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# Lecture – 60 Oxide Pigments, Luminescent Pigments, Corrosion Protection Pigments, Magnetic Pigments

Hello and welcome back to the class where we are talking about the white colored pigments only.

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So, after TiO 2 we will just now take the example of zinc oxide white. So, it can also be used like that of your titanium dioxide and it can also be used with in comparison to that of your lithopone that we will also see. So, it is more opaque than lithopone, so the choice for getting a white compound or as your white p inorganic pigment is that first is your titanium dioxide, then is your zinc oxide and then your lithopone. So, how we produce?

One process is the indirect process, we take the corresponding zinc as the metallic form, so zinc metal is melted in graphite crucible which is high temperature withstand crucible such that it can withstand a 1000 degree ting centigrade temperature and you get the zinc vapor and is allowed to react with oxygen at a high temperature, which is immediately giving you the corresponding zinc oxide and in a smaller particles only.

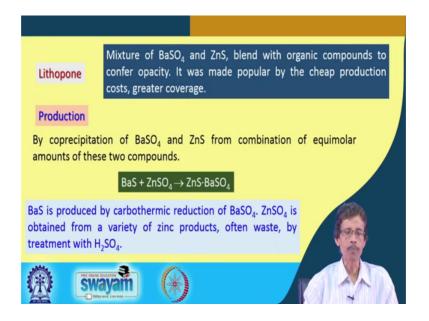
So, in the vapor state they are reacting; that means, the zinc vapor is reacting with the dioxygen and you go this particular form; that means, you can have the corresponding duct and the duct is taking away your zinc oxide and is going to the cooling duct which is not at the temperature of 1000 degree or more. And then finally, it can be collected in a bag type of area or is known as bag house.

And in the direct process what we get? Direct process is basically the reduction process which is carbothermic process. And, we basically use the coal based anthracite to produce the zinc vapor; that means, the coal based reduction can take place with that of your zinc vapor. So, that is your typically direct process based on your carbothermic reduction only.

Then wet chemical process you see that now we will be taking will always be very much fascinated particularly, the people like us the in organic chemist always try to see that what chemical processes we can take place we can see in the test tube. So, wet chemical process is one such process where you use some typical inorganic compounds which are readily available as ore or which can be very quickly converted from some other sources that of your scrap zinc metal ion or some other sources.

So, two such compounds are your zinc carbonate and zinc hydroxide can be precipitated from aqueous solutions for any zinc salt you can take. So, zinc chloride or zinc other material you can use and that can be precipitated; that means, they are insoluble in water as zinc carbonate or zinc hydrox and when you burnt it at 800 degree centigrade we get the zinc oxide as your pigment.

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Then we go for the lithopone; lithopone is nothing, but your mixture of barium sulfate and zinc sulfide and we blend them; that means, is a mixture so definitely you should add some blending material, sometime we can use some organic compound with adhesive in nature. So, with the presence of this organic compound those are not only blending material, but they can also the binder material also such that the uniform mixing of these two solid compound can take place and which can also give you the corresponding opacity, which is required for be considered as a paint material for your compound.

So, it was made popular by the cheap production costs and greater coverage, so it is if it is cheaper than that of your titanium dioxide, zinc oxide we definitely go for this and also sometimes for this wet chemical method we can use very cheaply available zinc compounds or zinc metallic zinc also we basically throw away from some industry. That means, industrial by product for the zinc industry can be used for making this particular zinc pigments or the zinc paints.

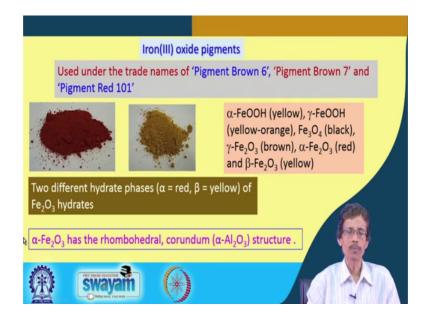
Production is therefore, the co precipitation of these two compounds, these two inorganic compounds together and the combination of equi molar compounds of this, so it is basically two of them are white in color. So, equimolecular mixture or equimolar mixture of these two will give you the lithopone.

