referInorganic Chemical Technology
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Lecture - 29
Paints and Pigments

Welcome to the MOOCs course in Organic Chemical Technology, the title of today's lecture is Paints and Pigments. In the last lecture, we started discussing about the Surface Coating Industries. So, we have seen what are the different types of surface coating industry products, what are their constituents, what for they applied. And then, each constituents, what is the role of a given particular constituent, on those kind of things we have seen.

Then, we have seen that paints is primarily having a vehicle which is a liquid portion and then a pigment which is a finely divided solid. So, then, paint in a crude way we can say that a finely divided the pigment solid is dispersed in a liquid vehicle, right. So, then it is mixed in mixed thoroughly, and then the dispersion has to be uniform. That is how we can say crudely.

Again for pigments, extenders are there, fillers are there for the liquids, then oils, dryers etcetera are also there. Those are all ingredients etcetera, their roles we have seen. So, primarily what we have seen from previous lecture is that paint is nothing, but a proper thoroughly mixed liquid and finely divided solid, right. So, dispersion whatever is formed that is the paint that is how we can say.

So, now we are saying, when we are saying it is a mixture of a liquid and then finely divided solids. So, the paint formation process is nothing but a unit operation only, mixing only occurring. Only mixing is occurring in the paint formulation. But before paint formulation, whatever the pigments that you wanted to manufacture, there are some chemical reactions. So, there are some unit processes, right.

After paint formation, when you apply on a structure or on a surface, then it has to dry. So, then for the drying or hardening of these layers, paint layers, you know some kind of oxidation and polymerization reactions occurs. Those things also we have seen. So, then after applying paints on a surface, then also there are reactions, so unit processes are there. But paint manufacturing process only primarily it is all you know kind of a you know unit operations involving mixing, grinding kind of these kind of operations.

So, now in this lecture, we are going to start discussing paint manufacture. So, paint manufacture, we as we said that it is mixing of a liquid vehicle and then finely divided solid pigments.

So, now the mixing has to be thorough, efficient, then only it will be proper, you know, emulsion, paint emulsion will form or suspension will form, and then, that suspension will stay longer for several years. What does mean by suspension staying longer for several years? That means that pigment particle should not settle down there. It should be in suspended conditions only in the liquid portion, right.

So, now if you do not have a proper mixing units or proper grinding units, then your paint formulated whatever is there that may not give the required characteristics. So, what is the point that I mean to stress on here is that the mixing is very essential part of paint formulation and then mixing equipment as well as the grinding equipments depends on the type of pigments that are using.

Whether it is dry and non-sticky pigment or if it is a, you know, wet and sticky pigment, similarly liquid is like you know, viscous like resin ones or a non-viscous like ketones kind of volatile components, etcetera. Based on those combinations, the selection of mixers and grinder should be done because if you do proper grinding and proper mixing, then operation is successful. Paint formulation is going to be successful otherwise not, ok.

So, now, we are going to discuss about paint formulation through a flow chart as well, paint manufacture.

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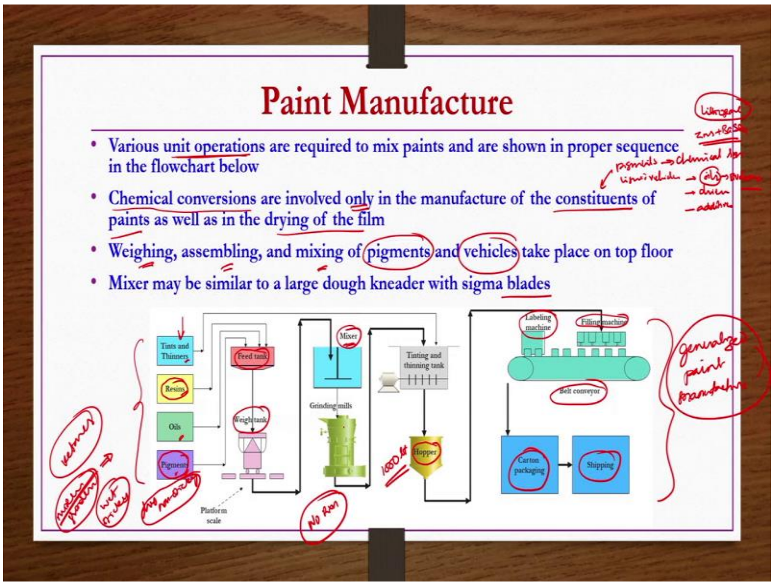

Various unit operations are required to mix paints as we will be saying subsequently. Chemical conversions are involved only in the manufacture of the constituents of paints as well as drying of the film.

Let us say constituents, you know, pigments. Pigments Making or manufacturing of pigments involved chemical processes, chemical reactions. So, we are going to see couple of, you know, these things, you know, pigments manufacturing also today we are going to discuss, alright.

So, paint also constituents liquid vehicles where we may need to have oils. So, that to enhance the film forming nature of a given suspension or to help in film forming not only helping in film forming, but also in aiding it to dry properly for that also oils are used.

And then, proper drying is required. So, dryers are required, then some kind of additives may also be required. So, then all these things, you know, when you mix, you know there may be some kind of reaction. Let us say, oils we have seen. Bodying, bodying of oils yesterday we have seen. So, there are some reactions. Different types of oils are used along with the liquid portion of the paints for different purposes as we have seen. And then these oils usually not used as a kind of a pure form.

They will be passed through certain kind of a pretreatment operations. One of them is like, you know, bodying of the oils, etcetera, then, you know, segregation, extraction, etcetera. Those kind of things we have seen yesterday several options are there. So, there also some reactions are involved, right.

Pigments also like, you know, we know that they are, you know, something like ZnS plus BASO4 mixture, that is zinc sulfide and then barium sulfate is known as the lithopone which is nothing, but kind of a white pigment.

So, in making of these pigments, then there are some extenders. Extenders also in making of the extenders are manufacturing of extenders, there are reactions. Reactions In the sense, the chemical conversions are unit processes are involved prior to making the paint or in the making of the constituents of the paints as well as the after making the paint when you apply for the drying of the film etcetera also, there are chemical reactions are unit processes are involved.

But in the manufacturing of the paint, we have only several types of unit operations as we are going to discuss. In the flow sheet, that we will be seeing now. Weighing, assembling, and mixing of pigments and vehicles take place on the top floor. Mixer may be similar to a large dough kneader with sigma blades.

So, pictorially, if you see actually, it can be arranged in other side also. These are the things which are supposed to be present at the top floor. So, that is pigments, oils, resins, sometimes tints and thinners are also required as per the requirement, right.

So, now let us say if your liquid portion is a viscous resin, then whatever the mixer that you are going to have you know for the volatile ketones kind of liquid portion is not going to be working properly. Because resins are very viscous, ketones often or aldehydes etcetera they are not that much viscous, ok.

Similarly, pigments if they are dry, non-sticky or sticky kind of material, you know, wet, these kind of things are also coming into the picture. So, accordingly, the mixers and then grinders should be chosen because these two are the important ones which are going to decide the success of the paint formulation. Final product that you are going to get.

So, in general, these ingredients if at all you need additives also, you can add them. Some kind of additives also you required. Let us say tints and thinners may be taken as a kind of additives as per the requirement. Sometimes you need to do pH control, sometime you need to have some anti-foam agents kind of things. So, many other things may also required to have in the process, right.

So, here what we are trying to understand? Very generalized paint manufacture process. It is not specific to any particular type of paint or color etcetera. Very generic one, there may be a few additions may also be there, there may be some deletions may also be there from the flowchart whatever we have shown the things are unit operations here, depending on the specific condition. This is very generalized one.

So, primarily pigments, oils, resins are the primary ingredients. Tints and thinners are optional ones. You can add pH control agents or anti-foam agents as per the requirement. Then, you weigh them and then take them to the feed tank, then weighing tank, you weigh as per the requirement, as per the weight, how much pigment should be there, how much you know resin should be there. Accordingly, you weigh them and then take them to the mixer, right.

So, in this mixer, you know all these things are mixed thoroughly, and then these tints and thinners sometimes you know not added directly along with the ingredients. They may be added later on also, right. So, now here when you are doing mixing, you know mixing is a unit operations and then its efficiency cannot be 100 percent as well as any of the crushing size reduction equipment.

So, here mixes you are using depending on the, you know selection of your mixer, how appropriate for a given combination of pigment and oil and resins, you know each performance will depend, right. So, obviously, everything will not be mixed up, some may be non-dispersed, you know solids may be there etcetera.

So, what you do after this mixes, everything you take to the grinding mills and then do the proper grinding etcetera further if you required. Then, you take to tinting and thinning tanks where thinners etcetera may be added if required, otherwise not. Otherwise directly whatever the paint that has formed that will be taken to a hopper or storage tanks where it can store 1000s of liters of final paint in a batch mode, right.

