Organic Chemical Technology
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Lecture - 08
Detergents Manufacture

Welcome to the MOOCs course Organic Chemical Technology. The title of today's lecture is detergent manufacture. Before going to the details of today's lecture, we will have a recapitulation of what we have discussed in the previous lecture. In the previous lecture, we started discussions on soaps and detergents industry, right? Then specifically we discussed about manufacture of soaps and glycerin or glycerol, okay? So here what is the purpose of either soap or detergent that you take? They usually lower the surface tension and then provide required cleaning action. These are taking place because of presence of some surfactants as a major ingredient in the soaps or detergents, right? So the soaps manufacturing is having two different processes like batch or continuous hydrolysis followed by saponification reaction process, right? So here the soaps are natural product industries output, why? Because in India especially we use vegetable oils for the soaps manufacturing, right? How the vegetable oils whatever are required for the soap manufacturing they will be having fatty glycerides.

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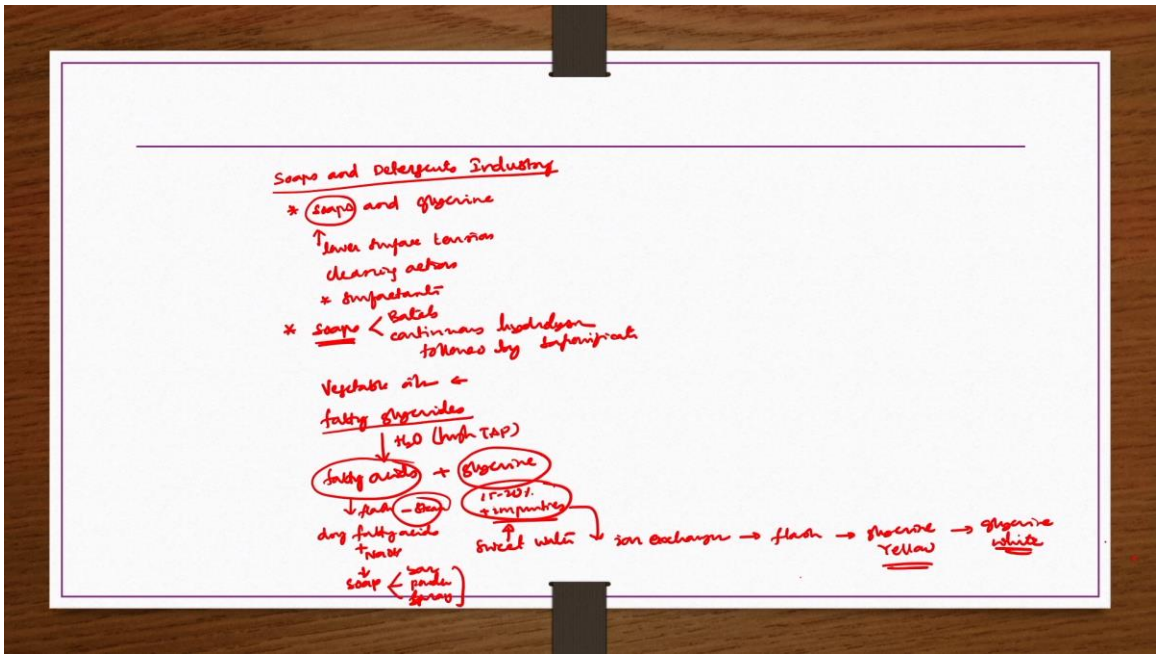

These fatty glycerides what we do? We react with high temperature water at high pressure or we try to interact water and fatty glycerides in counter current way at high temperature and high pressure so that whatever this fatty glyceride are there they will reduce into fatty acids plus glycerin, right? So, this glycerin is only 15 to 20 percent purity and then some impurities would be there, right? So, this we call sweet water, right? So, then this you can pass through some kind of series of ion exchanges to remove the colors and impurities then followed by purification by flash distillation etcetera to get the glycerin, right? So, this glycerin is often yellow in color. This yellow glycerin if you do the adsorption of yellow color by activated carbons then you get the glycerin which is white in color or white glycerin you get which is good for the human consumption whereas yellow glycerin is sufficiently good for the industrial applications, right? So this is how you get the glycerin whereas the soaps you get from the fatty acids. These fatty acids usually contain lot of moisture also because of this hydrolysis process. Then what you do? You pass this fatty acid through flash tanks to remove the steam and then moisture etcetera so that what you get? You get the dry clean purified fatty acids. This you react with the sodium hydroxide then you get soaps, right? The soaps you can make into the bars, powder or any other format, sprays etcetera. This kind of formats you can make as per the consumer's requirement, right? So, this is what we have seen in the previous lecture where we targeted primarily on the soaps and glycerins. In this lecture we will be talking about the detergents which are also lower the surface tension but they lower the surface tension to a much lower degree than the soaps plus these detergents are better in the hard water. Why? Because if you use the soaps in hard water what happens? They will form the components with the calcium, magnesium ions of the hard water and then they precipitate out as a insoluble lump. So that is not going to be good for the cleaning action. So that will reduce the forming action as well as the cleaning action. But if you use the detergents in hard water what will happen? It will form some kind of components with the ions of the hard water definitely as in the soaps but they will be either soluble in water or they will be colloidally uniformly dispersed in the solution, right? And then these detergents are synthetic as I already mentioned. So quite a lot of applications and then advantages are there for these detergents compared to the soaps. However, there are some kind of problems also associated with these detergents, all those things we are going to discuss in this particular lecture. Now let us start our discussion on our today’s topic on detergents. Before going into the details of its manufacturing process in the industrial scale or in the chemical plants, we will have a few basic details of detergents.

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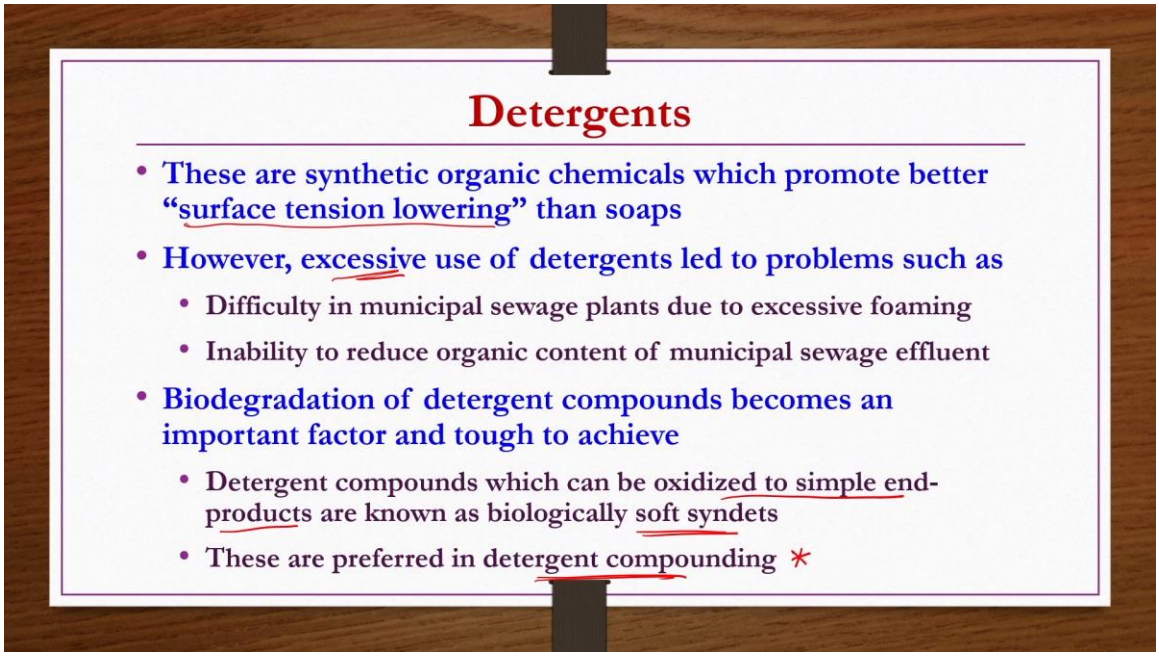

Detergents are synthetic Detergents are synthetic organic chemicals which promote better surface tension lowering than soaps. Soaps also lower the surface tension but detergents lower to a much lower level than the soaps. That is the reason we call them they promote better surface tension lowering than the soaps. However, excessive use of detergents led to certain problems in municipal sewage plants because in the household applications if you are using detergents, obviously you may be using for different purposes not only for the fabric cleaning purpose but also for the utensils cleaning purpose also in sometimes these are used. So, all the wash water after the cleaning that all goes into the drains and then goes to the municipal sewage.

This municipal sewage you know that has to be treated in municipal sewage plants because of the pollution concern but in the waste water that is going from the household into the municipal sewage if it is containing more amount of detergents what happens? Excessive foaming takes place in the municipal sewage sludge etc. So, because of that excessive foaming one cannot handle or operate the plants properly. Another disadvantage of this detergent is the components, the major cleaning component. Actually, the detergents are having surface active components which are having you know one long chain and as well as the functional group. Organic long chain whatever is there that is hydrophobic in nature and then that has to be biodegradable then it is good.

In the case of these are biodegradable such kind of chains are biodegradable but in the detergents some of them are not biodegradable. If they are not biodegradable again there would be problems from the environmental concerns. Such kind of problems are there by

excessive use of detergents. We cannot avoid using detergents they are essential for household purpose but they should be used appropriately, they should not be used excessively so that you know problems like difficulty in municipal sewage plants due to the excessive foaming should not be there and then also inability to reduce organic content of municipal sewage effluent. We are going to see sooner this surface-active component of detergents or soaps etc. they will be having you know long chain as well as the functional group like this. This long chain whatever is there that is organic in nature or hydrocarbons that can be linear or branched also possible like this. So, these are hydrophobic we do not like water. If these chains are like you know biodegradable then it is good. So, there is no problem but most of the detergents since they are synthetic it is possible that these chains may not be biodegradable always. So, it is better to have a chain which is biodegradable in general. So, biodegradation of detergent compounds becomes an important factor and tough to achieve in general. Detergents compounds which can be oxidized to simple end products known as biologically soft syndetes are good.

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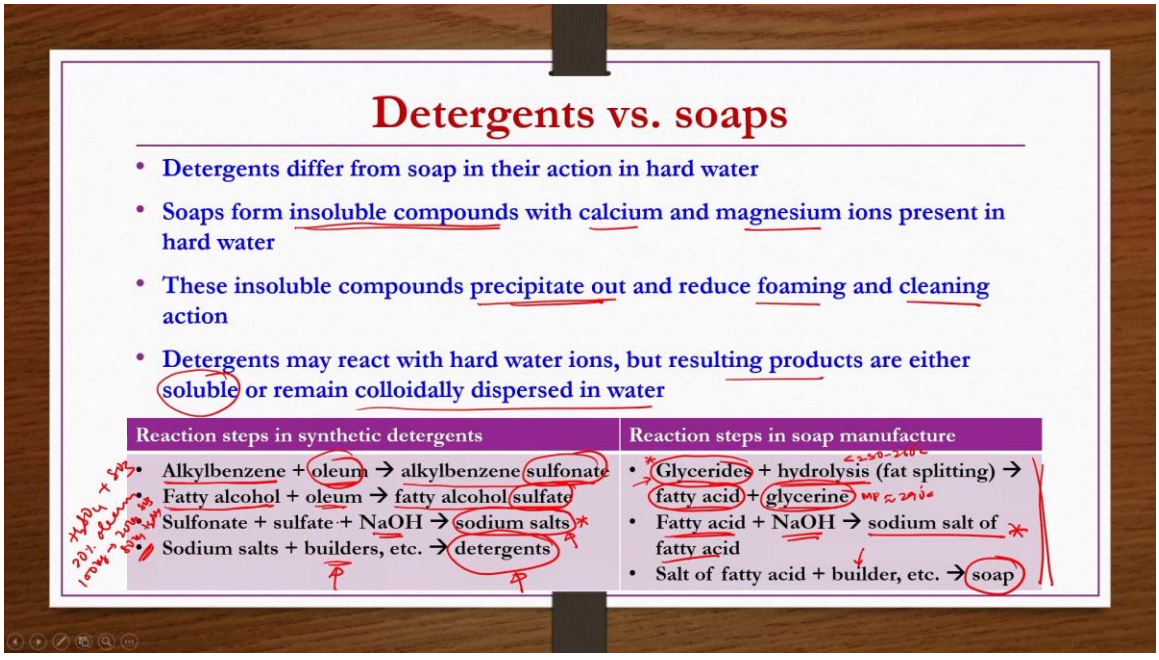

Actually, these soft syndetes are preferred in detergent compounding. They are preferred. So, if these kinds of components are there so then it is good anyway. So, we are going to see a few examples by structure of these detergents or the components of the detergent so that to understand which is easily biodegradable which is partially biodegradable and then which is very tough to biodegradable or biohard those kinds of things we are going to see in the subsequent slides anyway. Now, we see a few more differences between

detergents and soaps. Let us say if you have hard water. So, the action of detergent and then action of soap in hard water are going to be different from each other.