So, the reaction is basically with that of your barium sulfide at that of your zinc sulphate, giving you this which are co precipitated together as the salt mixed salt of zinc sulfide

and barium sulphate is not that we are mixing zinc sulfide and barium sulfate together by, but in the solution we produce it from barium sulfide and zinc sulfate. So, is produced by again this particular barium sulfate is produced from barium sulfate.

So, we have to produce this barium sulfate by reduction and zinc sulfate is obtained from a variety of zinc products even for the zinc metal often for the different waste, by the treatment of sulfuric acid which can be sometimes not very concentrated because the concentrated sulfuric acid we do not handle because it can also corrosive in nature and it can also oxidize the surface. So, it is basically less concentrated sometimes 1 is to 1 sulfuric acid can be useful for converting your any zinc metallic scrap to your zinc sulfate.

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Then we go for the other colored iron III oxide pigment which are not white in color we have already categorized these as the corresponding rate to brown pigment and under the trade name basically they are known as the pigment brown 6. So, when we take these names basically as the pigment name we do not have to know whether it is the iron 3 pigment based on iron 3 oxide; that means, Fe 2 O 3; Fe 2 O 3 is a trivalent iron or any other thing.

So, it can have some other brown compound to be mixed that is why we have the corresponding trade name at brown 6, brown 7 or red 101, but categorically the compound wise the pure compound wise we can have all these different compounds

starting from yellow to black. So, alpha iron oxo hydroxo compound and Fe OOH; that means this is the hydrated form of the oxide is not that of your pure oxide, but the hydrated form of the oxide, so oxo hydroxo compound is yellow in color, then the gamma variety is yellow orange in color.

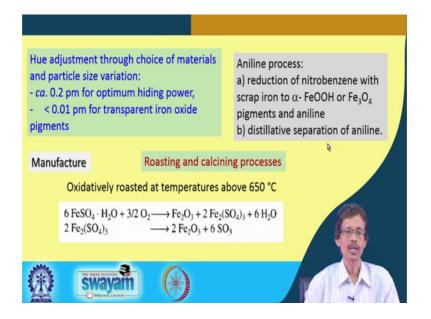
Similarly the ferrous of ferric oxide Fe 3w O 4 we all know that the magnetite particles are black in color, then gamma Fe 2 O 3 the ferric oxide in the gamma form is brown, alpha form is red in color and the beta form is yellow in color. So, the solid state structures are different and solid state colors are different that is why we can use them differently for different purposes for making different types of all these pigments.

So, two such different hydrated phases we can have is for the Fe 2 O 3 1 is alpha in the left hand side one is that is the your red form and another is the beta; beta is the yellow or the dark yellow type of compound because of that, so that is why we level to that of your inorganic solid material as whether you are having an alpha form or a beta form which is based on your iron oxide pigment that can be used for other additives to give you the corresponding paints and the use of that pigments in the soluble form.

Then you have the alpha Fe 2 O 3 which we have seen that is red in color and that alpha Fe 2 O 3 has a rhombohedral structure because the structurally they are different that is why the color for the light scattering is also different. So, they are giving a different types of color, so they have the corresponding alpha alumina structure alpha alumina is nothing, but your Al 2 O 3.

So, that has a very similar structure that of your aluminum sorry iron as trivalent. So, trivalent aluminum and the trivalent iron have very similar ionic radii and those ionic radii are matching giving you very similar structure for that particular purpose.

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Then we see what we have seen just now I told you also that how we go for the hue adjustment; that means, we can get different colors by knowing the corresponding color in our hand if we have a red pigment or a blue pigment we can mix them together to such that we can get a violet variety. So, like that of your when we know a artist can draws that pigment we can go for some basic color; that means, the primary color to the secondary color to the corresponding tertiary color.

So, how you get the primary color is the 3 different colors what do you all know the red, that blue and the green. So, the red blue and green, if we mix them together we can have the different hue and the different color. So, the hue adjustment can be achieved by mixing of the materials and of the particular size. So, we use in most of these cases at 0.2 picometer size of those particles.