So, this paint will be taken to a belt conveyor which is facilitated with the filling machine. So, a required amount of paint maybe 10 liters or 20 liters can should be there and then this tank would be poured into those cans in the filling machine range, and then that will be passed to the next level where labeling of the material will be done as per the manufacturer company name etcetera. Those labeling would be done, alright.

So, and these two operations done on a belt conveyor one after other. So, finally, labeled product whatever is there that will be taken to the carton packaging and then followed by the shipping to the consumer or customers, right. So, this is a very generalized paint manufacture process, there may be some additions, there may be some deletions of whatever we have shown here, but you know it is just to understand.

Now, what you understand here? In this process there is no reaction at all. Is there any reaction? No, only you know kind of grinding mixing kind of things only undergoing here. So, now what we see now in this process? We can divide the process into two categories, one is the grinding and mixing, or steps up to the grinding and mixing and then steps after the mixing, ok. So, that way we see now grinding and mixing of ingredients.

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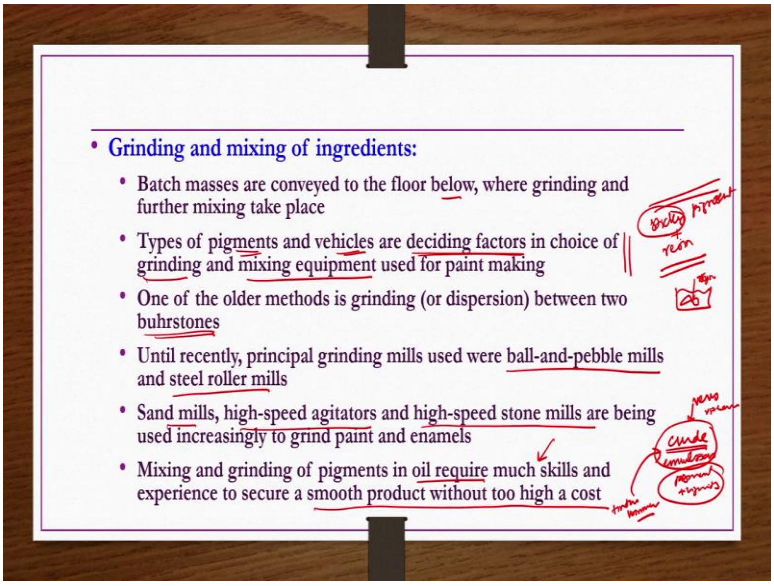

Batch masses are conveyed to the floor below where grinding and further mixing take place. Types of pigments and then vehicles used are going to deciding factors in choice of grinding and then mixing equipment used for paint making, right.

So, if you have a sticky wet pigment and then resinous liquid portion which is also sticky, then you have to have a kind of a mixer where you know needle kind of mixers are very essential. Having simple batch kind of reactor and then stator mixing them is not going to give a proper mixing of such kind of sticky and then resinous liquids, right.

So, that is what it means. Like, if you have a dry pigment and then very volatile liquid portion like ketones, aldehydes, etcetera, then you can have a simple batch reactor kind of thing and then pour them together. You have a stirrer and then stirrer different rotations as per the requirements to get the required you know mixture. That is possible. So, you know that is one.

And then also, grinding also grinding sticky materials is very difficult, right. If it is dry and then non-sticky kind of a ore, then it can be easily crushed. If it is a like you know sticky material, then grinding them also is a very difficult. So, then what kind of grinder should be use, like ball mill, pebble mill, etcetera those kind of things also come into the picture based on the choice of the pigments and then choice of the vehicles, right.

Choice of the grinder and then mixing equipment depends on the what kind of pigments and vehicles you are selecting, right. Selection also you cannot select as per the grinding and mixing equipment that you are having. Selection of pigments and vehicles should be done as per the consumer’s requirement, right. And then, based on the nature of this pigments and vehicles, accordingly you have to select the grinding and mixing equipment, but not the other way, ok.

One of the older methods is grinding or dispersion between two buhrstone's that is very conventional one. But until recent past, grinding mills such as ball and pebble mills, steel roller mills were used, but nowadays so many advanced equipment have come into the picture.

So, what you see, sand mills, high-speed agitators and then high-speed stone mills are being used increasingly to grind paint and enamels as well, ok. Mixing and grinding of pigments in oil require much skills. Actually, these are very viscous in general, right. Until when you have a crude emulsion where you have only pigments and then liquids have been you know dispersed together and mixed together.

So, then you get that crude emulsion, it is very viscous, very viscous in general. So, you cannot have very viscous paint also. If you have very viscous paint let us say, if you have apply an a surface or an architectural structure what will happen? You know on drying, it will form a very thick layer, and then, the layer if it is thick when it is drying it will be peeling out of the you know structure. So, viscosity is very much essential for the paints application point of view also.

So, then you have to add tinters or thinners etcetera in order to decrease the viscosity of this crude emulsions, right. So, now when you have this viscous material kind of thing you know, you need lot of experience, right. You cannot have, you cannot expect everyone able to do it, ok. So, in order to have a smooth product without too high a cost, then you need to have experienced persons to handle this mixing and grinding equipments in the plants.

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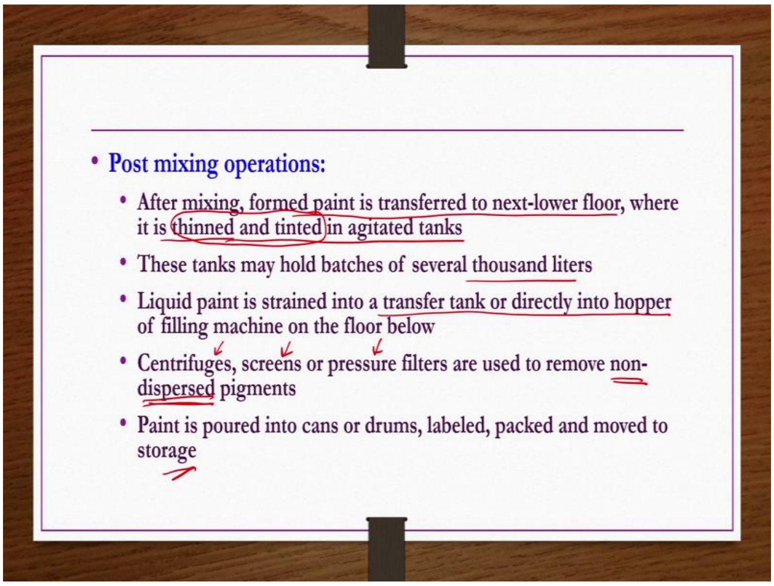

Post mixing operations, what we do? We usually formed paint is transferred to a next floor level where it is thinned and tinted in agitated tanks. These are the right you know in general required for most of them, but not necessarily for all of them, ok.

These tanks may hold batches of several 1000s of liters of paint. Liquid paint is strain into a transfer tank or directly into hopper of filling machine on the floor below.

Then obviously, as I said everything may not be dispersed properly because mixing also will not give 100 percent efficiency. There would be some kind of non-dispersed pigments in the emulsion. So, then they should be separated. For the separation of those non-dispersed pigments in general, we use the screens, centrifuges or pressure filters etcetera. Those are being used in general.

Paint is poured into cans or drums labeled packed and moved to storage after removing these non-dispersed pigments. So, that is about paint manufacture, very generalized approach. So, any paint you know that you are going to make latex based paint or emulsion based paints or you know enamels etcetera. Whatever you make you have similar kind of flow charts only, right.

So, that is the reason we are not going into the details of each and every different types of a paints individually, right. However, before completing this paint section what we will do? We will be having a discussion on how to make latex based paints or latex paints.

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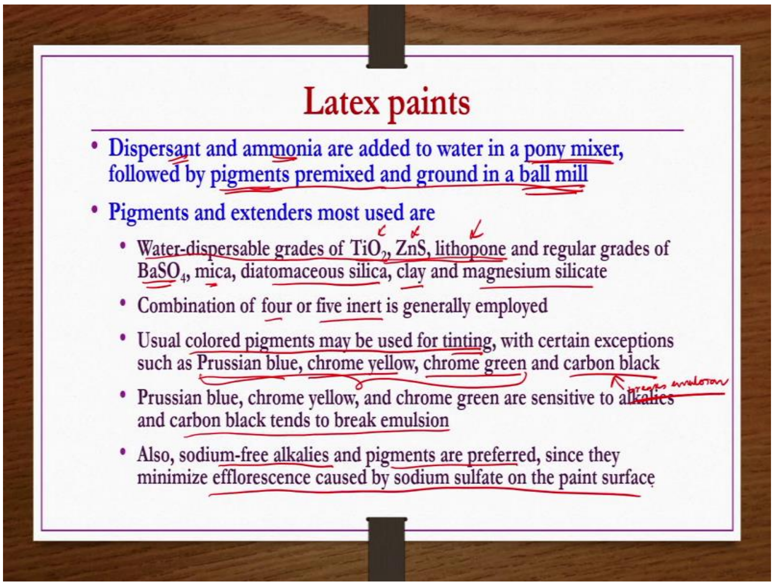

Dispersant and ammonia are added to water in a pony mixer followed by pigments, pre-mixed and ground in a ball mill.

