Chemical Technology
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Module - 9
Dye and Pesticide
Lecture - 2
Dye and Intermediates

We are discussing the module 9 of the organic chemical technology course, and we have discussed the how the chemicals industry in the various modules. We have discussed the how the chemical industry that has been playing important role in meeting the basic demands of the mankind. And the how the growth that has been there what are the driving force for the growth of the organic chemical industry, and starting from the soap to detergent from fertilizer to your means ammonia, which we discussed ammonia to pesticides, and then the petroleum to petrochemicals; and then the final end products the means the polymer elastomer, and the synthetic robot we discussed. But in all making one of the very important actually sector of the Indian chemical industry is there, which is the although it is not as a basic needs which is providing, but it is being used for making or like more colourful.

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And you can see the how the various actually the dyes that is whether you are celebrating the holy or you are wearing the colourful clothes, you are having the colourful toys, you are having the colourful. Now, the lot of the colour pants we are using where you may be

using the pigments, and the large number of other woollen blankets, carpets everywhere you are using huge amount of the dyes in some or other form, so this is the you can see the various seats.

Now, the requirement of the seat that have changed in the paper, it me it is not confined to the only the, because earlier the when people were talking about the dyes and they were thinking only it is being used for the textile purpose.

It is the wide application in the large number of the area that will be discussing about the, when we discussing in detail about the dyes intermediate. Because it is not confine with the textile, it is the paper, it is the laser, it is other number of the application of the here you see the even here, colour, colour different colour different colour we have maintained different colour of the taste we are maintaining and again the dying of the cotton, and then the synthetic fibre.

Because the different type of the fibre they require the different type of the dyes and that was the one of the initial problem, when we have these started making synthetic fibre dying, that was also one of the, because what we need fastness of the dye. So these are the some of the issue involved and at the same time environmental concerned that is also one of the important factors in case of the dyes and dyes intermediate manufacturing.

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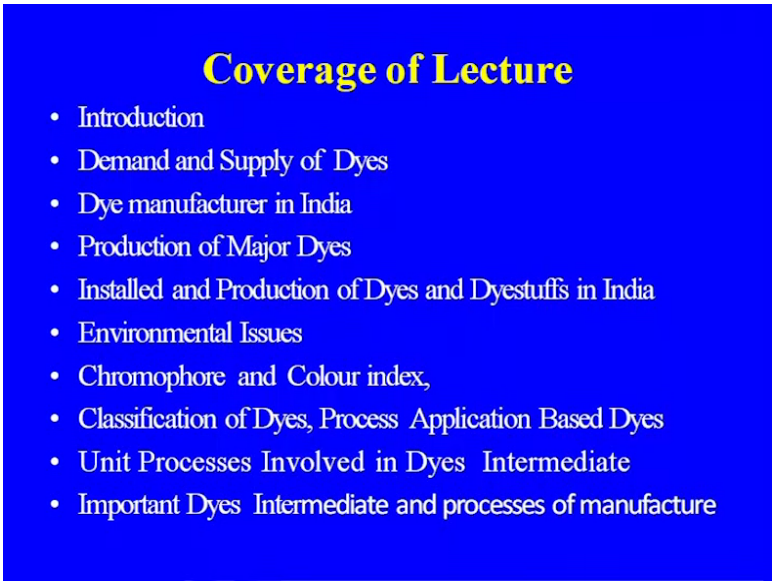

So, the coverage of the lecture that will be introduction classification of the dye, production of the major dyes, chromospheres in the important class of dyes, colour index install capacity of the dyes, environmental issue classification and the process application based dyes.

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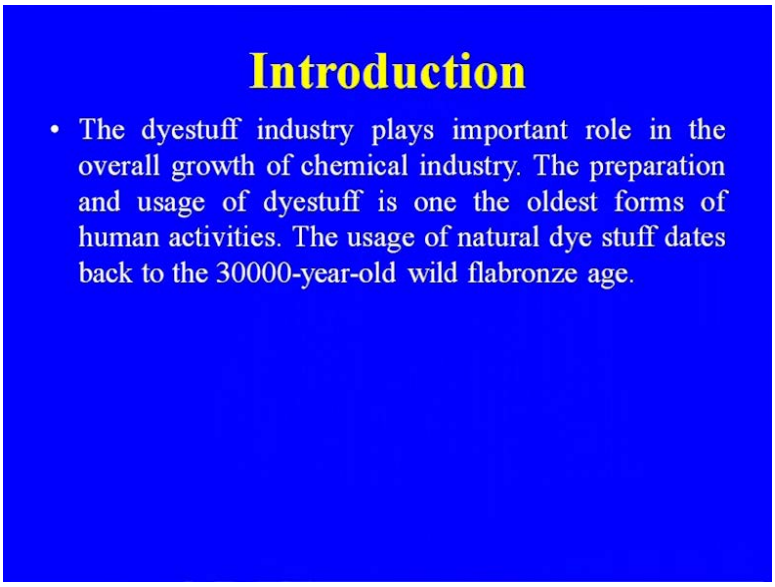

The dyestuff industry plays important role in the overall growth of the chemical industry. The preparation and usage of the dyestuff is one of the oldest forms of the human activities usage of the natural dyestuff. Because the God have provided the nature has provided the natural colours earlier, when it was not no colour was available, no synthetic colour or the manufacture of the colour, the various actually the natural material was there, and even you see the various type of the foods.

We are not using any colour, but it is the god gifted or it is the nature of colour, that is available in those similarly, the some of the colours was available in the nature, just you take the rose, rose is the your colour is the red colour. If you take the some of the vegetables, they are having the different colour. So, this is the how the dye dyes from the oldest forms of the human activities, that is been there usage of the natural dye stuff dates back to 3000 year old wild flabronze age.

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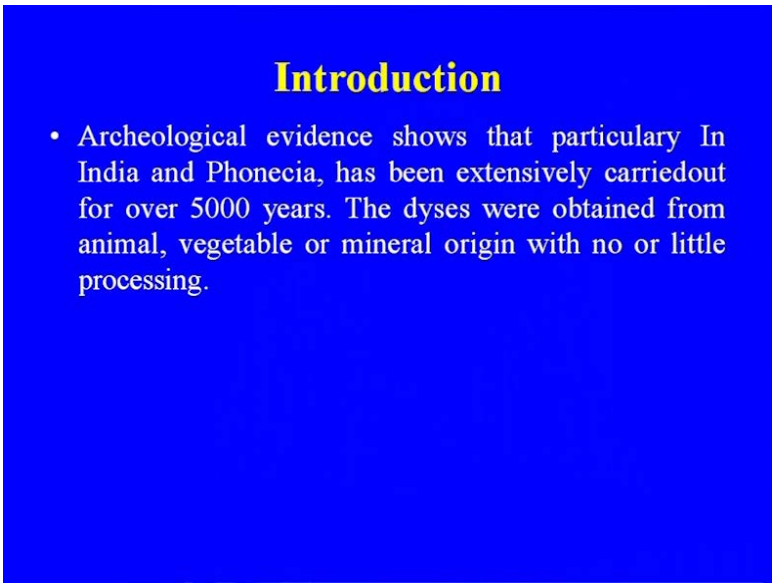

Archaeological evidence shows that the particular in India and the Phoenicia has been extensively carried out for over 5000 years, the dyes were obtained from the animal vegetables or mineral origins with no or little processing. So, this was the original route of getting the your dye.

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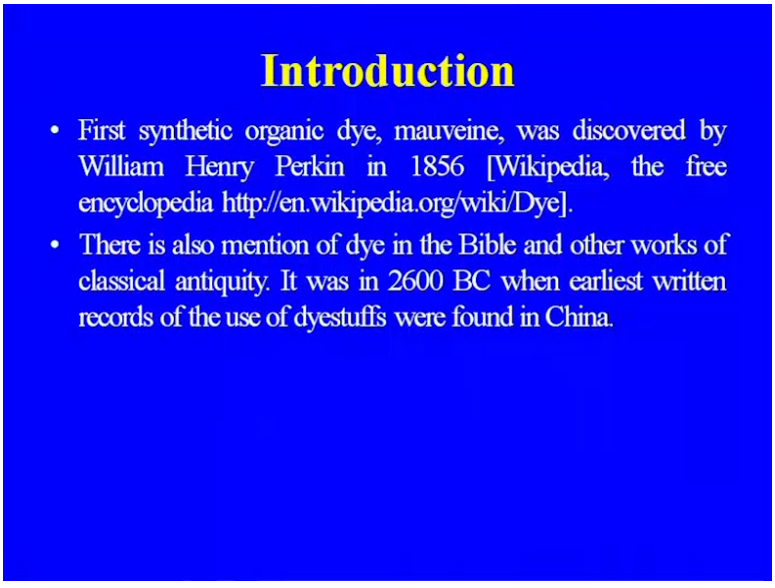

First synthetic organic dye mauveine was discovered by William Henry perking in 1856, there is also mention of the dye in the bible and other works of the classical antiquity, it

was in 2 2600 B C when earliest written records of the use of the dyestuff were found in China.