So, the particles are not in a particular range of this sometimes we have seen also that how the nano particles; that means, the nanometer regime size of those particles are useful some particular special purpose. Similarly in the picometer range of 0.2 picometer size of these will have the very useful hiding power and when they are little bit be corresponding little bit more; more smaller which is in the each 0.01 picometer are transparent for iron oxide pigment. So, these particular size are basically transparent for iron oxide pigment.

So, how we get the different sizes of all these things all these compounds is the manufacturing process is basically. One first step is your roasting process and following roasting you should go for the corresponding calcining process; that means, the heating. Then we go for the oxidatively roasted temperatures above 650 degree centigrade temperature we take the corresponding sample as your simple ferrous sulphate.

So, ferrous sulphate with oxygen you go for the roasting and is the basically the burning of these producing Fe 2 O 3 of one type not that of the type what we are looking for making the corresponding pigment, but along with that we get the ferrous sulphate. So, when you burn it; that means, for the calcining process that not only your ferrous sulphate is burning, but this Fe 2 O 3 which is originally formed in the first step of the reaction is also getting burn.

So, you get the full form of these; that means, Fe 2 O 3 you are forming and along with that your by product is also a very useful product which is a sulphur trioxide which we are getting from the sulfate anion and that sulphur trioxide we know that the sulphur trioxide can be useful for the production of the sulfuric acid industrially. Then one particular process which is very much useful also some time that the aniline process; that means, we use nitrobenzene, so nitrobenzene is being used with the scrap iron.

So, nitrobenzene ways is basically use for the formation of this alpha FeOOH or Fe 3O 4; that means, the scrap iron is basically oxidized with that of your nitrobenzene and we get these as the corresponding pigmental form as FeOOH and Fe 3O 4 and aniline is the corresponding reduced form of the nitrogen and aniline can be your very good by product also. The way we know the organic chemistry, when we try to convert nitrobenzene to aniline we add iron as iron particles or iron corresponding scrap iron in some acidic medium.

So, that particular reaction we can use for the production of your material what we are using earlier for the conversion of nitrobenzene to aniline because you have the corresponding by product of aniline. But that can also be a very good chemical process for the production of your iron based this material as your pigmental material. Then we go for the distillative separation of aniline; aniline has to be distilled out to get back your corresponding iron as your oxide form.

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Then we get for the corresponding cadmium pigments and these cadmium pigments are very useful of different colors from yellow to red. And already we have seen they are either sulfides or sulfoselenide because not only cadmium sulfide, but also cadmium selenide can give you or impart some useful color.

So, the color variation you see that from the red to yellow or some or some radish yellow type the darker yellow shade is also can be obtained. So, you can control the shades also when you go for mixing of the individual or the primary colors. So, cadmium sulfoselenide is a solid solution therefore, like that of thing what we get for your lithopone is the solid solution of cadmium sulfide and cadmium selenide, so is that so I known as the sulfoselenide compound.

And properties based on this cadmium compound because nowadays we have outdated this use of cadmium because the cadmium is not so good material is harmful also, but still we use for some special purposes like use of your cadmium as cadmium battery. So, cadmium (Refer Time: 13:32) we use, but the production is day by day it is deteriorating or declining, we are not producing huge amount of cadmium pigment for the red and the yellow or the orange type. Because the substitution the useful substitutions are there to avoid the cadmium which is a toxic metal iron even in the corresponding ionic form or the free elemental form. So, it has high tinting strength, it has high brightness that is why

they those have been chosen as your corresponding pigment material for inorganic paints.

Better thermal stability because high temperature withstand is there where you do not have the corresponding leaching property of that cadmium in some enamel or the ceramic material, we definitely can use this material because these are all chip. During the pigmentation of plastics also and because: it can withstand a very high temperature with temperature, the color quality, the color type and the color intensity is not fading away with the use of these pigments.

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The manufacturing process is dependent on the use of sodium sulfide and the calcination with that of your cadmium salts. So, you get the cadmium sulphide, the zinc salt and the sulfur if you want to get the corresponding yellow pigment and when you use sulfur along with selenium that the cadmium sulfoselenide that we have seen you can get the corresponding red pigment.

