (Carbon black)
2.	Drying oil or Vehicle	1. They form a protective film by oxidation and by polymerization of oil. 2. It supply toughness, adhesiveness and durability.	Glyceryl trilinoleate, Linseed oil, etc.,
3.	Thinners	1. It reduces the viscosity of paints. 2. It increases the elasticity of film.	Kerosene, Acetone, Turpentine oil, sprit, etc.,
4.	Fillers or Extenders	1. It fills the voids in the film. 2. It reduces the cost of the paint. 3. It reduces the cracking of drying paint.	Gypsum, Chalk, Silicon, Clay, etc.,
5.	Driers	1. To increase the rate of drying process. 2. To accelerate the drying of drying oil through oxidation, polymerization and condensation.	Metallic soap, Borax.
6.	Plasticizers	1. To provide the elasticity of paints. 2. To prevent the cracking of the film.	Triphenyl phosphate, Dibutyl tartarate, Dibutyl phthalate.
7.	Anti skinning agent	To provide the jelly and skinning of the paint.	Poly hydroxyl phenol.

Pigment Volume Concentration (P.V.C)

It is an important property of a paint. The following equation is used to calculate the P.V.C.

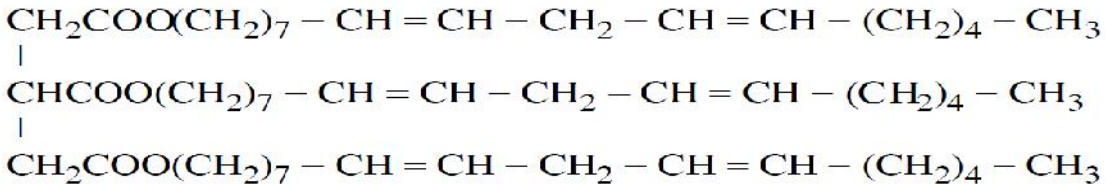
$$PVC = \frac{\text{Volume of pigment in the paint}}{\text{Volume of (pigment + vehicle) in the paint}}$$

Higher the volume of P.V.C, lower will be the durability, adhesion, consistency of the paint.

Mechanism of Drying oil of the paint:

Drying oils are the film forming constituents of the paint. These are glyceryl esters of high molecular weight fatty acids.

Structure of an Oil



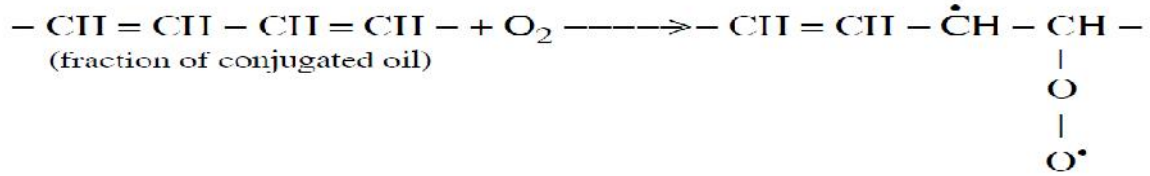
The mechanism involves oxidation, polymerisation and condensation reactions. The oil containing conjugated double bonds dry very faster than the non-conjugated oils.

Mechanism for Conjugated Oil

The various steps involved in the mechanism of drying of conjugated oil are given below.

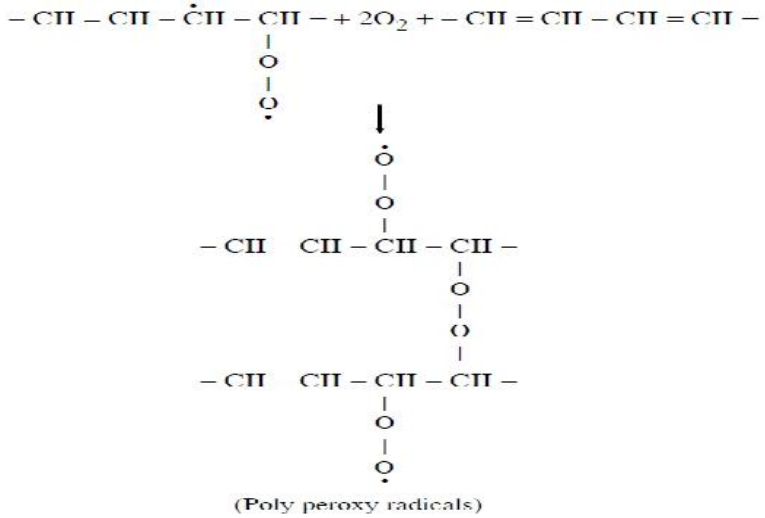
STEP -1

The oil absorbs oxygen and gives di-radical.