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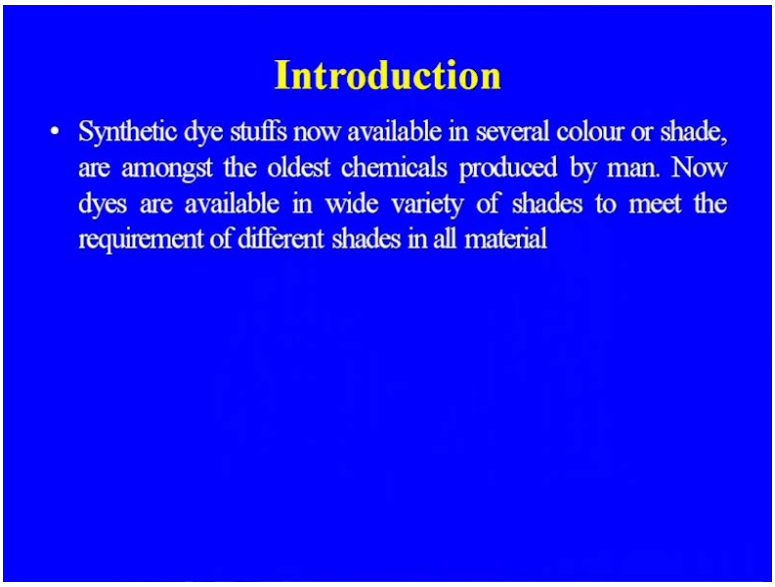

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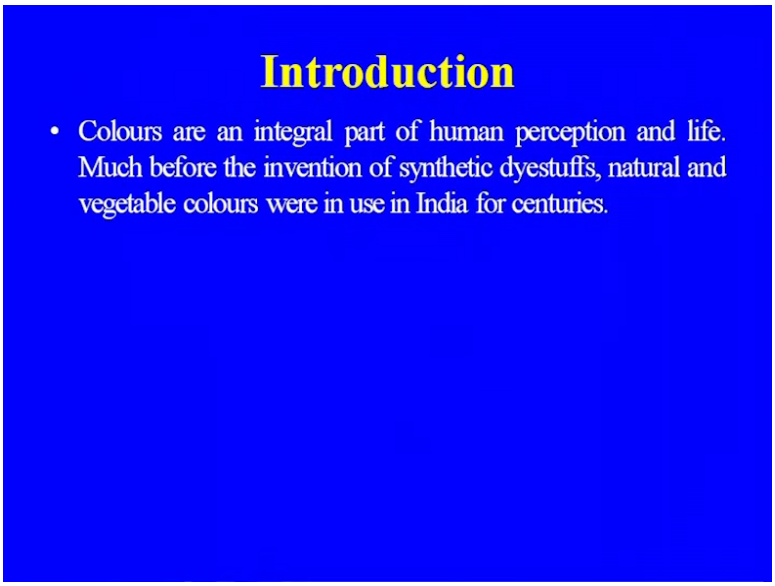

Synthetic dye stuff now available in several colour or shade are amongst the oldest chemical produced by man. Now dyes are available in the wide variety of shades to meet the requirement of different shades in all the material. All you see the whether you taking the cloth, you are taking the paper, you are taking the plastic material different type of

the colour even the colour coated colour, that you are finding on the metal colourful metal metallic materials are available for the decoration purposes.

Colours are integral part of the human perception, and life because this is making our life colourful as I told you earlier, also much before the invention of the synthetic dyestuff natural and vegetable colours were in use in India for centuries.

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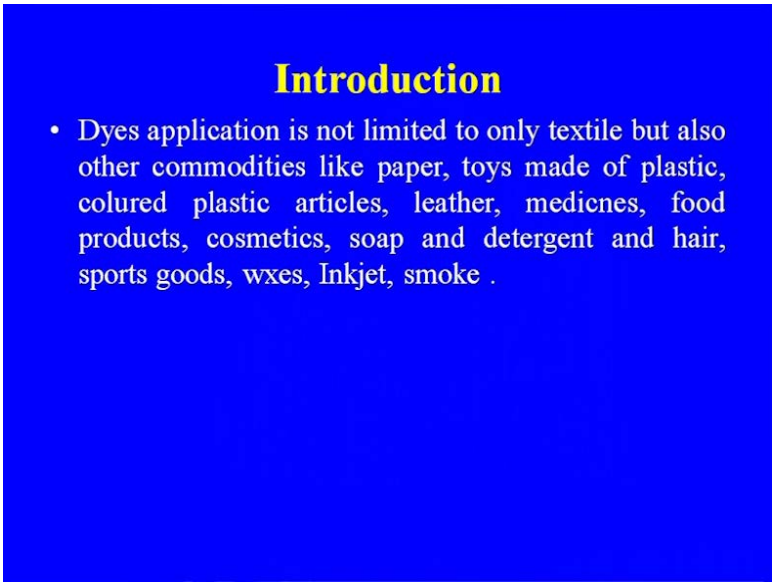

Dyes application is not limited to only textile as I told you earlier that the but also other com commodities like; paper, toys made of the plastic coloured plastic, articles, leather, medicines. You must have seen the colours that we are also using the medicine, food products, you go to sweet shop; you will find the colour of the sweets are available some are using the although the food colour colour that that has to be use. But different even they colouring the pulses, also many of the materials are to give the better appear, even the I have seen that the people they are colouring their vegetables also.

So, the product the dyes there are it is not limited to your textile cosmetics, different shades of the cosmetics that you are fine soap and detergent they are also the colour different shades of the colour that is available.

That the soaps are there detergent bleach, and the white is different colours are there in case of the hair dying people are using at the hair dye. And so that is also one of the dye,

sports wood, waxes different shades of the waxes that is available in market, Inkjet smoke that is for the military operation that we are using the colour.

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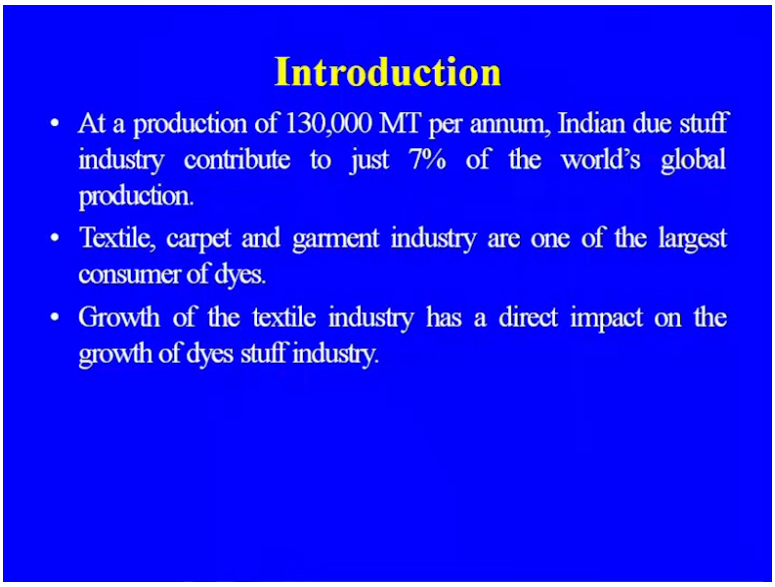

At a production of 130000 metric ton per annum, Indian dye stuff industry contribute to just 7 percent of the world's global production. Textile carpet and garment industry are one of the largest consumer of the dyes, because these are the huge amount of the dyes we are using, and depending upon the so far the textile carpet then garment industry concerned, depending upon the type of the whether you are having the cotton material, whether you are the synthetic fibre, you are having the viscose the requirement of the dyes and the consumption of the dyes increases. Even the depending upon the type of the you need the because the colour fastness that is very important, so the textile carpet and garment industry. These are the one of the largest consumer of the dye.

Growth of the textile industry has a direct impact on the growth of the dyes stuff and because, you see the most of the textile industry they were concentrated in the Maharashtra and the Gujarat, and they will find the large number of the manufacture of the dyes in those region of in India.

That the Maharashtra and Gujarat are there other states are also dying manufacture are there and just take the case of the Kanpur, where also we are having the textile industry and, so there also the some dyes but, the major producer of the dyes are in Maharashtra and the Gujarat.

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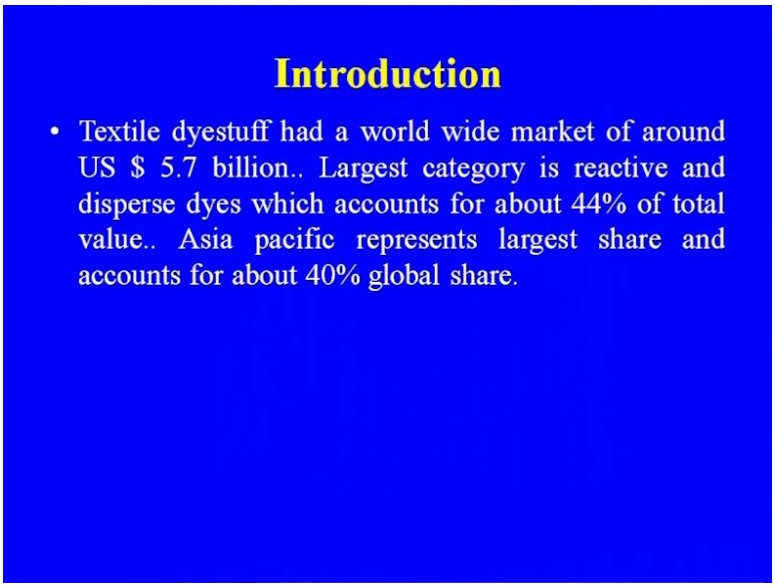

Textile dye stuff had a word wide market of around 5.7 billion; largest category is reactive and disperses dyes, which accounts for about 40 per cent of the total value. Asia pacific represents largest share and accounts for about 40 percent of the global share.

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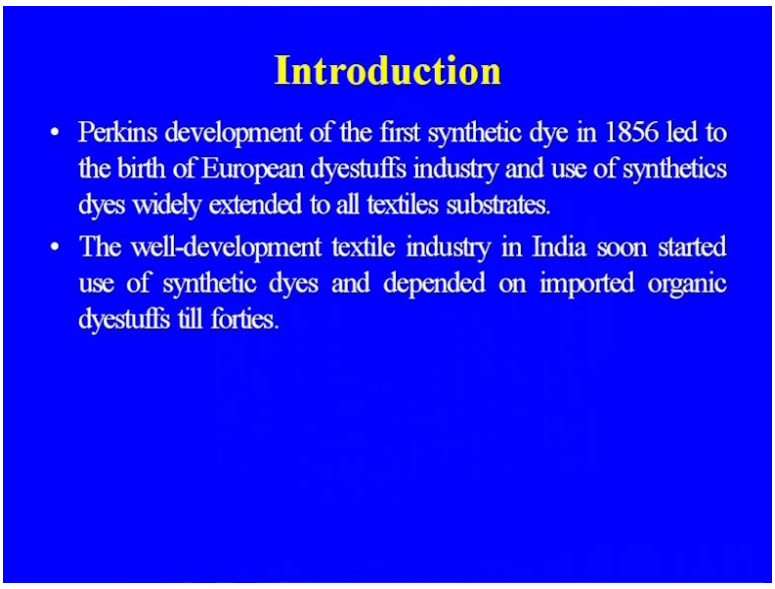

So, this already I discussed the Perkins was the first person who discovered the synthetic dye 1856 lead to the birth of the European dye stuff industry, and use of the synthetics dyes widely extended to all textile substrates.