So, individual salts you can ask the zinc as the corresponding reduction for somewhat the reduction material that sometimes the zinc salt is also used, along with their corresponding sulfide for getting cadmium sulfide and sulfur as well as selenium for getting the corresponding sulfoselenide form. And, particle size should be a little bit higher which is 0.2 to 0.4 micrometer in size not that in the picometer range for the very fine particle or in the nanometer range.

So, three different units basically used because most of the time because you can convert and you can think of the sizes also when you talk in terms of the corresponding nanometer size and also the micrometer size. Then one most useful material what we can use is your mixed metal oxide pigments for ceramic coloration, that ceramics material what we have seen earlier that we can make the ceramic material at a very high temperature firing.

So, if we go for some mixed metal oxide pigment mix metal oxide pigments are nothing, but your spinels because the spinels we all know they are mixed oxides. So, if they are colored we can get this for your high temporary resistant because the thermal stability of spinels are much more compared to or the individual oxides. So, you incorporate the color giving the transition metal ions all of them are colored as we know into the oxide host lattice because if you have the host lattice which is colorless like your alumina, aluminum oxide or magnesium oxide is there the host lattice.

And within that you incorporate the corresponding transition metal ion oxides you get the beautiful coloration, which we can heat at a temperature of 100 to 1400 degree centigrade. So, the firing or the heating of the solid at a very high temperature in the range of 1000 to 1400 is useful. So, if you consider say the magnesium which is not a transition metal ion as well as zinc also it can be doped with cobalt which is the coloring material.

So, if you have both magnesium and zinc side in magnesium titanate and zinc titanate, so you have individually if you have the compounds like magnesium titanate or zinc titanate and you dope both of them by cobalt, so cobalt can take the positions of the magnesium as well as zinc. That means, the substitutions in the solid state structure some of the positions by the cobalt, which can give you the corresponding cobalt as the coloring material and the family of cobalt greens because, those cobalt compounds in the solid state structure can impart a type of coloration which is not the corresponding cobalt in the solution which is giving you the corresponding green coloration.

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So, cobalt gets like that of your corresponding minerals or the corresponding stones, we all know that is the cobalt based if they are cobalt based this will be the corresponding coloration is the green coloration. Then we take the help of luminescence which is a very useful thing what we can understand that how we can use the corresponding luminescent behavior for the pigment.

So, they can so the corresponding fluorescence as well as the phosphorescence behavior when they are excited energetically. So, we take very fine particles of these solids when we talk in terms of the corresponding luminescent pigments. And those luminescent pigments are there which has to be activated either we giving rise to the photons or the impingement of the photons or any other radiation source, such that we go for the corresponding excitation of the material when the emit radiation, they are showing side their fluorescence or phosphorescence.

So, they give basically the luminescence behavior or the luminescence property upon excitation. So, you have the excited state, so you excite those particular species which is responsible for your luminescence behavior and when they come out from the excited state to the ground state, they basically give you the corresponding luminescence property which are completely different from that of your other property what we are seeing basically through scattering. So, the transition metal ions or the rare earth ions; that means, the lanthanides or lanthanides. So, the length transition metal ions and the lanthanides are basically can function as the luminescent centers.

So, if like that of your cobalt doping if we can dope the material with that of your transition metal ions or some of these rare earth ions because rare earth ions are functioning as your luminescence centers because the corresponding luminescent behavior of the corresponding lanthanides are well known well established. So, we will give this or add them as sensitizers.

So, sensitizers are basically some compounds of their corresponding lanthanides that be cerium europium and terbium. These three metal ions out of the 14 lanthanide ions we all know that you have the f elements of the 14 in number the first series. So, cerium europium and terbium will use along with antimony and lead also we can have they are also functioning trivalent antimony and bivalent lead can also function as their your the corresponding sensitizing material or incorporated to a very low concentration of 10 to the power minus 2 to 10 to the power minus 4 gram per mole of the material what we are using.