In this process actually, again mixing only taking place. What happens here? You have the pigments. These pigments are pre-mixed and ground in a ball mill, right. So, pigments there may be 1 or 2, 3, 4, 5 also required some time depending on application. So, different types of pigments are pre-mixed and ground in a ball mill. And they are added to a pony mixer, small mixer, that means, a batch type of mixer in which dispersant and ammonia are already added, right.

Pigments and extenders that are used often are water dispersable, grades of TiO2, ZnS, lithopone. These are actually white pigments to be frank. Water based or water dispersable, grades whatever this TiO2, ZnS and lithopone etcetera are there. They are white pigments. And regular grades of barium sulphate, mica, diatomaceous silica, clay and magnesium silicate etcetera are also used very often.

Combination of 4 or 5 inert is in general employed as I mentioned. So, it is not necessarily one single, but in this combination of many. Usual colored pigments may be used for tinting with certain exceptions such as Prussian blue, chrome yellow, chrome green and carbon black.

Why exception to this? Because these 3 are found to be like you know very sensitive to alkalis and this usually breaks the emulsions. You do not want emulsion to be break. Actually, you want emulsion to be stable for years, ok. So, Prussian blue, chrome yellow and then chrome green are sensitive to alkalis and then carbon black tends to break emulsion. That is the reason. These are certain exception. These are also used, but as per the requirement wherever the certain applications are there and then they are essential to add.

So, you add them, and then appropriately you change modification in the process, so that you know breaking of emulsion may not take place. Let us say if you are making black paint. So, carbon black is one of the pigment. You cannot avoid it, ok. So, accordingly you have to make changes in the process. Also, sodium free alkalis and pigments are preferred, since they minimize efflorescence caused by sodium sulfate on the paint surface.

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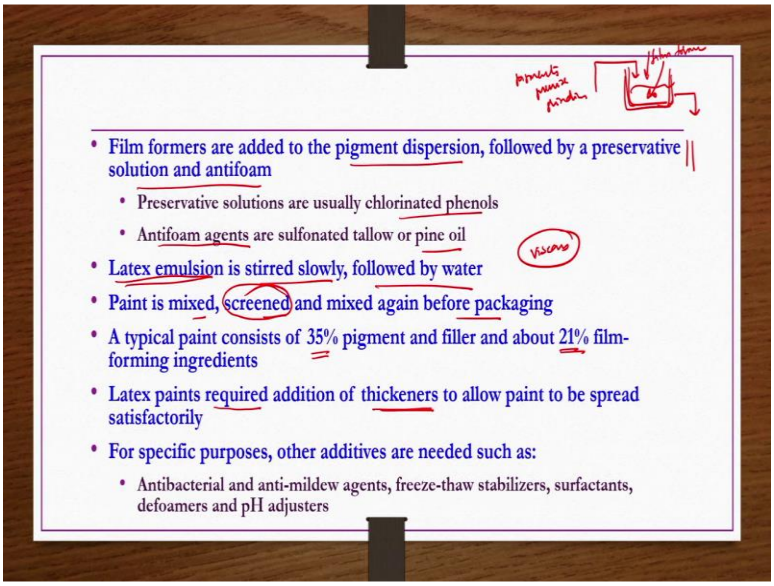

Then, film formers are added to the pigment dispersion, followed by a preservative solution and anti-form as per the requirement. See, now this all process like you know we are mixing the pigments, and then we are grinding them, and then we are pouring in a reactor like you know pigments, premix, then grind, then take to a reactor in which already dispersion ammonia etcetera are present, right.

So, now this to this reactor you can also add film forming agents or oils etcetera you can add. You can also add preservative solution and anti-form as per the requirement. So, it is all mixing kind of operation is only going on until now. Preservative solutions are usually chlorinated phenols, whereas, the antifoam agents are sulfonated tallow or pine oils.

Latex emulsion is stayed slowly followed by water because this latex emulsions are in general viscous in general very viscous in nature. So, then you cannot have a kind of a high speed agitators etcetera. That is the reason you know these are mixed slowly in a pony mixes, batch type mixes. Pony in the sense small which indicating batch kind of a mixers.

Paint is mixed, then screened and mixed again before packing because why screening? There may be some non-dispersive items that may be you know pigment, that may be a kind of a film forming agent or that may be anti-form agent or there may be preservative etcetera, whatever it may be. So, some kind of screens may be required. So, then you if at all anything is not dispersed properly that you remove, and then, you take it back to the mixture, and then, again mix before making packaging.

So, a typical paint consist of 35 percent pigment and filler and whereas, the 21 percent is film forming ingredients. Latex paints required addition of thickeners to allow paint to be spread satisfactory. For specific, purposes other additives are also needed such as anti-foam agents, anti-bacterial agent, pH adjusters etcetera. These kind of things, ok. This is very basic knowledge about the paint formulation, normal paint formulation and latex paint formulation etcetera.

Now, we cannot go into details of each and every paint because of the you know nature of the course and then has to be completed within stipulated time. So, then what we do? We go to the next topic of a surface coating industries that is pigments, right. So, we understand, then pigments is one of the most important constituent of any paint that you take.

Any paint without pigments it is not possible. It is not possible to have a satisfactory emulsion without a proper pigments. And these pigments are usually finely divided solids and then they provide different types of colors etcetera as per the requirement. These pigments are dispersed in or formed emulsions in a vehicle. Vehicle may be volatile, nonvolatile,resinous etcetera and all those things we have seen, ok.

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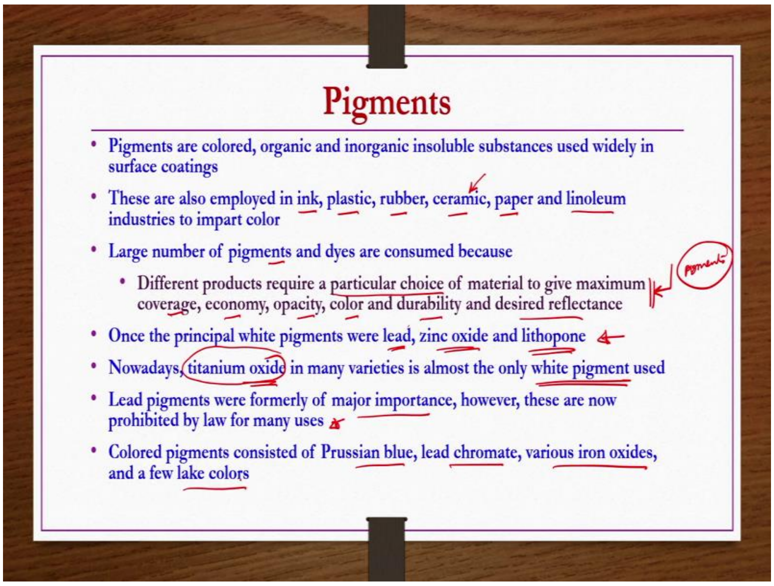

So, what are these pigments? What are their roles etcetera. These things we are going to see now. Also, we are going to see how to manufacture these pigments because naturally they are not available. You have to do such certain kind of processing, ok. So, pigments are colored, organic and inorganic soluble substances used widely in surface coating industries. In fact, without having these pigments it is not possible to have paints.

These are also employed in ink, plastic, rubber, ceramic, paper and linoleum industries to impart color different types of colors, colored paper different types of colored plastics or design plastics different types of colored rubbers, design rubbers, ceramics etcetera. There also you know you need these pigments, right.

Ceramics again next week we are going to study about the ceramics. There again we may be having role of these pigments again. Large number of pigments and dyes are consumed because different products required a particular choice of material to give a maximum coverage, economy, opacity, color, durability, desired reflectance. You see so many things are there. These many activities or these many requirements are there from the pigments point of view in the surface coating industry.

In fact, almost all of them you know whatever the requirements are then, whatever the expectation that you have from a surface coating industry product, all of them, almost all of them are coming from this pigments. Whereas, the liquid or vehicles you know they are kind of vehicles to form emulsions of this pigments only, ok. Including the opaque nature, including the reflectance, durability, color, coverage everything is coming because of this pigments and dyes only, ok.

Once the principle white pigments used were lead, zinc oxide, lithopone, these were very famous once upon a time. We will study about white lead in the section where we talk about white pigment.

