

Chemical Technology
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Module - 4
Soap and Detergents
Lecture - 2
Synthetic Detergent and Linear Alkyl Benzene

We are discussing the module 4 of the organic chemical technology course. In the lecture 1, we discussed about the soap and detergents some of the historical development, which has taken place in soap making, and the changes that took place on this soap to detergent and that was because of the ability of the raw material. In the lecture 2 of this module 4 will be discussing about the synthetic detergent and linear alkyl benzene LAB, which is the major raw material for making of the surf extent or this detergent.

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Detergent

- Synthetic detergent industry is now one of the largest chemical industry.
- Synthetic detergent became popular due to lower price of raw material, price stability, and effectiveness and biodegradable nature of new synthetic detergent like linear alkyl benzene.

Synthetic detergent in this stage now, one of the largest chemical industry, we can say and the synthetic, and that has been only possible because of the coming of the refinery and the petro chemical complex. Synthetic detergent became popular due to lower price of the raw material, price stability and effectiveness and biodegradable nature of the new synthetic detergent like a linear alkyl benzene, in the earlier stage it is because the detergent, which may that was non biodegradable nature. And so there was a problem

and so with the coming of the linear alkyl benzene, the synthetic detergent market that achieved this.

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Detergent

- A detergent is a surfactant or a mixture of surfactants having "cleaning properties in dilute solutions. Commonly, "detergent" refers to alkylbenzene sulfonates, a family of compounds that are similar to soap but are less affected by hard water.

A detergent is a surfactant or a mixture of surfactants having cleaning property in dilute solution, commonly detergent refers to alkyl benzene sulfonate, a family of the compound that are similar to soap, but are less affected by hard water because that was the problem. In case of the hard water use of the soap, for cleaning purposes that was not effective in case of the hard water, but with the coming of the detergent and the process that has been improved the cleaning process. Let us come to the because the starting of the how, we start with the a detergent earlier the material, which has raw material, which has used for the that was the sodium dodecyl benzene sulfonate because the sulphonation. Even in case of the LAB we are doing this sulphonation of the linear alkyl benzene finally, it has been used as a detergent.

So, earlier detergent market was primarily from the sodium, dodecyl benzene sulfonate made from benzene with propylene tetramer by Friedel Craft alkylation that was followed by sulphonation with oleum, then the alkylation that was the alkylation. Actually, the alkylation earlier that was the expect that was being used and now, we are using this solid that is castle in case of the LAB.

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Sodium Dodecyl Benzene Sulphonate and Linear Alkyl Benzene(LAB)

- Earlier detergent market was primarily from sodium dodecyl benzene sulphonate made from alkylation of benzene with propylene tetramer by (Friedel Crafts Alkylation) followed by sulphonation with oleum.
- It was found that detergent made from highly branched structure of propylene tetramer was not easily biodegradable.
- Later it was replaced by LAB which is biodegradable.

It was found that detergent made from the highly branched structure of the propylene tetramer was not easily biodegradable, this was the actually major constraint from the environment point of view. And later it was replaced by a LAB linear alkyl benzene, which is biodegradable in nature because we are able to take a definite carbon item fraction, and from the paraffin from the kerosene.

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Detergent

- High detergency in soft and hard water (they do not react with Ca and Mg solution.)
- Requirement of small quantity
- Detergency action at low temperature
- Do not hydrolyse

Detergent, high detergency in soft and hard water, they do not react with the calcium magnesium solution. Next, that is the hardness that we are having requirement of the

smaller quantity in comparison to the soap. Detergency action at a low temperature do not hydrolyze. Let us come to the historical review of the detergent industry of the development that has taken place. Now, we are seeing the whole clean and the soap market that have been captured other than the bathing purposes, which are using the by the detergent.

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Historical Review of Detergent

- World war I led to development of synthetic soap and detergent
- Earlier short chain alkyl naphthalene sulphonates and later in 1920's and 1930's long chain alcohol sulphonates
- Latter long chain alkyl aryl sulphonates in 1940

Actually, the world war I led to the development of the synthetic soap and detergent as I told you, in the lecture 1, because that was the area of the industrialization at the same time that was required of that time many of the petro chemicals, many of the finish product at that time that was developed, manufacture was large scale manufacture that was started. So, earlier short chain alkyl naphthalene sulfonates and later in 1920s and 1930s long chain alcohol sulfonates that was used as a raw material for the detergent later long chain alkyl aryl sulfonate in 1940 that was there.

During 40s and 50s the detergent market was primarily captured by dodecyl benzene, a product formed by alkylation of benzene with the propylene tetramer, in a hard detergent alkylation. So, this was the problem in case of the when we use the benzene with the propylene tetramer that was the, of the non biodegradable nature.

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Historical Review of 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.

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Historical Review of Detergent

- It was found, 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.

It was found that the branched structure of the alkyl group was responsible for the poor biodegradability of the detergent because we are using detergent, and that the municipal water. The waste that was getting the that that was creating problem there and the linear alkyl benzene was introduced in the early 60s, have substantially replaced its counterpart, and the most of the detergent that is depending up on the linear alkyl benzene other raw materials are also there, because of this again, the improvement in the quality of the detergent because of the coming ethoxylene.

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Historical Review of Soap and detergent

- Latter long chain alkyl aryl sulphonates in 1940
- Proctor and Gamble introduced synthetic detergent TIDE
- Branched chain compounds in 1950's to 1960's non biodegradable
- With availability of tetrapropylenebenzenesulphonate replaced the soap as the key surfactant.

Latter long chain alkyl aryl sulfonate that was in 1940, Proctor and Gamble introduced synthetic detergent in the that is the tide. Branch chain compounds in 1950's to 1960 that was the non-biodegradable nature, which I told you. With the availability of the tetra propylene benzene sulfonate replace the soap as the key surfactant, during the initial stages. Again the problem of biodegradability was there and that was again replaced with the linear alkyl benzene.

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Historical Review of Detergent

- Linear alkyl benzene sulphonates during 1960's to have biodegradable detergent
- Real Break through in detergent industry was due to development of UOP LAB process and availability of LAB from petrochemical complexes
- Availability of paraffins from kerosene fractionation and for olefin and benzene from refinery and petrochemical complex led to large scale development of synthetic detergent industry

As I told you the linear alkyl benzene sulfonate during 1960's, that came to the market and to have the because it was the biodegradable detergent and so, that was the adhere non biodegradable detergent, was replaced with the linear alkyl benzene because of the environmental concern. And the real break breakthrough in the detergent industry was due to the development of the UOP lab process, and availability of lab from the petrochemical complexes.

We have the UOP they developed one palex, the molex process for the separation of the paraffin from the kerosene, and even the whole process of the LAB that was developed by the UOP, it was the actually depend in case of the UOP process there was lot of the development at RDL, they started the alkylation using the hydro fluoric acid. And then it was replaced with the solid acid catalyst, availability of the paraffins from the kerosene fractionation and for olefin and benzene from the refinery, and petrochemical led to the large scale development of the synthetic detergent industry, this was the how the development in case of the synthetic detergent industry that took place.

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Historical Review of Detergent

- Major breakthrough in LAB process has been development of environmentally friendly solid acid catalyst which replaced the conventional old HF catalyst

Major breakthrough as I told you the in case of the LAB has been development of the environmentally friendly solid acid catalyst, which replace the conventional old hydrofluoric acid catalyst because normally, in this case of the alkylation process, first we started with the sulfuric acid and then it was the hydrofluoric acid. Again the problem in case of the hydrofluoric acid was there more.