So, for example, if you take soaps they form insoluble components with calcium, magnesium ions that are present in the hard water not only forming insoluble actually if they are forming insoluble components they are not going to be perform or participate in the cleaning action. So that should be avoided further not only forming these insoluble components they also precipitate out and reduce foaming and then cleaning action. So, that is the reason soaps are not preferred if the water is hard water, but if you have detergents then you can use them even in the case of hard water why because detergents may react with hard water and but resulting products are either soluble that is a good thing or they remain colloidal dispersed in the water uniformly it is dispersed. So, that way detergents are you know better options if the water is hard water. Now, from the reaction steps that are included in the manufacturing of soaps and detergents if you see and compare in general glycerides fatty glycerides or tallows etc. are taken as a raw material for the soaps manufacturing then you do the hydrolysis by reacting with hot water at high pressure and high temperature. So, that splitting of these glycerides fats will take place you get fatty acids and glycerin as a mixture. This glycerin its melting point is approximately 290 degrees centigrade whereas this hydrolysis is done less than 250 to 260 degrees centigrade. So, whatever this glycerin is there in this product mixture that will be forming as a bottom product only that bottom product glycerin plus impurities you take it as a sweet water and then further processing you do to get the glycerin as we discussed in the previous lecture. Whereas the fatty acids you know they are important for the soap making but they are having excessive of water after this fat splitting reaction that excessive of water what you do you remove by passing through this dilute fatty acid through a flash tank to which steam is provided. So that these fatty acids moisture content would be relieved and then pure fatty acid or dry fatty acids you get then you react with sodium hydroxide to get the sodium salts of fatty acid. This is the major component of the soap. So, to this soap you add the builder's additives etc to get the soap of requirement soap of required properties as per the consumer. This is what happens in the case of soap manufacturing. Similar kind of reactions takes place here also in the case of detergent were slightly different let us say here whatever the raw material is the alkyl benzene that organic is synthetic organic whereas the glycerides etc here in the case of soap they are natural products. These synthetic alkyl benzenes they react with the oleum or excess of 98 percent H_2SO_4 to get alkyl benzene sulfonate. Other reaction is possible that whatever the fatty alcohols that are present or you know may be taken as a raw material and then they will also react with oleum or excess of 98 percent H_2SO_4 to get the fatty alcohol sulfate. So, this sulfonate and this sulfate components you react with sodium hydroxide to get the sodium salts. These sodium salts are you know surface active material and now these are the primary components which are bringing required foaming as well as the cleaning action. But we cannot have 100 percent of this one.

It necessary to be added some builders and additives to increase the detergents power as well as to have the corrosion resistance as well as the antimicrobial action, blowing action etc all those kinds of requirements may be there. So those can be brought in by adding appropriate builders. So, this sodium salts when you add the builders additives etc then you get the final detergents that are in general you get in the market. This oleum is nothing but you know H2SO4 plus SO3. Let us say you have 20 percent oleum means what? It is if you have the 100 kgs out of which 20 kgs would be SO3 and then 80 kgs would be H2SO4 that is what it means by 20 percent oleum. So, all these manufacturing of oleum etc is part of the other course in organic chemical technology. There you can find details which are also available in the MOOCs portal.

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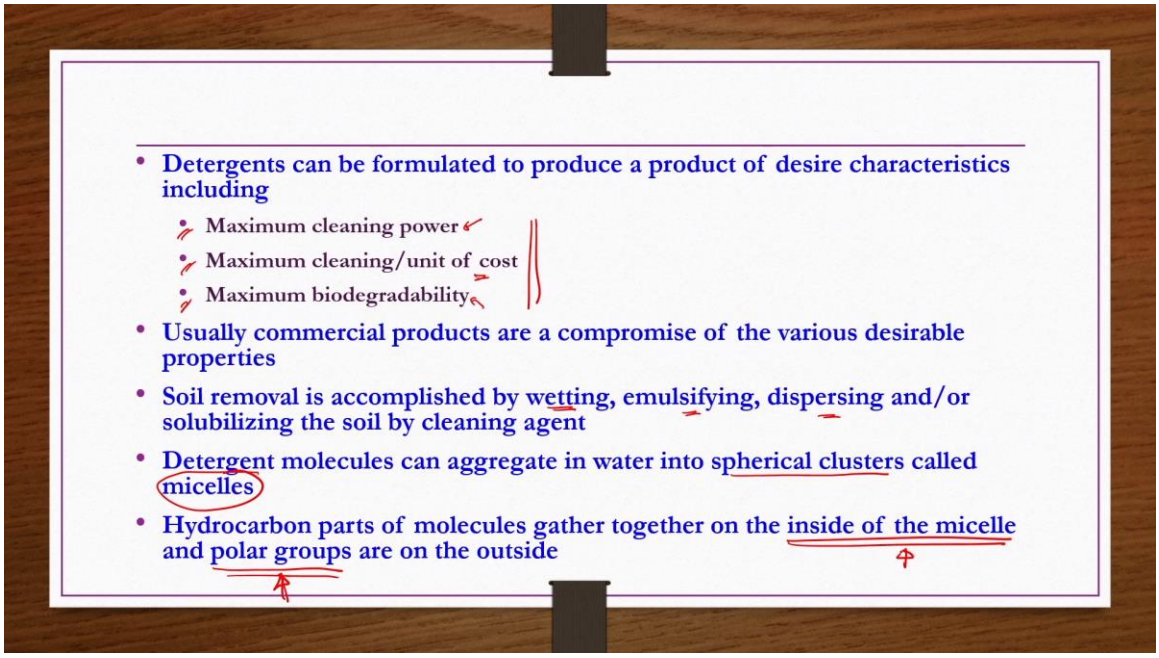

Now these are some basic differences between soaps and detergents both from the manufacturing purpose as well as from the action point of view. But what is the purpose of detergents? Why do you want to prepare or what are the properties that you would like to have in detergents? So, there are 3 important properties or characteristics are required in the detergents. First one is the obviously maximum cleaning power.

Second one is the maximum cleaning per unit of the cost. It should not be very expensive and then third most important is that the component of the detergent they should be biodegradable. So maximum biodegradability should be there. Now any detergent if you see its composition you will not able to find out all these properties together. So all the commercial detergents are having some kind of compromises.

One detergent may be having a compromise on the cleaning power, another may be having compromise on the biodegradability, another may be having good cleaning power, good biodegradability, but maybe cost may be higher. Such kind of compromises are unavoidable at the present industry situations as per the present industry situations. So usually commercial products are a compromise of the various desirable properties. Now the cleaning action is the important task that we are looking forward that detergent should provide. So how does it occur? That we are going to see now.

Soil removal is accompanied by wetting, emulsifying, dispersing and or solubilizing the soil by cleaning agent. How? That all details we are going to see now. Detergent molecules can aggregate in water into spherical clusters called micelles. So pictorially we are seeing in the next slide. So, when you dissolve these detergents in water what happens? These surface active components of the detergents they will aggregate such a way that spherical clusters would be formed. Hydrocarbon parts of the molecules gather together on the inside of the micelle whereas the polar groups are on the outside.

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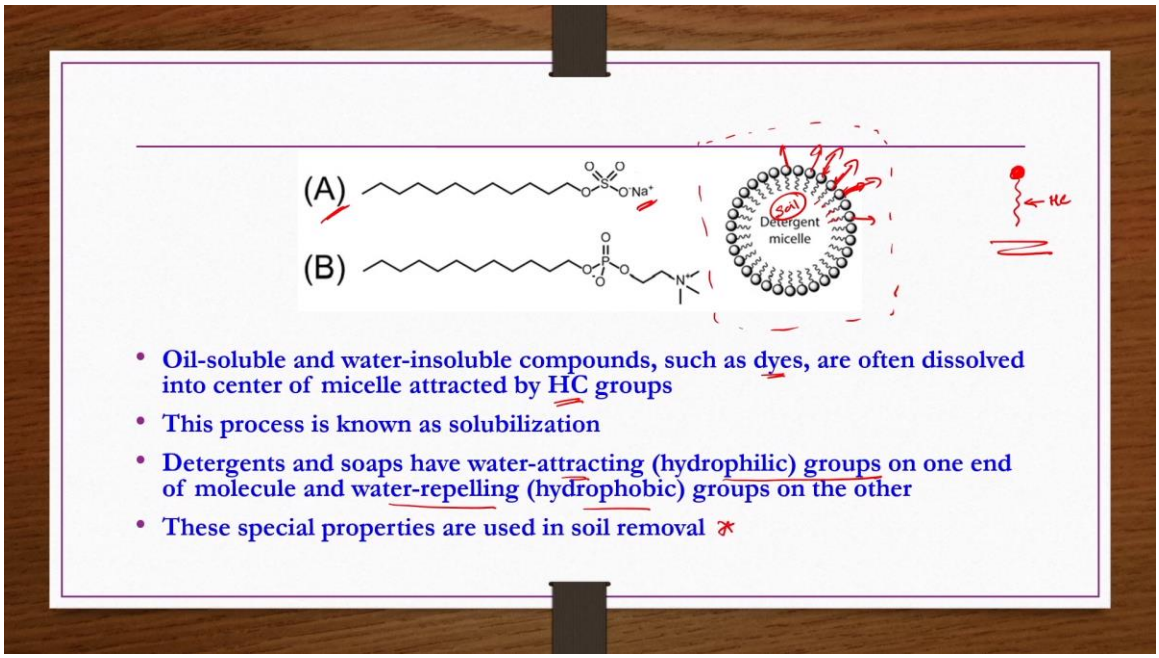

So, these are dissolvable or soluble in water whereas these are not soluble in the water. So that means this is A is one type of detergents, anionic detergents because it is giving this whatever this major portion is this one is there that provides the cleaning action organic the chain lengths. So that is having negative charge. So, then this is one example of anionic detergent same is this one as well.

So now pictorially these are represented, especially surface-active materials like you know chains like this at one end you are having functional groups and then the remaining

chain is usually taken as the hydrocarbon, right? So in the case of detergents in general I am talking, right? So, when you have so many of these things and then dissolve in the water, all these hydrophobic things kind of thing they form together and then they join together and then form a spherical cluster like this, right? So in this spherical cluster, so these the circles, smaller circles whatever are there, they are hydrophilic components, you know which like the water, water loving component, right? So let us say if the surrounding is all water, so they will try to go towards the water side like this, right? Whereas the tail side or the chain side whatever is there that is hydrophilic side or hydrophilic nature they will be having. So, they try to go towards the soil or the hydrophobic surface kind of thing. In general, if you are applying this principle for the fabric cleaning point of view, the soil whatever is there that soil usually you know they will be hydrophobic in nature that will not dissolve easily in the water. That is the reason it is not possible to clean it properly without using the surfactants or the detergents. So these micelles which are these clusters which are forming they go towards such kind of soils because both of them are hydrophobic, they allow together and then they form a cluster like this.

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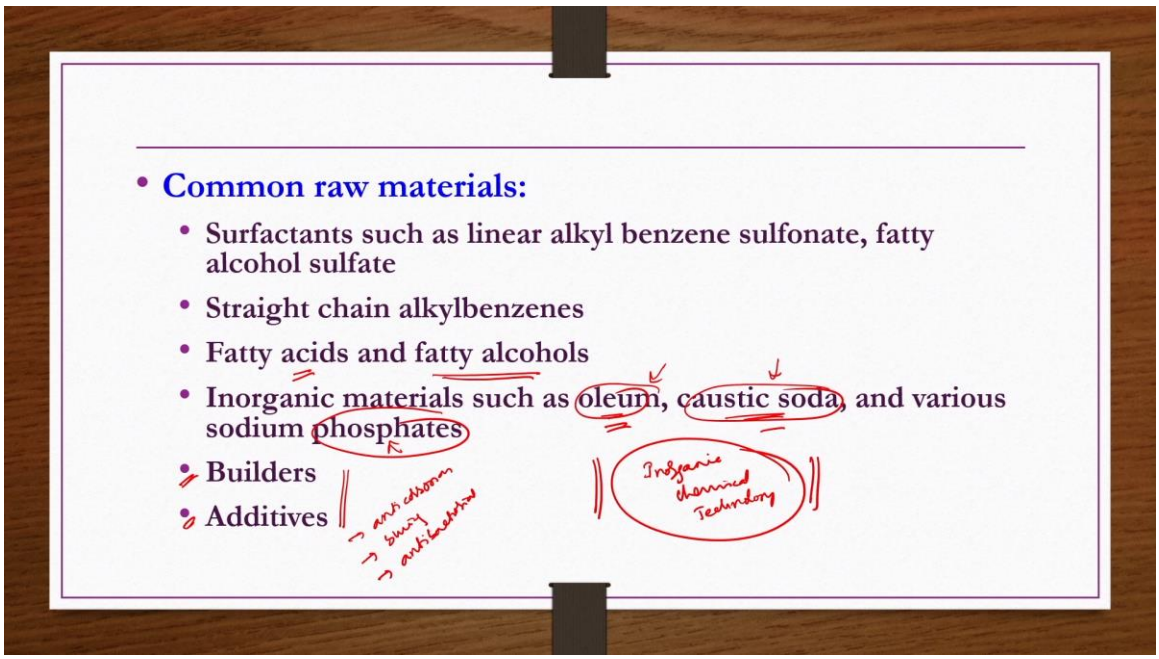

Now in the water because of the mechanical agitation, etc., as well as the natural tendency, these heads whatever are there they will try to go towards the water and then these chains they try to go towards or they attract the soil or attract the hydrocarbon whatever the dirt, etc., is there that will be attracted by this hydrocarbon chain, right? So in this process the soil would be loosened and then that will come out of you know detached or removed from the fabric surface and then cleaning action takes place, okay?

So, oil soluble and water insoluble components such as dyes or soils, etc., often dissolve into center of micelle attracted by the hydrocarbon group which is hydrophobic in nature. This process is known as the solubilization, this is only one we have taken. So mostly these such kind of actions are taking place when you dissolve you know detergents in water. Detergents and soaps have water attracting hydrophilic groups on one end of molecule and water repelling hydrophobic group on the other end as shown here, right? So, these special properties are used in general in soil removal, okay?

So that is about a few basics about detergents, soaps and all those things. Now we talk about the raw materials that are required for manufacturing detergents at the industry level, right? So, the raw materials are we are talking about common raw materials because they are not specific one particular commercial detergent may be having one particular surface active material, other industry may be having or other commercial detergent may be having different types of surface active material as a major ingredient. So, like different you know variations are possible from one plant to the other plant or from one commercial detergent to the other commercial detergent. That is the reason the raw materials we are going to discuss as a common phenomenon rather specific to one particular product, okay? So common raw materials, so surfactants such as linear alkyl benzene sulfonate, fatty alcohol sulfate, etc., straight chain alkyl benzene, etc., fatty acids and fatty alcohols, etc. Then inorganic materials such as oleum, caustic soda, various sodium phosphates, etc., are required either for the reaction to occur or as a builder or additive purpose these inorganic materials are required. Some builders' additives are also required. So, let us say in some cases these builders and additives are studied together assuming the same thing, they are having different roles.

