SOAPS AND DETERGENTS

(K. R. JANARDHANAN)

In olden days clothes were cleaned by beating them on rocks in the nearest stream. This practice is followed even today in many villages. Sometimes plants such as soap nuts are used as cleaning agents. Such plants contain saponins, chemical compounds that produce a soapy lather. These saponins were probably the first detergents used.

History : Ashes of plants contain potassium carbonate (K_2 Co_3) and sodium carbonate (Na_2 Co_3). The carbonate ion present in both these compounds, reacts with water to form an alkaline solution. The basic solution has detergent properties. These alkaline plant ashes were used as cleaning agents by the earliest civilizations at least 4000 years ago. Europeans were using plant ashes to wash their clothes as recently as 100 years ago. Sodium carbonate is still sold as washing soda and is being used for cleansing purposes. The discovery of disease causing micro organisms and subsequent public health practices brought about an increased interest in cleanliness by the late eighteenth century. Soap was in common use by the middle of the nineteenth century.

The first written record of soap can be seen in the writings of the Roman pliny the Elder. He described the Phoenicians' synthesis of soap by using goat tallow and ashes. By the second centaury A. D, sodium carbonate was heated with time (from limestone) to produce sodium hydroxide (lye). The sodium hydroxide was heated with animal fats or vegetable oils to produce soap. Other societies made soap in much the same manner.

The large scale manufacture of soap was not possible until the discovery of practical methods of manufacturing alkalies on a large scale. This did not take place until about 1800. Soaps are compounds formed by the reaction of bases with fats, chemically known as fatty acid esters. The most important fatty acid esters. The three most important fatty acid esters are

Palmitin [(C_{15} $H_{3\,1}$ $COO)_3$ C_3 H_5)

Stearin [(C_{17} H_{35} $COO)_3$ C_3 H_5)

and

Olein [(C_{17} $H_{3\,3}$ $COO)_3$ C_3 H_5)

They are found in lard, tallow, olive oil, cotton seed oil, and other animal and vegetable fats or oils. Soap is usually made by the reaction of animal fat or vegetable oil with sodium hydroxide. The process of treating fats with bases or alkalies is called ‘Saponification’. Vegetable oils, with unsaturated carbon chains, produce soft soaps. Animal fats yield hard soaps. Coconut oils with shorter carbon chains, yield soaps that are more soluble in water.

Soap to day : In modern commercial soap making, the fats and oils are often hydrolysed with super heated steam. The fatty acids then are neutralized to make soap. The process takes place in large cylindrical vessel. The next step in the manufacture of soap is called graining or Saltingout. This involves the addition of common salt (NaCl). During this process the soap becomes insoluble in brine and separates from the solution. The soap may be washed several times with brine to rid it of free alkali.

The molten soap may be run into large frames from which bars may be cut, or it may be run over cold rollers, producing thin sheets which are scraped to form soap chips. The molten soap may also be squirted from a nozzle as a spray into hot air to form powdered soap.

Soft or liquid soaps are made by using potassium hydroxide (KOH) instead of lye. Potassium soap produces a finer lather. They are used alone or in combination with sodium soaps in liquid soaps, shampoo soaps and shaving creams.

Very often certain foreign materials are added to soap as it leaves the reaction kettle. These fillers may be such inert adulterants as chalk and suphates of sodium, calcium or barium. Another very common filler is talc (magnesium acid silicate). Sodium silicate is also used. Silicates give firmness to soap and enables it to hold more water. Rosin is also sometimes added to soap especially to laundry soap. Although not a fatty acid, it reacts with sodium hydroxide to form a sodium salt which resembles soap in many respects. It is soluble and has a high frothing power. The cleansing power of rosin soap is much lower than that of ordinary soap. The presence of rosin in any quantity is undesirable. If soap contains more than 15 percent rosin, it is known as low grade soap. Permitted dyes are added to soaps to impart than a pleasing colour. The most expensive ingredient of toilet soap is the perfume, which is responsible for its characterstic odour.

<u>Ads' and soaps</u> Among the consumer products aggressively advertised, bath soap's are in the top of the list. Although, a both soaps basic function is to clean the body, the advertisements confer exotic qualities to it. Soaps are being advertised as

- Beauty soaps
- Health soaps
- Complexion soaps
- Deodorant soaps
- Freshness soaps

- Cinema stars are their brand ambassadors
- Sports person used to sponsor them

- Baby soaps and
- Herbal or medicinal soaps

None of the advertisements speak of what exactly, goes into the making of such soaps. Can medicated soaps readily cure skin diseases? Are glycerine transparent soaps really gentle to the skin ?