The well development of the textile industry in Indians seen started use of the synthetic dyes, and dependent dependent on the imported, because that was totally the imported organic dyestuff till forties, and after that after getting because as it is I told you earlier the petroleum or the petrochemical industry.

The revolution in the chemical production that is started after coming of the petrochemical complexes, and production of the chemicals from the same thing because here, also in case of the dye industry we are using the huge amount of the raw material, which is derived from the petroleum rate, now earlier it was derived from the coal route which was earlier route as I told you in case of the many of the chemicals also the coal to the calcium carbide, and then acetylene other routes were there or the from the coke oven plant if you see the a large number of aromatics we are producing, which are being used in the dye industry also in the case of the your pesticides manufacture.

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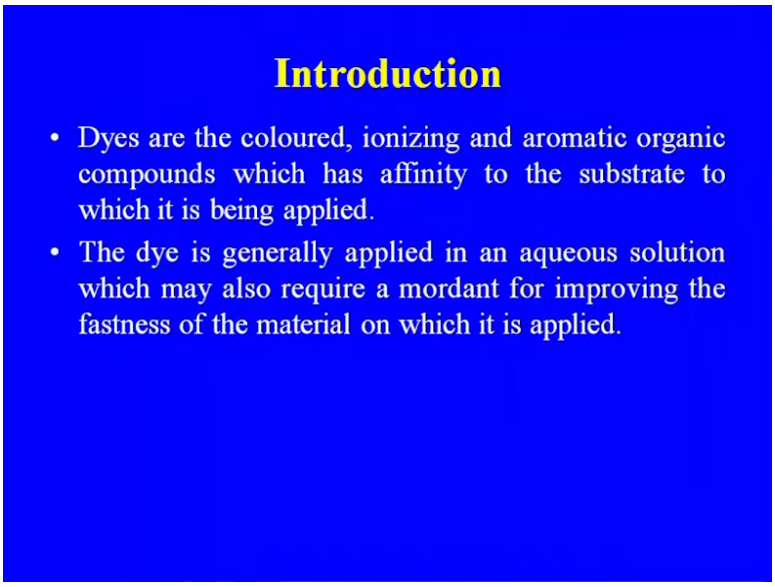

Dyes are the colour, ionizing aromatic organic compounds which has affinity to substrate to which it is being applied. The dye is generally applied in an aqueous solution which may also require a mordant for improving the fastness of the material on which it is applied. Because, fading of the colour that was the major issue earlier but, now you will find the with development of the large number of the dyes. Now the colour fastness is there they your colour fading is less. So, this is the one of the major development in case of the use of the dye in the textile industry that has been there.

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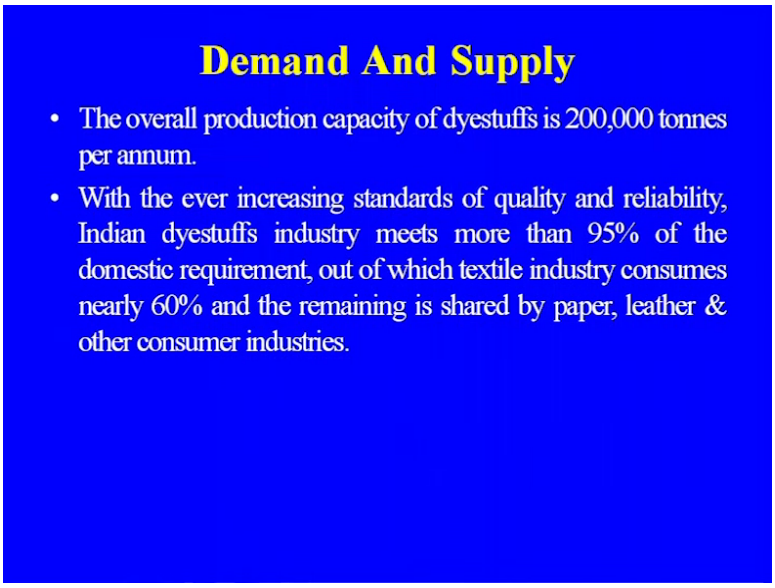

The overall production capacity of dyestuffs is 200000 tonnes per annum with the ever increasing standards of quality and reliability, Indian dyestuffs industry meets more than 95 percent of the domestic requirement, now out of which textile industry consumes nearly 60 percent, and remaining is shared by leather, paper and other consumer industry.

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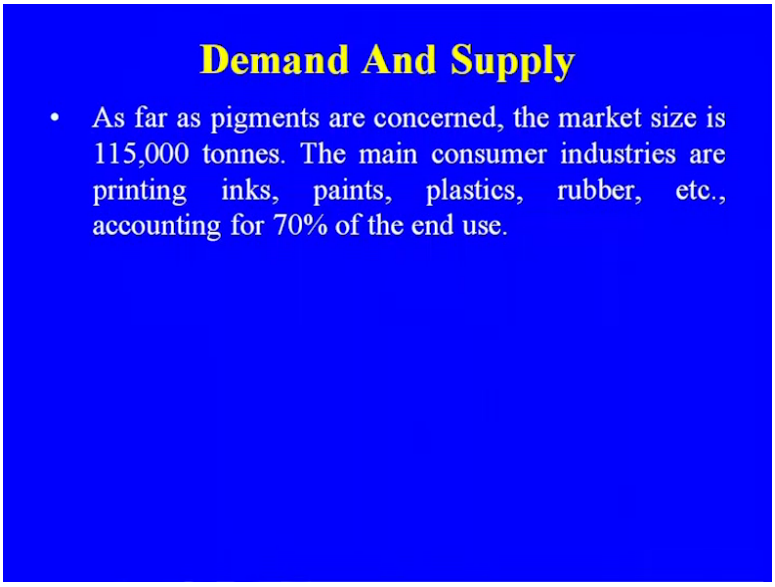

Because as I told you earlier also that the dye or colouring of the fabric is not only there but, the dyes are also being used for the colouring of the wide variety of the material

articles starting from the paper, leather to cosmetics, and so on n number of products which we discussed earlier.

As for as the pigment, because pigment is also one of the very important part of the dyes industry, so as far the pigments are concerned the market size the 115000 tonnes. The main consumer industries are printing inks, paints, plastics, rubber and accounting for about 70 percent of the total end use.

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Installed and Production of Dyes and Dyestuffs in India,000 tonnes

Major Groups/Products	Installed Capacity (2009-10)	Production (2010-11)
Azo Dyes	8.70	2.80
Disperse Dyes	6.50	0.53
Fast Colour Bases	0.60	0.09
Ingrain Dyes	0.50	0.70
Optical Whitening Agents	3.40	3.04
Organic Pigment Colours	11.00	21.83

These are the some of the data available from the ministry of chemical and fertilizer and the from the annual report, you can see that the installed and production of the dyes and dye stuff industry. So, this is installed capacity and this is the production figure azo dyes, disperse dyes fast colour, bases ingrain dyes, optical whitening agents, organic pigment colours. So, this is the installed capacity and this is the production is the figure is multiplied by 1000.

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Installed and Production of Dyes and Dyestuffs in India,000 tonnes

Major Groups/Products	Installed Capacity (2009-10)	Production (2010-11)
Pigment Emulsions	6.30	5.63
Reactive Dyes	7.90	2.40
Sulphur Dyes(Sulphur Black)	3.30	8.60
Vat Dyes	3.00	1.60
Solubilised Vat Dyes	0.10	0.04
Napthols	3.60	0.07
TOTAL	54.90	47.33

The pigment emulsion, reactive dyes, sulphur dyes, vat dyes, solubilised vat dye, naphtha's etcetera.

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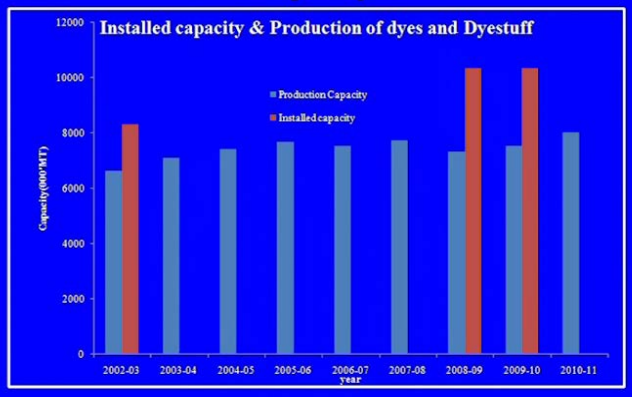
Product wise installed capacity & production of Major dyes



So, this is the product wise installed capacity of the production that the of the various dyes capacity, and production that is given their production is the in the blue and this is the your installed capacity. So, the here you can see the capacity utilization in this definitely lower in case of the dyestuff industry.

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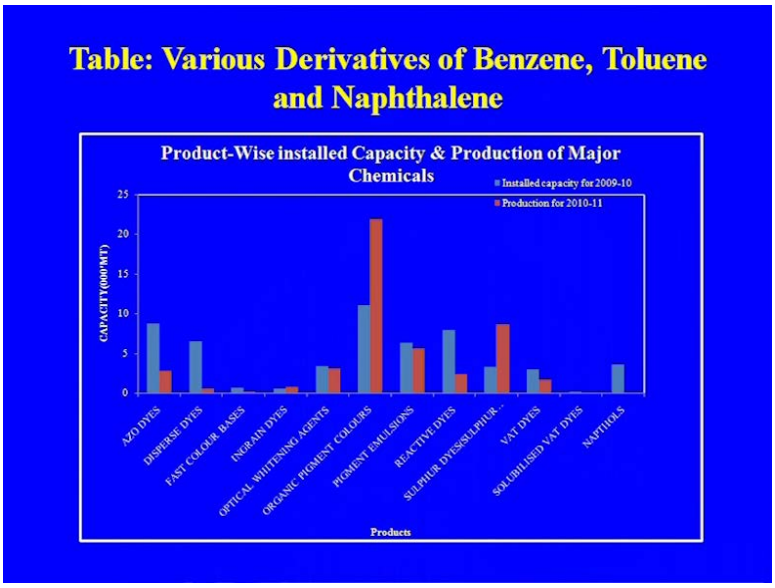

This is also the various derivatives of the benzene, toluene, naphthalene which are the major chemicals, which are being used in making of the number of the your dyes, which are the azo dyes, and other dyes are there disperse dyes, so these dyes are consuming the raw material benzene, toluene or the naphthalene.