Nowadays, titanium oxide in many varieties is almost the only white pigment used, right. Earlier all these zincs zinc oxide, zinc sulfate, lead, lithopone etcetera were used, but nowadays primarily titanium oxide is only $TiO2$ is used in many varieties to have this white pigment or used in the paint industries.

Lead pigments were formerly of major importance. however, these are now prohibited by loss for many uses. Because of the loss of a given country these lead pigments are not being used because of their impact on the environment as well as the inhabitant as well as the painter as well.

Colored pigments consisted of Prussian blue, lead chromate, various iron oxides and a few lake colors as well.

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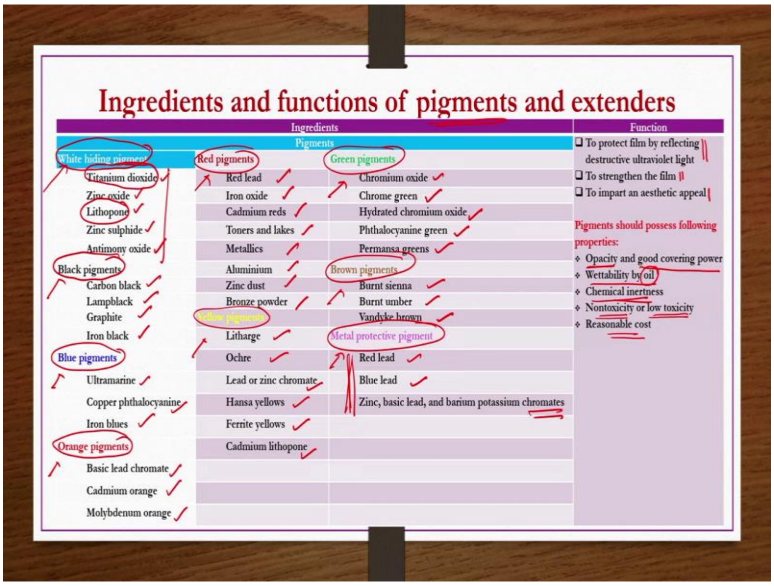

So, now what we see? We see ingredients and functions of different types of pigments and extenders. First, we start with the pigments, right. Pigments, now they are the ones they are providing opacity, color, reflectance or you know resistance to the reflectance, durability etcetera, right. So, what are these pigments? Right. When you are talking about the color, so then each type of color if you need to have. So, then certain types of pigments are there, right. So, like why like that way we group these pigments, right.

Let us say ingredients of the pigments, you have a white hiding pigment. So, what are the things? Then, similarly if you wanted to have a black pigments, black color, blue pigments, so then what are the constituents like orange pigments, red pigments, yellow pigments, green pigments, brown pigments and metal protective pigments etcetera all these things are there, right.

Now, we have already seen the functions of this pigments, but however, again presented here these pigments are used to protect film by reflecting destructive ultraviolet light and to strengthen the film and to impart an aesthetic appeal. And then, pigments should posses particular properties those things are requirements of pigments also we have seen basic requirements. They should be opaque, opacity, good covering power they should have, wettability by oil because oils are essential part of the paint.

And then, if these pigments though majority of the characteristics of the paints are coming through pigments, if these pigments are not wetterable by the oil or liquid portion or vehicle of the paints. So, then that is not going to be useful anyway.

So, the wetterability by oil has to be there, then they should be chemically inert, right. So, when you apply these paints on a surface, if they are chemically active, so then they may destroyed or destruct the surface itself. So, they should be chemically inert and then they should not be toxic. They should be completely non-toxic, if possible. If not possible, at least they should be low toxic and then they should be low cost or reasonable cost.

So, these functions as well as the basic requirements basic characteristics of the pigments there are things we have seen. These are very common for all of the different types or different colors of pigments, right. However, each pigment providing a different color, right. Let us say if you wanted to have a white hiding pigment, then you should use titanium dioxide pigments or zinc oxide or lithopone or zinc sulfide or antimony oxide see how to use.

Let us say if you wanted to have a black color, then carbon black, lampblack, graphite iron blacks are useful. Likewise for blue color blue pigments like such as ultramarine, copper phthalocyanine, and then iron blues are required. In order to impart orange color, orange pigments are required which include like you know basic lead chromate, cadmium orange, molybdenum orange etcetera.

Likewise, if you need to impart red color, then red pigments such as red lead iron oxide, cadmium red toner and lakes, metallics, aluminum, zinc dust, bronze powder etcetera are used. If you prefer to have yellow color in the paint, then yellow pigments are going to be useful such as litharge, ochre, lead or zinc chromate, hansa yellows, ferrite yellows, cadmium lithopone etcetera.

If you wish to have a green color in the paints, then green pigments such as chromium oxide, chrome green, hydrated chromium oxide, phthalocyanine green, permansa greens are used in general. Similarly, to have a brown color, brown pigments something like a burnt sienna, burnt umber, Vandyke brown etcetera are used.

Likewise, if you wanted to have metal protective pigments then red lead, blue lead, zinc, basic lead and barium, potassium, chromates etcetera are used, alright. So, based on the color. So, not only the color based on the other required properties also you have to select appropriate you know pigments for the paint formulation.

Now, you see different colored pigments 1, 2, 3, 4, 5, 6, 7, 8, 9 only shown here. There may be many more, there may be a combination of these also. Nowadays, different color patterns are there, they are neither fall in one particular color or nor the other color, it may be in between of these two. So, then mixture of colors, pigments are required.

So, n number of combinations are possible. And then, which in each of them there are several different types of a pigments are there. So, manufacturing of each and every pigment is not at all possible for us. So, now what we do?

Since, we cannot discuss manufacturing process of each and every pigment, as a learning process, we try to understand you know manufacturing of lithopone, white hiding pigment as well as the titanium dioxide white pigment, we are going to discuss in detail.

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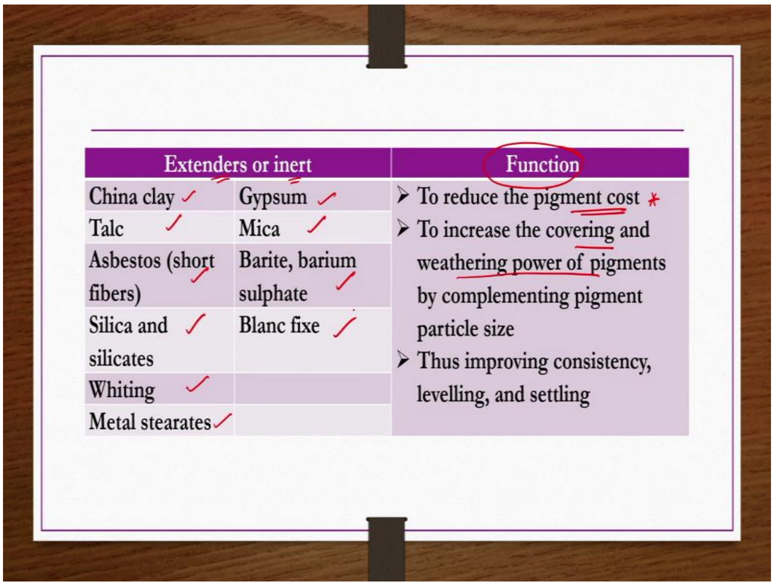

Now, before going to the manufacturing process of white pigments what we will have? We will have a discussion on the extenders or inerts as well and their functions. Their functions also we have already seen, we have seen that they reduced the cost of pigments because some of the pigments. What you see there? Almost all of them are chemicals, solids, chemical solids and then finally, divided solids, right. So, they may be expensive, some of them may be very expensive, right.

So, if you have some kind of extenders or inert which may not decrease the quality of the product, but decrease the cost of the overall paint or pigment it is going to be very useful. So, one of the role of these extenders or inert is to reduce the pigment cost. To increase the covering and weathering power of pigment by complementing pigment particle size. And thus, improving consistency, leveling and settling, right.

For these purposes, extenders or inerts are used. So, what are the common types of extenders or inerts? China clay, talc, asbestos, silica and silicates, whiting, metal stearates, gypsum, mica, barite, barium sulphate, blanc fixe etcetera. These kind of extenders are used. There may be many other types are also possible.