As mentioned earlier soaps are salts particularly sodium or potassium of long chain fatty acids. These carboxylic acids are derived from fatty oils. The principal active cleaning agent is sodium carboxylate.

Total Fatty Matter (TFM)

Soaps are graded in terms of total fatty matter or TFM. Bureau of Indian Standards (BIS) has catogorised bath or toilet soaps as ‘normal’, ‘baby, transparent, and antibacterial soaps. The last three are called specialty soaps targeted to specific users. A toilet soap is a cosmetic by law and it must fulfil the requirements of the relevant Indian standard.

T. F. M or total fatty matter is a measure for identifying the amount of fatty matter present in soaps. TFM of a sample of soap can be determined as follows. A known weight of the soap is dissolved in water and the solution is treated with dilute sulphuric acid. The soap decomposes to sodium suplphate and fatty acids. The fatty acids so formed can be estimated. From this TFM can be calculated. On the basis TFM, toilet soaps can be classified into three grades.

Grade 1	TFM	Moisture	Free salt (NaCl)
I	above 80	Max : 13.5	Max : 0.7
II	65 – 80	13- 15	0.8
III	55- 65	15-20	1.5

Grade I toilet soap should have TFM value above 80 percent, except in ayurvedic soap. Any soap which has a TFM value less than 55 percent is not considered as toilet soap at all. TFM is what lends soap its soapy feel and it is the TFM and the insoluble matter in the soap that largely distinguishes one soap from the other. The three grades should have less than 0.05 % of free alkali as sodium hydroxide and less than 1% of carbonate alkali. The salt content should not go above 1.5 %.

Bathing bars: - To day 85 percent of bathing soaps available in the market are not toilet soaps even if they are promoted by some celebrities. The bathing bar shall be a product containing acceptable surface active agents which could be used for bathing purposes. One or more of the following surfactants confirming to the relevant Indian standards, can be used

Soap of fatty acids.

Fatty acid ester sulphonates

Fatty alkanolamide

Fatty alcohol ethoxylates

Sarcosinates

Taurides

Fatty isothionates

Alpha olefin sulphonates

Alcohol sulphates and

Amphoterics such as betaines.

In addition to surfactants and perfume, the bathing bar may contain other ingredients such as electrolytes, bar structuring and processing aids, colouring matter, permitted antioxidants, preservatives, permissible germicides super fatting agents, humectants and such additional substances that are declared on the label.

All ingredients except moisture should be declared. All of them should be non-injurious to skin.

Why bathing bars:

Bathing bars were introduced in India in 1985, when the country was facing acute scarcity of vegetable cooking oils. Much of the vegetable oils were being used by industry. The government started importing palmoil from abroad. In order to control the use of vegetable oils for soap making, the government allowed the manufacturers of soap to introduce bathing bars. The introduction of bathing bars reduced the use of cooking oils for soap making. Thus more cooking oil became available for domestic use. The price of bathing bars were determined according to the total fatty matter contained in them and more importantly the type of fatty matter used. Due to this step government could reduce the quantum of import of vegetable oil and could save a lot of foreign exchange.

Types of bathing bars

There are two types of bathing bars (1) made up of partial soap and partial synthetic detergent (syndet). (2) Made up of wholly synthetic detergent. The first type is usually known as combination bars or combars. These contain 50 percent TFM and 30-35 percent mineral matter like talc and Kaolin. They are simply structured toilet soaps. Bureau of Indian standards (BIS), warns the customers of bathing bars. “It is important to guard against the removal of the beneficial skin lipids by bathing bar and over cleaning resulting in defatting of the skin is undesirable”.

High clay content in bathing bar may reduce its solubility and hence increase its durability. But after bathing with a bathing bar, whole body may be coated with a white powder, (two-in-one soap + talcum powder) Children and old people can not tolerate high syndet containing bathing bar, because it would degrease their skin.