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Demand dye manufacture in India, most of the dyes and intermediate industries are located in Gujarat and Maharashtra both the states are responsible for the 75 percent of the total output, as I told you earlier also, because these are the state, where the textile

industry that was developed and the large number of the variety of the textiles starting from the cotton to polyester the acrylic fibre that we are making.

And, so the major consumption is also there, and these are the list of the some of the major actually the manufacture of the dyes in Gujarat atul dyes and chemicals, amar dyes that is in Maharashtra also, if they are having the Gujarat unit, Kolar jet, Mumbai jay chemicals, Gujarat Kevin's, India Ciba dyes, Sandoz colour chem and this is only the major manufacturer, which are there but, a long list of the pasties this dyes manufactures are there. Even some of the companies are there what are doing the only the marketing part of the even for making of the...

So, for the difference shades are this of the same colours are concerned, that is also art you can show because they are mixing the different type of the dyes and making the different shades.

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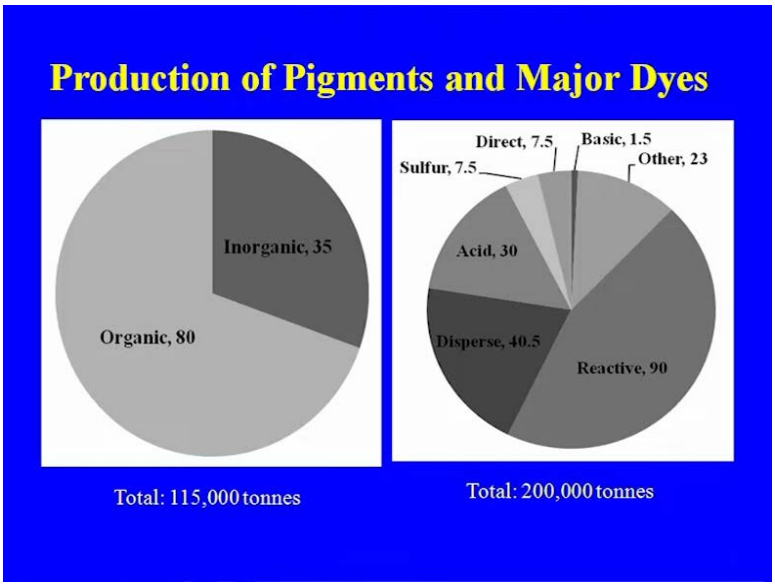

So, this is about the production about the pigment and major dyes. So, organic is 80 percent and the rest is your inorganic. So, this is the acid disperse and the reactive dyes and other, so here again you can see the reactive disperse acid dyes and the basic dyes, or more this is the then as I told you the earlier also the environmental regidation. Environmental resource that has main concern, even I while discussing the pesticide I told you, same problem here also in case of the dyes.

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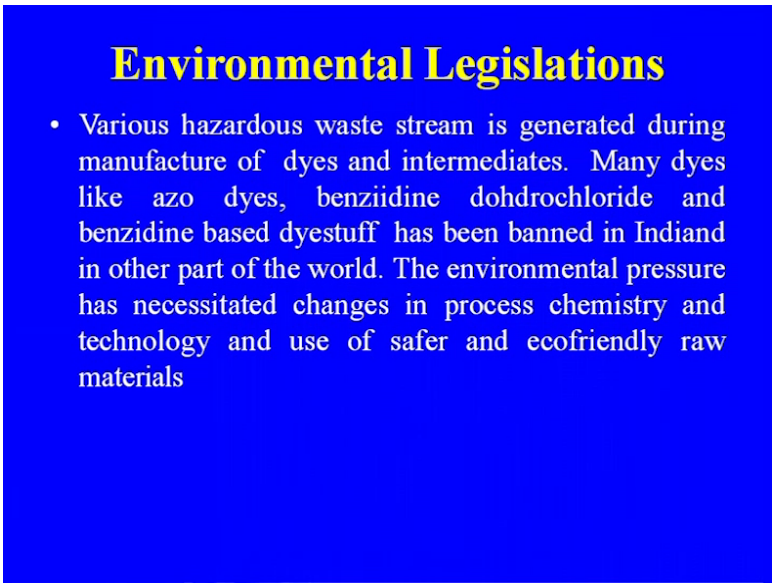

Various hazardous waste streams is generated during manufacture of dyes and intermediates many dyes like; azo dyes, Benzedrine do hydrochloride and the Benzedrine based dyestuff has been banned in India and in other part of the world. The environmental pressure has necessitated changes in process chemistry and technology and use of the safer and the eco-friendly raw materials ah.

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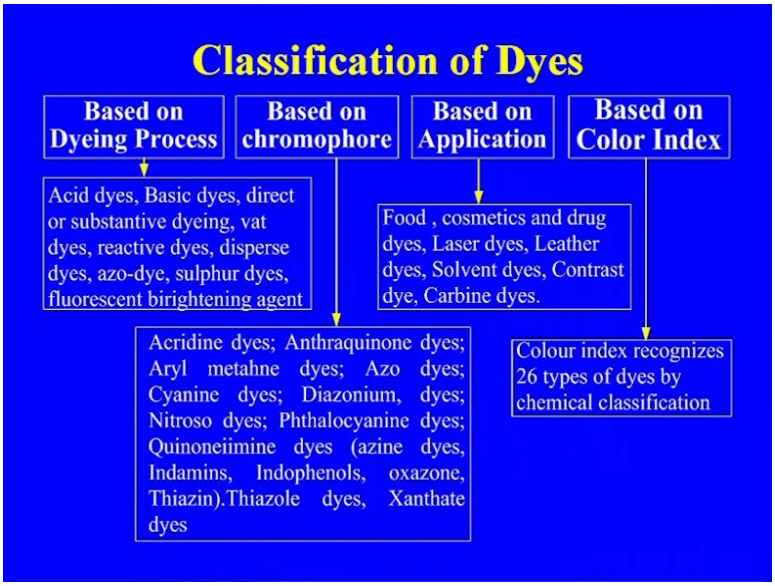

This is the broad classification of the dyes based on the dyeing process based on the chromophore, based on the application, based on the colour index. So, the acid dyes,

basic dyes, direct dyes type of the dyeing your vat dyes, reactive dyes, disperse dyes type of the based on the dyeing process based on the chromophore acridinedyes, anthraquinone dyes, aryl methane dyes azo dyes. So, this is based on the chromo based on the application food, cosmetics, drug, dyes, laser dyes, leather dyes, solvent dyes, contrast dyes, carbine dyes.

So, different grades based on the application also the classification of the dye, because you see the food dyes, food dyes that should be the for the addible dyes, that we can say that the otherwise it will be because many of the dyes are carsogenic. So, will have to take care while using the dyes for the colouring of the food material. Based on the colour index that I will be discussing module; colour index that has been given to the different dyes, and based on this because that is one of the major broad method of classification of the dyes, also there based on the colours if you are giving the colour index number, so you can find the same shade of the dyes otherwise lot of the variation from batch to batch is there while making, the dyes from one batch to another batch there may be the variation.

So, the based on the colour index we are maintaining the particular shade of the colour. So, the just to summarise because the how the dyes that has been classified natural or synthetic dyes, because already I told you the earlier the route of getting the dyes were the natural material, and the nature has provided the different colour of the material, and that was being used earlier and synthetic dyes, which are being made from the various chemicals that we are using.

And the acid, azoic, basic, reactive, disperse, sulphur, optical brightness. Leuco dyes; electronic industry they are using oxidation dyes for hair that we are using leather dyes, fuel dyes, smoke dyes, inkjet and sublimation, so these are the different grades of the dyes that we are using in some or other form.

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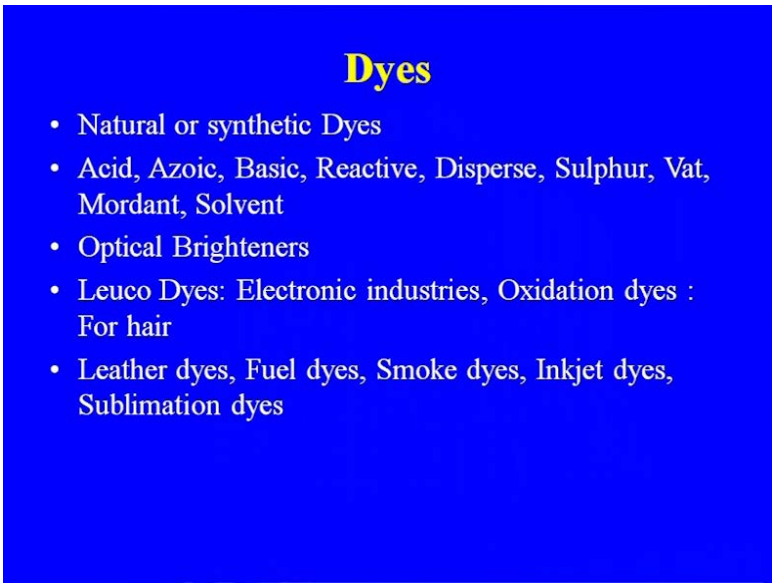

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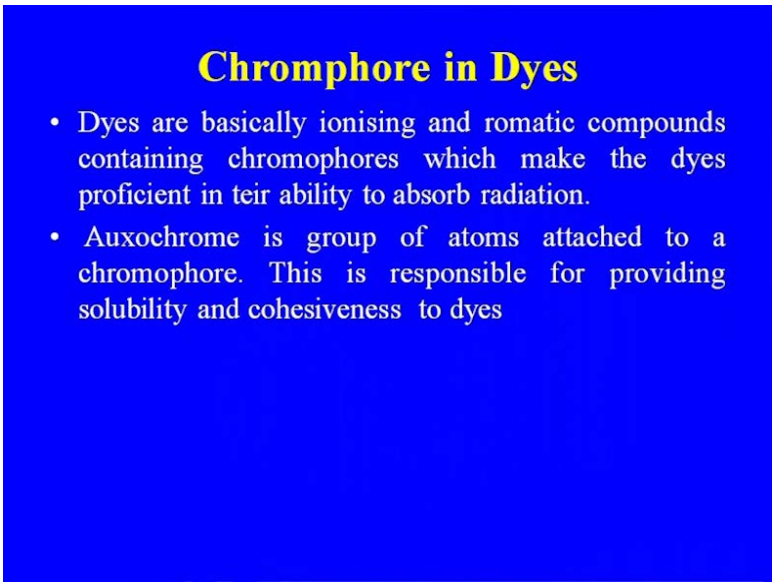

Now, let us see the chromophore because this is very important dyes are basically ionising and ionizing compounds containing chromophores, which make the dyes proficient in their ability to absorb radiation. Auxochrome is group of atoms attached to a chromophore. This is responsible for proving solubility and the cohesiveness to the dyes.