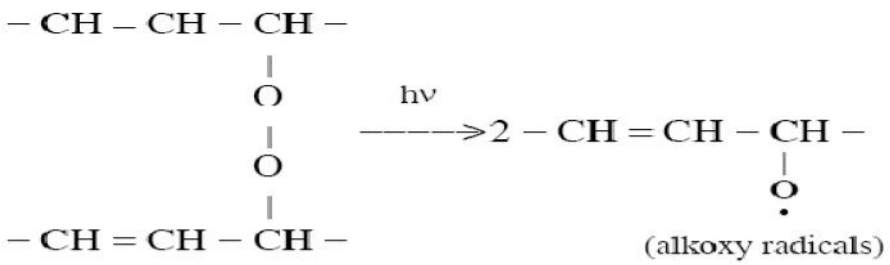
STEP -2

The di-radi calagain reacts with oxygen and fatty group to give peroxy and poly peroxy radicals.



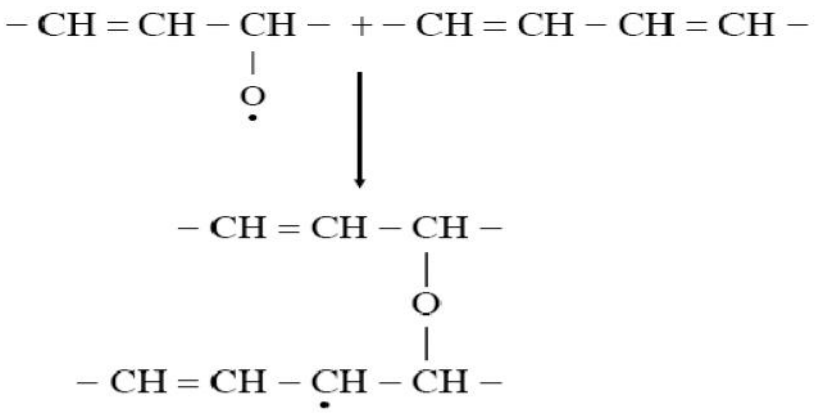
STEP -3

Polyperoxides are decomposed by heat and light to give alkoxy radicals ($RO^{\cdot}$)