Actually, the requirement of this it was there in case of the sulfuric acid, but in case of the HF because it is a hydro highly corrosive in nature. So, again the people had started searching the alternative for the sense. So, that was the development of the solid acid catalyst for the alkylation part, which we will be discussing in detail in the in the next few slides.

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This is the various type of the detergent and the various name it maybe Wheel, Ariel, Sulfur, the Surf, Nirma number of the it may be in the powder form, liquid detergent that may be available. So, this is the how the detergent industry is growing because of the more and more usage of the detergent, and that is the driving force for that is the one driving force is you its consumption, rise in the population second is the availability of the raw material. The development in the technology of the separation process, which has lead to the lot of the economical production of the L A B, these are the application of the LAB in India at the various stage; not only for the fabric, but other uses are also there.

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LAB Application in India	
Application	Share (%)
Consumer Cleaning Products	96.2
a. Synthetic detergents for fabric wash	90.1
Popular	68.3
Mid-Price	13.3
Premium	18.4
a. Scouring products	8.7
a. Liquid detergents	1.2
Industrial & Institutional Cleaners	1.3
Other Industrial Application	2.5
Non-surfactant Applications(varnish, cable fluid oil, lubricant)	0.1
Total	100

So, these are the consumer and application consumer, cleaning products, synthetic detergent for fabric wash, popular, mid price, premium, scouring products, liquid detergent, industrial and institutional cleaners, other industrial application, non surfactant application just like in varnish, cable fluid oil, lubricant, some of the detergent that we are using. So, this is the how they and the percentage here you see the percentage here of the application that is there 96 percent that we are higher percentage, in the case of your. So, classification of the detergent you see the detergent that has been classified in different.

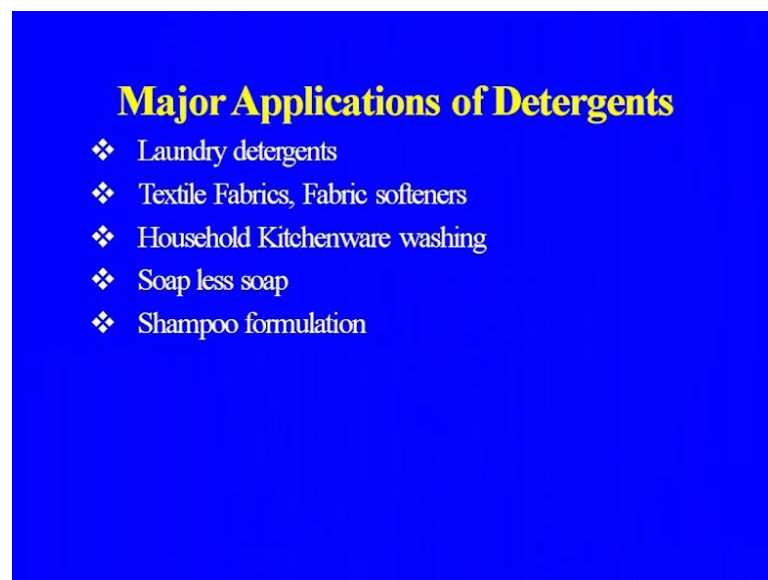
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Classification of Detergent
<ul style="list-style-type: none">• Anionic(negative charge): used in laundry and Hand dish washing. Long hydrophobic alkyl chain is the anionic part• Cationic(positive charge): Used in fabric softeners and fabric softening laundry• Nonionic (no charge): Used as dishwasher detergents and rinse aids.• Amphoteric(either positive or negative): used in personal cleansing and household cleaning products.• Ethoxylates

So, one classification anionic negative charge used in the laundry and the hand, dish washing long hydrophobic alkyl chain is the anionic part, this is about the anionic we are having the anionic, cationic, nonionic, amphoteric. So, in case of the cationic positive charge used in the fabric softeners, and the fabric softening is laundry nonionic no charge lose used in as dishwasher, detergents and rinse aids.

Amphoteric either positive or negative charge that maybe there used in the personal cleansing and household cleaning product ethoxylates. Now, the that is come in a big way from the ethylene, the ethylene oxide because now, this ethylene oxide that is being produced from all the crackup. We are getting ethylene and the ethylene oxide, and from then the ethoxilate that has become a very important product.

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Major applications these are the already, we have we have discussed about the even the sample formation also, we are using the. So, laundry detergent textile fabric, fabric softener, household kitchen ware washing, soap less soap, shampoo formulation.

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Types of Speciality Surfactants			
Anionic	Amphoteric	Cationic	Nonionic
Ether carboxylates	Amphoteric acetates	Amine Oxide	Alkyl polyglucosides
Acylisethionates	Betaines and siltaines		
Phosphate esters			
Sarcosinates			
Sulfosuccinates			
Taurates			

Again these are the some of the various type of the specialty surfactant that is available in the market, let the anionic, amphoteric, cationic and nonionic. Here is the alkyl polyglucosides amine oxides in some of the cases, this is some nitrogen compounds are also there here ether carboxylates, acylisethionates, phosphate esters. So, these are the some of the coming in case of the anionic detergent.

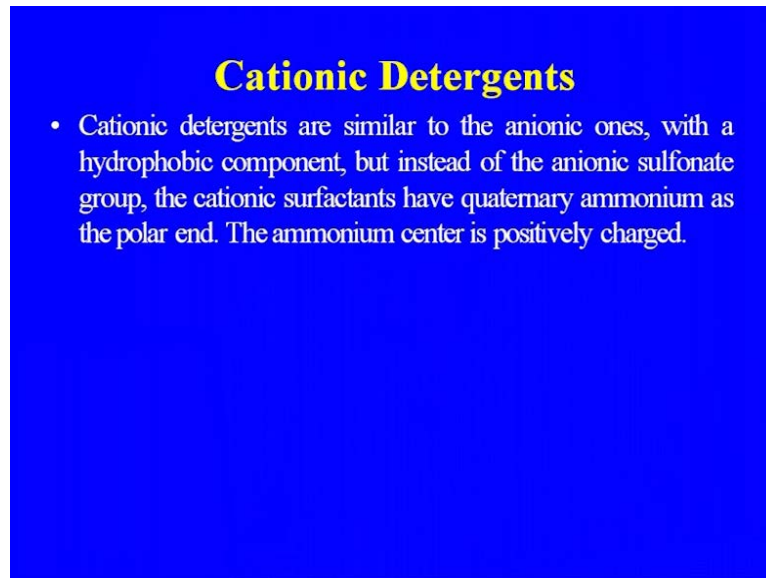
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Anionic Detergents
<ul style="list-style-type: none">• Typical anionic detergents are alkylbenzenesulfonates. The alkylbenzene portion of these anions is lipophilic and the sulfonate is hydrophilic.• Two varieties have been popularized, those with branched alkyl groups and those with linear alkyl groups.

Anionic detergent, let us now come to the typical anionic detergents are alkyl benzene sulfonates. The alkyl benzene portion of these anion is the lipophilic and the sulfonate is

the hydrophobic hydrophilic. Two varieties have been popularized; those with the branched alkyl group, and those with the linear alkyl group because in case of the linear group definitely it is more biodegradable in nature.