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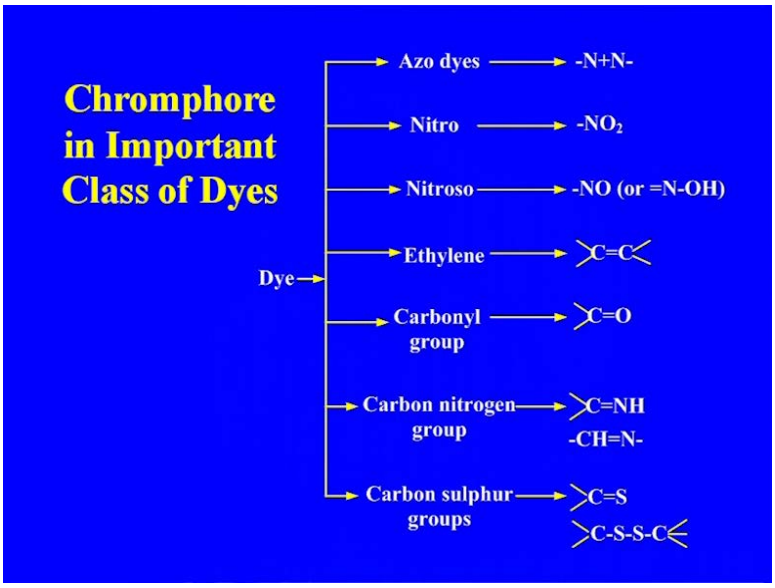

These are the different chromophore in the important dyes; azo dyes, nitro dyes and these are the actually the groups that is available nitro so, ethylene, carbonyl group, carbon nitrogen group and then the carbon sulphur group. So, this is the about the various chromophore in the important dyes and based on this the you are getting the (( )).

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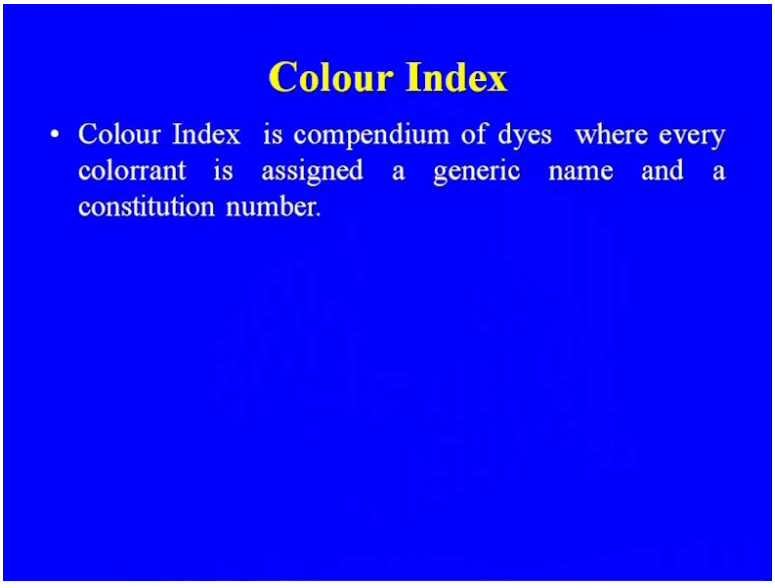

Another actually the classification that is based on the colour index; colour index is the compendium of the dyes where every colorant is assigned a generic name and a constitution number, that has been the European dye industry and the us in the American

dye industry also they have given the colour index here. Now the process application based dye, because normally you see the in the literature and the process we are using the term acid dyes, bad dyes, disperse dyes, direct dyes.

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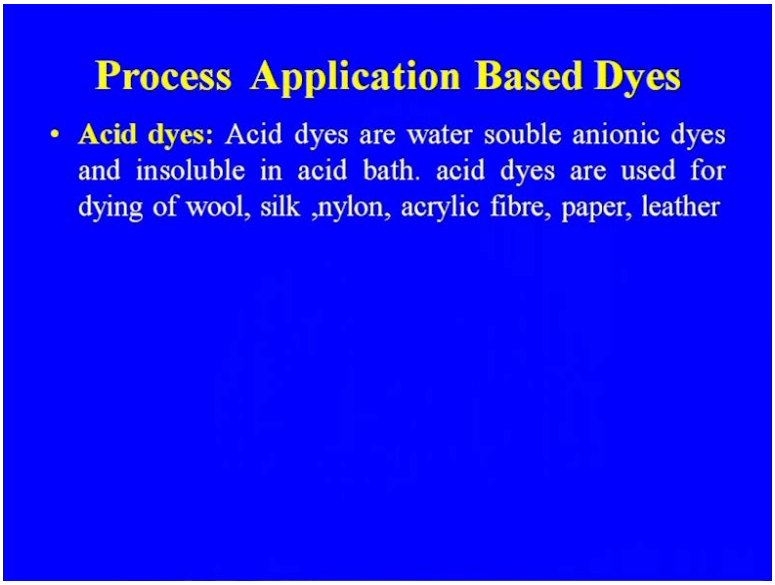

So, let us see thee ach and definition of these dyes. Acid dyes are water soluble anionic dyes and insoluble in acid bath, acid dyes are used for dying of the wool, silk, nylon, acrylic fibre, paper, leather.

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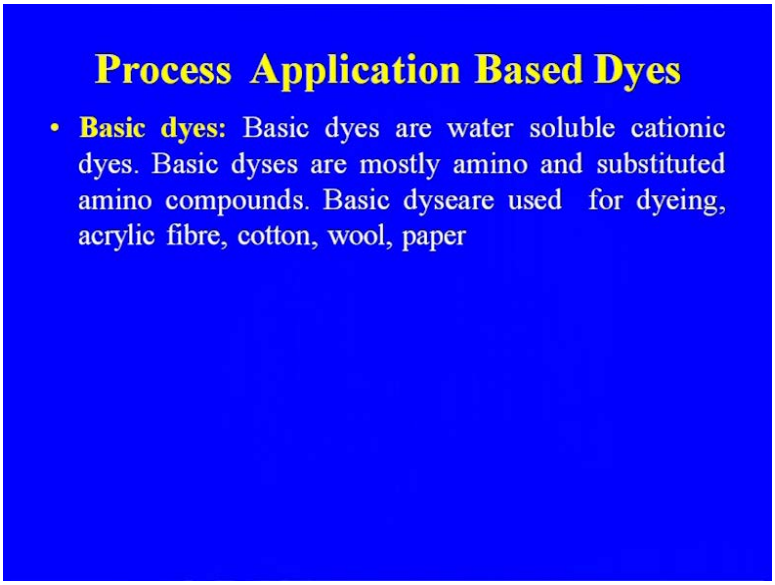

Basic dyes; basic dyes are water soluble cationic dyes; basic dyes are mostly amino and substituted amino compounds. Basic dyes are used for dyeing acrylic fibre, cotton, wool and paper.

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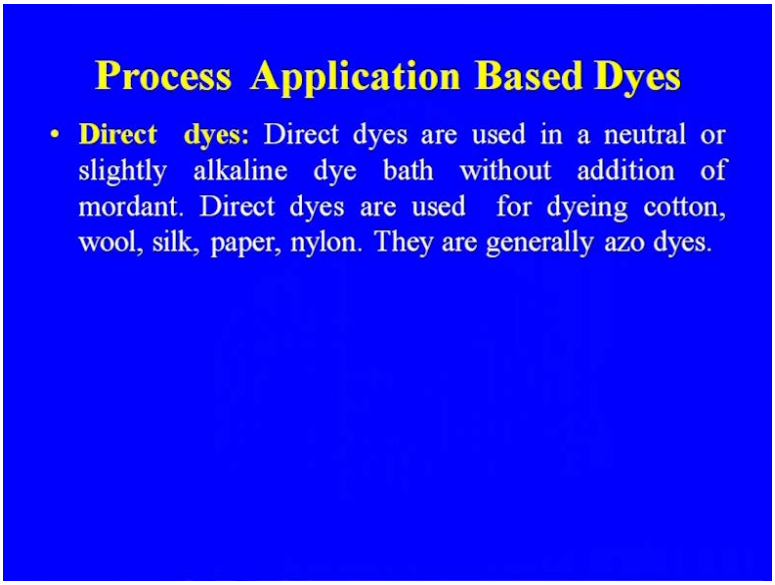

Direct dyes; direct dyes are used in a neutral or slightly alkaline dye bath without addition of mordant, direct dyes are used for dyeing cotton, wool, silk, paper, nylon. They are generally azo dyes.