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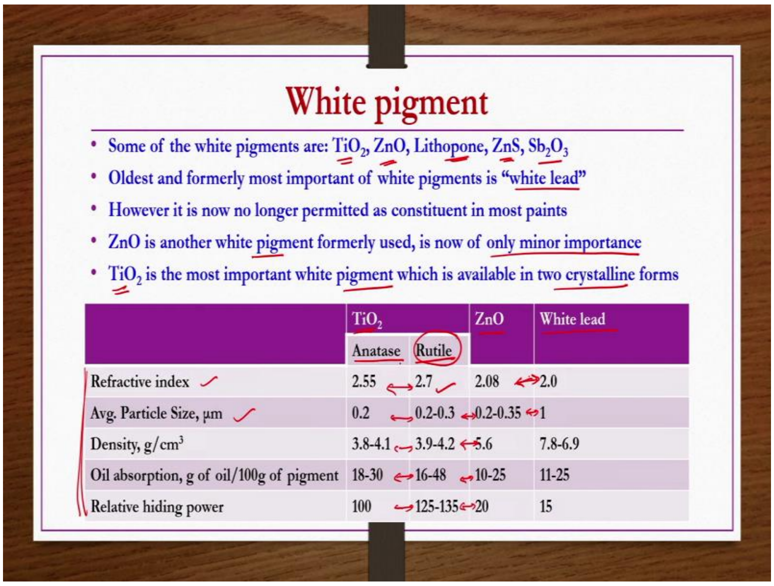

Now, we discuss about white pigments. Some of the white pigments are titanium oxide, zinc oxide, lithopone, zinc sulphide, antimony oxide etcetera. Oldest and formerly most important white pigment is white lead.

However nowadays, it is not used as a constituent in most of the paint industries because of certain restrictions. Zinc oxide is another white pigment formerly used and it is now only a minor importance, right. Because so many different types are being produced gradually and then, older ones may be supplanted by the newer ones in general, ok. Titanium oxide is the most important white pigment which is available into crystalline forms, anatase and then rutile.

Now, what we do? We take a conventional white lead and then older zinc oxide and then presently used titanium oxide in two different forms and then compare their properties. If you take the refractive index, refractive index of TiO2 is higher compared to the remaining two.

Similarly, average particle size also you know it is within the control compared to the other two ones. White lead particle size is very high, one micron in general. Whereas the density also, if you see it is low density compared to the ZnO and then white lead, ok.

If it density is higher, what will happen? Emulsion may not be stable. It may settle. Particle may be settle in quicker time. Rather in 2 years it may be settling in 1 year only. So, we after 1 year you cannot use that emulsion in general. So, density has to be low as much as possible. So, that way TiO2 is better compared to the previous ones. Oil absorption characteristics also you see.

The TiO2 oil absorption characteristics are better. And then, relative hiding power also, if you see this TiO2, they are having high power. So, individually TiO2 also, anatase and rutile if you compare, rutile is found to be better from these numbers mostly, from all these characteristics point of view. That is refractive index, average particle size, density and then oil absorption.

How many grams of oil per 100 grams of pigment is required, from that point also and then the relative hiding power point of view also, this rutile is better. Because it is most stable compared to the anatase. But anyway, you can get the rutile from the anatase as well by heating it at high temperature. So, those things we are going to see anyway.

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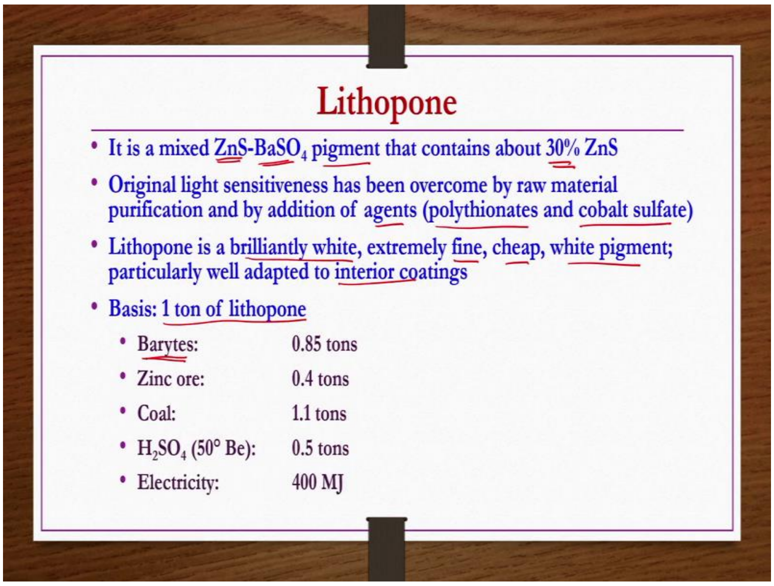

Now, we talk about the manufacturing of lithopone. It is mixed zinc sulfide and barium sulfate pigment, that contains about 30 percent zinc sulfide remaining is barium sulfate. Original light sensitiveness has been overcome by raw material purification and by adding agents such as polythionates and cobalt sulfate etcetera. Lithopone is a brilliantly white, extremely fine, cheap, white pigment, particularly well adopted to interior coatings.

From the production point of view, if you take 1 ton of lithopone as basis, the barytes which are nothing, but barium sulfate ores, you need 0.85 tons. Then, zinc ore you need 0.4 tons, coal you need 1.1 tons, sulfuric acid 0.5 tons, electricity 400 megajoule you required.

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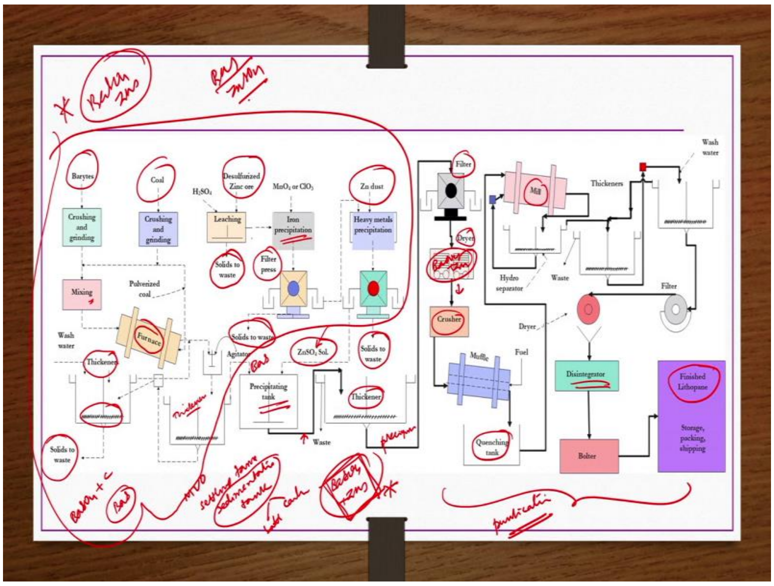

Now, this is the flowchart that is used for making finished lithopone, right. So, now it is what we are having as per the raw material, that barytes ores are there, coal is there and then zinc also there, zinc ore is also there, right.

So, all these things are individually processed, right. You know the processing is also indicated by the different lines. For example, barytes are taken crust and grinded, similarly coal is also crust and grinded, pulverized coal is taken. And then, these are added together in a mixer or they are individually taken to a furnace.

First, before taking to the furnace they can be individually mixed and then send the mixture to the furnace or individually they can be taken to a furnace where the required reaction takes place and then you get barium sulfate. It is coming from ore is having barium sulfate and then when it reacts with this one you get a barium sulfate from this reaction.

So, that mixture whatever the from the furnace whatever the product is there, that you take to a agitator, right. So, from the agitator you mix these contents of the product whatever are they, thoroughly you mix them and then the product mixture you send to thickness. These are nothing, but the thickener.

Thickeners are you know settling chambers kind of thing. You see in mechanical unit operations, these settling tanks or sedimentation tanks etcetera you might have studied.

So, these sedimentation tanks can be continuous and batch. Now, here we are having a continuous one. So, what happens? The heavy particles or you know when you are doing crushing, so all size of particles may be there. You may have the proper screens before sending them to the furnace, even then also some kind of oversize or undersize would be there.

So, heavier particles bigger size would be collected from the bottom and then they would be sent to a second thickener where again the same process is being done, right. So, large particle or mud etcetera those things are not required, they will be taken as a solids to waste. Whereas, the overflow which are the required ones, they will be sent back to the agitator again, right.

From the first thickener whatever the product is there that will be taken to a precipitating tank to which zinc sulfate solution is added. So, here from where is it coming? It is coming from the de-sulfurized zinc ore, right. Zinc ore and then H_2SO_4 react together to get the zinc sulfate $ZnSO_4$, right.

So, from here whatever the solids which are not you required for the process, they will be taken to the waste. Whereas, the zinc sulfates etcetera would be taken to the iron precipitation units. And then, the product from this iron precipitation units will be taken to a filter press.

There are two filter press are there. So, after doing the filtration whatever the solids, cakes etcetera are there, you can collect them as solids to waste. Whereas, the filtrate that you take to heavy metal precipitations to which zinc dust may be added if required, otherwise not.