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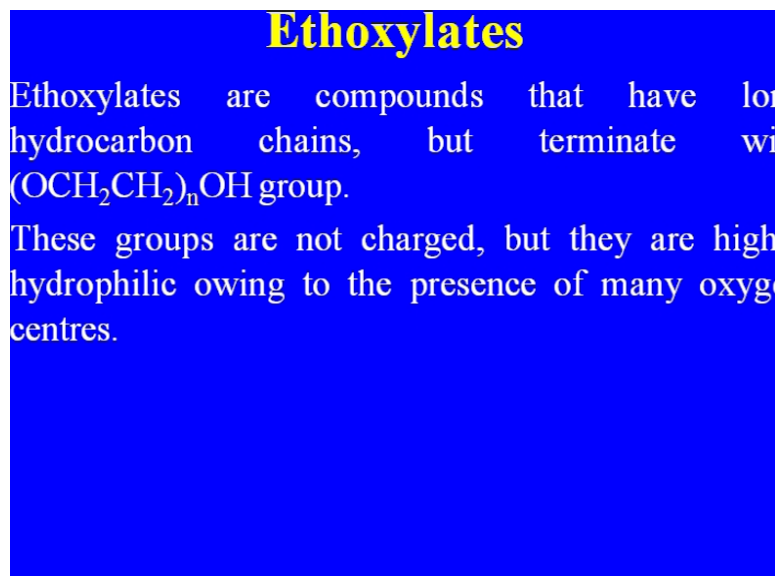


Cationic Detergents

- Cationic detergents are similar to the anionic ones, with a hydrophobic component, but instead of the anionic sulfonate group, the cationic surfactants have quaternary ammonium as the polar end. The ammonium center is positively charged.

Cationic detergents are similar to the anionic one with a hydrophobic component, but instead of anionic sulfonate, the cationic surfactants have quaternary ammonium as the polar end the ammonium center is the positively charged. So, this is about the cationic detergent.

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Ethoxylates

Ethoxylates are compounds that have long hydrocarbon chains, but terminate with $(\text{OCH}_2\text{CH}_2)_n\text{OH}$ group.

These groups are not charged, but they are highly hydrophilic owing to the presence of many oxygen centres.

Ethoxylates are compounds that have long hydrocarbon chain, but terminate with it is group these groups are not charged, but they are highly hydrophilic owing to the presence of many oxygen centres.

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Non-ionic detergents

- These are characterized by their (net) uncharged, hydrophilic head groups. They are based on polyoxyethylene glycol (i.e. Tween, Triton and Brij series), Chaps, glycosides (i.e. octyl-thiogluconide, maltosides), bile acids such as DOC, lipids (HEGAs), or phosphine oxides.

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Basic Components of Detergent

- Detergent
- Builders
- Filler and processin Aids
- Anti redeposition agent
- Fabric Brightners
- Corrosion inhibitors
- Antimicrobiol agents
- Enzymes
- Bluing

Non-ionic detergent these are characterized by their net uncharged, hydrophilic head groups they are based on the polyoxyethylene glycol. These are the some of the various varieties that are available. Now, the what are the various component of the because the basic raw material is the your detergent part. So, along with the detergent in case of the

various formulation, if you are getting other materials also to improve the detergency, to improve the cleaning, efficiency, and to sometimes to reduce the cost also.

So, builders perform because foam is also very important filler and processing aids, anti re deposition agents, fabric brighteners are also being used corrosion inhibitors are there, antimicrobial agents are there. Now, the enzymes because the enzymes are also being added, and the this is the what the different type of the grades of the your detergency are available in the market, they are claiming at the better if they are and it is the premium detergent like that. So, then the bluing because normally you must have seen the detergent slightly bluish from is there.

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Basic components of detergent

- Detergent (Linear alkyl benzene sulphonate)
- Builders : Phosphate (Sodium tripolyphosphate, boost detergent powder), citrates, silicates, carbonates, zeolite
- Filters and Processing Aids : Sod. carbonate, sodium sulphonate

Basic component of the detergent you see, the detergent that is the base is the linear alkyl benzene sulfonate because most of the detergent all the detergent. They are now, using the linear alkyl benzene sulfonate builders, phosphate sodium tripolyphosphate and boost detergent powder, citrates, silicates, carbonates, zeolite these are the builders filters and processing aids sodium carbonate and sodium sulfonate that we are using.

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Basic Components Of Detergent

- Corrosion inhibitors : Sod. Silicate
- Anti redeposition agent : Carboxy methyl cellulose
- Fabric Brightners : Fluorescent dyes

Corrosion inhibitors that it also either it has sodium silicate, anti re deposition C M C methyl cellulose that was fabric brighteners fluorescent dyes that we are using, in case of the fabric brighteners.

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Basic Components Of Detergent

- Antimicrobial agents : Carbinilides, salicylanilides
- Enzymes :Decompose or alter the composition of soil and render the particles more easily removable.
- Bluing : improve whiteners by counteracting natural yellowing tendency

Antimicrobial agents that is the carbinilides and the salicylanilides enzymes decompose, or alter decomposition of this valve and render the particles more easily removable, so that they helping in the cleaning. So that is why enzymes are also there bluing improve the whiteness by counteracting, the natural yellowing tendency.

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Linear alkyl benzene

- Linear alkyl benzene (LAB) is the basic raw material for production of most widely used detergent Linear alkyl benzene sulphonate
- Linear alkyl benzene was introduced as substitute for non biodegradable branched alkyl benzene.
- LAB is a clear colourless liquid with characteristic odour.

Now, let us come to the linear alkyl benzene because this is the major raw material, we are making in India also, the linear alkyl benzene is the basic raw material for production of the most widely used detergent, linear alkyl benzene sulfonate. Linear alkyl benzene sulfonate, was introduced as substitute for non biodegradable branch alkyl benzene LAB is a clear colorless liquid with the characteristic odour.

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Linear Alkyl Benzene

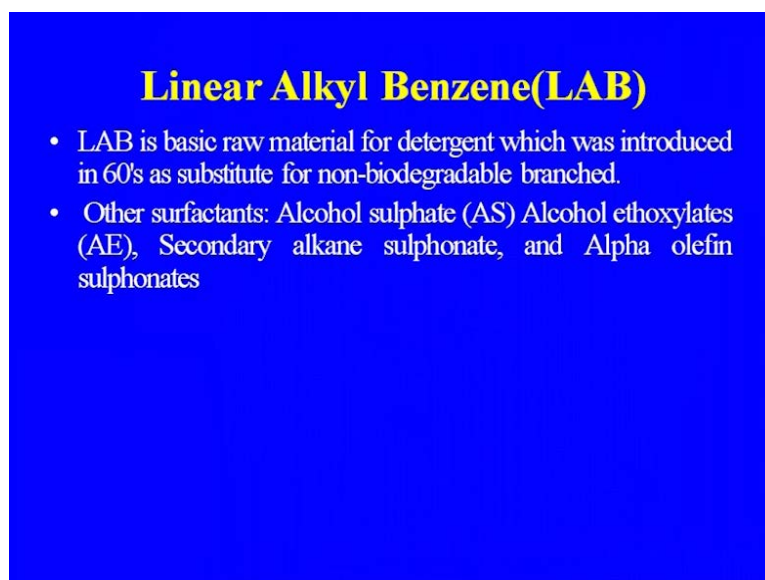
- Linear alkyl benzene (LAB) is most widely used as the basic raw material for the manufacture of synthetic detergent.
- The linear alkyl Benzene produced from the $C_{10} - C_{13}$ or $C_{11} - C_{14}$ linear mono olefins are useful detergent intermediate and can be readily sulphonated to yield linear alkyl benzene sulphonates.