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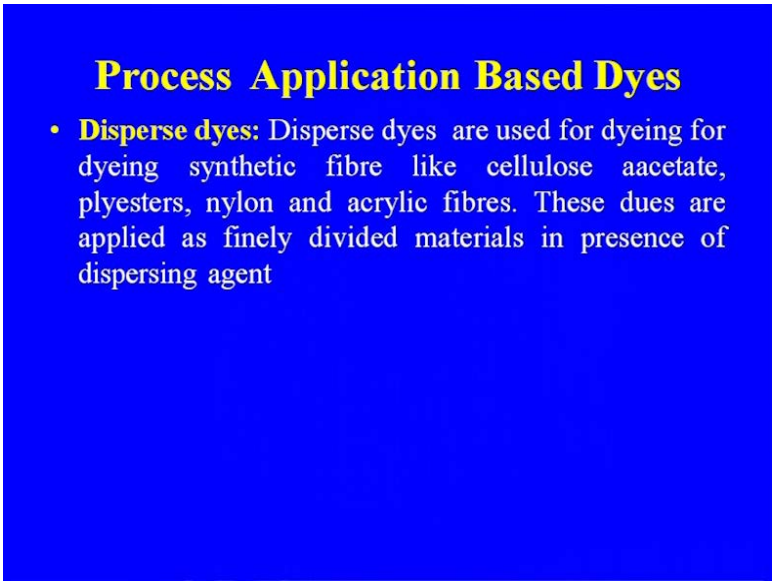

Disperse dyes; disperse dye are used for dyeing for dyeing synthetic fibre like; cellulose acetate, polyester, nylon, acrylic fibres. These dyes are applied as finely divided materials in presence of dispersing agent.

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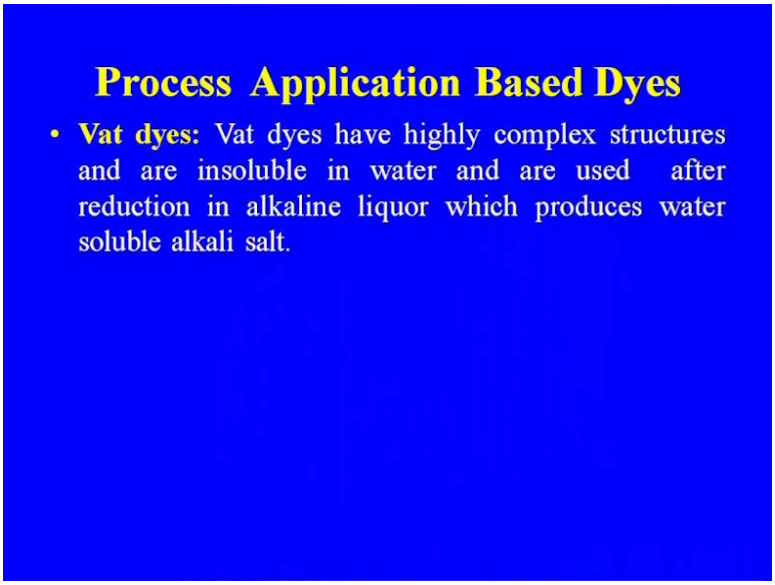

Another type of dyes that is vat dyes; vat dyes have highly complex structures and are insoluble in water and are used after reduction in alkaline liquor which produces water soluble alkali slat.

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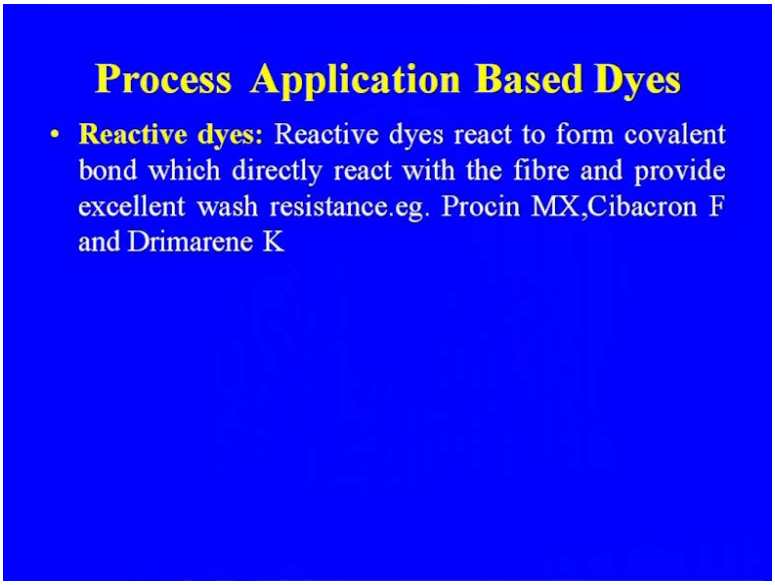

Reactive dyes; reactive dyes react to form covalent bond which directly react with the fibre and provide excellent wash resistance is procin, MX, cibacron and the drimarene k. These are the reactive dyes and as I told you in case of the all the dyes, the fastness of the colour that is very important especially vast resistance, because many of the case of the you must have observe, when you having the cotton fabric the colour fading is more than the your synthetic fibres.

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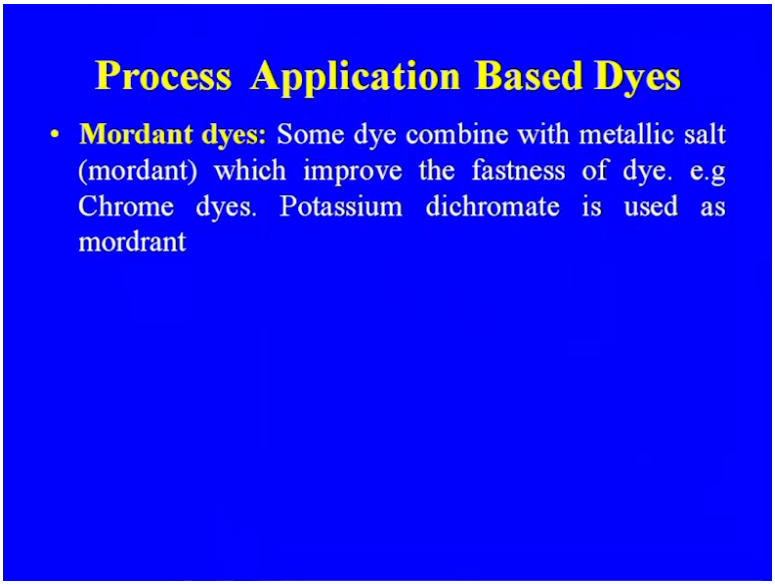

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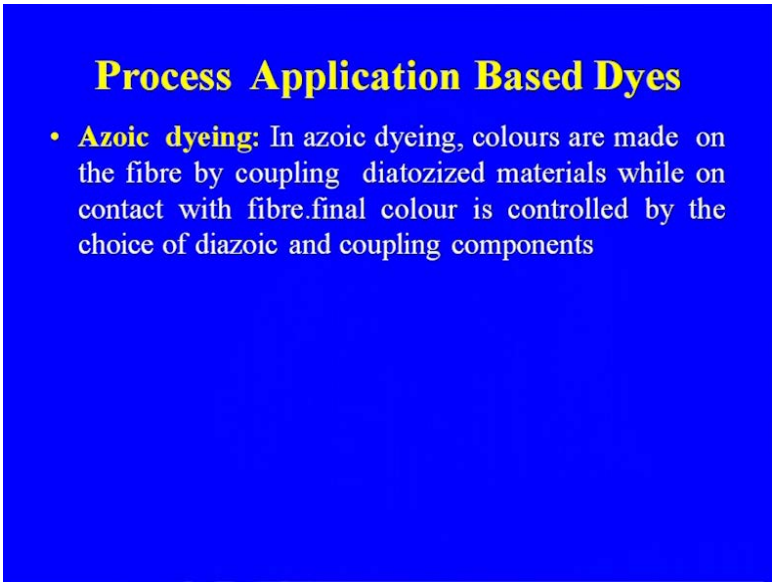

Modern dyes; some dye combine with metallic salt which improve the fastness of the dye. Chrome dye, potassium dichromate is used as mordant. Azoic dyes in azoic dyes colours are made on the fibre by coupling diatozized materials which on contact with fibre, final colour is controlled by the choice of the diazoic and the coupling compounds.

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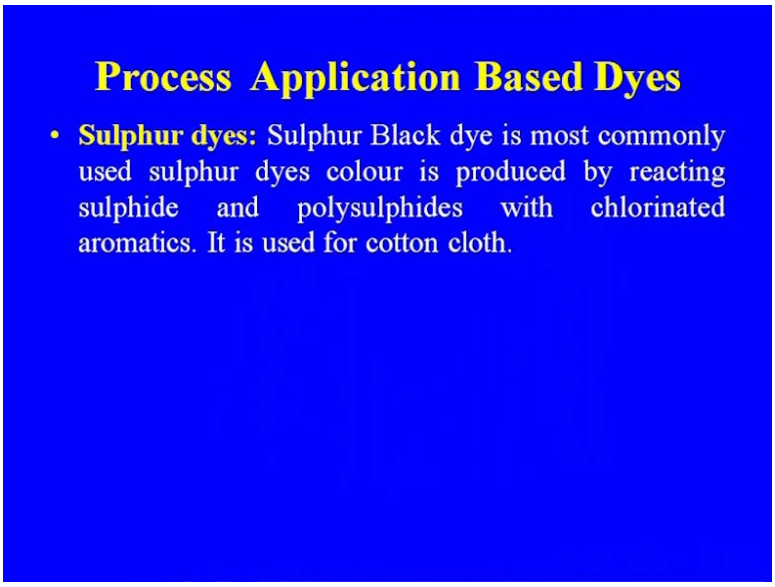

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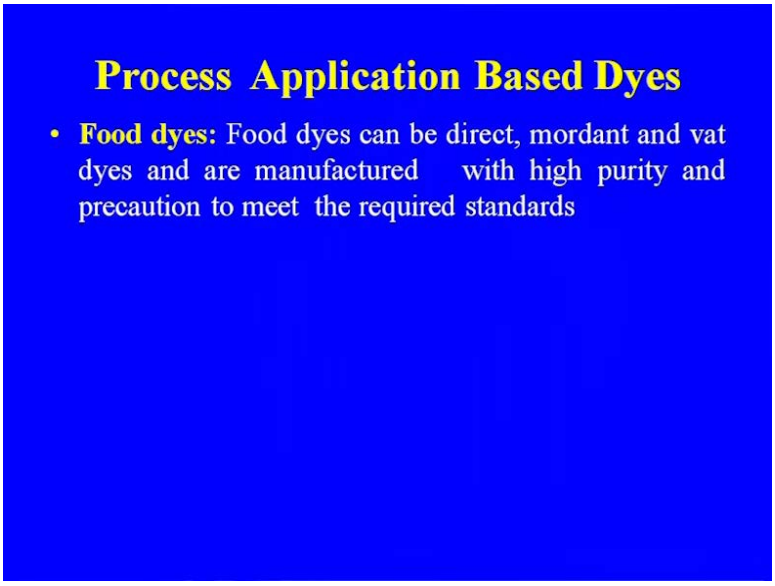

Sulphur dyes; sulphur black dye is most commonly used sulphur dyes; colour is produced by reacting sulphide and polysulphides with chlorinated aromatics it is used for cotton cloth. Now the another and it is use food dyes, food dyes that is uses increasing

day by day even you must have seen in different shades of the colour that is available, whether you are using this chocolates, whether you are going for the ice cream, whether you are going for the sweet or even in case of the various food gills also we are using the colour.