Special processes have been developed by Indian scientists to upgrade cheaper and easily available raw materials to make good quality toilet soap. Techniques have been developed to obtain good quality fatty acids for soap making from fish oil, neem oil and Karanja oil. India is the second largest producer of castor oil, the first being Brazil. A process was developed in India to convert castor oil into good quality soap making oil. Textured castor oil is found to be very good for making transparent soap.

Transparent soap

Transparent soap is a clear soap with high glycerin content often referred to as glycerin soap. Transparent soap is less drying than opaque soap and can have additional emollient oils added to it such as Shea butter or jojoba oil. It is basically partly soap and partly solvent. Sodium hydroxide causes big crystals to form in soap and that is why the soap becomes opaque. In order to make it transparent, we have to dissolve the soap in enough solvent to make the crystals so small that light will feely pass through the soap which makes it look transparent. The solvent used can be glycerol, alcohol or glycerol alcohol mixture.

Baby soap

Bay soaps are not much different from ordinary soaps, but they are comparatively of high purity. Baby's skin is soft and sensitive. Hence the oil used for making baby soap should be clean and bleached. No pigments are allowed in baby soap and fragrance materials added should be bare minimum. Free alkali content present in baby soap should not exceed 0.05 percent Ordinary soap may contain rosin and metallic impurities such as nickel. But a bay soap should not contain such things. Actually baby soap should be cheaper than luxuary soap because costly perfumes or colouring materials are not present in it.

Medicinal soap

As per many advertisements medicinal soaps are supposed to contain deodorants antiseptics and some medicines that cure skin diseases. They say that medicinal soaps are cleansing agents well as antiseptics. Here soap is treated as a carrier of medicines that is it serves the purpose an ointment or oil. But we should remember that soap is essentially a cleansing agent. After applying soap to the body, immediately we used to wash with water, when together with dirt the medicines if any would also be washed out. We are not giving enough time for the medicine, to be absorbed by the skin. Then how can they cure skin diseases? Germicidal soap usually contains the germicide Trichloro carbanilide (TCC) upto 1 percent. When warmed to 60^{o} C, It is converted into chloromine which is toxic to skin.

Herbal soaps contain some fragrant essential oils. Some soaps contain ‘Shekakai (Acacia sinuate) which has saponin as an active agent. Saponin is a good emulsifier. Soft soap: - Soft soaps are usually used in shaving soaps and in liquid soaps. They are more soluble in water than ordinary soaps. While ordinary soaps are sodium soaps, soft soaps are potassium soaps.

How Soap works

Dirt and grime usually adhere to skin, clothing and other surfaces because they are combined with greases and oils – body oil, cooking fats, lubricating greases and a variety of similar substances – which act a little like sticky glues. Since oils are not miscible with water, washing with water alone does little good.

Soap molecule have a split personality. One end is ionic and dissolves in water. The other end is like a hydrocarbon and dissolves in oils. If we imagine the ionic end of the molecule as ‘head’ and hydrocarbon chain as ‘tail’, then we can explain the clearing action of soap clearly. The hydrocarbon ‘tails’ stick into the oil. The ionic ‘heads’ remain in the acqueons phase. In this manner, the oil is broken into tiny droplets and dispersed throughout the solution. The droplets don't coalerec because of the repulsions of the charged groups (the caboxl anions) on their surfaces. The oil and water form an emulsion, with soap acting as an emulsifier. With the oil no longer "gluing" it to the surface, the dirt can be removed easily. This mechanism applies to synthetic detergents also.

Disadvantages of soaps.

For cleaning clothes and for other purposes, soap has been largely replaced by synthetic detergents. This is because soaps have two rather serious short comings. One of these is that, in acidic solutions, soaps are converted in to fatty acids. The fatty acids unlike soap (sodium salt of fatty acids) do not ionise much. Lacking the split personality, they can't emulsify the oil and dirt that is they do not exhibit any detergent action. What is more these fatty acids are in soluble in water and separate as a greasy scum.

The second and more serious disadvantage of soap is that it does not work very well in hard water. Hard water contains certain metallic ions, particularly magnesium, calcium and iron ions. The soap anions react with these metal ions, to form greasy, insoluble curds. These deposits make up the familiar bathtub ring. They leave the freshly washed hair sticky, and forms kettle fur.