In a crystal lattice generally consisting of colorless oxides, colorless oxysulfides, sulfides silicates, phosphates, borates and halides of what the metal ions are zinc, the zinc sulfide is colorless that is why because other transition metal ions sulfides are colored you should be careful at this point to understand these what we are talking. Then alkaline earth metal ions like barium, magnesium, calcium, oxides to halides all of them are colorless.

So, the metal ions we are changing we are not using transition metal ion and the rare earth metals we are using. So, rare earth metals are also using which are colorless; that means, the corresponding oxides. So, the emission decay time, so a particular emission decay time you can have and the color are mainly dependent upon the choice of the activators.

So, what activators we are used? Those activators like the transition metals and rare earth basically function as the luminescent centers there. So, is dependent so depending upon the metal ion what we are using, so your emission process as well as color will be dependent and which are in the solid state crystal field because this is in the oxide host you have. So, all the oxides basically it is the lattice of oxide ions and you can have the

corresponding holes basically or so the cavities you can have. So, tetrahedral sites or the octahedral sites are occupied by those metal ions depending upon their available ionic site and you get the corresponding crystal field and that crystal field is basically can control the corresponding color.

Because we all know that when water is coordinating to the metal ion you know that is the corresponding crystal field in your hand, but in a solid state when the oxide centers are available which is around the metal ion, that is also imparting the corresponding crystal field such that, you can have the corresponding dd transitions between the corresponding splitting, for the crystal field splitting and you get the corresponding dd transitions to obtain a particular type of color.

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So, this luminescent pigments are therefore, basically we can manufacture by repeated again heating; that means, the calcination process along with sintering of homogeneously mixed raw material because we can have different components which we first homogeneously mix. So, that homogenizer we can also say that the solid state homogenizer you can use, to get the raw material of uniform composition. If we are not happy we can take out the sample and we can analyze for your homogeneity.

And the temperature already I discussed I told you that is in the range of 1000 to only 400 1400 degree centigrade under reducing conditions because the most of the thing we want to reduce in the reducing atmosphere we can have. So, once you get these as the

corresponding luminescent material in your hand, then we want to see that how we can apply those materials. So, the application of those basically we can have for the cathode ray tubes.

So, what we are talking about the inorganic paints and pigments basically and once we introduce those as the corresponding luminescent form; that means, you can simply the paint we can have the corresponding painting or the corresponding coating of the surface, for the cathode ray tubes also which is a very sophisticated item what we can make out of this application.

Then we can have the fluorescent light also that the coating on the glass surface with this particular paint. So, when you go for painting of some particular part we can get something; that means, some effect will getting will be getting out of those surfaces only and very small amount of that material depending upon its power of cover, the coverage power of that particular paint we can have the corresponding uniform very thin covering of that and we can so for your fluorescence behavior when that can be painted for your fluorescent lights; that means, our day to day we use for our tube lights.

Then for your television screens also they placed the screen surface, the screen the glass plate can also be painted. Then radar screens also we can paint with this particular pigment. Then flying spot scanner if you want to spot something with that over the flying object that can also basically a scanner.

Then image intensifiers also we can use for that, then different types of X-ray screens are also used for this particular printing process and sometimes the safety marketing process also we can use with that of your luminescent paints. So, these luminescent paints are therefore, very useful for this particular purpose that from a range of cathode ray tubes to that of safety marketing we can use that particular material.

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Then we can have the corrosion protection pigments and that corrosion protection pigments what we can protect basically day to day we also use that aluminum powder or the red led or the iron oxides. So, we can inhibit the corresponding corrosion of a particular iron surface or the corresponding rod surface with the use of that processes which are basically dependent on the passivation of the surface, how we inhibit the corresponding corrosion.

Then cathodic protection, formation of the protective layer on that particular surface, formation of metal soaps and the pH change also sometimes and neutralization of the corrosion promoters which is responsible for creating that particular corrosion of the surface of that material.