So, food dyes can be direct mordant of the vat dyes and are manufactured with high purity and precaution to meet the required standards that is there for the food dye, especially for separate standards are there for the food grade dyes. So, important dyes intermediate, because you see the one of the process is the first make the intermediation final dyes are made.

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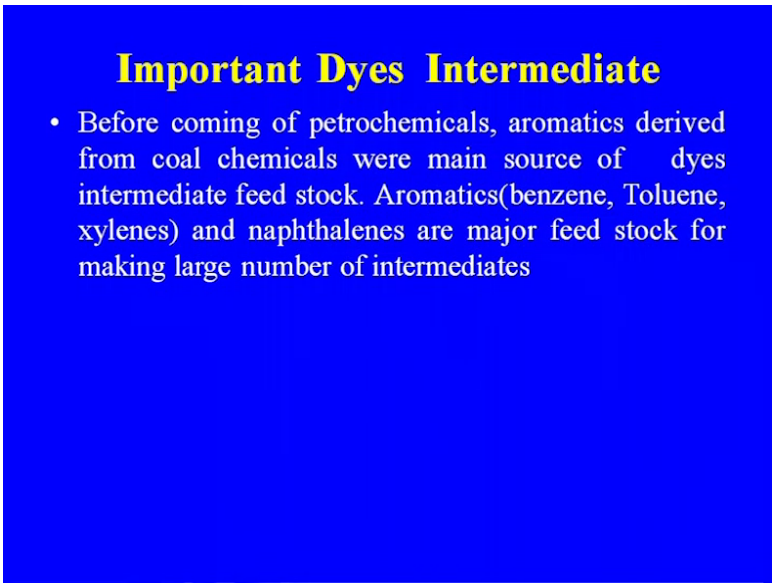

So, before coming of petrochemicals, aromatics derived from coal chemicals were main source of dyes intermediate feed stock, there is aromatics; benzene, toluene, xylene, naphthalene's then are major feed stock for making large number of intermediates. Because, the when you are talking about the aromatics the entire compound, whether these all being manufacture from the aromatics. Similarly from the naphthalene anthondis from the naphthalene, earlier it was orthozile which is also being used in manufacture of dyes intermediate. So, important yes intermediate and if you see the lays most of the cases it is all aromatic compound that we are using.

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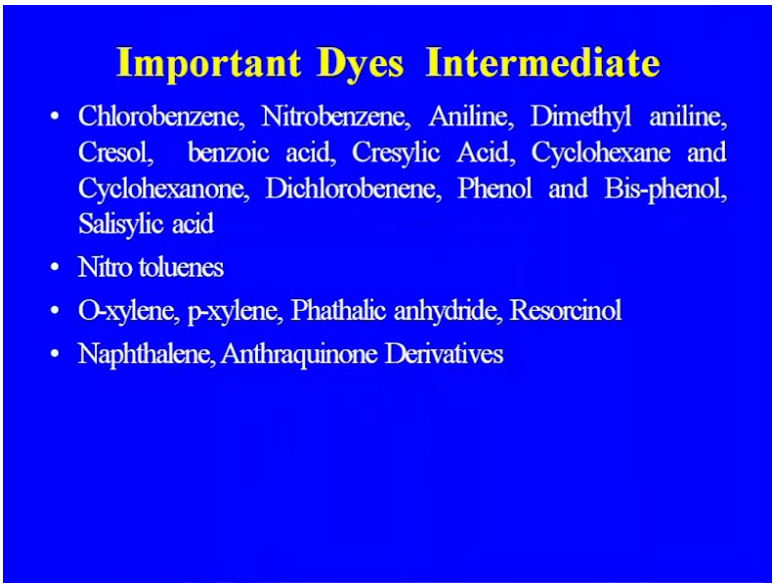

Some are other form this is chlorobenzene, nitrobenzene and finally aniline; these aniline that is being used as the intermediate for making of the number of the tie, that is dimethyl aniline. Cresol, benzoic acid, cresylic acid, cyclohexane, cyclohexanone dichlorobenzene, phenol, bis-phenol, salisylic acid. Salisylic acid also again a product we are getting from aniline but, salisylic also salisylic acid hug amount of that is being used in the gaspine, but here also this some of the usage of the salsylic acid, there are there in dye intermediate.

Nitro toluene, ortho xylene, para xylene phathalic anhydride, resorcinol, naphthalene, anthraquinone, derivatives, so these are the various intermediated and if you see that the manufacture of these and cost reduction that is there only because of the coming of the petro chemical complexes and the petrol (()), where we are getting aromatics are the other petro chemicals.

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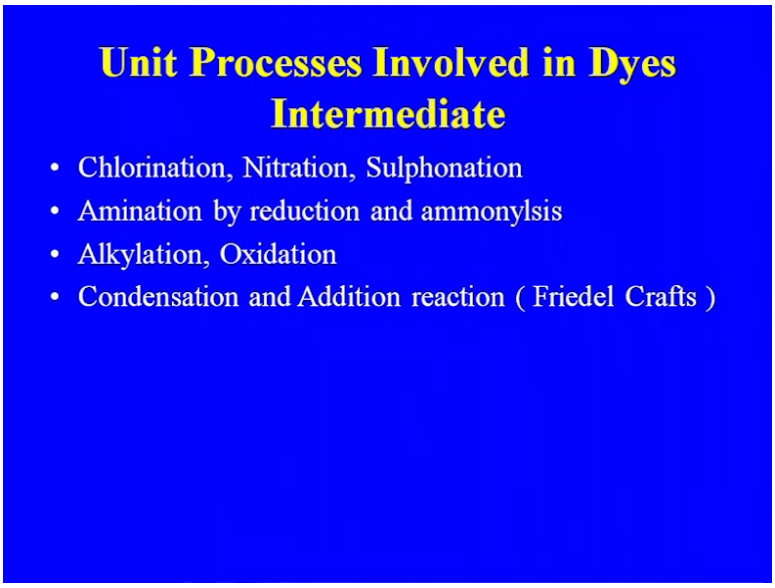

These are the various unit process involve in dyes intermediate. That is chlorination, nitration, sulphonation, amination by reduction ammonylsis, alkylation, oxidation, condensation addition reaction nitration, here the mix acids some of the cases we are using in mix acid. So, the use of the nitric acid, sulphuric acid both are there similarly, chlorination for each that we need the chlorine, so, the requirement of the chlorine will be there.

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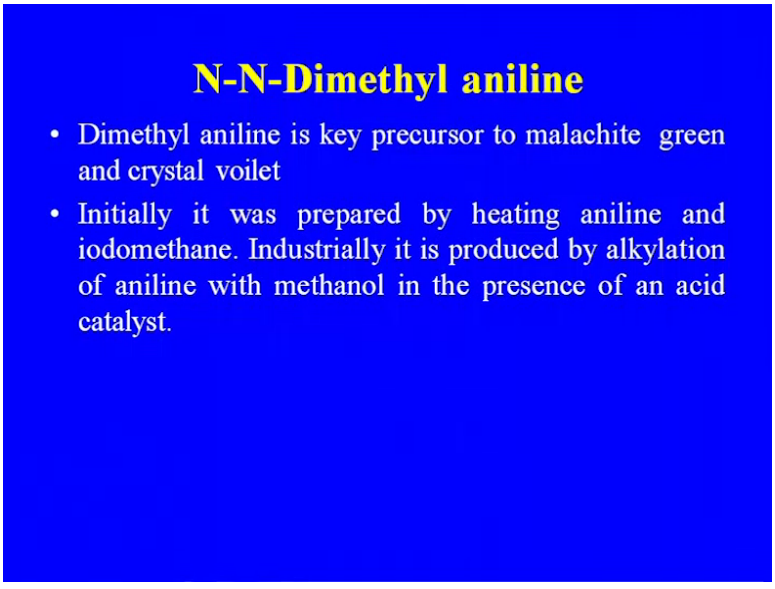

So, ammonia that is also needed, alkylation the same we already discussed about the alkylation process what are the alkylating media that we arriving. So, this these are the some of the major unit process involved in making of the dyes intermediate. now let us come to the individual intermediate some of the compound.

Dimethyl aniline is key precursor to malachite green and the crystal violet, initially it was prepared by heating aniline and iodomethane, industrially it is produced by alkylation of aniline with methanol in the presence of an acid catalyst. So this is the many application large application the aniline has aniline has chemical intermediate is there. Orthochlorobenze acid again benzelic acid either the italine route that you can make benzelic acid.