Let us say some additives are required as anti-corrosion purpose. Sometimes fabrics tend to have the natural alloying tendency over the period of time. So that has to be reduced or removed for that bluing kind of agents are required. Then sometimes you know if the weather is damp, so then fabrics may not be drying up easily when you do the cleaning or after the cleaning or washing the fabrics using the detergents, right? So then if they are not drying quickly or within stipulated time, so then some kind of stains are forming on the fabrics because of the bacterial activity. So, to avoid such kind of thing anti-bacterial agents should be used.

Like that several options are there. So, these are all added as additives, we are going to see details anyway, right? So, these what kind of builders or additives in general use that is what we are going to see. This oleum, caustic soda, their production, etc., that we have seen including the phosphates, etc., are part of other course that is inorganic chemical technology. So, in that course you can find how these are being produced, but now for this part we are directly taking them, okay? So, anybody interested they can go through other course on inorganic chemical technology where you can find production of the inorganic chemicals like this, right?

Some of the fatty acids productions from the vegetable oils, etc., or by the continuous hydrolysis process, etc., that we have already seen in the previous lecture, but there are other processes also there where we can get the fatty alcohols as well as the fatty acids, those things we are going to discuss now, right? Likewise, you know some details of the surfactants, etc., are also we are going to discuss now, right? Before going into the main manufacturing process of the detergents. So, let us start with the surfactants.

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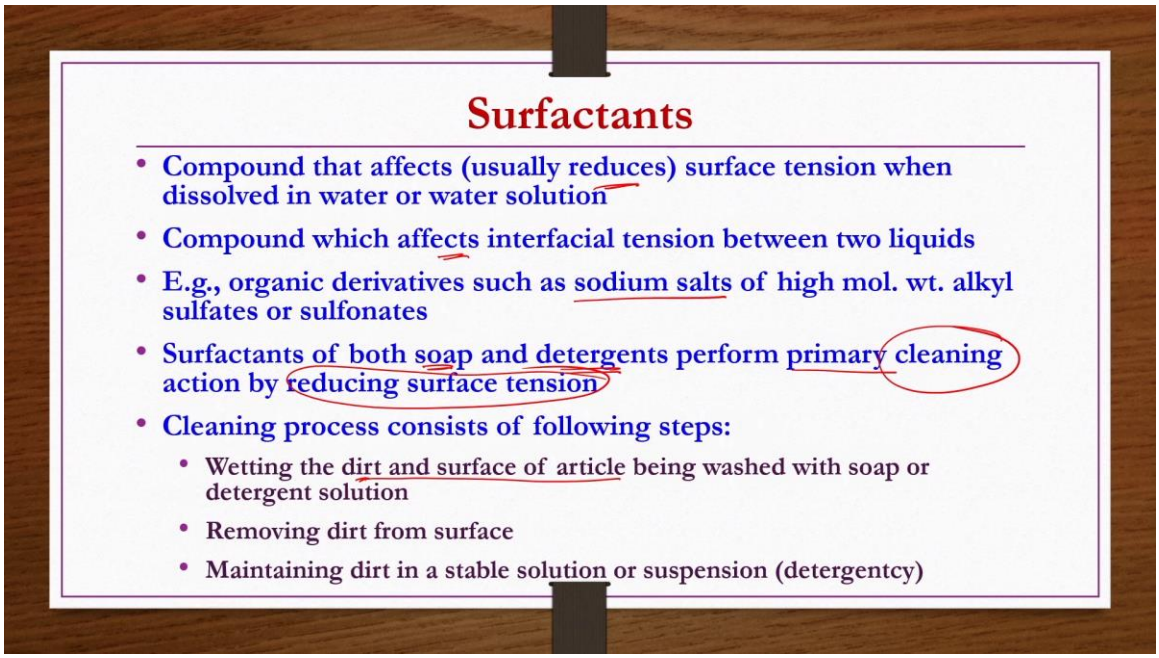

Surfactant what it is? It is a component that affects usually reduces surface tension when dissolved in water or water solutions, but if you have two liquid solutions, two immiscible liquid solution, there is possible that the surface tension or interfacial tension is there between two immiscible liquids. So, in such case also surfactant can be seen as a component which affects that interfacial tension between two liquids.

This is how a surfactant probably you can define easiest way, okay? Example organic derivatives such as sodium salts of high molecular weight, alkyl sulfates or sulfonates, we are going to see their structure soon. Then surfactants of both soap and detergents perform primarily what? The cleaning action. How they do? They do it by reducing the surface tension. So, this colloidal chemistry principles are very much essential from the understanding point of view of the surfactants. Now we are saying that either soap or detergent they are used for the cleaning purpose.

So, then how this cleaning process takes place? If you list out the steps primarily we have wetting the dirt and surface of article being washed with soap or detergent solution that is one step. Then removing the dirt from the surface is the second step and then finally

maintaining dirt in a stable solution or suspension, right? You remove the dirt by applying the detergents etc. in water solution and then after some time when you stop the washing machine and then after 1 hour if you remove it should not be the case that you know this dirt are deposited back on the fabric surface. That should not be the case, okay? So, redeposition should also be avoided that is also important not only the cleaning one. So, how these occur? We have already seen but once again we see the steps here.

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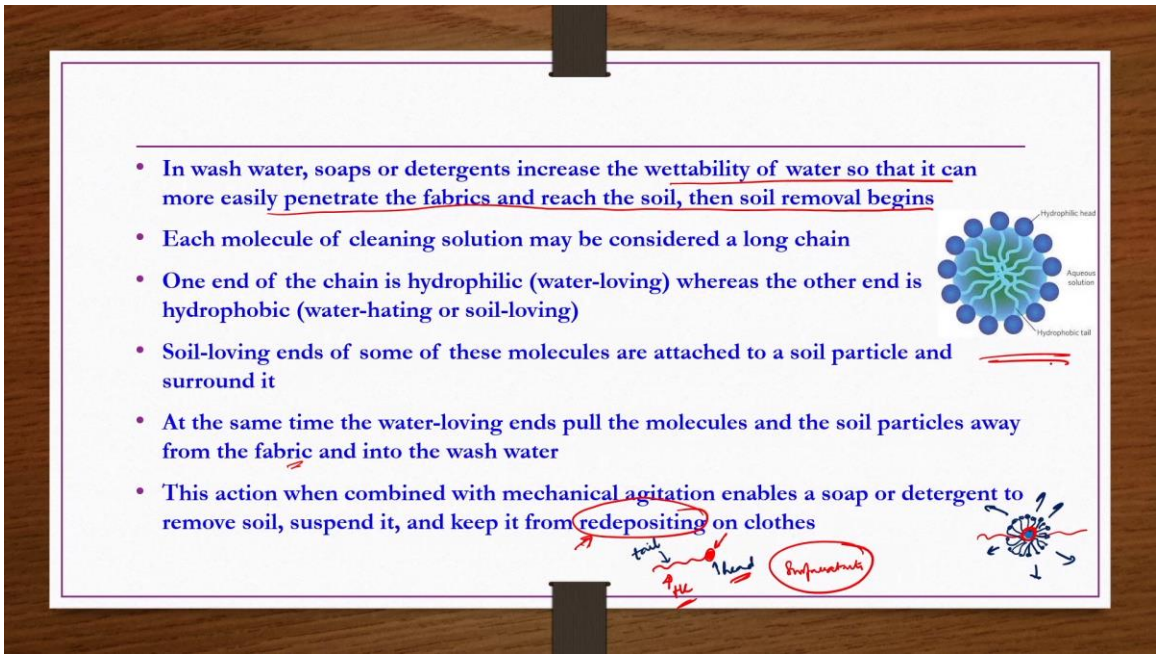

In wash water soaps or detergents increase the wettability of water so that it can more easily penetrate the fabrics and reach the soil then soil removal begins. Let us say you have a fabric here, fabric surface and then there is a stain here, right? Now, this stain if you wanted to remove what you have to do? How these detergents are acting here, right? So, these detergents are having surface active component that we are talking about surfactants, right? So, now it is having a kind of long chain kind of structure, long chain hydrocarbons with some functional group at one end, right? So, that long chain whatever is there that is hydrocarbon which is hydrophobic whereas this one is hydrophilic. When you dissolve these detergents in water and make solution to wash the clothes and then you put these clothes in that one then what happens? These surface active components of the detergents they will form spherical micelles like this or you know clustering of the surfactants takes place like this because of their tendency. Their normal tendency is that the hydrophobic part of the surfactant that is long chain hydrocarbon part that do not like water so that will move towards the hydrophobic stains or soil that is blue color like this whereas the hydrophilic part of the surfactants they like water so they move towards the water, right? So, now this process the heads, now dots you can call it the heads, the

different terminology is there. So, people also call it as a head and then the chain as a tail, right? So, these heads they try to move towards the water, okay? Whereas these tails they try to move towards the soil.

So, because of this action what happens? So, whatever the stain is there that will be removed and then this will be aided by so called you know mechanical agitation of the washing machine or hand wash whatever you are doing. So, by this way it will be removed, the stain would be removed from the fabric surface and then you get a clean washed fabric, okay? Each molecule of cleaning solution may be considered as a long chain. One end of the chain is hydrophilic water loving that is head side whereas the other end is hydrophobic or water heating or soil loving which is the chain side, the tail one. Soil loving ends of some of these molecules are attached to a soil particle and surround it and then form spherical muscles like shown here in the picture. At the same time the water loving ends pull the molecules and the soil particles away from the fabric and into the wash water so that the cleaning action takes place.

So, this action when combined with mechanical agitation enables a soap or detergent to remove soil, suspend it and keep it from redepositing on the cloth. This is also important. All these activities are done by the surface active components of the detergents. Remember detergents consist of primarily surface active materials but not 100 percent.

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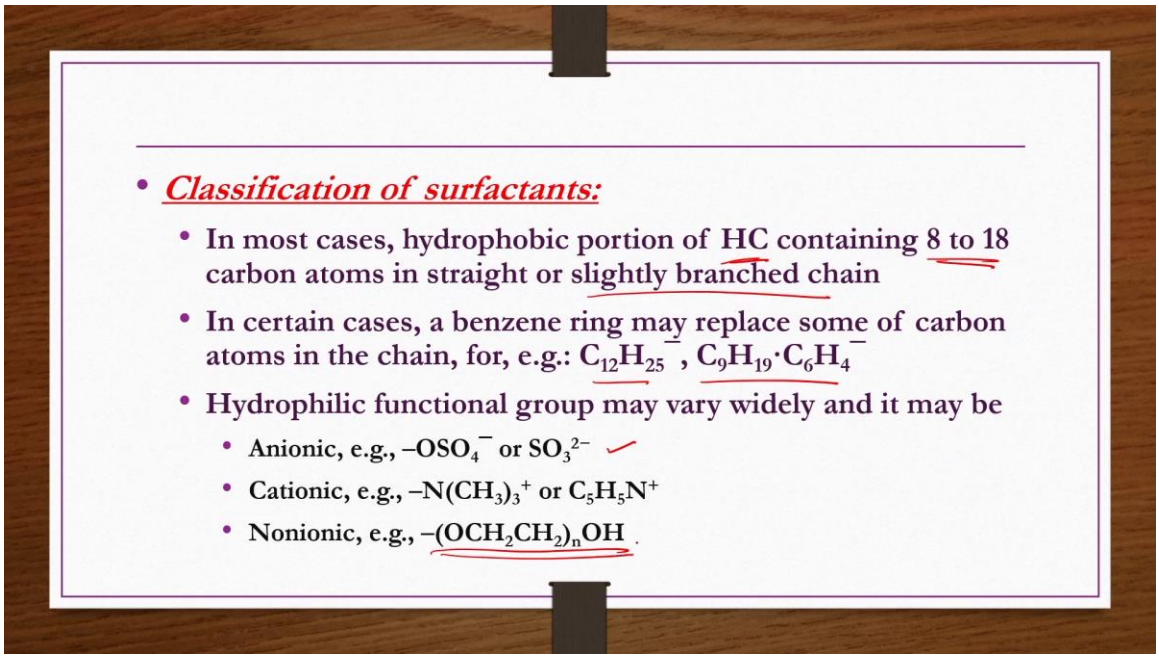

There are some builders and then additives etc. are also there, okay? So this surface active material they should also do the duty of not allowing the soil to redeposit on the fabric. The same is pictorially shown here once again. So now if we see the classification

of surfactants, in most cases hydrophobic portion of hydrocarbon that is long chain containing either 8 to 18 carbon atoms in straight or slightly branched chain. If they are slightly branched, so then they will be less biodegradable. If they are straight chains, then they are easily biodegradable in general, okay? In certain cases a benzene ring may replace some of the carbon atoms in the chain for example, like you know shown here, right? Cationic functional group may vary widely and it may be anionic like this, like you know OSO4 minus or SO32 minus, cationic like NCH3 thrice plus or C5H5N plus, then non-ionic like this one, okay? Now we talk about fatty acids and fatty alcohols.