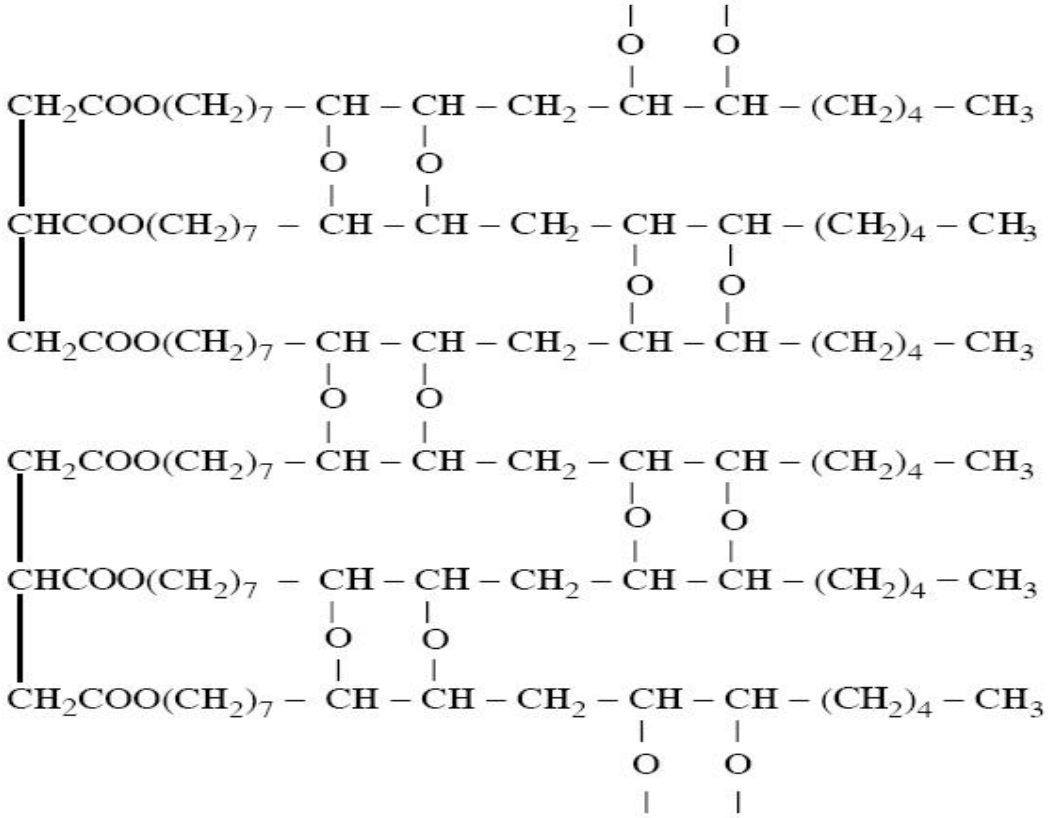


STEP -4

These alkoxy radicals react with another fatty groups, form ether linkages.



Thus, the various oil molecules are linked through ether linkages and forms highly cross-linked macromolecular film. The structure of macromolecular film is shown below.



Failure of a Paint

A paint may fail due to the following reasons.

(i) Chalking

It is the progressive powdering of the paint film on the painted surface. This occurs due to improper dispersion of pigment in vehicle.

(ii) Cracking

Cracking of paint film is due to the unequal expansion or contraction of paint coats.

(iii) Erosion

It is very quick chalking.

(iv) Blistering

This is due to improper surface exposure of paint to strong sunshine.

(v) Flaking

It is the peeling of the paint film from the painted surface. This occurs due to the presence of dust particles (or) greasy matters in the paint. These foreign matter results in poor adhesion of the paint on the painted surface.

Special paint

Heat resistant paint

These paints can withstand very high temperature. These are silicone based paints containing metal powders like zinc, aluminium and heat resistant pigment like titanium peroxide, chromium oxide, etc.

Uses

These paints are used as a finish furnace, oven, etc.

Temperature indicating paints

These paints contain thermochrome, which decomposes and undergoes colour changes at different temperature.

Eg. Silver Iodide(AgI), Amine complexes of metals like Fe, Cu, Cr, Mn, Co, etc.

Uses

These are coated on the outer walls of the reactors and furnaces to indicates the temperature of the reaction so that the reaction can be stopped or controlled at a particular state.

Fire retardant paints

These paints contains chemicals like chlorinated rubber, carbonate pigments, urea formaldehyde.

Uses

Wherever timber is intended to be fire resistant, it may be coated with these paint.

Water repellent paints

Silicones and silicone based paints are generally used as water repellent paint. These are used in ships, boat and marine equipments.

Varnishes

Varnish is a homogeneous colloidal dispersion solution of natural or synthetic resin in oil or thinner or both. Varnish is used for both protection and decoration of metal surfaces.

Types of varnish

Depending upon the solvent used, varnishes are classified as follows.

1) Sprit varnish

2) Oil varnish

1) Sprit Varnish

Sprit varnish is prepared by dissolving natural or synthetic resin in a sprit. This type of varnish dries just by the evaporation of the solvent (sprit). The film formed is brittle and not strong.

It is used for polishing wooden surfaces.

2) Oil Varnish

Oil varnish is prepared by dissolving natural or synthetic resins in a drying oil and solvent(volatile).

This type of varnish dries by the evaporation of the solvent followed by oxidation and polymerisation of drying oil.

Oil varnishes dry slowly but the film is hard.

It is used for interior and exterior works.

Constituents and functions of varnish

S.No.	Constituent	Functions	Example
1.	Resin	Provides elasticity Good adhesion	Natural resin : Shellac Synthetic resin: Vinyl resin, Phenol formaldehyde.
2.	Drying	These are film forming materials of varnish	Soya bean oil, Linseed oil, Dehydrated castor oil.
3.	Solvents / Thinners	These are volatile liquids They reduce the viscosity of varnish	Turpentine oil, Kerosene.
4.	Driers	These are added to increase the rate of drying.	Phthalates, Linoleates of Zn, Co, Mn, etc.,
5.	Anti skinning agent	These are added to prevent jellying and skinning of varnish.	Poly hydroxyl phenol.