Soap powders and washing powders

Soap powders are not be confused with powdered soaps, which is merely soap in powdered form. Most soap powders are mixtures of soap and alkali substances known as builders. Such builders include sodium carbonate, trisodium phosphate, borax and sodium sulphate. Most frequently used one is sodium corbonate. Some washing powders also contain a beaching agent, such as sodium perborate. These usually are called oxygen washes and often contain part of the word oxygen in the commercial name. As a rule, the cheaper the washing powder, the larger the proportion of alkali present. The builder is added to soften hard water and to act as cheap detergent, or cleansing agent. It should be remembered, however, that the builder is a less efficient cleansing agent than soap.

<u>Synthetic Detergents</u>

Detergent is a cleansing agent. In that sense soap is also a detergent. But the word detergent usually refers to a synthetic substance other than soap. A detergent contains an active agent called surfactant, that wets the fabric, emulsifies oily matter, solubilizes grime and keeps the soil in suspension. This active agent contains two groups one oil loving lipophilic and the other water loving – hydrophilic.

The first synthetic detergents synthesized were derived from fats by reduction with hydrogen, followed by reaction with sulphuric acid, and then neutralization.

Example

$$\mathit{Triaurin} = \frac{\mathit{Nickel}}{\mathit{Reduction}} > \textbf{Lauryl alcohol} = \xrightarrow{\textbf{Surphuric acid}}$$

$$\mathit{Laurylsupнate} = \frac{\textbf{Nickel}}{\textbf{Neutrilization}} > \text{Sodium lauryl sulphate (Sodium dodecyl sulphate)}$$

Thus sodium lauryl sulphates are the first such detergents synthesized. But this process was found to be expensive. Within a few years, cheap synthetic detergents were produced from petroleum products.

Made largely from a material called aeid clurry which is chemically linear alkly benzence (LAB). LAB is sulphonated to get linear alkyl benzene sulphonate (LABS). This is reacted with sodiumhydroxide or sodium carbonate (Sodaash) to form its sodium salt soluble in water. The products for use in homes and commercial laundries usually contain much more than LABS molecules. The LABS is called a surface active agent or surfactant. In addition to the LABS modern detergent formulations contain a number of other substances to improve detergency, to bleach, to lessen redeposition of dirt, to brighten, or simply to reduce the cost of the formulation.

An substance added to a surfactant to increase its detergency is called a builder. Common builders are the Phosphates. An example is sodium tripoly phosphates ($Na_3 P_3 O_{10}$). It ties up Ca^{2+} and Mg^{2+} in soluble complexes this softening water. It also produces a mild alkalinity, proving a favourable environment for detergent action. Other builders and fillers added include soda ash, sodium silicate, sodium chloride, sodium sulphate and Zeolite (special form of clay - hydrated sodium aluminium silicate.

Detergents are graded on the basis of their active matter, and poly phosphate content. Detergents can be used in hard water, but removal from fabrics requires a to lot of rincing. Detergents can be used in cold and hot water as well as acidie and alkaline conditions.

Cotton fabrics can be washed with detergents heavy with phosphates and soda ash. Wool, nylon and silk fabrics should be washed with detergents, which have less alkali, less phosphates, and less soda ash.

Heavy duty detergent powders are two types. one suitable for handwashing and the other for machine washing. Detergents used for hand washing should give copious lather. That would satisfy the aesthelic sense of the customer. But the fact is that the amount of form is not a measure of the effectiveness of the detergent. however a small amount of foam is necessary to trap the dirt and carry it away during rinsing. But detergents used in washing machine should not produce much foam, because it may damage the machine parts, especially of the front loading machines.

The optimum concentration of active matter is found to be0.05 percent or half gram per litre or 5 gram in ten liters. 50 g of a popular low priced detergent powder is needed in 10 litres of water for optimim economy and efficiency. Preference of sodium triploy phosphate in detergent increases its clean ring powder. For localized cleaning it is better to use detergent bar.

TYPICAL COMPOSITION DIFFERENT TYPES A DETERGENT POWDERS AND DETERGENTS BARS.