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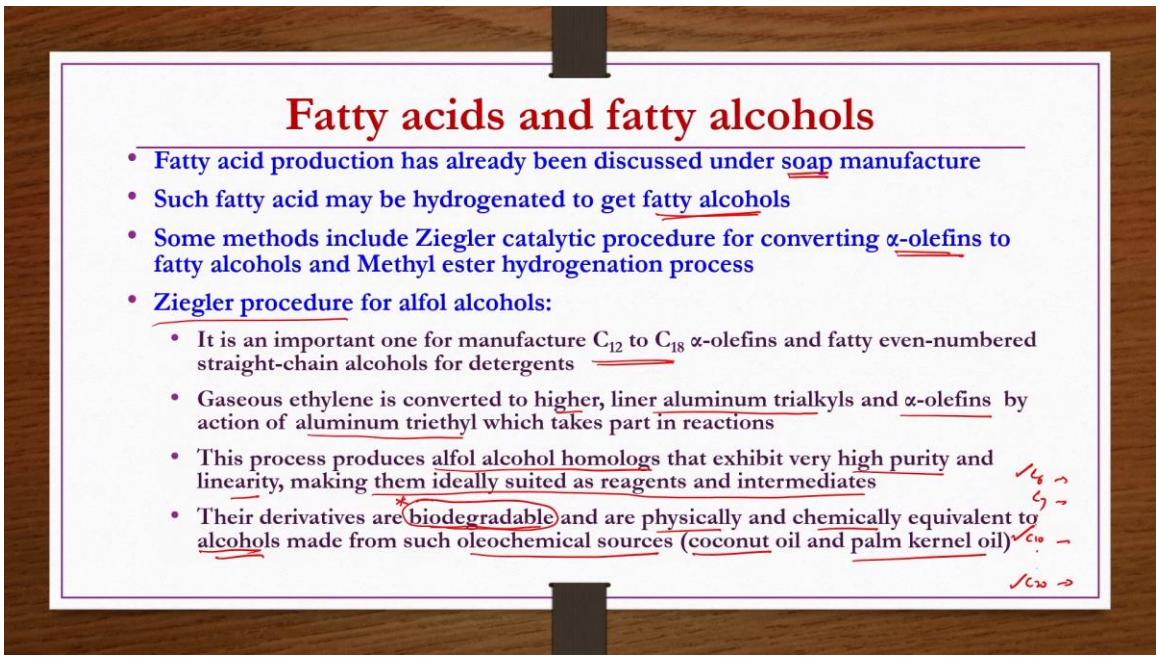

Out of the common raw materials, we had a required amount of information on the surfactants. The next common raw material is either fatty acid or fatty alcohol or both, okay? So fatty acid production has already been discussed under soap manufacturing where triglycerides have been reacted with hot water at high pressure to undergo the so-called hydrolysis reactions to produce fatty acids and glycerin, then further purification you do to separate the products. You get fatty acid one product, other product is glycerin that we have already seen in the previous lecture. Such fatty acid may be hydrogenated to get fatty alcohols. Simple catalytic hydrogenation reaction of fatty acids if you do, then you get the fatty alcohols.

However, some methods like you know, Ziegler Catalytic Procedure for converting alpha olefins to fatty alcohols and methyl ester hydrogenation process are discussed here. So, we are discussing two more processes to get these fatty alcohols which are required for making detergents. Let us start with Ziegler procedure for alfol alcohols. It is an important one for manufacturing of C12 to C18 alpha olefins and fatty even numbered

straight chain alcohols for the detergents. In this process in general what happens gaseous ethylene is converted to the higher linear aluminum trialkyls and alpha olefins by action of aluminum triethyl which takes part in the reactions.

So, we are going to see the flowchart for this process in the next slide anyway. This process produces alphal alcohol homologs. Actually, alphal alcohols are produced by Jiggler procedure, but this is not one alcohol. There are you know C6, C2, C20 alcohols are possible like this. So, you get all these catalogs and then what you have to do as per your requirement whether it is C6 is required for you, C10 is required for you, C20 is required for you, fractionation you have to do because in this process you get the mixture of all these things.

So, after doing the fractionation as per your requirement you can use the specific alcohol fatty alcohol for your specific application. So, this process produces alphal alcohol homologs that exhibit very high purity and linearity making them ideally suited as reagents as well as intermediates for many organic syntheses. Their derivatives are biodegradable that is very much essential very important one because whatever the hydrocarbon portion of detergents are there, they should be biodegradable. Otherwise, we may have issues of excess using detergents. In addition, they are physically and chemically equivalent to alcohols made from such oleochemical sources natural sources like coconut oil, palm, kernel oil, etc. when you use whatever the alcohols fatty alcohols you get such nature both physically chemically such property alcohols are also produced by this method. In addition, they are also biodegradable though these are you know synthetic ones, they are having the properties equivalent to the natural ones.

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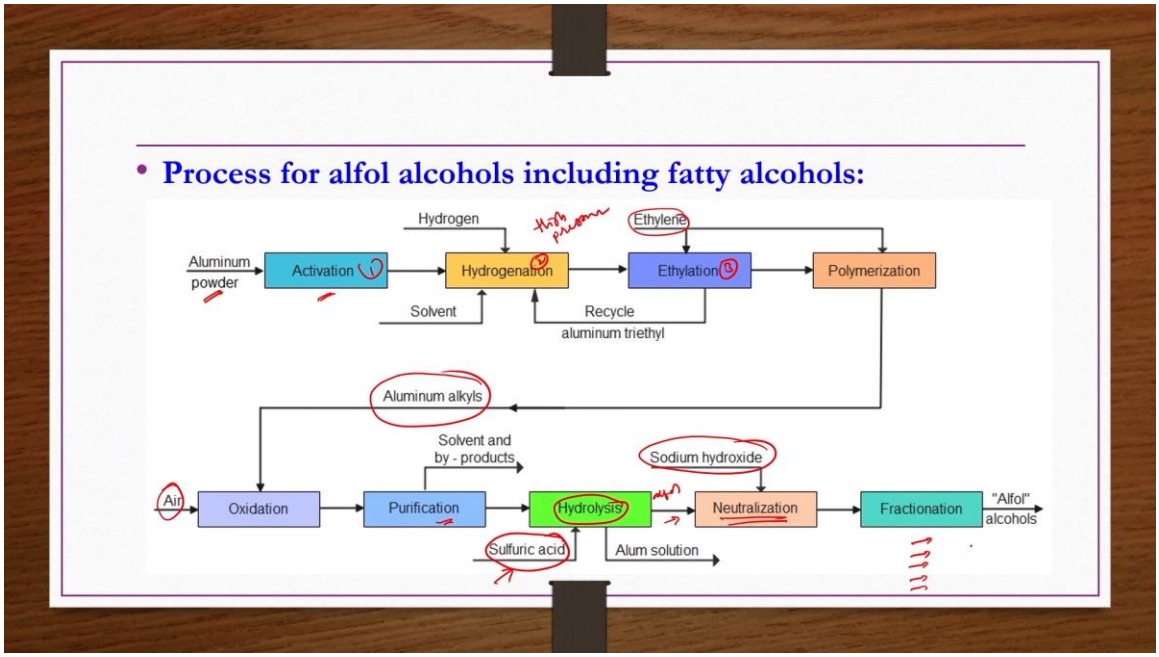

Process for alphal alcohols including fatty alcohols is provided here. In this process what you do you take aluminum powder, you do the activation of this one using the hydrogen or by the hydrogenation reaction. So, all this activation hydrogenation reaction and then ethylation of that aluminum powder using the ethylene has to be done. All these things are required to be done at high pressures this 1, 2, 3 steps. So, when you take the activated aluminum and then react with ethylene, then what you get aluminum triethyl that you can recycle back to the hydrogenation chamber as per the requirement. If not, what you can do? You can do the polymerization of that one using the ethylene so that you can get aluminum alkyls. This aluminum alkyls if you do the oxidation using the air, then you get alkoxide, then you get aluminum alkoxide. These alkoxides followed by the purification and hydrolysis using sulfuric acid you get alphal alcohols actually, but they are not pure enough.

You may be required to do the neutralization using the sodium hydroxide because hydrolysis you are doing using the sulfuric acid. So, some traces of the sulfuric acid may be there in the mixture that crude alphal alcohols whatever you are getting. So for that purpose this sodium hydroxide is added to do the neutralization followed by the fractionation. Fractionation you do as per your requirement to which C number alcohol is required. In general, in this process even numbered fatty alcohols are obtained like C6, C8, C10 something like that.

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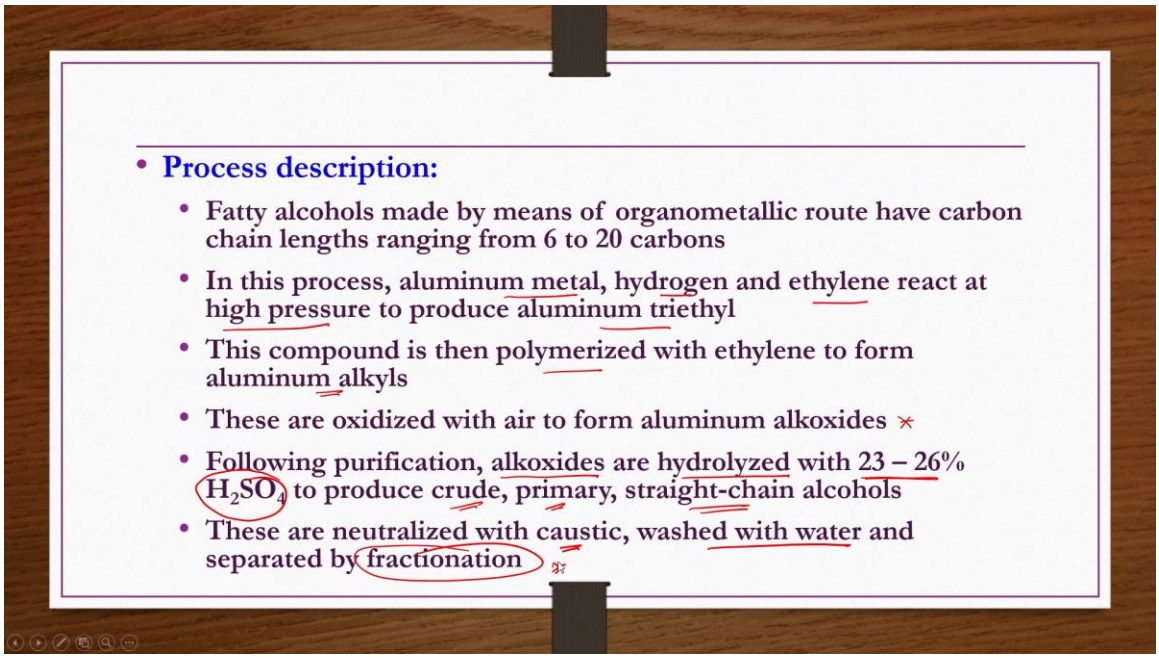

Description of the process is presented here once again. Fatty alcohols made by means of organometallic route have carbon chain lines ranging from 6 to 20 carbons. In this process aluminum metal, hydrogen and ethylene react at high pressure to produce

aluminum triethyl. This component is then polymerized with ethylene to form aluminum alkyls. These are oxidized with air to form aluminum alkoxides. Following by purification alkoxides are hydrolyzed with 23 to 26 percent sulfuric acid H_2SO_4 to produce crude primary straight chain alcohols. These are neutralized with caustic washed with water and separated by fractionation.

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So that final alphal alcohols you can get. Now alphal alcohols are available in various purities as well as blends and single cuts as per the fractionation how are you going to do and then obviously when various blends or purities are available their application should also be too many. Some of the applications of this alphal alcohols are presented here. They are used in plastic additives, cosmetics, pharmaceuticals manufacturing, water evaporation, retardants also for that purpose also these are used.

In paper industries foaming is not allowed is not good. In paper industries froth flotation kind of operations are done in order to remove some kind of impurities, but froth flotation occurs by the froth formation by adding some froth forming agents. That froth formation should not be too much. If that is too much then de-foamers has to be added such for that purpose also these alphal alcohols are used. Power point depressions for crude oil also is one of the application or in order to reduce the power point of crude oil then also you can use these alphal alcohols. Also used as additives for leather and textile industries, flotation aid purpose, detergents and cleaners' purpose, metal processing purpose also they are used.

They are also used in agrochemicals, flavors, fragments, purpose etc. And then paints, inks, coatings and adhesive industries also these are being used in general.

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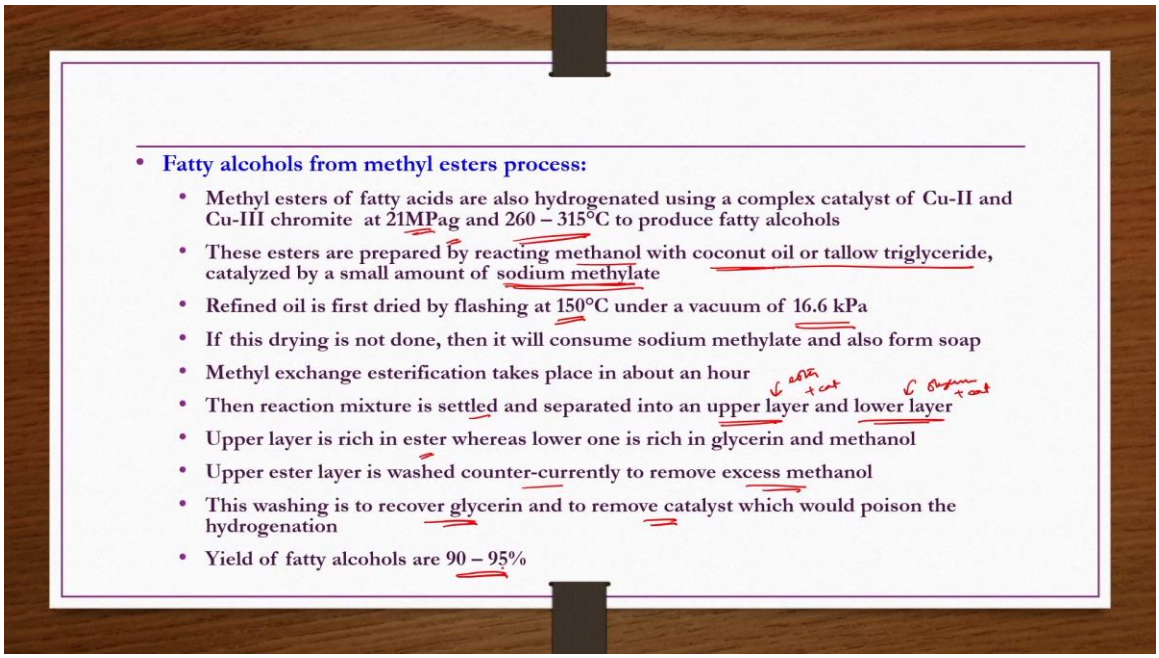

So this is about a fatty alcohols production by the Jiggler processor and then applications of such fatty alcohols. Now we try to see the process how to get the fatty alcohols from methyl esters. Fatty alcohols from methyl esters process. Here methyl esters of fatty acids are also hydrogenated using a complex catalyst of Cu2 and Cu3 chromate at 21 mega Pascal gauge 260 to 315 degrees centigrade to produce fatty alcohols.