So, I already discussed about the importance of the linear alkyl benzene, which is the basic raw material; and normally because this is the biodegradability of the linear alkyl

benzene. So, it is very important factor and so for getting the biodegradable nature, what we need is the specific carbon atom in the raw material that is needed.

So, the linear alkyl benzene produced from the C 10 to C 13 or C 11 to C 14. So, linear mono olefins are use because the if you are increasing the carbon number, if it is more than this, then the non biodegradable nature of your linear alkyl benzene will be produced. So, this actually the after getting the linear alkyl benzene, this is sulfonated to the linear alkyl benzene is sulfonate, which is the actually the basic detergent that we are using. Earlier also I discussed about the L A B, which is the it was introduced it in the it came into the market in 60 a substitute for the non-biodegradable.

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Linear Alkyl Benzene(LAB)

- LAB is basic raw material for detergent which was introduced in 60's as substitute for non-biodegradable branched.
- Other surfactants: Alcohol sulphate (AS) Alcohol ethoxylates (AE), Secondary alkane sulphonate, and Alpha olefin sulphonates

Other surfactants are also there that is getting important that the alcohol sulphate alcohol ethoxylates, which I was telling about the ethoxylate secondary alkane sulfonate and alpha olefin sulfonate, these are also being use in the detergent industry because these are the some of the alternative raw materials also.

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Linear alkyl benzene

- These compounds constitute the “active” ingredients of many house hold detergents.
- They are surface active compounds (surfactants) which are combined with various builders (often inorganic salts) to make up a detergent formula

These compound constitute the active ingredient of many house hold detergent, that is the LAB. They are surface active compound, which are combined with the various builders, often inorganic salt to make a detergent formula that is the final detergent which we are getting.

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Linear Alkyl Benzene

- Although LAB demand grew by 14% per annum during 1984-90, future demand in the country is projected to increase at a healthy growth rate of 7-8% as against 2-4% worldwide.
- India and China with huge population are the largest market for LAB

Although the LAB demand grew by 14 percent per annum during 1984 to 90, future demand in the country is projected to increase at a healthy growth rate of 7 to 8 percent, as against 2 to 4 percent worldwide because India and China, there have been huge

population. The largest market for LAB is in these two country. So, for a production of the LAB in India is concern, we started manufacturing LAB in 1985 that was the first point by the IPCL and it was followed by reliance industry at Pathal Ganga.

Reliance was the first plant IPCL, now it is taken about by the reliance industry at Vadodara that was the first plant, and this is the IPCL at that time when it was started that was the large petro chemical complex was which was manufacturing, a number of the petro chemicals. So, here the they are having the catalytic reforming for getting the benzene and so, that benzene that was being used here then the paraffins, which was used for the making the olefin that was actually, produced by the fractions of the kerosene.

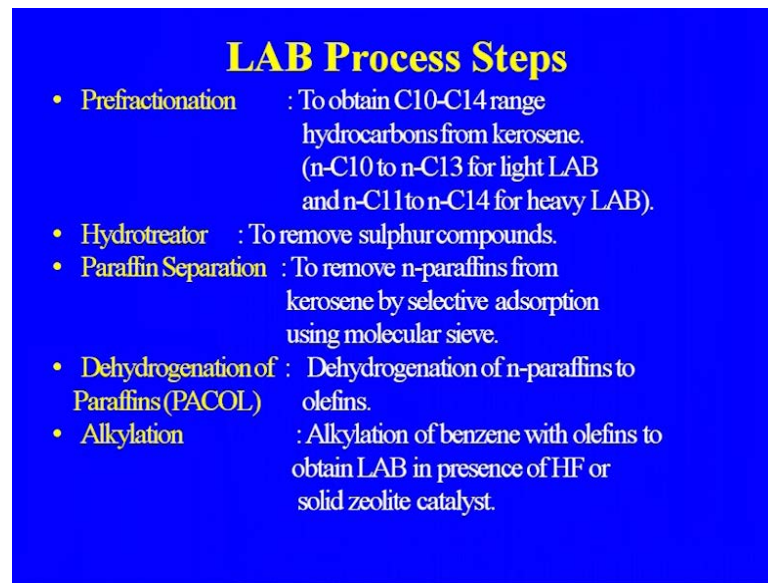
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Linear Alkyl Benzene

- LAB manufactured in India started in 1985 by IPCL in 1985 followed by Reliance Industries, Tamilnadu Petro products, Nirma, Indian Oil corporation
- IPCL, Vadodara: 50,000
- Reliance Industries: 1,00,000
- Tamil Nadu Petro Products: 1,20,000
- Nirma: 75,000
- Indian Oil Corporation: 1,20,000
- Total: 4,65,000

So, these are the some of the units which we are manufacturing that is the IPCL. Now, the reliance, reliance industry Tamil Nadu reliance, the Patal Ganga, Tamil Nadu petro products, Nirma and new plant which came later that was the Indian oil corporation they have started their plant at Vadodara unit. That even it is based on the solid acid catalyst the earlier other units they are they are using the hydrofluoric acid, but Indian oil corporation they started their UOP LAB plan based on the solid acid catalyst. Now, let us go to the detail of the LAB process. So, first step in case of the LAB manufacturing at the pre fractionation because the pre fractionation means, the here leads the paraffins for the changing to the for making your olefin.

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LAB Process Steps

- **Prefractionation** : To obtain C10-C14 range hydrocarbons from kerosene. (n-C10 to n-C13 for light LAB and n-C11 to n-C14 for heavy LAB).
- **Hydrotreater** : To remove sulphur compounds.
- **Paraffin Separation** : To remove n-paraffins from kerosene by selective adsorption using molecular sieve.
- **Dehydrogenation of Paraffins (PACOL)** : Dehydrogenation of n-paraffins to olefins.
- **Alkylation** : Alkylation of benzene with olefins to obtain LAB in presence of HF or solid zeolite catalyst.

So, to obtain the C 10 and C 14 range hydrocarbon from kerosene, we are taking so that will be the in case if the carbon item for light LAB, and if the carbon item is high then there will be LAB. So, these two type two gates are there hydrotreater, because always the raw material changing that may contain some sulfur compound, and removal of the sulfur compound that is very important. And so that has to be removed before it is going to the paraffin separation just, because it will poison the catalyst, and the adsorption also in the substantial stages. So, that is the important of the hydrotreating to remove sulfur.

Paraffin separation to remove the n paraffins from kerosene by selective adsorption using molecular sieve and this process, we call it the molex process that has been developed by UOP, then dehydrogenation of the paraffins to olefins that is the pacol process, we called the in case the UOP process. They have named it the pacol process. So, dehydrogenation of normal paraffins to olefins the next step is the alkylation of benzene with olefins to obtain LAB in presence of HF or the solid acid catalysts.

