Lecture 1

Introduction to Soap And Detergent, Soap Making And Recovery of Glycerine
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SOAP MAKING AND RECOVERY OF
GLYCERINE

INTRODUCTION

Soap is one of the oldest chemical produced over two thousand years ago by saponification animal fats with the ashes from plants. Although soap are mainly used as surfactant for washing, bathing cleaning, but they are also being used in textile spinning and as important constituent of lubricating grease. Now soap and detergent have become integral part of our society. There has been continuous development Soap making technology starting with batch kettle making process in cottage industry and to present continuous modern soap making process using either fat saponification or by fatty acid neutralization utilizing a wide variety of natural and synthetic feed stock [Zhu et al., 2004]. Soaps are also key components of most lubricating grease which are usually emulsion of, calcium, sodium, lithium soaps and mineral oil.

Synthetic detergent is an effective substitute of washing soap have become now very popular replacing the soap. All soaps and detergents contain a surfactant as their active ingredient. However detergent has better cleaning properties than soap because good detergency and has increasingly popular. Environmental issues during initial stages because of non biodegradable nature of the detergent caused major concern. With the production of linear alkyl benzene there has been continuous increase in detergent production because of the biodegradable nature of the detergent.

During 40’s and 50’s the detergent market was primarily captured by the dodecyl benzene (DDB), a product formed by alkylation of benzene with propylene tetramer in a hard detergent alkylation unit. However, that the branched structure of the alkyl group was responsible for the poor biodegradability of the detergent, and the linear alkyl Benzene (LAB) was introduced in the early 60’s have substantially replaced its counter parts.

India is one of the largest producer of soap in the world. However, per capita consumption of toilet bathing soap in India is 0.8 kg against 6.5 kg in USA, 4.0 kg in china, 1.1 kg in Brazil and 2.5 kg in Indonesia. Soaps are the largest portion of the fast moving consumer Goods (FMG)
markets with bathing soap and toilet soaps contributing about 30% of the soap market. In India soaps are available in five million retail stores out of which 3.75 million are in the rural area. The major player in the personal wash soap market are HUL, Nirma and P & G. In soap industry, the popular sector has witnessed growth with toilet soaps [http://www.cirec.com/2011/01/soap-and-detergent-industry-in-india].

Soap and Detergent differ in their action with hard water. Soap form insoluble compounds with hard water containing calcium and magnesium ions which precipitates and reduce foaming and cleaning while detergent may react with the ions responsible for hardness but the resulting product is either soluble or colloidal dispersed in water [ Austin 1984].

**SOAP**
Soap is the alkali salt of fatty acid. Some of the important fatty acids used in soap manufacture are lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, reicinolenic acid. Fatty acids have varying chain length and may be saturated or unsaturated. Fatty acid content of the oils vary. Unsaturated fatty acids give softer soap with lower melting point and are less stable while soap from saturated fatty acids are firm, slowly soluble, milder and have good detergency [Dixit,2011]. Total fatty acid is considered beneficial ingredient of toilet soap. Property of soap depends on the chain length of fatty acids in blend, amount of saturation and unsaturation, formulation and soap structure. A judicious blend of oils and fats are necessary to obtain soaps of ideal properties.

**Catogrisation of Soap**
Soaps has been graded in terms of total fatty matter. Soap may be catogorised as toilet soaps or bathing soap or specialty soap like baby( comparatively of high purity), transparent( soap with high glycerine content), herbal and antibacterial soap. Bureau of Indian standards (BIS) has catogrised on the basis of total fatty matter(TFM): Grade I ( Minimum 76%), Grade II(minimum 70%), Grade III(minimum 60%), bathing bar (minimum TFM 40%). Soft soap are made by using potassium hydroxide instead of sodium hydroxide. Bathing bars may be made from partial soap and partial detergent or wholly synthetic detergent
Raw Material