These esters are prepared by reacting methanol with coconut oil or tallow triglyceride catalyzed by small amount of sodium methylate. Actually, whatever the coconut oil or tallow triglycerides are there that you react with the methanol to get these methyl esters and then from those methyl esters you further you know do separation process to get the required alcohols. That is what we are going to see primarily. But here in the coconut oil we already know that fatty glycerides are there. If these are reacting with ethanol and in the presence of sodium methylate catalyst so then sometimes what happens if the oil is not dry enough that may be consuming some amount of sodium methylate and forming soaps also.

But you do not want to make soaps you wanted to make fatty alcohols. So, you have to reduce or control that reaction. How it is possible you have to use the dry coconut oil refined oil has to be dry enough. For that purpose, what you do refined oil is first dried by flashing at 150 degrees centigrade under vacuum of 16.6 kilopascal. So that to make sure that the refined oil is not having any moisture. If the moisture is there then there is a

danger of saponication taking place because the catalyst is there is nothing but sodium methylate. If this drying is not done then it will consume sodium methylate and also form soap which is not desirable in this case. Then methyl exchange esterification reaction takes place in an about hour. Whatever the reaction mixture is there that would be settled and separated into upper layer and then lower layer. This upper layer is rich in the esters, lower layers are rich in the so called glycerin methanol etc.

But both of them would also be having the catalyst. So, then these layers individually separate out to recover the catalyst. If the catalyst is still reusable so then that would be sent back to the catalyst tank otherwise they will be discarded as a spent catalyst. After removing the catalyst those 2 layers whatever are there they will be hydrogenated to get the so called fatty alcohols. Upper layer is rich in ester whereas lower one is rich in glycerin and methanol. Upper ester layer is washed counter currently to remove excess methanol. This washing is to recover glycerin and to remove catalyst which would poison the hydrogenation. Yield of fatty alcohols in this process is about 90 to 95%.

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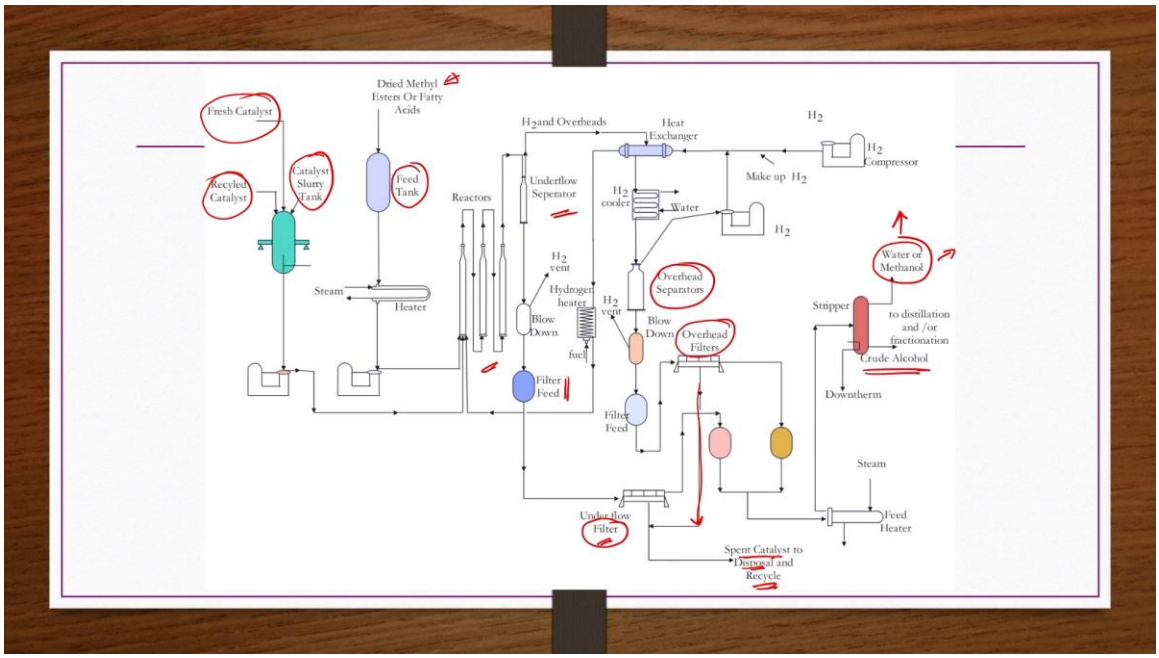

If you see the flow chart for this process here what we have? We have catalyst slurry tank in which either you have a fresh catalyst or recycled catalyst can also be taken. We have a feed tank separately in which you have dried methyl esters that is very essential or fatty acids directly. So, if they are not dried enough what you do? You dry them by passing them through a flash tank to which steam is provided so that enough drying is taking place.

So then after drying of this methyl esters or fatty acids raw material what you do? You take them along with the catalyst to the reactors where the required hydrogenation of fatty acids takes place so that you get the fatty alcohols. So now after the reaction whatever the mixture is there that would be separated out into 2 layers overhead layer and then separated out as a top layer or upper layer and then bottom layer. Underflow separator after separation of this one that material whatever is there underflow material is there that is primarily rich in the glycerin, methanol and then catalyst. So that once you pass through the filter then what will happen? Here whatever that mixture glycerin, methanol and then catalyst is there that you pass through filter press so that you recover the catalyst and then check if the catalyst is sufficiently pure or not. If it is sufficiently usable then it can take it as recycle to the catalyst slurry tank otherwise it can be disposed of.

Whereas the filtrate of this filtration is nothing but primarily glycerin, methanol, etc. that will be collected. Likewise, the upper layer is also that would be separated out because it is also having some amount of the catalyst. So those things would be removed by the overhead filters. Those catalysts will also be checked whether they are good enough to recycle otherwise they will be discarded as a spent catalyst. So, the filtrate from this overhead filters are there primarily they are either esters or alcohols, fatty esters or fatty alcohols they will be taken to the fractionation column where water and methanol are separated out as a top product because water and methanol are more volatile compared to the crude alcohols that are present.

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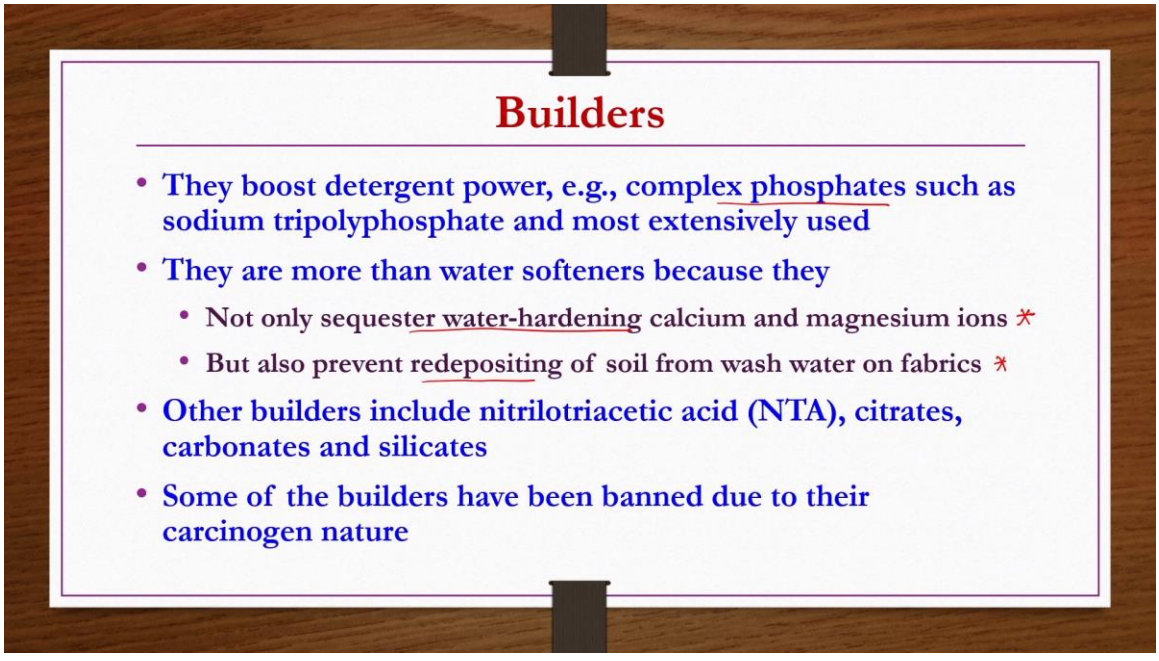

These alcohols are collected from the bottom as the bottom product whereas the water, methanol, etc. are collected from the top as the top product. This is the methyl ester process to get the fatty alcohols. Now we have seen the surfactants. Until now also we are discussing about the common raw materials required for the surfactants manufacturing.

So surfactants we have discussed fatty acids, fatty alcohols we discussed. So now what we are going to discuss? We are going to discuss about the builders. Builders and additives are sometimes taken combinedly but however we are discussing separately. These builders are usually used to increase the power of a detergent. They boost the detergent power. Some example are complex phosphates such as sodium tripolyphosphate and it is the most extensively used one.

They are more than water softeners because they not only sequester water hardening calcium and magnesium ions, but they also prevent redepositing of soil from wash water on fabrics. So, both of them are important. So sometimes if the surface active material is not sufficient enough to prevent the soil to redeposit on the fabric such duty can be taken care by the builders as well. Other builders include nitrilo triacetic acid, citrates, carbonates, silicates, etc. Some of them are banned due to their causes in nature.

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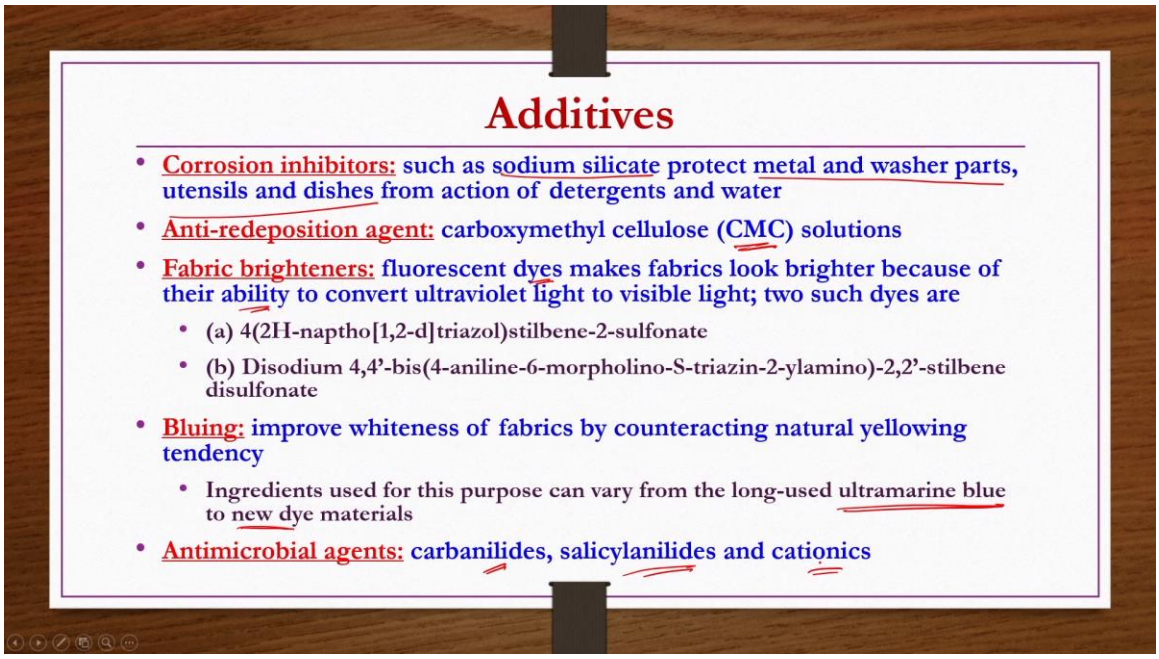

Next is the additives. Let us say one of the additives is corrosion inhibitors such as sodium silicate. They are very important in most of the detergents that may be present because they protect metal and washer parts, utensils, dishes from action of detergents and water so that there should not be any corrosion to take place. Next is anti-redeposition agent. We do not want redepositing of the soil onto the fabrics. So that can

be avoided if the soil is properly suspended or dispersed in the water and then that can be done properly by using CMC solution that is carboxymethylcellulose solutions.

Then fabric brighteners. Usually fluorescent dyes are used because they make fabrics look brighter. How? How they do it? Because of their ability to convert ultraviolet light to visible light and two such dyes are given here, chemical names are given. Both of them are sulfonates. Bluing. These additives improve whiteness of fabrics by counteracting natural alloying tendency.

In general, fabrics have the natural tendency of alloying over the period of time. That can be reduced if you add additives like bluing additives. Ingredients used for this purpose can vary from the long used ultramarine blue. They have been used for long time, several decades or even maybe several centuries. There are some new dye materials are also developed for this purpose of bluing. Then antimicrobial agents are also sometimes required. Something like carbanilides, salicyl anilides and then cationics, etc. are used for this purpose. So, this is all about the different types of raw materials or the ingredients of the detergents, some of them how to produce etc. also we have seen.