Characteristics of good varnish

1. It should be soft.
2. It should produce a shiny and glassy film on drying.
3. It should dry quickly.
4. It should not shrink or crack after drying.
5. The colour does not fade.
6. It should produce a protective film.

Uses of Varnishes

1. It is used for the protection of articles from corrosion.
2. It is used a brightening coat of varnish.
3. It is used for improving the appearance and intensifying the ornamental grains of wood surfaces.

Soap

Any substance having cleansing properties in water, which can remove dirt or grease from our body or fabric is called detergent. The oil based soapy detergents are called soaps.

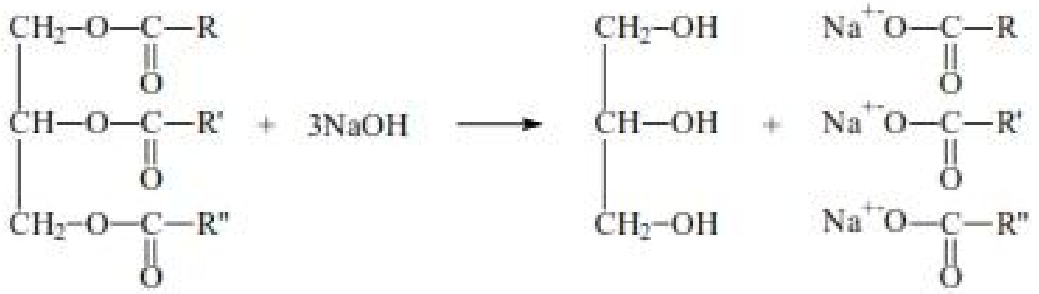
Methods of Preparation of soaps

Soaps are made by the saponification of oils and fats. Higher fatty oils are reacts with sodium

hydroxide or potassium hydroxide to form soap.

Fat + 3NaOH → Glycerol + 3 soap

The saponification reaction is given below



Fat or Oil Alkali Glycerol Soap

The saponification of a fat or oil with NaOH or KOH solution may be done by Hot process or Cold process.

Hot Process:

It is carried out by the following steps:

(i) Boiling:

It involves boiling of fat with NaOH with the help of steam in soap pan or kettle unless the greasy nature of the mixture has disappeared.

Fat + 3NaOH → Glycerol + 3 soap (Hard soap)

(ii) Salting out:

It is done by adding either solid NaCl or brine to the mixture of soap and glycerol. Due to the common ion effect, soap is insoluble in concentrated salt solution, while glycerol is readily soluble. As the soap is having lower density so it floats to the surface and thus can be separated, it is called neat soap.

(iii) Finishing:

Finishing is done by (a) adding colour, perfumes, germicides, etc, to the soap obtained from step (b) moulding of soap in desired shape.

In this method is used to prepare Hard soaps.

Cold Process:

In cold process, saponification is allowed to take place in cold.

Oil or Fat + 3KOH → Glycerol + 3 Soft soap (Washing soap)