Now, let us go in more detail about the process to obtain the C 10, C 14 obtain the hydrocarbons from the kerosene, because the kerosene that is one of the major raw material for making of the LAB. And that we are getting because kerosene that contains higher or the lower paraffins also and so, those paraffins has to be removed only what we need in case of the LA B that is C 10 to C 14 carbon item paraffin tetraionin.

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Process steps in LAB manufacture

- Prefractionation
- To obtain C10-C14 range hydrocarbons from kerosene. (n-C10 to n-C13 for light and n-C11 to n-C14 for heavy LAB).
- The LAB unit requires a very specific feed in terms of carbon number. The prefractionation unit is designed to process a high purity C₉ to C₁₅ linear (normal) paraffin feed and to separate out a heart cut with the desired carbon number which will range from n C₁₀ to n₁₃ for light LAB and n₁₁ – n₁₄ for heavy LAB.

So, the LAB requires a very specific feed in terms of the carbon number. The prefractionation unit is designed to process a high purity C 9 to C 15 linear normal paraffins, feed and to separate out a heart cut with the desired carbon number, which will range from the C 10 to C 13 for light LAB and C 11 to C 14 for heavy L A B. So, prefractionation and the to get a particular cut that we are having during the prefractionation stage and rest of the kerosene, which we are getting that will be again recycled to the system.

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Process steps in LAB manufacture

Hydrotreater

- To remove sulphur compounds from feed stock
- The purpose of this unit is to remove sulfur and nitrogen from the feed without greatly changing its B.P. If not removed, sulfur and nitrogen would poison the sieve in the Molex Unit.

Hydrotreater as I told you, this is important for removal of the sulfur compounds from the stock, the purpose of this unit is to remove sulfur, and nitrogen from the feed without greatly changing its boiling point, if not remove sulfur and nitrogen would poison the sieve in the molar unit that that is how we are going to use it in the molar process.

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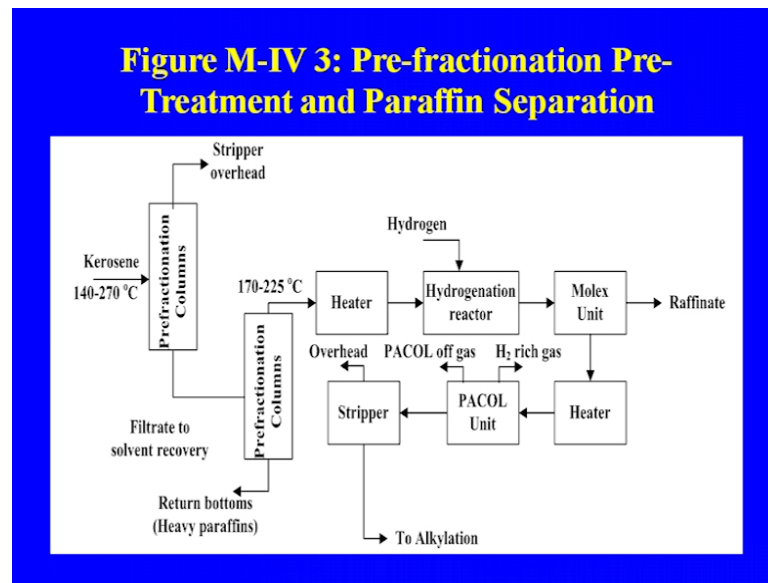
Process steps in LAB manufacture

- Paraffin Separation(Molar process)
- To remove n-paraffins from kerosene by selective adsorption using molecular sieve. The UOP MOLEX process is an effective method of continuously separating normal paraffins from a stream of co-boiling hydrocarbons by means of physically selective adsorption.
- The feed stock is separated into a high purity normal paraffin fraction at high recoveries and a non-normal paraffin.

Then the next step is the paraffin separation, you have the continuous separation that is taking place and this process molar process based on the adsorption. To remove the normal paraffins from the kerosene by selective adsorption using molecular sieve, the UOP molar process is an effective method of continuously separating, separating normal paraffins from a stream of co-boiling hydrocarbon by means of physical selective adsorption process. And so the to get a defined fraction of the kerosene, as a paraffin because we need as I told you we need this C 10 to C 14.

The feed stock is separated into a high purity, normal paraffin fraction at high recoveries and a non normal paraffin because the other fraction that has to so, this is the selective absorption of the normal paraffin by the molar adsorbent. So, this is very important to get the high purity product, this is the pre treatment and the paraffin separation process that is taking place, you see this is the kerosene.

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Pre-fractionation column then the stripper overhead again filtrates to solvent recovery, this is going to the, this is not part of this, this is coming in the other. So, pre-fractionation column and then the finally, the return bottom to the heavy paraffins that will be jumped to this, and that will be used a fuel again and so, it will go to the heater hydrogenation reactor hydro treatment means, the pre treatment of the paraffins, which we are separating from the fractionation column.

And so after the hydrogenation means, that is the desulphonation for the removal of the sulfur and nitrogen compound, and then it will go to the molex unit, molex unit means the definite and the extract faced that will be there. And so the adsorbent means, that you are getting here. There the finally, it will go to the pacol unit, pacol unit where the that will be your because here we are getting the paraffin.

So, paraffin separation is taking place and the paraffin separation that the and here in case the molex process that continuous regeneration of the adsorbent is there and that adsorbent again continuously, that has been done and the separation is very efficient in case of the molex process. So, that was the real breakthrough also you can say in case of the LAB because the development of the some of the adsorbent. Especially, because the UOP has been definer they have developed a number of the adsorbent, one is the olex another the parax, which is being used for the olex for the olefins.

Separation parax is for the parasailing separation and here, it is the molex for the separation of the paraffin. So, finally this molex unit from the molex unit paraffin that will go to the pacol unit and then from the pattern the olefin that will go to the alkylation section. Let us come to the, because the next step after the separation of the required carbon number of the paraffins. The next step in LAB manufacture is to have the dehydrogenation of the paraffins to get the olefins.

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Process steps in LAB manufacture

Dehydrogenation of Paraffins (Pacol Process)

- This process dehydrogenates the high purity linear paraffin feed stock from the pre-fractionation unit into the corresponding mon-olefins, suitable as feed stock for the down stream detergent alkylate unit.

This process dehydrogenates, the high purity linear paraffin feed stock from the pre-fractionation unit into corresponding mon-olefins, suitable as feed stock for the alkylation purpose, this is downstream detergent alkylates. And unit some of the actually, the catalyst poisoning because we are having the different type of the catalyst poisons, one is the temporary another, the permanent. Temporary means that can be removed by some treatment and this is the reason why, we are having the pre-treatment of the feed which is going to the molex process.

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PACOL Section: Catalyst Poisoning)

Sulfur: Excessive amounts of sulfur in the liquid feed will attenuate metal function. Accordingly higher operating temperatures have to be kept. It will reduce the catalyst life.

Organic Nitrogen Compounds: It will readily form ammonia and can react with chlorides to form ammonium chloride salts.

Oxygenates: Most would react to form water. Low levels are not a problem.

So, sulfur excessive amount of sulfur in the liquid feed will attenuate the metal functions and accordingly higher operating temperature have to be kept, it will reduce the catalyst life also. Then the other impurities, which may be present because you see the sulfur compound, nitrogen compound energy present in the raw material and so, it will readily form ammonia and can react with the chlorides to form the ammonium chloride salt again, it will poison the catalyst oxygenates most would react to form water low levels are not a problem.