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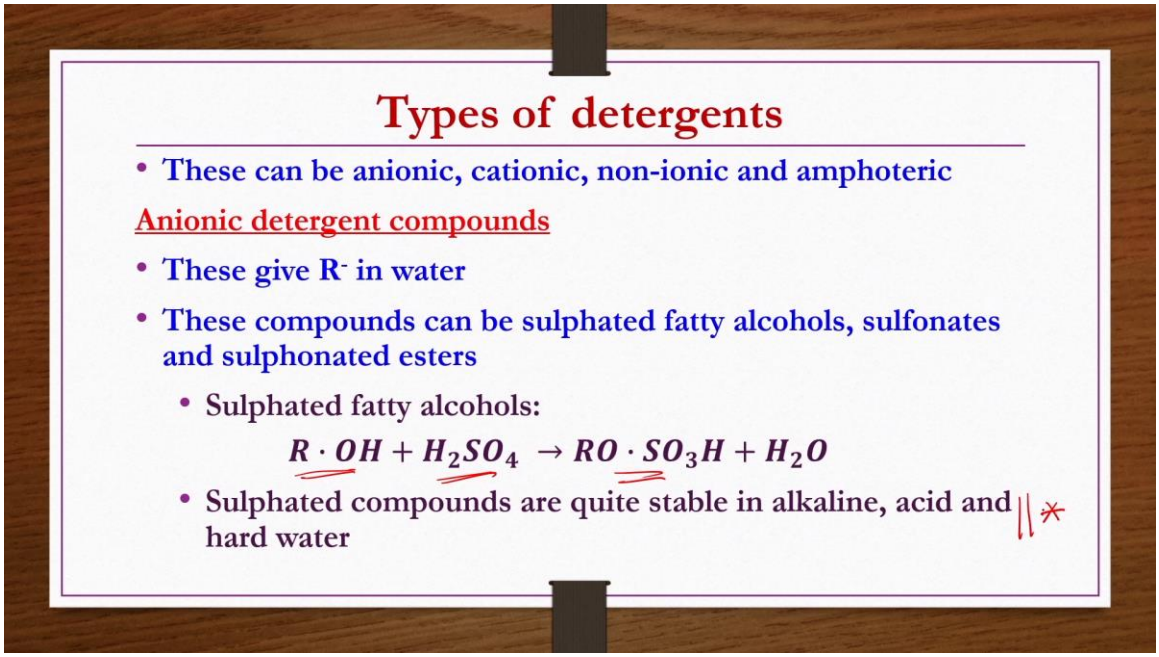

Now we talk about types of detergents. These can be anionic, cationic, nonionic, amphoteric as well. Let us start with anionic detergent components. They give R minus in water. These compounds can be sulfated fatty alcohols, they can be sulfonates or sulfonated esters also possible different types are there. So, we see a few examples. So, sulfated fatty alcohols like when you do alcohol and then oleum are excess of 98 percent H2SO4 reaction, then you get these sulfated fatty alcohols. When you react these one

with sodium hydroxide, then sodium salts of the sulfated fatty alcohols you get, which is nothing but anionic detergent. Most of the detergents are anionic because of their superiority. Sulfated compounds are quite stable in alkaline, acid and hard water because of such reasons and then we are going to list out some more reasons also. These anionic detergents are mostly used in most of the detergents because cationic detergents, their foam forming as well as the cleaning action is not that good as in the case of anionic detergent compounds.

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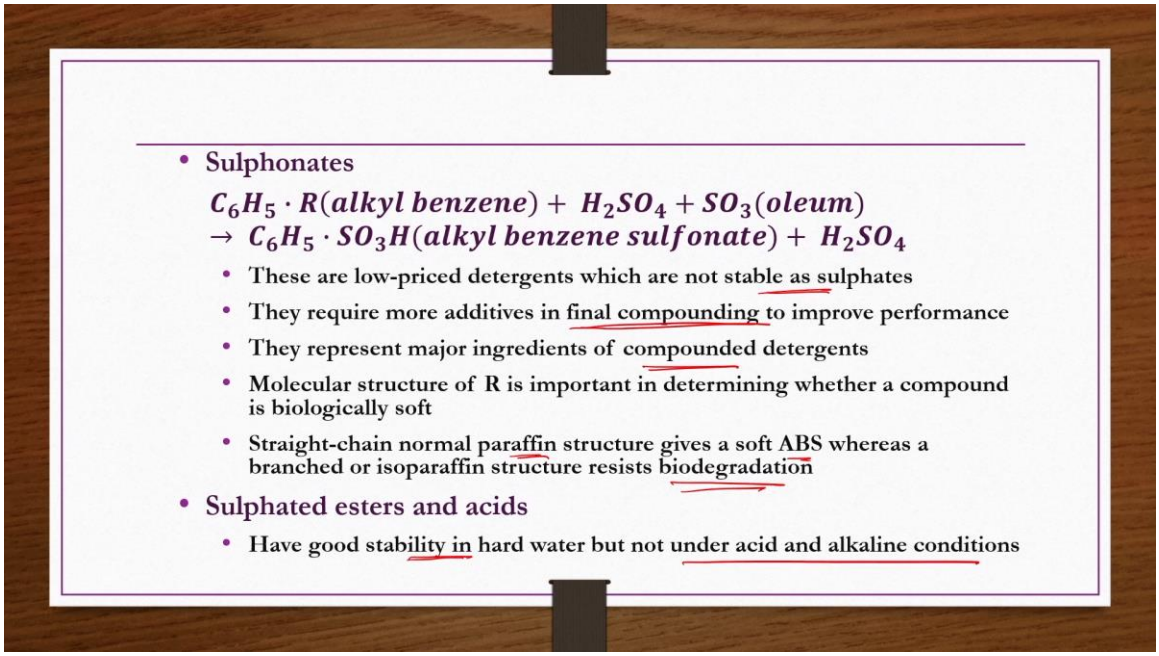

Another type of anionic detergent compounds is sulfonate. Here let us say alcohol benzene you have and then you react with oleum which is a mixture of H2SO4 and SO3, then you get alcohol benzene sulfonate, but these sulfonates are low priced detergents which are not stable as sulfates. They require more additives in final compounding to improve performance. What do you mean by final compounding because we need to add additives, builders, etc. So, in the final composition you have to have more sulfonates because they are not stable as sulfates.

They represent major ingredient of compound and detergents. Compounded detergents are nothing but they are mixture of sulfonates as well as the sulfates. Molecular structure of R is important in determining whether a component is biologically soft or not. Straight chain normal paraffin structure gives a soft ABS whereas a branched or isoparaffin structure resists biodegradation. That pictorially we see the structure in the next slide.

Likewise sulfated esters and acids are also there which fall under the category of anionic detergent compounds. They have good stability in hard water but not under acid and

alkaline conditions. Some examples of anionic detergents, so this one. So, now when you dissolve this one, what you get? This one whatever you have this will be having anionic nature.

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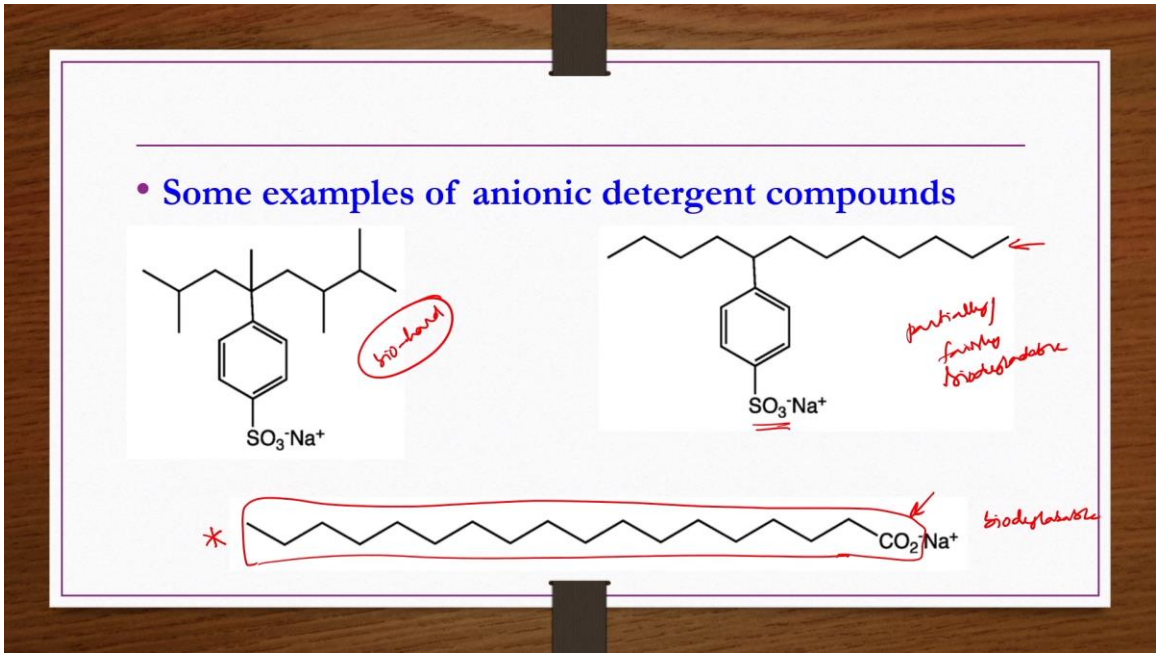

That is the reason it is known as the anionic detergent component. Likewise, the same thing here also. So, now what you see here in both these 2 examples when you dissolve in water definitely they are going to form anions of this part here again. But what is the thing to observe here? So, now this is benzene ring is there but it is connected to long chain. So, linear long chain is there to there, benzene ring is connected to that this functional groups are attached. Here whatever the benzene ring with functional group is there that is attached to a branched one not a linear chain. Branched chain it is attached, it is what it mean by. This may be taken as biohard or very difficult to biodegrade compared to this one. This is partially or fairly biodegradable compared to the third one. Now this is easily biodegradable because it is a linear chain is there.

So, it is possible that it can be easily biodegradable. This one also when you dissolve in water you get anion component. Next is cationetic detergent compounds, they give R plus in water, do not have strong detergent characteristics, but do have germicidal properties. These are also important. Non-ionic detergent compounds if you take some examples like alkyl, aryl, ethylene, oxide derivatives, aliphatic, polyhydric, alcohol, esters, fatty acids, amides, etc. are used as a non-ionic detergent compound. These non-ionic compounds produce little foam but good thing is that they possess excellent soil removal action and grease emulsification characteristics.

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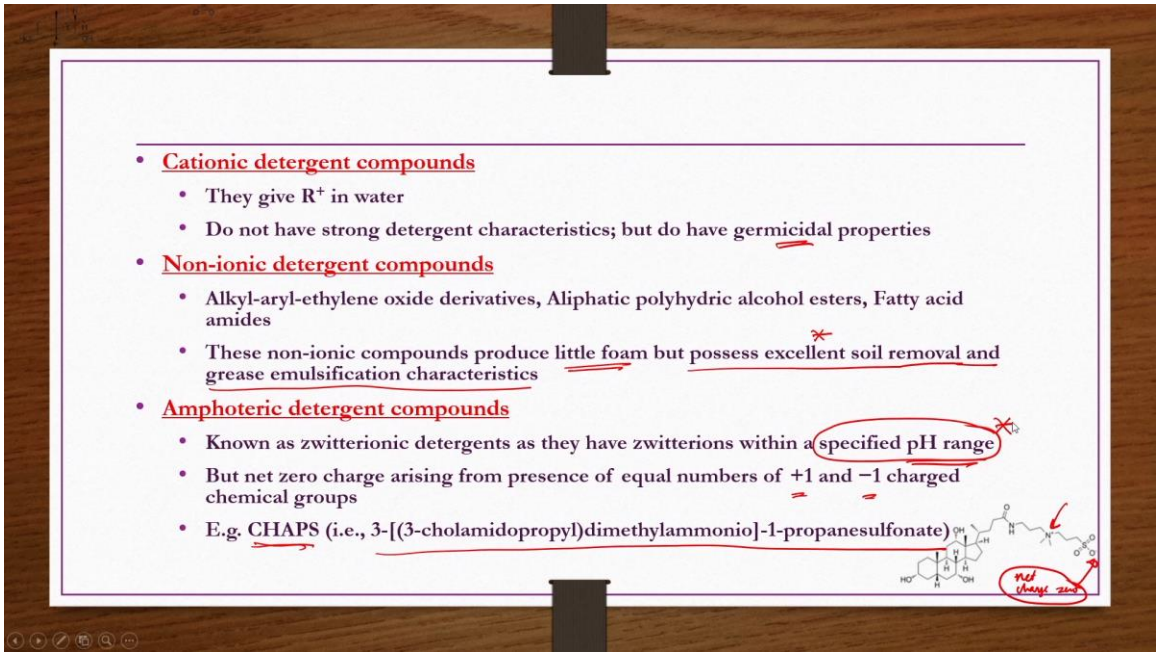

So, wherever this grease etc. are there and then you need excellent soil removal characteristics so then better to go for non-ionic detergent components. Next is amphoteric detergent compounds. They are known as zwitterionic detergents as they have zwitterions within a specified pH range, but net zero charge arising from presence of equal numbers of plus minus charged chemical group present in that one. Example is CHAPs, its abbreviated name, the chemical name of this component is given here and then structure if you see the structure is given here.

So, now here you have the plus ion, 1 plus ion here, 1 minus ion is there. So, overall net charge is becoming 0 and in such kind of characteristics it may be having over a specified pH range only. That is the reason these are not categorized as non-ionic detergents. They are specially categorized as amphoteric detergent compounds. Now, detergent builders are essential compounds used for various purposes such as foam forming, brighteners etc. Phosphates such as sodium, tri-polyphosphate and tetrasodium pyrophosphate used that is 30 to 50 percent in detergent formulation to extend the foam when these components are present then foaming is better.