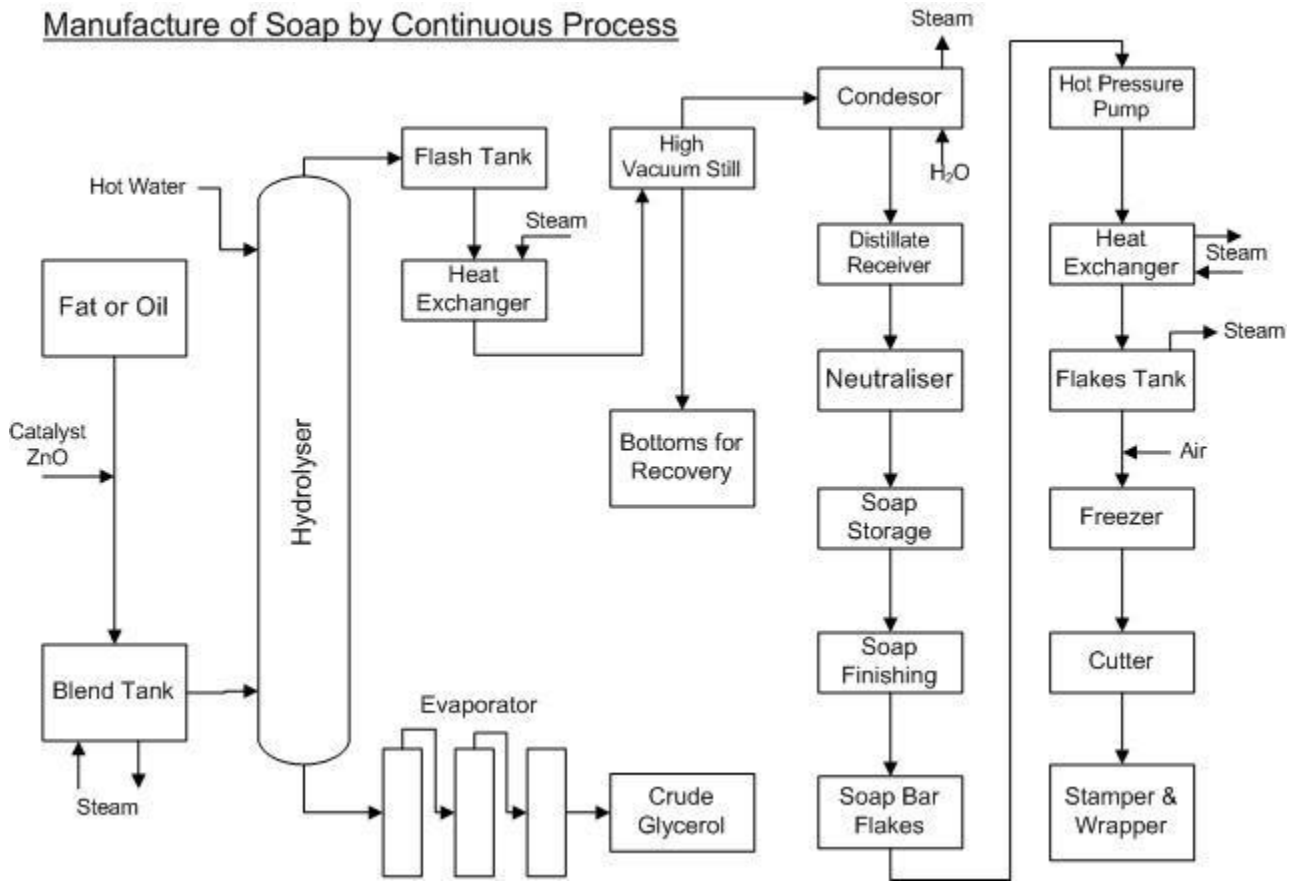
Types of Soaps

(i) Hard Soap (ii) Soft Soap.

S.No.	Hard Soap	Soft Soap
1.	They are sodium carboxylates RCOONa and are harder.	They are Potassium carboxylates RCOOK and are softer.
2.	It is prepared by saponification of fats having	It is prepared by saponification of vegetable

	higher % of saturated fatty acids with NaOH via hot process.	oils having higher % of unsaturated fatty acids with KOH via cold process.
3.	Ex: Common toilet soaps.	Ex: Liquid Soaps(Shampoo) and shaving creams.

Industrial Bar Soap Making



The industrial soap making involves four basis steps -

- Saponification
- Glycerin Removal
- Soap Purification
- Finishing

These different steps involve various processing steps and operations in their own. A brief description of these different steps is given below –

Saponification

The saponification process involves the mixing of tallow (animal fat) and coconut oil with sodium hydroxide and the application of heat. The process results in formation of soap, which is a salt of long chain carboxylic acid.

Glycerin Removal

Glycerin is more valuable than soap, and hence most of it is removed for its uses in more expensive cosmetic products. Some of the glycerin is left in the soap to make it soft and smooth. Soap

is generally not very soluble in salt water, while glycerin is, hence the salt is added to the wet soap thereby causing it to separate out into glycerin and soap in salty water.

Soap Purification

In the soap purification stage, any remaining sodium hydroxide is neutralized with a weak acid, like citric acid and two thirds of the remaining water is removed to obtain pure soap.

Finishing

The final stage of industrial soap manufacturing process, finishing stage involves mixing of additives, such as colors, preservatives, and perfume into soap, which is then shaped into bars for sale.