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Process steps in LAB Manufacture

Alkylation

Alkylation of benzene with olefins to obtain LAB in presence of HF or solid zeolite catalyst.

This process alkylates benzene with linear olefins produced by the Pacol unit in the presence of HF acid catalyst to yield linear alkyl benzenes, LAB.

Now, let us come to the alkylation process the alkylation of the benzene with the olefins to obtain LAB in the presence of HF, or the solid zeolite catalyst that we are what we call is the acid catalyst. This process alkylates benzene with a linear olefins produced by the pacol process because in the pacol process, what we are getting? In the pacol process we are converting the paraffins to olefins, and these olefins that we are using here for alkylating the benzene again, the benzene you see the benzene that we are getting from the catalytic reforming process.

And the reformat, which you are getting for the because in the catalytic reforming that is the integral part of any refining, and the petro chemical because depending upon the requirement, if you are going for the improving the octane number and the you are interesting in the gasoline. So, simply the reformat that will put the gasoline form. If you are interested for the getting the recovery of the benzene, talien or the jolene then the reformat from the catalytic reforming that will go for the separation of the benzene, talien and jolene.

As you know the separation of the benzene or the use of the benzene, that is very important for the polyester manufacture where we are making the, but benzene separation because the first amongst the all the aerometrics benzene, talien and jolene. Benzene is having the lower boiling point and so, the benzene is separated from the reformat, which we are getting after the catalytic reforming and so, that benzene that is available from the refinery, and this is the reason why some of the refiner.

Although, they do not have the TPA plant, or the TMT plant still they are separating benzene because that benzene that has been used in the your LAB manufacture either to may be other application just like you. Take the case of the manufacture of the captor-electron where we the need your raw material and so, from the benzene to captor-electron that we are using as a raw material.

So, this is how the benzene we are getting. So, alkylation of benzene with the olefins to obtain LAB in the presence of hydro fluoric acid and solid acid catalyst, this is the process that we are using in the alkylation. This process alkylates benzene with the linear olefins produced by the pacol unit, in the presence of HF acid catalyst to yield the linear alkyl benzene.

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Process steps in LAB manufacture

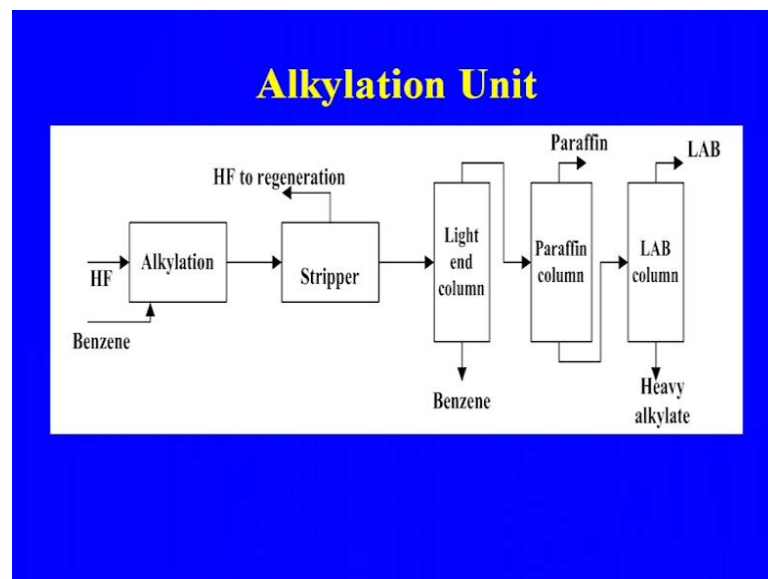
Alkylation

The LAB thus produced can be readily sulfonated to form a suitable ingredient for many household detergents. This unit consists of three processing section :

- i. Alkylation Section.
- ii. Fractionation Section
- iii. Acid Regeneration Section.

So, the next in case of the LAB thus produced can be readily sulfonated to form a suitable ingredient for many a household detergents. This unit consist of alkylation because the product of the alkylation that you have the alkylation section, fractionation section, acid regeneration section because the acid recovery that is very important if you are using the hydrofluoric acid.

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And still many of the units they are using the hydrofluoric acid. So, acid regeneration that is very important but in case of this solid acid catalyst, again the regeneration of the

catalyst is there, but here the you are effluent at the environmental from the environmental point of view. This process, HF hydro, HF alkylation process notice are available. So, that is the reason why it led to the solid acid catalyst.

This is the alkylation unit and it may be the benzene, benzene and then the input that is here it is not shown, but in the your olefins from the pacol process that will come to the alkylation unit HF is catalyst. Then this stripper light end columns, you see paraffin columns were some of the paraffins, that may be there which is removed and then the finally, it will go to the LAB column and where the linear alkyl benzene that will be getting and heavy alkylate that maybe there and so that has. Now, I discuss about the why the shifting from the hydro fluoric acid catalyst to the solid acid because this has been a major development in case of the alkylation process, even in the refinery where we are using the alkylation process for getting more number. So, alkylation process, there also and now solid acid catalyst that been used.

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Hydrofluoric Acid catalyst

HF acid has been the principal catalyst for the production of LAB from linear olefins.

However, the handling of corrosive catalysts such as HF acid have always had some disadvantages

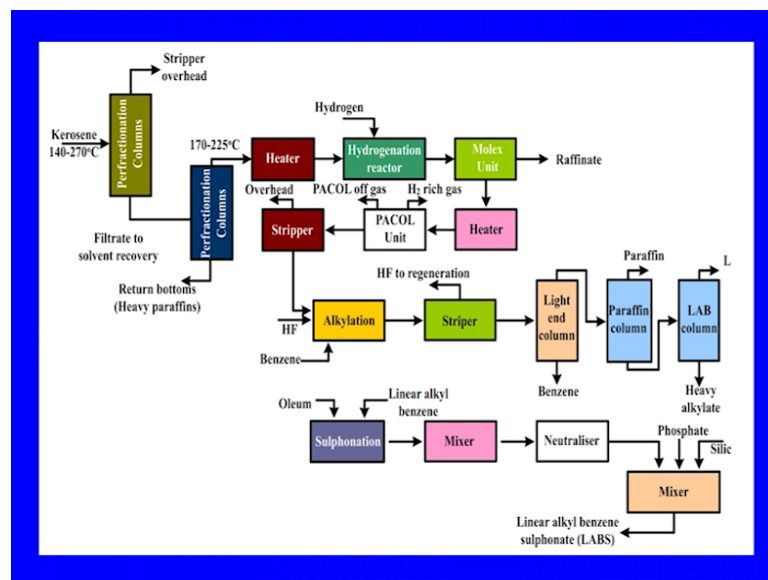
- ❖ Highly corrosive environment
- ❖ Higher equipment capital cost,
- ❖ Disposal of small quantities of neutralization products generated by the process.

So, HF acid has been the principal catalyst for the production of LAB from the linear olefins, and most of the plans before coming of the Indian oil plant at Vadodara in India. All the plant there are based on the H F's hydro fluoric. How about the handling of the corrosive catalyst such as hydrofluoric acid? They have always some disadvantage, that I told you the corrosiveness, and from the environmental norm highly corrosive

environment is there because of the hydrofluoric acid, and the that will result in the higher equipment capital cost.