	HIGH PRICED POWDER	MEDIUM PRICED POWDER	LOW PRICED POWDER	HIGHT PRICED BAR	LOW PRICED BAR
Active matter	15-18%	11-14%	8-10%	18-20	12-15
Phosphates/Zeolites	15-20%	5-8%	Nil	10-15	5-15
Soddash	5-10%	12-20%	30-70%	Nil	5-15
Sodium silicate	4-5%	15-30%	Nil	-	-
Sodium Sulphate	24-40%	23-36%	3-5%	2-3	2-3
Sodium Chloride	Nil	Nil	7-50%	5-10	10-20
Clay	Nil	15-20%	10-20%	30-50	40-60
Moisture	8-10%	10-15%	15-20%	5-10	10-12
Starch/				10-15	5-10
Wax				1-3	0-2

POWDER

GREADE	PERCENTAGE ACTIVE MATTER	MAXIMUM PERCENTAGE OF SODIM CABONATE ALLOWED.
1	19	30
2	16	40
3	15	50
4	12	60

Health and Detergents

The basic function of a detergent is to remove dirt. In our country most of the people are washing their clothes with their hands. The detergent which removes the dirt and grime from the clothes also degreases the skin while washing the clothes. Thus natural oils from the skin are removed which may lead to certain skin diseases. Alkaline materials which are also present in the detergent powders and bars will intensity this. LABS can penetrate, the epidermis causing irritation of the skin. More over the alkaline builders and fillers added to the detergents are also harmful to the sensitive skin. If the clothes are not washed very well with water, the residual detergent sticking to the cloth also may irritate the skin. Metallic impurities like nickel present in the detergent powders or cakes are also harmful.

Alpha olefin sulphonate (AOS) is now days used as detergent instead of LABS. Some time AOS is mixed with sultones which are also good surfactants. Sultones are very sensitive to skin. One advantage of AOS is that it is completely biodegradable.

Spray dried and Drymix powders

The grains of spray dried detergent powder are hollow globules. They look like beautiful little pearls. The powder is freed flowing and very well soluble in water. Since it is very attractive customers prefer it even though it is bit costly.

Drymix detergents are made by mixing the pre-dried ingredients throughly either manually or using a mixer. The density of this powder is higher than that of spray dried powder. There is not much difference between them in detergent action. But drymix powder tend to cake on contact with moisture.

Compact detergents

Concentrated or compact detergents contain about 25 percent of active matter; and the rest consists of builders and fillers. Now a days in order to reduce packaging cost, compact detergents containing 40 to 60 percent of active matter have been introduced by leading companies.

Detergents and environment

Use of phosphates, enzymes, bleachers, and brightening agents in detergents is a subject of debate among environmentalists. Even though phosphates are perfect builders they suffer from one overwhelming defect: they are superb, nutrients for the algae and other small plants and grow on the surfaces of lakes and streams. Algae, nourished by a steady supply of phosphates, can cover the surface of body of water and prevant atmosheric oxygen from reaching the marine life below the surface. The resulting death of fish and other aquatic animals sometimes occurring on a large scal in lakes and rivers covered by algae, has led many countries to ban the use of phosphates as detergent builders. This type of water pollution is known as Eutrophieation. In india 80 percent of the detergents marketed are phosphate free, hence eutrophieation from detergents does not happen. The most promising substitute for phosphates is a class of compounds of aluminium, silicon and oxygen known as zeolites.

Chemical composition of a detergent does not correctly reveal its cleaning capacity. For a practical and realistic evaluation, it is necessary to determine the actual performance of detergents. Detergency is measured by reflectance. Infact there is not much difference in detergency between low grade and high grade detergents.

All the surfactants discussed so far, including soap are anionic surfactants; The working part of the molecule is an anion with a nonpolar part and anionic end. Some liquid detergents contain nonionic surfactants. Examples are alcohol ethoxylates and alkyl phenol ethoxylates. The several oxygen atoms, by their attraction for water molecules, make that end of the molecule water soluble. Nonionic surfactants are great for removing oily soil from fabrics. They are more soluble in cold water than in hot water.

There are eat ionic surfactants also, in which the working part of the molecule is a action. The most common of these are called quaternary ammonium salts. An example of such an eat ionic surfactant is hexadecyl timethylammoniumchloride. These are not very good detergents, but they have a degree of germicidal action. Sometimes they are used along with nonionic surfactants, as cleaners and disinfectants in good and dairy industries. Eat ionies cannot be used with anionic surfactants.

Of all the house hold chemicals, the detergents and related cleaning compounds make up the greatest volume. Extensive use of these chemicals has led to an increasing number of health and environmental problems. Hence care should be taken to use them in homes with proper regard to the directions or precautions given on their labels. It would be nice if every one knew a lot of chemistry.