Toilet Soap Manufacturing

Toilet soap generally has less water and more fatty material than laundry soap and because of this, the base soap intended for manufacturing toilet soap usually has extra fatty acids that are blended with preservatives before it is vacuum dried. These measures ensure that there is no unreacted caustic remains in the soap by the time it reaches the consumer, and also make the soap softer. Additives, such as perfume, dye and opacifier are then mixed to the dried soap and the mixture is milled to ensure even mixing. It is then plodded and extruded out as a continuous bar, which is cut into billets and stamped ready for packaging and sale.

Cleansing Action of Soaps and Detergents

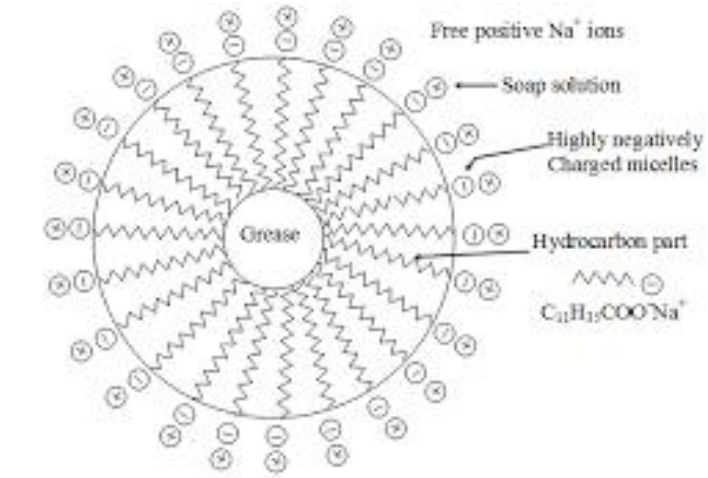
Most of the dirt is oily in nature and oil does not dissolve in water. The molecule of soap constitutes sodium or potassium salts of long-chain carboxylic acids. In the case of soaps, the carbon chain dissolves in oil and the ionic end dissolves in water. Thus the soap molecules form structures called micelles. In micelles, one end is towards the oil droplet and the other end which is the ionic faces outside. Therefore, it forms an emulsion in water and helps in dissolving the dirt when we wash our clothes.

Soap is a kind of molecule in which both the ends have different properties.

- ***Hydrophilic end***
- ***Hydrophobic end***

The first one is the hydrophilic end which dissolves water and is attracted to it whereas the second one is the hydrophobic end that is dissolved in hydrocarbons and is water repulsive in nature. If on the surface of the water, soap is present then the hydrophobic tail which is not soluble in water will align along the water surface.

Micelles



Cleansing action of soap. Soap micelle entraps the oily dirt particle

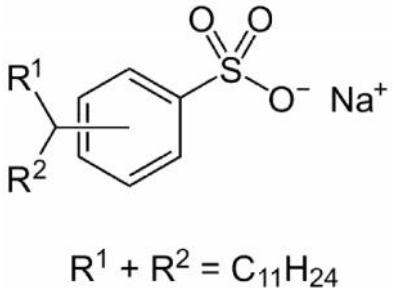
In water, the soap molecule is uniquely oriented which helps to keep the hydrocarbon part outside the water. When the clusters of molecules are formed then hydrophobic tail comes at the interior of the cluster and the ionic end comes at the surface of the cluster and this formation is called a micelle. When the soap is in the form of micelles then it has the ability to clean the oily dirt which gets accumulated at the center. These micelles remain as colloidal solutions. Therefore the dirt from the cloth is easily washed away. The soap solution appears cloudy as it forms a colloidal solution which scatters light.

Detergents

Detergents are synthetic soap like cleansing agents and are also known as syndets.

Example: Sodium salt of alkyl benzene sulphonic acids.

Alkylbenzene sulfonates are a class of anionic surfactants, consisting of a hydrophilic sulfonate head-group and a hydrophobic alkyl benzene tail-group. Along with sodium laureth sulfate they are one of the oldest and most widely used synthetic detergents and may be found in numerous personal-care products (soaps, shampoos, toothpaste etc.) and household-care products (laundry detergent, dishwashing liquid, spray cleaner, etc.



$R^1 + R^2 = C_{11}H_{24}$