In case of the hydrofluoric acid disposal of the small quantity of the neutralization products generated by the process that is also getting some environmental problem. And so these are the some of the disadvantages, which we are having because of the use of the hydrofluoric acid has catalyst this is the complete actually, the process that we are using in case of the any LAB plant we have the kerosene.

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And this particular fraction of the kerosene because if the kerosene that is in between the naphtha and the diesel part. And so, the boiling point may be in the some of the 140 minutes naphtha range also in the one around 200 times. So, kerosene with the this fraction and then it will go for the fractionation. So, that the you are getting a particular cut of the kerosene that will be the year rest of it is written already, I discussed this diagram. So, the again it will go to the, after the separation in the pre-fractionation, it will go to the hydrogenation or the, we are doing the hydro de-sulfiration removal of the other input is also.

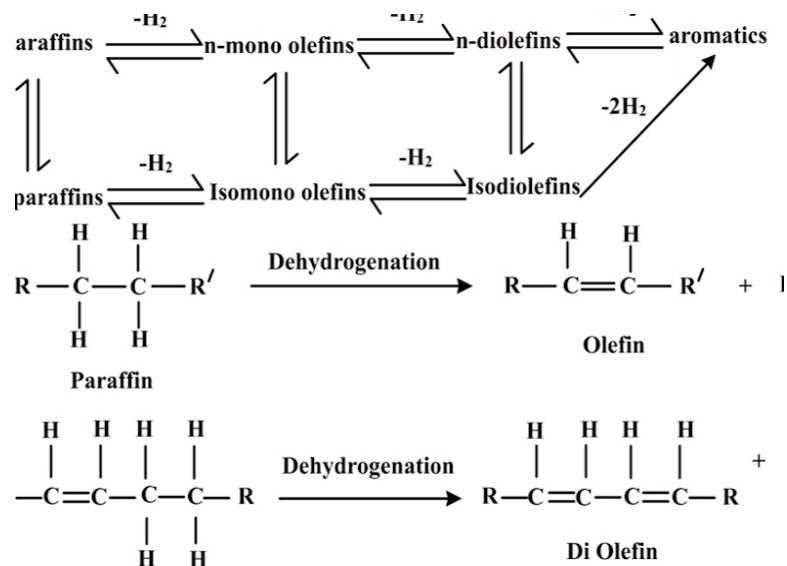
And then it will go to the pacol unit, pacol unit to the alkylation unit where you are getting the HF catalyst here. It is the olefins which we are getting, after the hydro treatment also and the, because hydro treatment usually, before going to the pacol. We are removing all the your impurities, which are present as sulfur compound as in the

catalyst. So, hydrofluoric acid that we are this is the actually, the in case when we are using the hydrofluoric acid slightly, some changes have there in case of the flow diagram when we are using the solid acid and this benzene as I told, this benzene we are getting from the catalytic reforming then you to the stripper.

Then the HF hydrofluoric acid that will be the regeneration, and the lightened columns where some of the undetected paraffins that may remain. So, and the benzene that will be against separated and that will be reused, and this paraffin again it will go to this and the finally, we are getting this. Next, step actually in case of the your making of the final detergent, this is the steps involved.

We are using the oleum for sulfonation of the linear alkyl benzene that will be the mixture, where adding the various ingredient neutralization. Then finally, here it is the neutralization part and finally, because the treasure of the acetate will be not desirable. So, finally in the mixture we are adding the various additives phosphates enzymes all the things. Then the near linear alkyl benzene sulfonates that will be available from the process.

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This is the reaction that is taking place in case of the paraffin process. Now, the next step as I told you in case of the after making of the linear alkyl benzene, this is the sulfonation of the linear alkyl benzene.

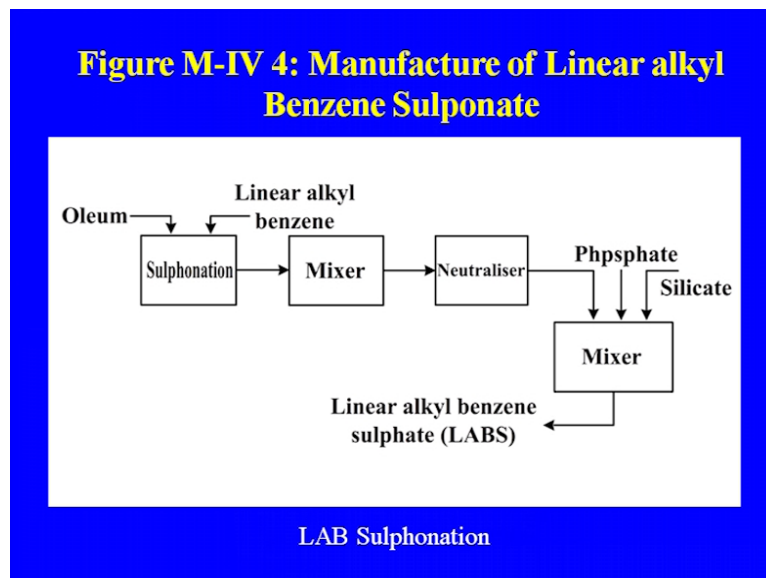
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Sulphonation of LAB

- This involves sulphonation of LAB using sulphuric acid to produce Linear alkyl Benzene Sulphonate which is the main ingredient of detergent

This involves using sulfuric acid to produce linear alkyl benzene sulfonate, which is the main ingredient that of the detergent.

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This is the process which I discussed earlier the linear alkyl benzene sulphate, where the you are doing the sulfonation mixture, neutralizer and then silicate phosphate as a filter. And other ingredients of the surfactant that we are and the final, you will be getting the L A B. Again the final formulation of the detergent, which you are getting the finished product, because this is the basic raw material that has been supplying by the LAB

manufacturing, either they can because again here, you see that maybe in the case of the plant, it may be only the LAB that is available from the major pollution, they will provide the LAB.

The rest of the process sulfonation mixing, mixing of the base ingredient mixing of the filler sometime because if they want to reduce the cost, they will have they are adding the fillers. Also all those activity that is taking place at the formulation stage, where they are making the final surfactant, or final detergent and the quality because the cost of the detergent, cost of the because if this you take the surf. A various grades of the surf are available in the market and they are declaiming better, and better cleaning efficiency with the, and the cost is also increasing with it different kinds. So, the addition of the various ingredient that will depend upon the quality of the your raw material.

So, that was the actually about the I was telling about the formulation part, that is the part of the final making of the detergent bars, soaps, flakes all those thing that will be that the plan separately that is being done because these major producers, they have supplying the linear alkyl benzene. Now, let us come to the solid acid catalyst and this is the real breakthrough in case of the alkylation process whether, it is in case of the LAB manufacture or in case of the refinery.

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Lab by Solid Acid Catalyst

- The conventional catalyst AlCl_3 , H_2SO_4 and HF commercially used has the disadvantage of causing corrosion of equipment as well as waste production.
- There has been continuous search for development of non corrosive solid catalyst with similar catalytic properties.

Because the conventional catalyst we use the mini-employed and then it was the H_2SO_4 and from the H_2SO_4 and HF because the HF was found better catalyst for alkylation

than H_2SO_4 . Amount of the H_2SO_4 that was about more than it was around 3 to 4 times more than what we are using. And so, that was the reason why it was and the even the quality.