After adding this zinc dust in a heavy metal precipitation whatever the final precipitate is coming that will be again sent to another filter press. Here again the cake final solid cake whatever is there that is taken as a waste. So, whatever the filtrate is there that filtrate is nothing, but the $ZnSO_4$ solution. That $ZnSO_4$ solution is coming to the precipitating tank to which we are sending barium sulfate solution anyway.

So, now here the required reaction takes place and then you get barium sulfate plus zinc sulfide mixture you get from here, from the below of this precipitating tank. So, that mixture is taken to series of thickeners. We are showing 1 or 2 only depends on the requirements.

So, again here thickeners when you do the processing, you know here now final precipitate whatever this that is the product. Earlier, in this thickeners, the other side around. So, here final precipitate solution slurry whatever is there, that is the product that you take to another filter, right filter press.

Again, you try to remove the so called the filtrate whatever the solids are there or the cakes are that formed in the filter press, those cakes are taken to a dryer. So, then these are nothing, but the required $BaSO_4$ plus ZnS mixture only that you are getting after this drying.

So, these are crushed. And then passed through muffle furnace, again if required and then quenching is done. After this they will be sent to you know mills, hydro separators etcetera, thickeners etcetera as per the requirement. And then dried finally, disintegration of these, because all these processes are occurring, so the lumps of the particles may be taking place or they may be forming a kind of lumps.

So, those lumps would be disintegrated, and then, sent to the bolt as followed by the packing of a lithopone. So, this lithopone is forming here only as a product $BaSO_4$ and then ZnS after this thickener unit coming after the precipitating tank. So, here itself the product is there, but all this remaining step here is that purification step.

Now, here you see it is a pigment making or manufacturing of a pigment. Now, you see so many reactions were involved here, right and then followed by the purification steps. Whereas, in the paint formulations there are no reactions only mixing, grinding and mixing operations were there or maybe separation of non-dispersed pigments are maybe there, but there are no reactions, ok.

So, this looks very big, but sequence wise you know if you see like you know, if you already processed barium sulphate and processed zinc sulphide you are having. So, then all these steps may not be required, if you are already having them. Directly you can take to the precipitation tank followed by the thickener and then followed by the purification etcetera, steps you can follow.

This is all not required if you directly have a pure BaSO4 and then ZnS. If you are trying to get this BaS and then ZnSO4 from their corresponding ores, then only all these steps are required.

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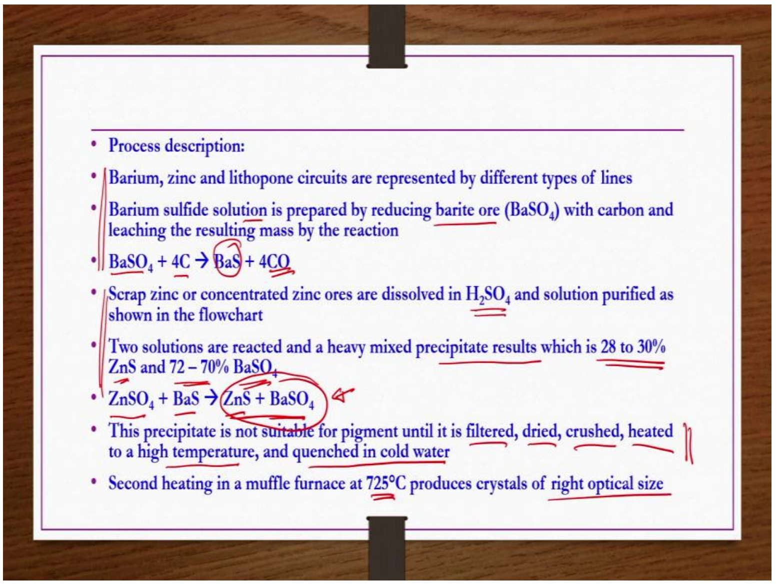

So, whatever we have seen in the previous slides you know same thing is a provided as a text here for understanding, for learning process. Barium, zinc and lithopone circuits are represented by different types of lines, some are the dotted lines, some of them are you know thick lines we have seen.

Barium sulphide solution is prepared by reducing barite ore which is majorly consisting barium sulphate with carbon and leaching the resulting mass by the reaction BaSO4 plus 4C giving raised to BaS plus 4CO, right. So, this is the processing of a barite ore. Now, zinc ore processing that we are seeing now. Scrap zinc or concentrated zinc ores are dissolved in H2SO4, and then solution purified are shown in the flowchart.

Then, two solutions are reacted and a heavy mixed precipitate results which is having 28 to 30 percent of ZnS and then 70 to 72 percent barium sulphate, right as per the reaction that is ZnSO4 reacting with BaS to give ZnS and then BaSO4. This is nothing, but the lithopone, ok.

This precipitate is not suitable for pigment until it is filtered using filter press then dried, then crushed, then heated in a muffle furnace to high temperature, then quenched in a cold water. All these steps we have seen in the flowchart. Without doing these purification steps this is not going to be useful as a pigment.

Chemically, it is the same composition ZnS and BaSO4 mixture. But in order to have or in order to bring pigment basic requirements in this mixture you have to do all these steps as well. Second heating in muffle furnace at 725 degree centigrade produces crystals of right optical size.

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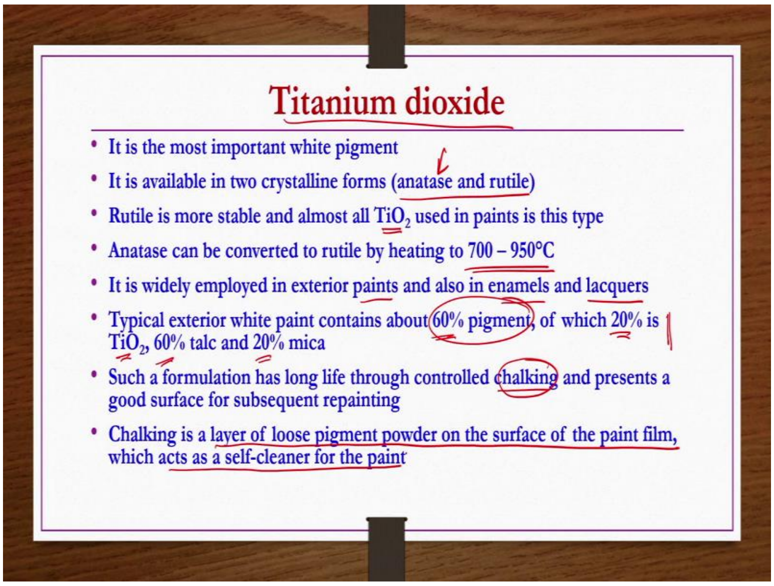

Now, we talk about titanium dioxide pigment, ok. It is also white pigment. It is the most important white pigment nowadays used in most of the paint industries. It is available in two crystalline forms anatase and rutile.

Rutile is most stable and then almost all TiO2 used in paints is this type. However, you can get rutile from the anatase also by heating it to 800 or 900 degree centigrades. Anatase can be converted to rutile by heating to higher temperature like 700 to 950 degree centigrades. It is widely employed in exterior paints also in enamels and lacquers.

Typical exterior white paint contains about 60 percent of pigment, out of this 60 percent pigment 20 percent is TiO2, 60 percent is talc, and 20 percent is mica. These are you know not exactly the same one, there may be slightly variations or may be there plus or minus 2 to 5 percent may also be there in general from one paint industry to the other paint industry.

Such a formulation has long life through controlled chalking and presents a good surface for subsequent repainting. So, what is the chalking? It is a layer of loose pigment powder on the surface of the paint film which acts as a self-cleaner for the paint, ok.

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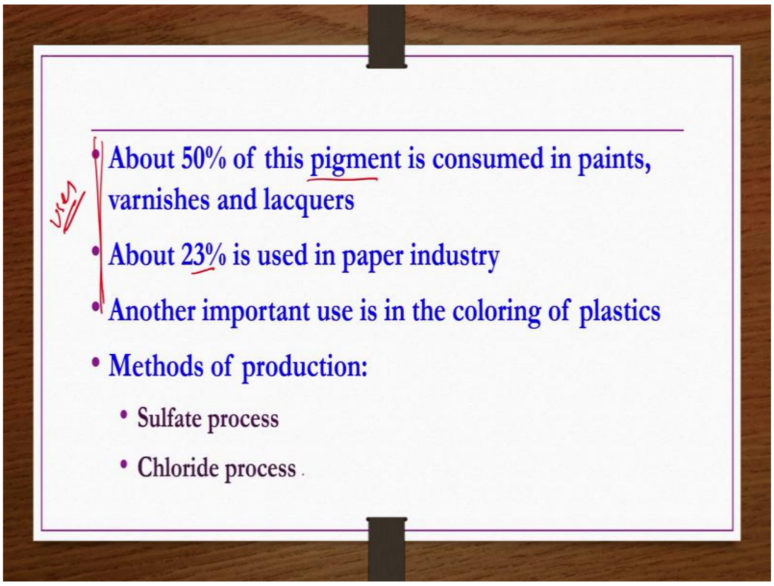

Now, about 50 percent of this pigment is consumed in paints varnishes and lacquers. About 23 percent is used in paper industry. Another important use of this TiO2 is in the coloring of plastics, right. So, these are the end uses, uses of or economics of a TiO2.