Sodium carboxyl cellulose if you use that will improve the soil and dirt suspension. It will not allow the redeposition of this soil and dirt onto the fabric for that purpose it is used like carboxyl methyl cellulose as well. Fluorescent dyes as brighteners they are used in order to avoid corrosion of aluminum or other metal parts of the washing machine etc. or utensils etc. sodium silicates are used. Dyes as alternative phosphorus free builders being used in general nowadays. Now, we talk about methods of detergent manufacture. Two anionic type detergents are mostly used in India and we are going to discuss about

them only because they are mostly used in India as well as in other countries also because of their merits compared to the cationic as well as non-ionic detergents. One is the sulfated fatty alcohol type other one is the alkyl aryl or sulfonates type. So, sulfated fatty alcohol type detergents they are manufactured via following steps.

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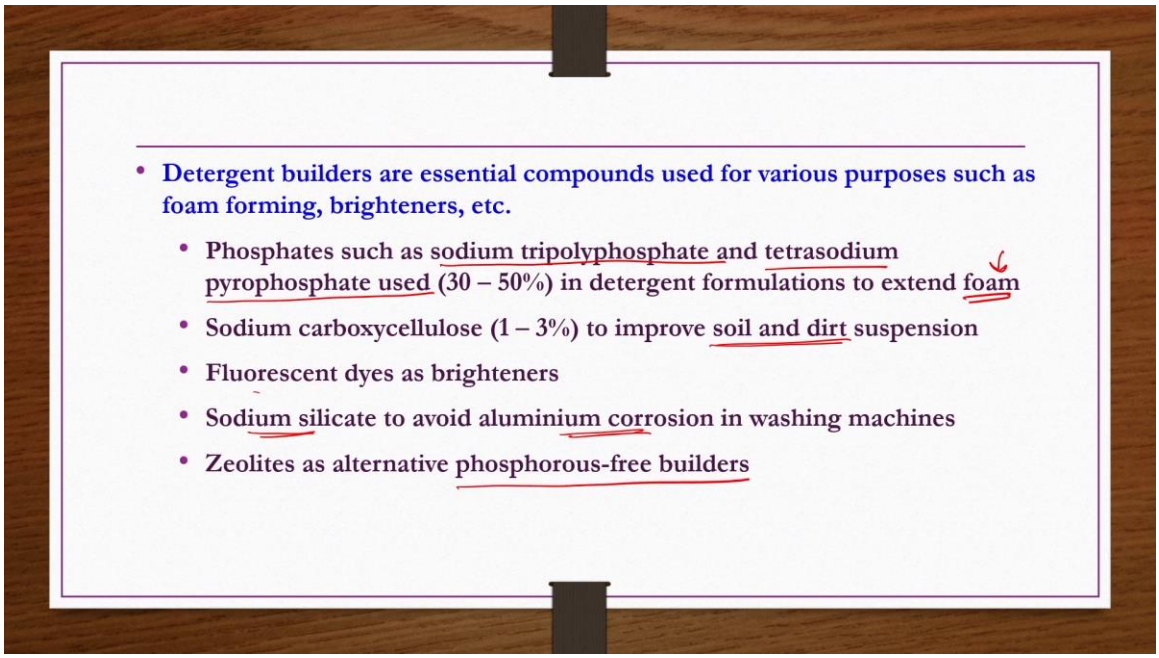

High molecular weight alcohol such as the group from laurel alcohol up to olel alcohol are used. These are derived from coconut oil either by catalytic hydrogenation or by sodium reduction. So, we see both of these processes then sulfating of these alcohols follows to get detergents as per the requirements. So, we see these two steps and then we see the reactions for this step as well. Catalytic hydrogenation of coconut oil, hydrogenation is done at high temperature and then high pressure temperature is approximately 200 to 300 degrees centigrade whereas the pressure is very high 100 to 200 atmosphere. Catalyst for this purpose is copper salts. In addition to hydrogenation at carboxyl linkage saturation of double bonds also occur which is not desirable in the case of best detergent action. If there are no double bonds that is good for the edible oil purpose, but it is not good in the case of detergents. In the other method where sodium reduction of coconut oil is taking place. So, along with esterifying alcohol molten sodium is slowly added to coconut oil in an aliphatic solvent.

Commonly used solvents are esterifying alcohol such as amyl alcohol and aliphatic solvent such as xylene or toluene. In this process following reactions occur. The alcohol reacts with the sodium to give the salts of sodium here and then releasing the active hydrogen. This active hydrogen reacts with the triglycerides to form the esters and then

finally by dehydration reactions you get the fatty alcohols. It is a very generalized representation this reaction we have already seen previously.

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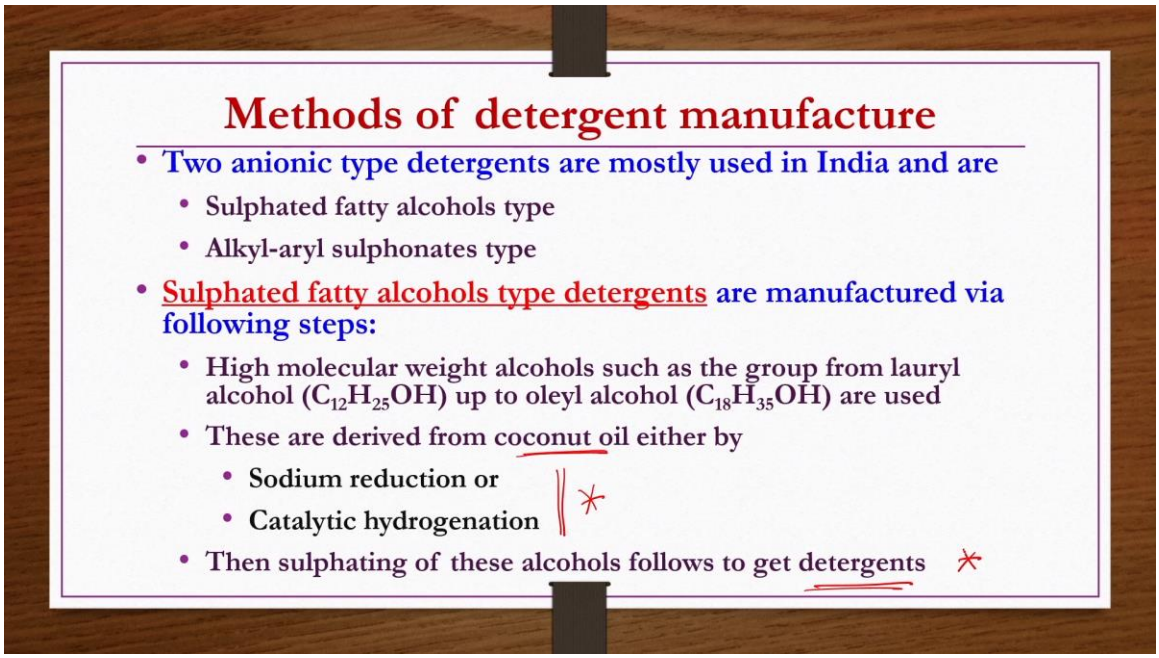

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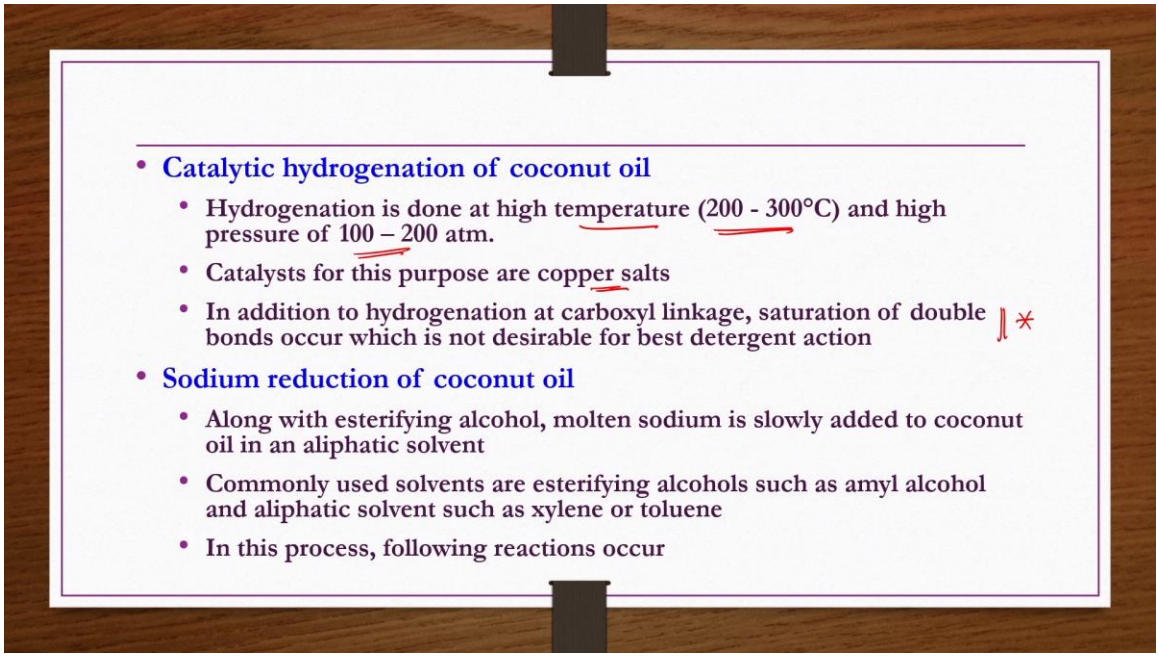

To these fatty alcohols then you do the required reaction with the NaOH and then additives addition etc. if you do you get the detergents. At the end of the reaction batch is

pumped into a water tank. In this tank mixture settles into 3 layers. Top layer is high molecular weight alcohol which you have taken as a raw material primary raw material. Intermediate layer contains regenerated reducing alcohol that you produce whereas the bottom layer has caustic soda and glycerin for recovery.

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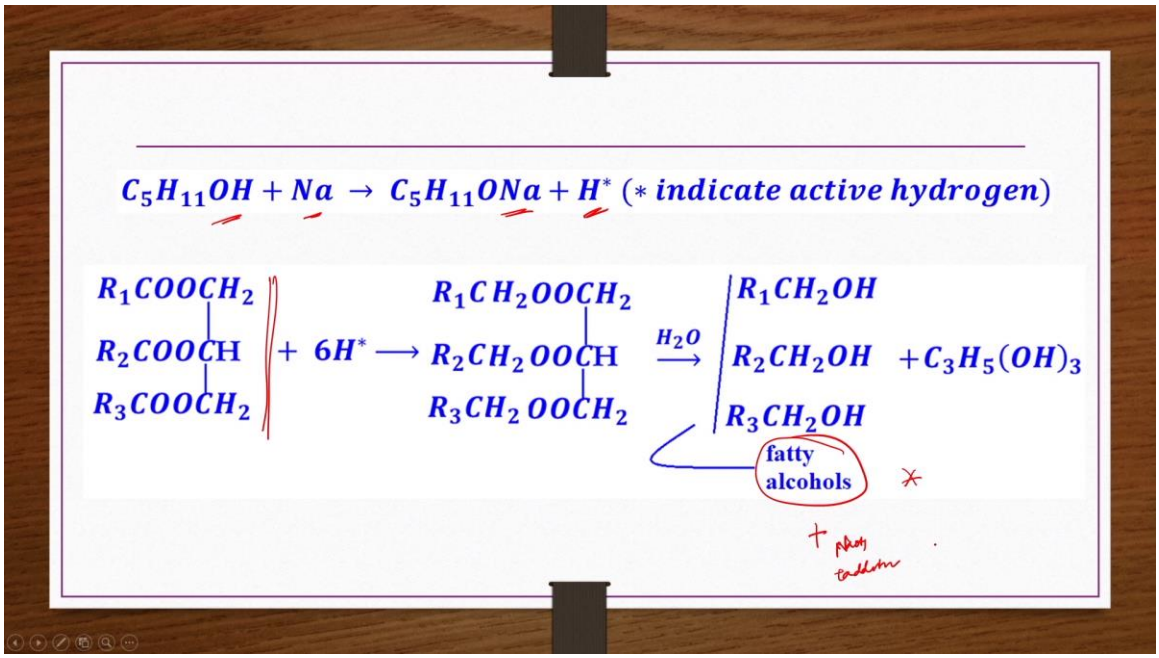

Economics of process compared to the hydrogenation involves an economic balance between following two costs. One is the catalytic hydrogenation if you do what you need you need hydrogen. Hydrogen at 100 to 200 atmosphere and 200 to 300 degrees centigrade is very dangerous very very dangerous. So, then in which such reaction is taking place that equipment has to be constructed with such a kind of high cost material. So, that is one factor higher cost of high pressure hydrogenation equipment.

But if you go for this sodium reduction approach and that case you know higher cost of sodium reductant is there. But in addition to that one more complex product separation is required. Whatever the product you get by this sodium reduction process you get more complex product distribution and then you have to separate it that is going to be additional cost more unit operations may be required. So, as per your requirement you have to decide which one is going to be more economical for you economic balance is required this one cannot say generalized one this is better this is not better. Sulphation of fatty alcohols, oleum or an excess of 98 percent H2SO4 is added to purify fatty alcohols then acid sulphate is then converted to the sodium salts by this reaction. So, now here whatever the fatty alcohols are there they are reacting with the H2SO4 to give the acid sulfate which are reacting with the sodium hydroxide to give sodium salts.