So, we shifted from H_2SO_4 to HF alkylation and so, this was the some of the disadvantage, which I discuss earlier also causing corrosion of the equipment as well as the waste production. There has been continuous search for development of non corrosive solid acid catalyst with the similar catalytic property. And so, this was the how the UOP, they were able to develop the solid acid catalyst for manufacture of the linear alkyl benzene.

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Lab by Solid Acid Catalyst

- Some of the catalyst which have been developed are $SiO_2-Al_2O_3$, H-montmorillonite, amberlyst, H-Y, H-Beta, HM World LAB capacity was around 3 million tones with nearly 85% based on HF alkylation, 5% on the aluminum chloride process, and 10% on the newly developed fixed bed
- The fixed bed alkylation was first introduced on commercial scale in 1995 in Canada by Petresa

Some of the catalyst which have been developed are SiO_2, Al_2O_3 combination H-montmorillonite, amberlyst H-Y, H-Beta, HM world LAB capacity was around 3 million tones with nearly 85 percent. You can see the waste on the HF alkylation only 5 percent on the aluminum chloride and 10 percent on the newly developed fixed bed, but then in the future because the environmental, from the environment point of view things are becoming more and more stringier, more stringier standards are there.

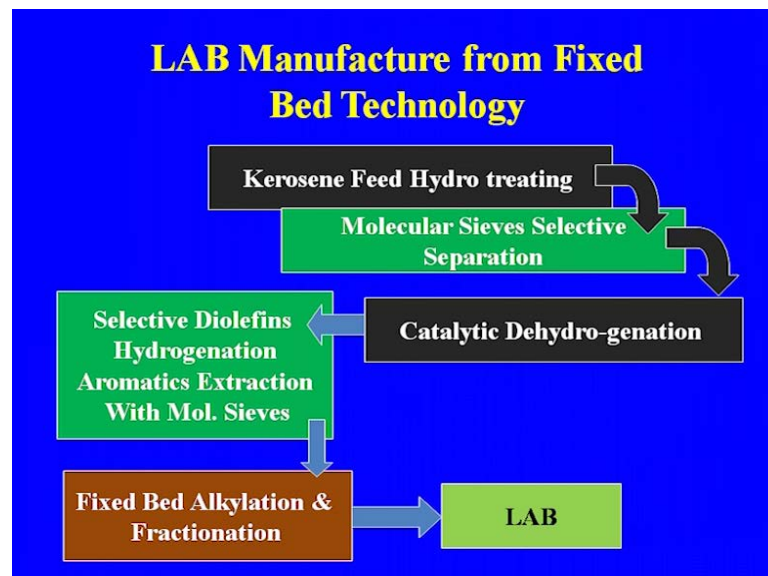
So, the now the people definitely they will have to shift from the HF catalyst to solid acid catalyst, but only thing that the cost definitely, the cost of the solid acid catalyst that is higher than the what we are using in case of the HF method. So, that is but may be one of the constant for shifting from the HF catalyst to solid acid catalyst, but it cannot go on

compromising with the environment. So, they will have to shift from the HF to solid acid catalyst a fixed bed alkylation was first introduced on commercial scale, in 1995 by Canada and the this is the actually, fixed bed technology based on the solid acid catalyst.

We are having had the I O C Indian Oil Corporation, Vadodara unit which is started manufacturing it was around 2005 and because of the Indian oil, they have come in big way in the making of the petro chemical, they are just integrated their refinery with the petro chemical and in that actually step, they started manufacturing LAB at the IOC, Vadodara. Then, TPA terry-ethylic acid at the Panipat refinery and in the now, the Panipat refinery that is one of the a big hub for the petro chemical, that is the petroleum and petro chemical of the another part of India.

So, this is the how the development that has taken place and the new plans, which are if it is coming definitely that will be based on this solid acid catalyst. Here also the most of the processes, which are involved in case of the HF catalyst up to the olefin production that is same except the alkylation stage, where will be doing the alkylation not in presence of the HF catalyst, but it will be on the present of presence of solid acid catalyst.

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So, here again as in the case of the HF catalyst the process, which we discussed kerosene feed hydro treating after the fractionation because here, this is only the simplifies flow diagram with that will have to fractionate. The kerosene we will have to get the paraffin

of the required carbon atom, and then it will go for the hydro treating or the removal of the catalyst poison, or which may poison the herein in case of the your paraffin separation in the molecular sieve.

So, that has to be removed during the hydro treatment process and then after that it will go the molecular sieve, selective separation which was there in case of the in the process, which we will discuss earlier. Then, the catalytic dehydrogenation again this is the converting the paraffins to the olefins, and because here we will be getting. Again the olefins of the higher carbon not higher means, desired carbon atom, which will be the of the because the alkylate, which will be getting of the alkylation of the benzene and olefin that will be of this higher carbon atom because just to have the more, and more biodegradable nature.

So, this is the selective hydrogenation aromatic extraction of the molecular sieves and the finally, the fixed bed alkylation unit, where we are using the acid catalyst. Finally, we are getting the linear alkyl benzene. So, this is the process that is being used and so, in future of the LAB plan that will based on the solid acid catalyst and now, we see the we are also having the powder detergent.

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Powder Detergent

- The solid and liquid raw ingredients are dropped into a large tank known as a slurry mixer.
- As the ingredients are added the mixture heats up as a result of two exothermic reactions: the hydration of sodium tripolyphosphate and the reaction between caustic soda and linear alkylbenzene sulphonic acid.

The solid and liquid raw ingredient drop into a large tank known as a slurry mixer, and as the ingredients are added the mixture heats up. As a result of the two exothermic

reactions, the hydration of the sodium tri-phosphate and the reaction between caustic soda and the alkyl benzene sulphonic acid.

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Liquid Detergent

- Liquid detergent contains soap as well as synthetic surfactants. This is usually made first as a premix, then other ingredients are blended into it.
- This step simply consists of neutralizing fatty acids (rather than fats themselves) with either caustic soda (NaOH) or potassium hydroxide.

The liquid detergent contains soap as well as they are actually the spring. The spring process is also there for making the your detergent and liquid detergent contains soap, as well as synthetic surfactant this is usually made first as a premix. Then, other ingredients are blended into it this step simply consists of neutralizing fatty acid rather than, fats themselves with either caustic soda or the potassium hydroxide. So, in the market you see the detergent powder detergent even the size of the granules, which are getting even you see the detergent manufactured at the finite detergent part of plot, of the manipulation part is also there just to increase the weight of the soap.

If you see the surf it is bulk, density will be lower, in some of the detergent in bulk density because they are adding more sodium carbonate or sodium silicate. So, the cost that will reduce and, but the detergency power definitely that will be in case of the, if the less and less fillers also, this is the about the LAB plant. The manufacture of detergent and so, because as you see the more and more detergent plans are coming, so in the future detergent plan that will be definitely on the solid acid catalyst, not on the HF catalyst.

One of the major reason for the growth of the detergent industry, has been the availability of the raw material whether, it is the paraffin from the kerosene or benzene

from the refinery or the petro chemical complex, that is the one of the driving force along with the population for the development of the detergent industry. At the same time we have been able to reduce, the cost of the detergent because with the availability with the production, mass production of the liquid of the L A B. And as I told you that we are having 5 major units, which are producing linear alkyl benzene. So, this is the how the development and that is taking place and the driving force and why, the cost factor because that is has been very important and that was the one the reason also from the soap to detergent.