Soaps are commonly made from fats and oil and sodium hydroxide. Oils and fats can be classified either lauric or nonlauric oils /fats. In soap making palm oil, coconut oil, caster oil, neem oil, kernel oil, ground nut oil, rice bran oil and animal fat especially tallow are used. Fatty acid present in tallow are mysteric acid, palmitic acid, stearic acid, oleic acid, linoleic acid whereas the coconut oil contains lauric acid, mysteric acid, palmitic acid, stearic acid. Different oils produce soaps of varying hardness, odour and lathering properties. Normally 75-85% tallow and 15-25 % coconut oil is used in soap making. C_{12} and C_{14} soaps lather quickly but they produce an unstable, coarse bubble foam while C_{16} and C_{18} lather slowly but lead to stable, fine bubble foamed. For saponification caustic lye (50% caustic soda) is used. Some of the other ingredient in soap are talc as filler which also act as carrier for perfume, fragrance. sodium silicate to give firmness to the soap, sodium carbonate, dyes to impart colour

Soap Making Process

The soap making process consists of reaction of animal fats along with coconut oil with sodium or potassium hydroxide. The traditional process consists of direct saponification of oil and fats in batch process. The commercial process consist saponification in a kettle pan boiling batch process or a continuous process The production of soap comprises saponification(soap making), removal of glycerol, soap purification, finishing which consist of mixing and homogenisation of the soap base with additive such as perfumes , coloring matter, skin grooming substances and final extrusion, cutting shaping and packaging.

Basic Steps in Soap Manufacture are saponification, glycerine removal, soap purification, finishing [Table M-IV 1.1]. Figure M-IV 1.1 illustrate the process diagram for soap manufacturing. Process for toilet soap bar making is shown in Figure M-IV 1.2
Table M-IV 1.1: Basic Steps in Soap Manufacture

<table>
<thead>
<tr>
<th>Basic Steps in Soap Manufacture</th>
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<tbody>
<tr>
<td><strong>Saponification</strong></td>
</tr>
<tr>
<td>A mixture of tallow (animal fat), coconut oil, sodium hydroxide and salt are mixed in fixed proportion and fed to a reactor (Kettle or pan) with and heated with steam. Effective mixing and proper blending of raw material is very important to ensure a consistent reaction. The soap batch is boiled using steam sparging. The soap produced is the salt of a long chain carboxylic acid.</td>
</tr>
<tr>
<td><strong>Opening of grain of soap and Glycerine removal</strong></td>
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<tr>
<td>Upon completion of saponification additional salt to the wet soap causing it to separate out into soap and glycerine in salt water as soap is not very soluble in salt water. Glycerine is very valuable by product soap, so effective removal is very important process. Upon addition of salt the single phase soap is converted to two layer. The bottom layer is high level of salt, glycerol and only small amount of soap while the top layer is soap which is allowed to settle for several hours. Aqueous solution called lye is drawn from the bottom which consist of most of the glycerine which is sent to the glycerine recovery plant where glycerol is recovered, purified.</td>
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<tr>
<td><strong>Soap purification and drying</strong></td>
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<td>The soap remaining in the kettle still contains some glycerine which is removed by adding small amount of caustic soda in the wash column. The soap and lye are separated. The lye removed is reused in the process. The top neat soap layer still contains some caustic soda which is neutralised with a weak acid such as citric acid. The separated soap containing water are further dried by heating under vacuum.</td>
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<tr>
<td><strong>Finishing</strong></td>
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<tr>
<td>Finally additives such as preservatives, colour and perfume are added and mixed in with the soap and it is shaped into bars for sale.</td>
</tr>
</tbody>
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Reaction in saponification process:

\[
\begin{align*}
\text{A TRIGLUCERIDE} & \quad \text{CAUSTIC SODA} & \quad \text{GLYCERINE} & \quad \text{METAL SOAP} \\
\text{CH}_2\text{O} & \quad \text{C}(\text{CH}_2)_n\text{CH}_3 & \quad 3\text{ NaOH} & \quad \text{CH}_2\text{OH} & \quad 3\text{ NaO} & \quad \text{C}(\text{CH}_2)_n\text{CH}_3
\end{align*}
\]

Continuous Saponification Process

Continuous saponification process has now replaced old batch process for making soap. Although there are variety of commercial system available, however all the process rely on high speed saponification using intense mixing and continuous separation of soap, lye and glycerol, drying and finishing of the soap. In the continuous process the blended oils and fats along with appropriate amount of caustic lye and salt is continuously fed to the pressurized, heated autoclave (temperature 120 °C and pressure 200 kpa). The saponification process is very fast and proceeds very quickly requiring about 30 minutes or less. After saponification in autoclave with short residence time the reaction product are fed to cooling mixer where further saponification is completed. The soap stream from the cooling mixer is sent to the static separator where lye phase containing, glycerol, caustic soda and salt are separated from the soap layer. The soap layer still contains glycerine which is washed in a washing column with lye and salt solution to remove impurities and allow further separation of glycerol. The soap solution is added at the bottom column while the fresh caustic lye is added at the top for washing. Final separation of lye with soap is achieved in centrifuge.