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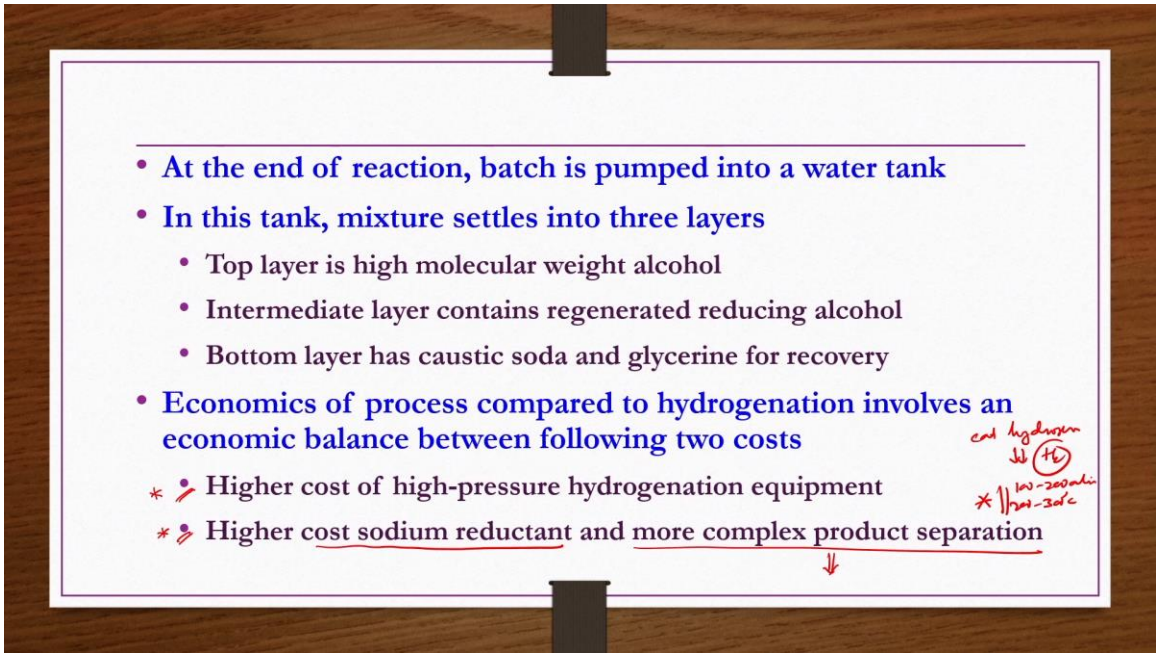

These are nothing but the detergent components. Any excess sulfuric acid is there that would be neutralized and sodium sulfate is usually left with the entire mixture and dried. The last slide of the lecture is alkyl aryl sulfonates. Compounds under this classification are prepared in 3 step process using economic petroleum raw materials. Here in this process kerosene feedstock may be fractionated by molecular sieve process in vapor phase.

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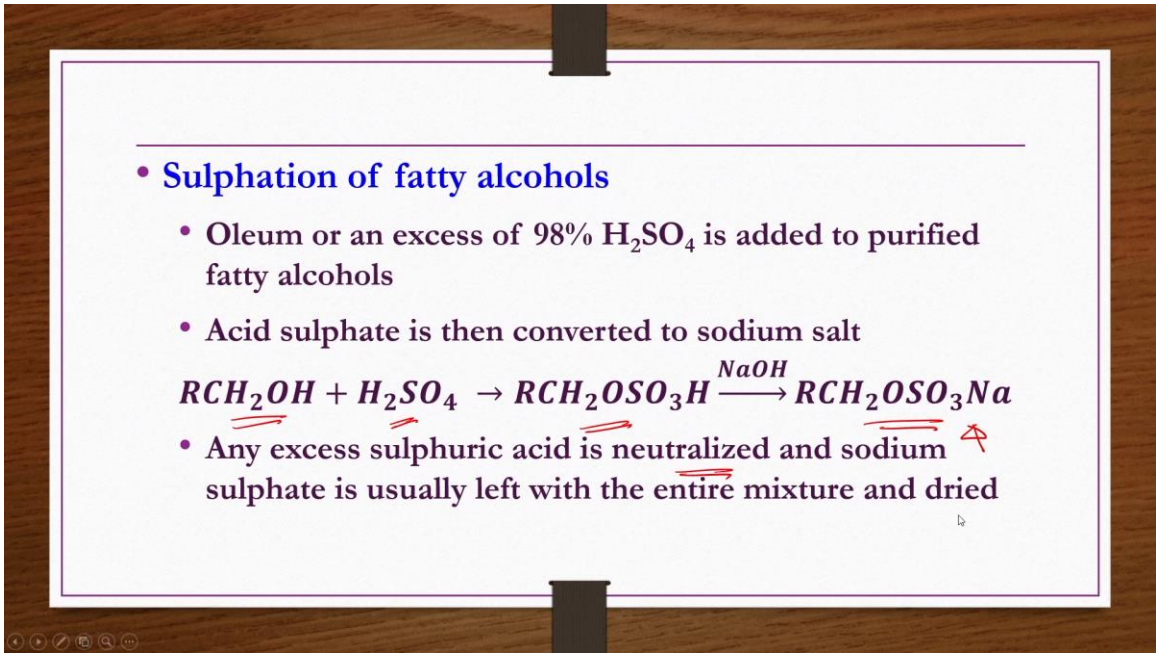

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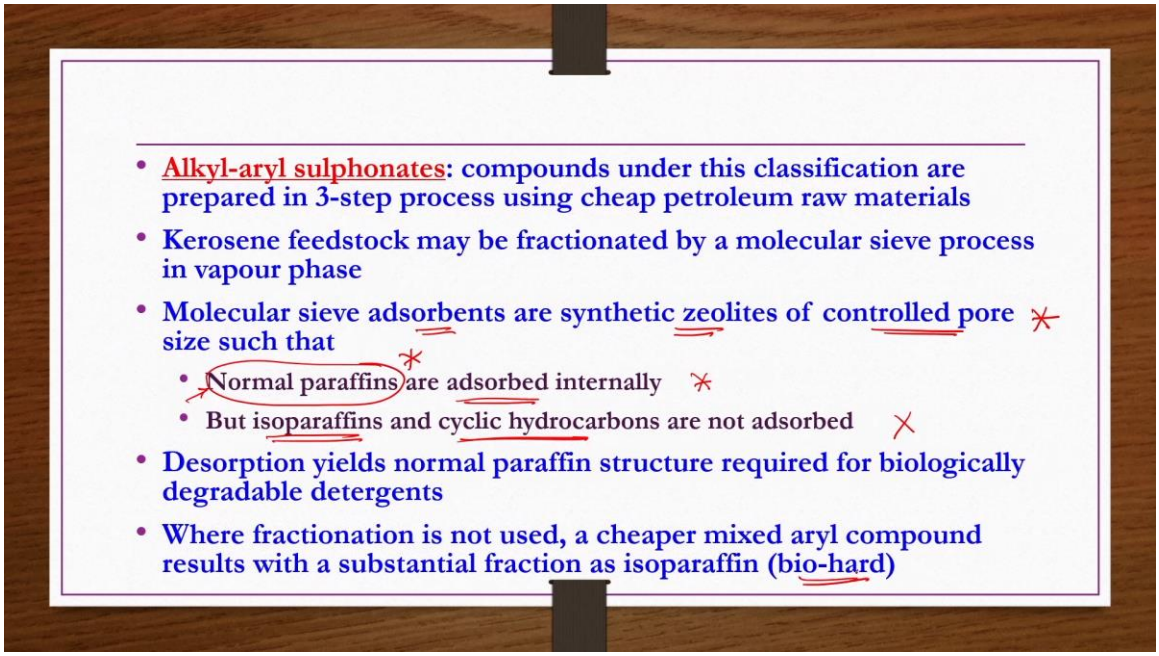

These molecular sieves are nothing but the absorbents which are synthetic zeolites having controlled pore size they are having several applications. But what they do they adsorb internally the normal paraffins which are required for you know for this process that is a good one. But they do not absorb isoparaffins and then cyclic hydrocarbons.

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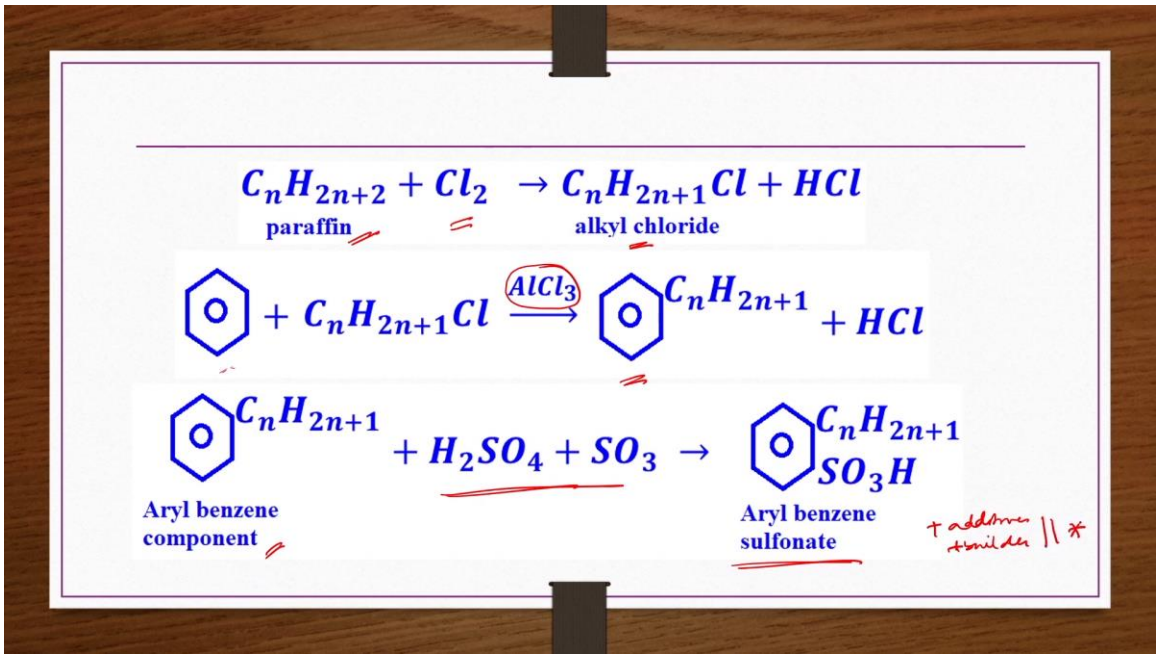

So, the molecular sieves are synthetic zeolites so they made such a way that they will be absorbing only normal paraffins but they will not be absorbing isoparaffins or cyclic hydrocarbons because you need normal paraffins. Because if you have normal paraffins what happen whatever the final surfactant or the detergent component that you are going to get that is going to have a linear chain and then that is going to be easily biodegradable. So, that way it is very advantageous.

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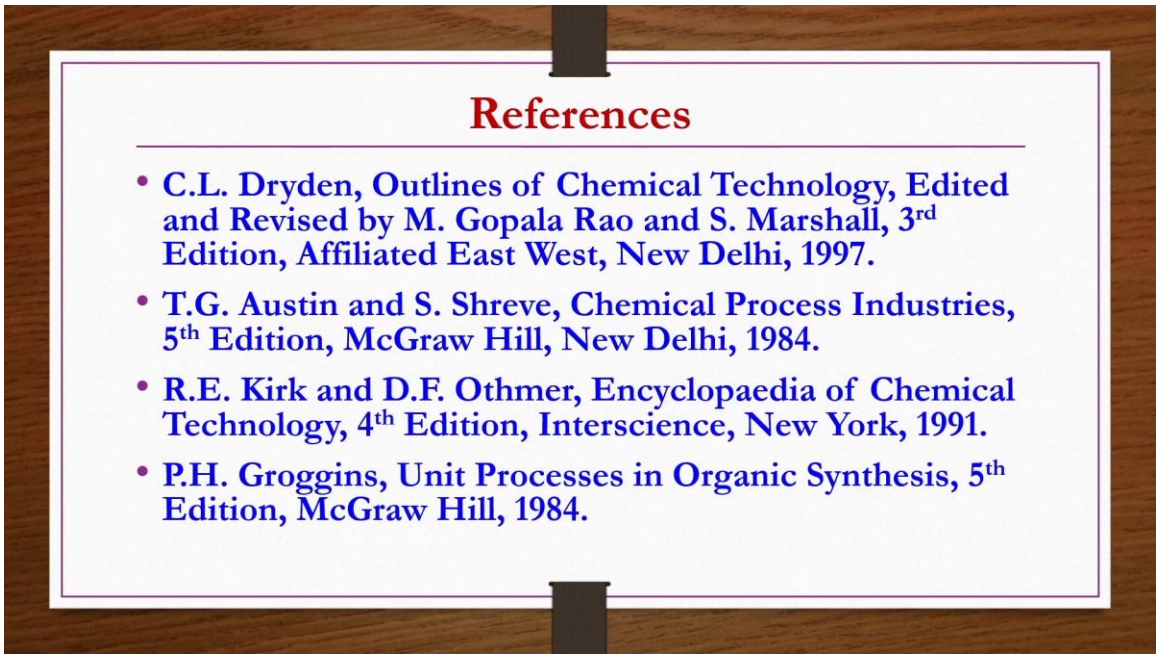

Disorption yields normal paraffin structure required for biologically degradable detergents. Where fractionation is not used an economical mixed RL component results with a substantial fraction as isoparaffin which is biohard not easily biodegradable. That reactions taking place in this process whatever the normal paraffin that are being separated from the petroleum feedstock they undergo chlorination reaction to give alkyl chlorides. These alkyl chlorides react with benzene so that alkylation reaction takes place in the presence of aluminium chloride catalyst to get aryl benzene component. This aryl benzene component further reacts with oleum to give aryl benzene sulfonate which is the important component of this detergent. And then now to this one you add the additives, builders, etc. to have the final so called detergents as per your requirement. This is all about detergents, the raw materials, classification of detergents, manufacturing of the detergents. With this we complete our discussions on the soaps and detergents industry. References for this lecture are provided here. Thank you.