Coming to the methods of production, there are two important methods of production one is the sulfate process, another one is the chloride process. Sulfate process is the older process, whereas the chloride process is a newer one.

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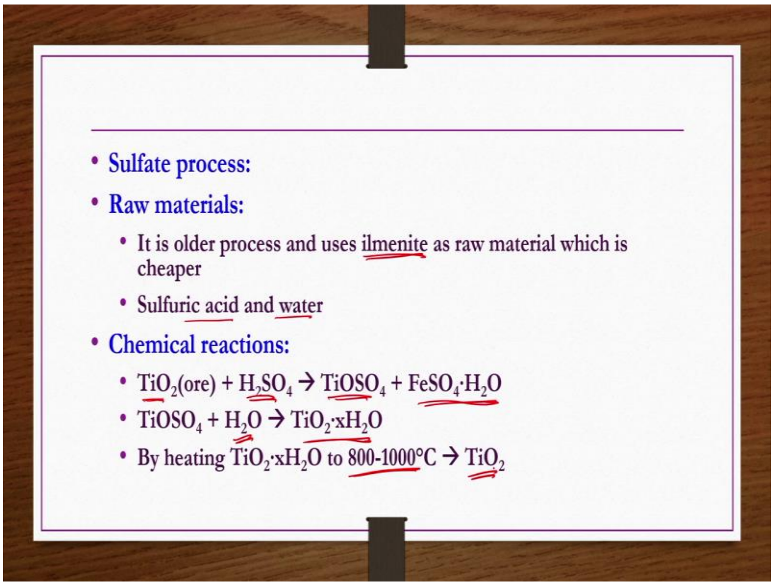

So, we start with sulfate process. Raw materials, ilmenite is used as raw material which is cheaper and then as I mentioned this process is a older process. In addition to ilmenite, you also need sulfuric acid and water.

Then, chemical reactions this ilmenite which is having TiO2 ore reacts with H2SO4, it will give TiOSO4 plus hydrated iron sulfate, ok. This TiOSO4 further reacts with the water to give hydrated TiO2. This hydrated TiO2 if you heat it to higher temperature to 800 to 1000 degree centigrades, then you get a TiO2 pigment.

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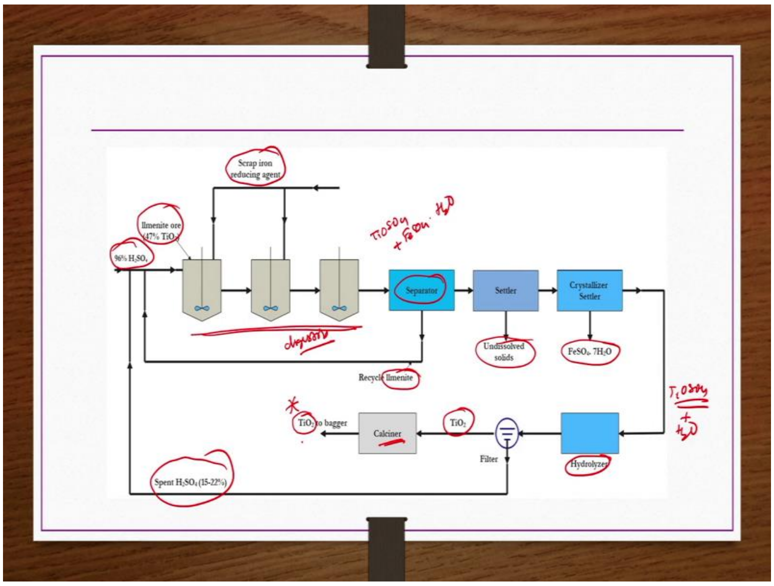

Now, we discuss process of TiO_2 manufacture or TiO_2 pigment manufacture using sulphate process through this flowchart. Here what we have? We have several number of digesters. These are nothing but digesters, only 3 have been shown, they can be in dozens, right.

So, here sulfuric acid and then ilmenite ore which is containing 47 percent TiO_2 after crushing, size reduction, crushing, drying and then washing all those things you do, and then you take that ore in a digester to which sulfuric acid is being added, right. To these digesters scrap iron is also added which is acting as reducing agent, right.

So, n number of other in a sequence, the product coming out of the one digester is going to the next one like this it is keep on going on, right. So, now here what happens? In this process, what you get? $TiOSO_4$ plus $FeSO_4.H_2O$ you are getting, right.

So, after passing all the digesters whatever the product mixture that you are getting from the last digester that is taken to a separator, where unreacted ilmenite if at all is there that would be separated and then that would be recycled to the first digester along with this sulfuric acid again.

Then, product mixture is taken to settler where undissolved solids, in the mixture if at all undissolved suspending solids are there they will be removed. Then, that mixture is taken to a crystallizer settler where this hydrated iron sulphate is separated out and then remaining $TiOSO_4$ whatever is there that is taken to a hydrolyzer. So, that this reacts with water to give TiO_2 or hydrated TiO_2 would be given.

And then, it would be a kind of slurry, so then filter would be there. So, whatever the filter is there when this mixture or the hydrated TiO_2 is there, when you pass it through filter, so whatever the acids etcetera are there they will be collected as spent acids and then mixed with the sulphuric acid and then sent to the sequence of digesters. Whereas, the hydrated TiO_2 would be calcine to high temperature like 700 to 900 degree centigrade to get the TiO_2 pigment of proper optical size, ok. So, this is the process.

Now, coming to this reaction these reactions whatever occurring between ilmenite and then H_2SO_4, they are very violent and then you know lot of fumes are forming so, H_2SO_4 etcetera may be going out along with the you know water vapors. So, that is very dangerous. So, then that reaction may be controlled if you use the dilute acid or spent acid in the process, ok. This is about the sulphate process to get TiO2 pigment.

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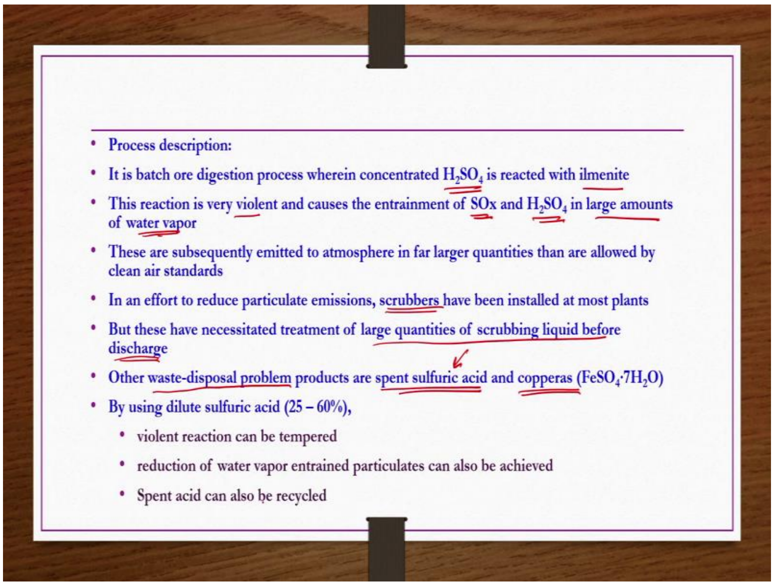

Description of the process is given whatever we have seen in flow chart, the same description is given here. It is a batch ore digestion process wherein concentrated H2SO4 is reacted with ilmenite. This reaction is very violent and causes the entrainment of sulphur oxides as well as the H2SO4 in large amounts of water vapor as well, right.

So, in previous days, they used to be discovered as it is, but now ever it is not possible because of the environmental pollution constraints or restrictions. So, then this has to be treated. So, for that purpose large number of scrubbers are being installed to reduce the particulate emissions from these water vapors, ok.

But these have necessitated treatment of large quantities of scrubbing liquid before discharge as well, that also increase the cost of the plant operation as well as the installment both.

Other waste disposal problem products are spent sulfuric acid, and then copperas that is FeSO4.7H2O. This can be used in the process again because if you are used dilute or spent sulphuric acid this violent nature of the reaction would decrease, right. And then this can be used to recover the iron sulphate. By using dilute sulfuric acid, violent reaction can be tempered. Reduction of water vapor entrained particulates can also be achieved, and then spent acid can also be recycled.