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Corrosion Protection Processes with Different Pigment Types		
type of process	mode of protection	typical examples
electrochemical	passivation by development of ar appropriate potential	n chromates, Pb <sub>3</sub> O <sub>4</sub>
	cathodic protection	Zn dust
chemical	formation of protective layers on metal surfaces	chromates, phosphates
physical	coverage of undercoat	micaceous iron oxide
	-3.0	<b>P</b>
SV SV	vayam (*)	

And with different pigment types what we can have the type of the process basically, what we can see? That for the mode of protection we can have the electrochemical type of process if it is, so we can go for passivation using chromates and lead oxide, you can go for cathodic protection using zinc dust only the zinc painting zinc powder painting.

If the process is chemical, then we can go for the corrosion based on chemical only we can go for the formation of protective layers by using chromates on the metal surface using phosphates. We can also the only the physical process which is operating for your corrosion. So, the physical process of corrosion you can be basically consider by coverage with the undercoat only and micaceous iron oxide because the mica type very small iron oxide particles can be used for this particular purpose.

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So, lastly we will just finish this particular course as well as the pigment area by seeing the very important very well known pigment type is your magnetic pigment. So, it can be used very easily or you can use for different areas for the magnetic information storage, for the tapes the audio tapes or any other tape material.

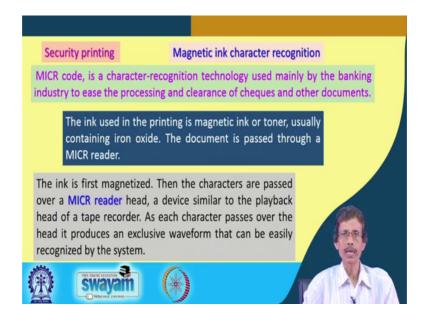
Then drums, the magnetic drums basically we all know the rigid and the floppy discs is based on the magnetization of miniscule solids which are known as magnetic solids, which are dispersed within organic binders that is why giving you the corresponding magnetic pigments. So, when you make all these electronic gadgets and all these things very useful we use some inorganic pigment only thing that your particles should be magnetic in nature.

So, the needles shape particles are their 0.03 to 0.1 picometer, so you the diameter is very less and the aspect ratio what we call the length versus a weight the ratio is 5 to 1 to 10 to 1 10 is to 1 can be also be useful and the products what we are used basically for these are the ferrimagnetic compound, not ferromagnetic these are ferrimagnetic compound like your gamma Fe 2 O 3.

So, the already we know how we can produce the gamma variety of your ferric oxide or ferrosoferric oxide the hematite ore type of thing is the Fe 3 O 4 or other ferromagnetic substance like that of a chromium oxide CrO 2 which is in the tetravalent state and

metallic iron, the metallic iron particles only these are ferrimagnetic compound and those ferrimagnetic compounds are very useful for giving you these magnetic pigments.

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Then for one most important thing that we can use using this magnetic pigment is for your security purpose, the security printing process we use which you all know that MICR the term we already know the day to day we also know that we use it the magnetic ink character recognition process can also be used with that magnetic ink.

So, inorganic pigment is used for producing or magnetic ink and that is used for your MICR code which is nothing, but a character recognition technology which is mainly used in the bank checks in banking industry to ease the processing and clearance of the cheques and other documents by automation; that means, by your computer or some scanner which can read this your MICR code.

The ink is used basically in the printing in the magnetic ink or toner, usually containing that iron oxide just now what we have seen and the document then is passed through your MICR reader. So, MICR reader will read what material is there in your magnetic code in the magnetic coded form within the check. So, the ink is first magnetized, then the characters are passed over the MICR reader head like that of your audio or tape what do we know the head is there.

And that a device similar to that of playback head or the tape recorder and each character when it passes over the head it produces an exclusive waveform. The magnetic signal basically that can be easily recognized by the signal, by the system by the reader. So, you have the MICR reader which can read then and which can identify the check in terms of his number is originality the bank name and the branch everything is known by that of your MICR.

So, you see that the application of the typical inorganic compounds as your paint which can go from your luminescent property to your magnetic property of that particles, it can be oxide particle or it can be metallic particle which can be useful for some useful purposes ok.

Thank you very much.