The soap from the crutcher is fed to feed tank where it is preheated in heat exchanger and then sprayed into the spray dryer for drying. Removal of excess moisture from vapor and entrained soap is achieved. Soap is separated by passing the vapor in a cyclone. The dry soap is fed to noodles which is screw extrududes. The extruded soap is cut into small noodles. The measured base soap for through the vortary air value blower is fed to noodles. The soap from noodle silo is fed to noodles through sigma mixer and roll mill. After milling it goes to pre plodder, vacuum chamber and final plodder, bar cutter and packing, wrapping and storage.
Figure M-IV 1.1: Soap Manufacturing Process Direct Saponification of Oils and Fat and Glycerine recovery
GLYCERINE RECOVERY

Glycerol is important by product of soap manufacture. The process of soap manufacture from fats and oils usually yield glycerol to about 10% of the value of the soap formed and because of its application in many uses, its recovery is very important for better economy of soap manufacture. Some of the major industrial application of glycerol include manufacture of alkyl resins and flexible polyurethane for plastic industry. It is also an important ingredient of in
cosmetics and adhesive manufacture [Israel et al. 2008]. Sweet water from wash column and lye from the static separator containing glycerol is processed for producing glycerine. First step in glycerine recovery is the pretreatment of lye for removal of traces of soluble soap in the lye. Ferric chloride is added to the lye to precipitate the soluble soap as ferric soap which is separated by filtration. The acidic filtrate after removal of soap is acidic and contains excess ferric chloride. This is treated with caustic soda and ferric chloride is separated as ferric hydroxide precipitate which separated by filtration. The filtrate after removal of soap is sent to evaporation section. In multiple effect evaporator dilute glycerine is concentrated to 52percent glycerine. Some salt is separated at this stage. The concentrated liquor after separation of salt is centrifuged and the concentrated glycerine is sent to another single effect evaporator to achieve a concentration of about 84percent glycerine. This is called crude glycerine which is further refined in special distillation column at 140 °C and 755 mmHg. The distillation column contains three condenser in series from which different fraction of glycerine are recovered which is further treated with activated carbon to achieve the finished product.

**SOAP REMOVAL:** The spent lye contains a small quantity of dissolved soap which must be removed before the evaporation process. This is done by treating the spent lye with ferrous chloride. However, if any hydroxide ions remain the ferrous ions react with them instead, so these are first removed with hydrochloric acid:
\[
\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}
\]
The ferrous chloride is then added. This reacts with the soap to form an insoluble ferrous soap:
\[
\text{FeCl}_2 + 2\text{RCOONa} \rightarrow 2\text{NaCl} + (\text{RCOO})_2\text{Fe}
\]
This precipitate is filtered out and then any excess ferrous chloride removed with caustic:
\[
2\text{NaOH} + \text{FeCl}_2 \rightarrow \text{Fe(OH)}_2(\text{s}) + 2\text{NaCl}
\]
This is filtered out, leaving a soap-free lye solution.

**Salt removal:** Water is removed from the lye in a vacuum evaporator, causing the salt to crystallise out as the solution becomes supersaturated. This is removed in a centrifuge, dissolved in hot water and stored for use as fresh lye. When the glycerine content of the solution reaches 80 – 85percent, it is pumped to the crude settling tank where more salt separates out.
**Glycerine Purification:** A small amount of caustic soda is added to the crude glycerine and the solution then distilled under vacuum in a heated still. Two fractions are taken off - one of pure glycerine and one of glycerine and water. The glycerine thus extracted is bleached with carbon black then transferred to drums for sale, while the water/glycerine fraction is mixed with the incoming spent lye and repeats the treatment cycle.

**REFERENCES**
2. Dixit,S.” Toilet soaps and bathing bars” Chemical business, October,2011,p.18