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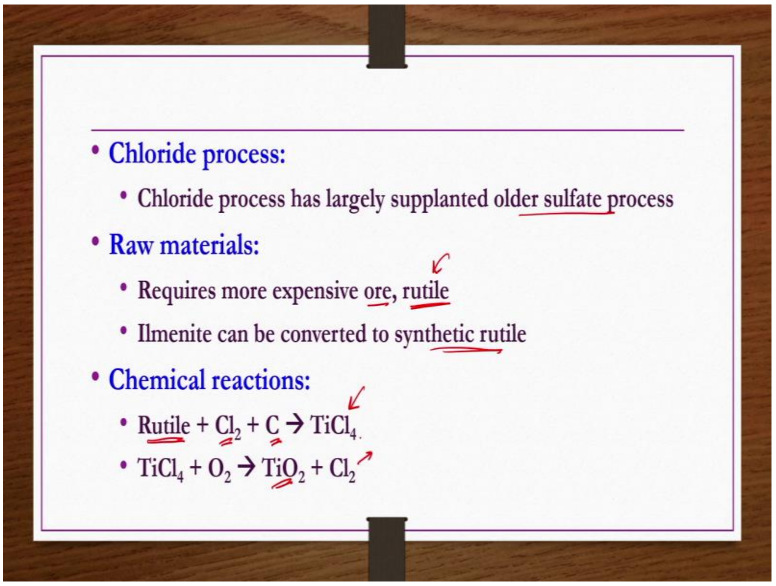

Now, before closing today's lecture we will be discussing chloride process to get TiO2 pigment. Chloride process has largely supplanted older sulphate process. It uses more expensive ore, rutile.

Rutile is more expensive though it is stable. It is stable because it has been processed through a calcination section at high temperature, so it has become stable. So, when you do additional processing then obviously, cost will increase. So, that is the reason it requires more expensive ore, rutile.

Ilmenite can be converted to synthetic rutile. Chemical reactions included in this chloride process are rutile which is having TiO2 that reacts with the hot chlorine gas and then coke to give chlorates of titanium. Titanium tetra chloride you get it, right. So, this titanium tetra chloride will be oxidized to give titanium oxide and then hot chlorine gases again which can be recycled.

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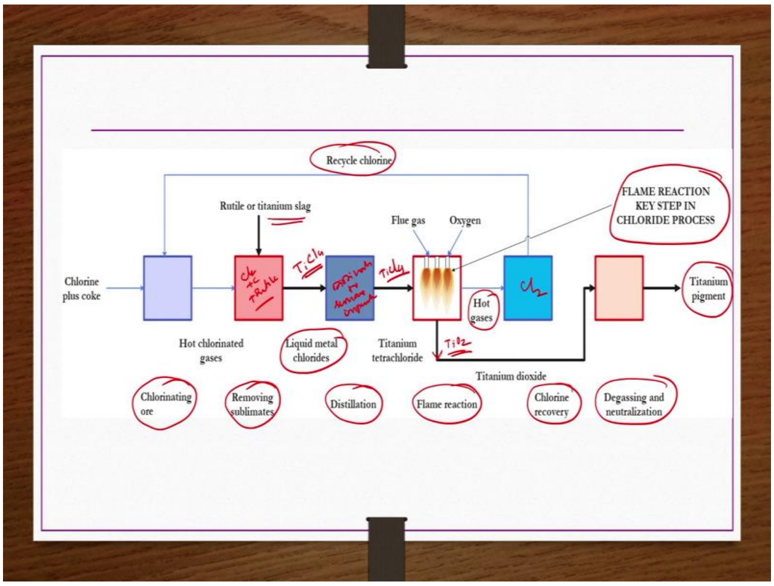

Process flowchart we will see here. Now, in this process, we have different section chlorinating ore and then removing sublimates and then distillation flame reaction, chlorine recovery, degassing and neutralization sections are there. So, here chlorine plus coke whatever is there, that is taken to a reactor, right.

In this reactor, what we will have? Again, they will be mixed together and then they will be sent to a another reactor where removing of sublimates are being done here. You know this Cl2, C and then this rutile will react together. This rutile or titanium slag can be used here.

So, when you do it here. So, what you get? You get TiCl4 as per the reaction, but there would be some impurities also. Liquid metal chlorides would be taken here and then there will be some kind of distillation would be done. Distillation to remove impurities, impurities from the liquid metal chlorides whatever are there they will be removed by the distillation. And then after removing these impurities you have almost pure titanium tetra chloride.

So, that will be oxidized using a flame reaction where the flame gases are coming and then oxygen is coming, and then, when do the combustion the flames are forming. When this TiCl4 passes through these flames, what happen? Oxidation will takes place and then hot gases of chlorine will be collected and then recycled. Recycled chlorine to the initial chlorinating over section.

Whereas, the bottom products or the solids from here you are nothing, but TiO2 that is titanium dioxide they will be process to degassing and neutralization. And then once the neutralization has been done, titanium pigments are collected as the process. Now, the success of this process depends on the flame reaction, how effectively it is being implemented, based on that one it depends.

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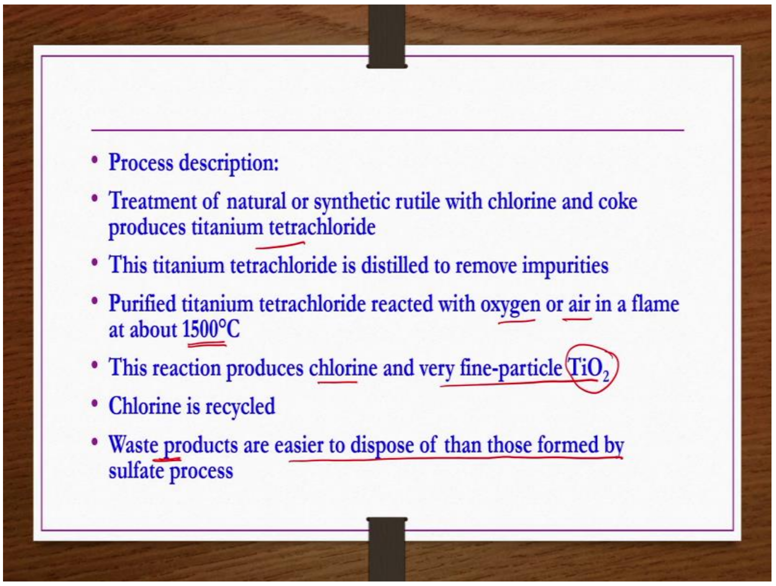

Steps of this chlorinated process are provided here. Treatment of natural or synthetic rutile with chlorine and coke produces titanium tetrachloride. This is distilled to remove impurities if at all present obviously, they will be present. Purified titanium tetra chloride reacted with oxygen are air in a flame at about 1500 degree centigrade. So, that oxidation of this TiCl4 takes place and TiO2 produced. This reaction produces chlorine and very fine-particle TiO2.

Chlorine is recycled whereas, the very fine particulate TiO2 is there that is collected as a product after degassing and neutralization. Waste products problem is there in both sulfonated process as well as this process as well, but here in this process waste products are easier to dispose than those formed by the sulfate process. Sulfate process spent H2SO4 are being formed, you cannot throw them easily, right. So, such problem is not here, in this process.

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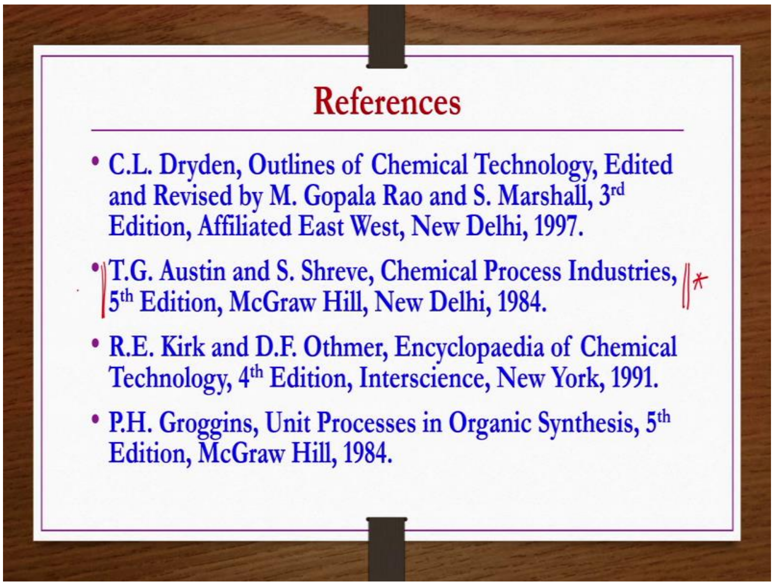

References for this particular lecture are provided here. But however, the entire lecture is prepared from this book Chemical Process Industries by Austin and Shreve, 5th Edition.

Thank you.