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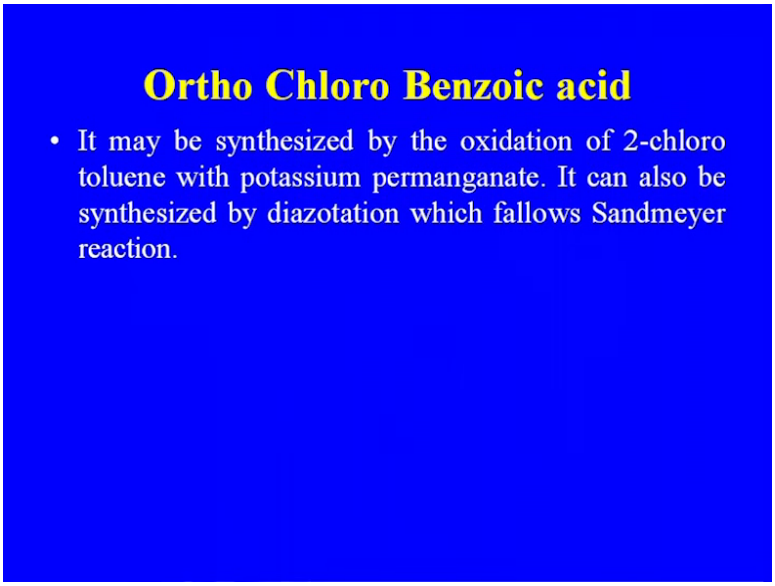

It may be synthesized by the oxidation of 2 chloro toluene with potassium permanganate, it can also be synthesized by diazotation which fallow sandmeyer reaction. Para nitro benzoic acid, it is prepared by oxidation of 4 nitro toluene using oxygen or nitric acid as an oxidant. Alternatively it can also be prepared by nitration of poly styrene fallowed by oxidation of alkyl substituent.

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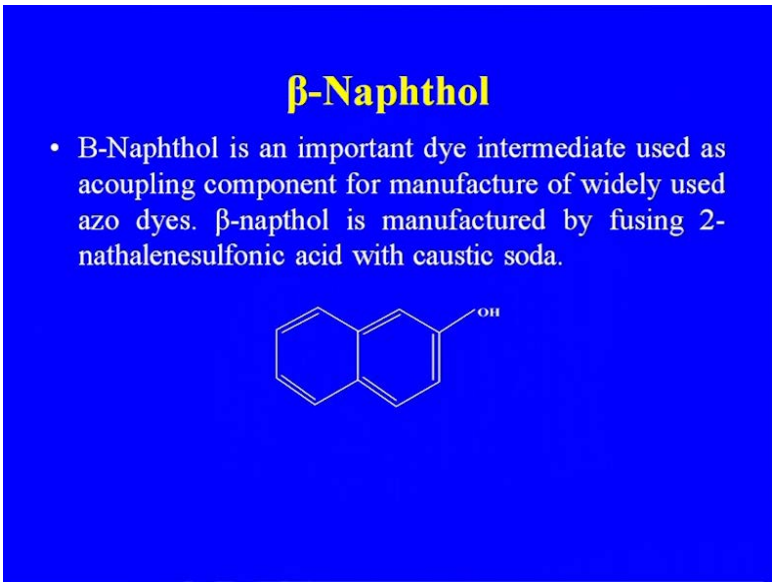

Beta naphthol that is one of the very important di intermediate used as the coupling component for manufacture of widely used azo dyes. Beta naphthalene is manufactured by fusing 2 nathalene sulfonic acid with caustic soda. So beta naphthol earlier because now there is ban on the azodile, otherwise the beta naphthol that was concerned very important dye intermediate.

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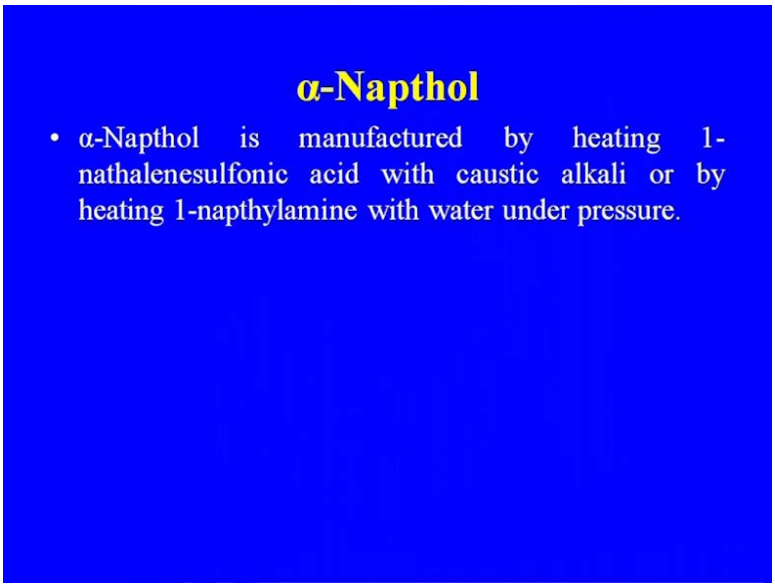

Alpha napthol is manufactured by heating 1-nathalenesulphonic acid with caustic alkali or by heating 1-naphthalene with water under pressure resorcinol.

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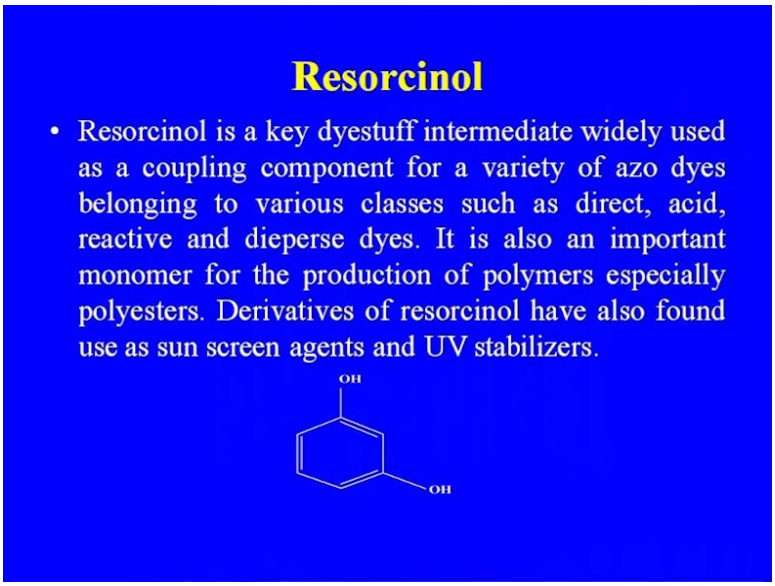

Resorcinol is a key dye stuff intermediate widely used as a coupling component for variety of azo dyes belonging to various classes such as direct acid reactive and disperse dyes, it is also an important monomer for the production of polymers, especially the polyesters derivatives of resorcinol have also found use as sun screen agents and U V stabilizers.

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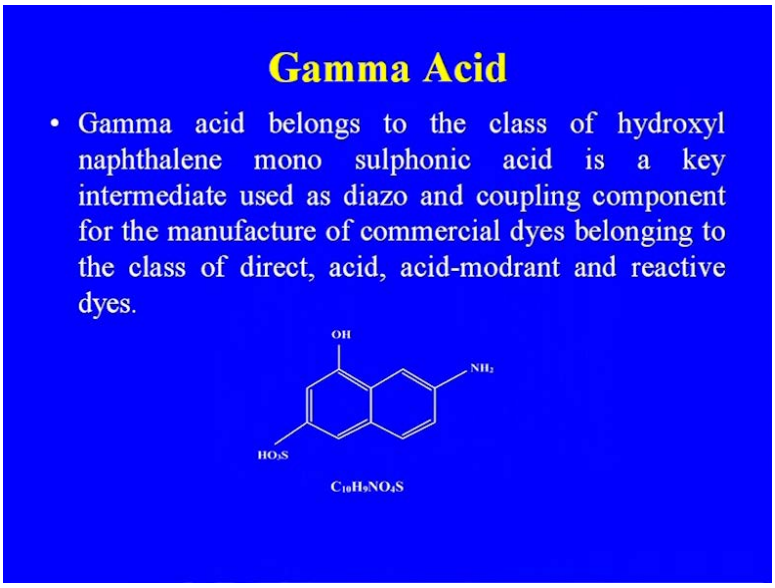

Gamma acid; gamma acid belongs to the class of hydroxyl naphthalene mono sulphonic acid is a key intermediate used as diazo and coupling component for the manufacture of commercial dyes belonging to the class of direct, acid, acid-mordant and reactive dyes.

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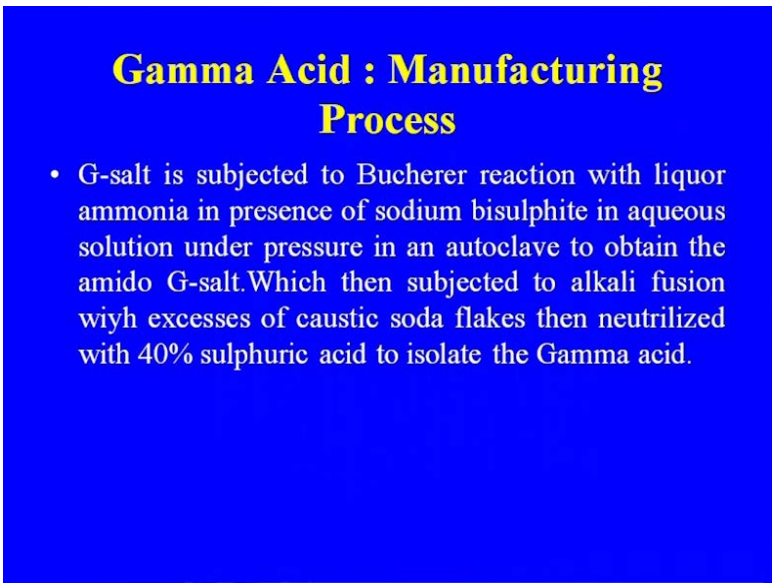

This is the manufacturing process G-salt is subjected to Bucherer reaction with liquor ammonia in presence of sodium bisulphate in acqueous solution under pressure in an autoclave to obtain the amido G-salt. Which then subjected to alkali fusion with excesses

of caustic soda flakes then neutralized with 40 percent sulphuric acid to isolate the gamma acid.

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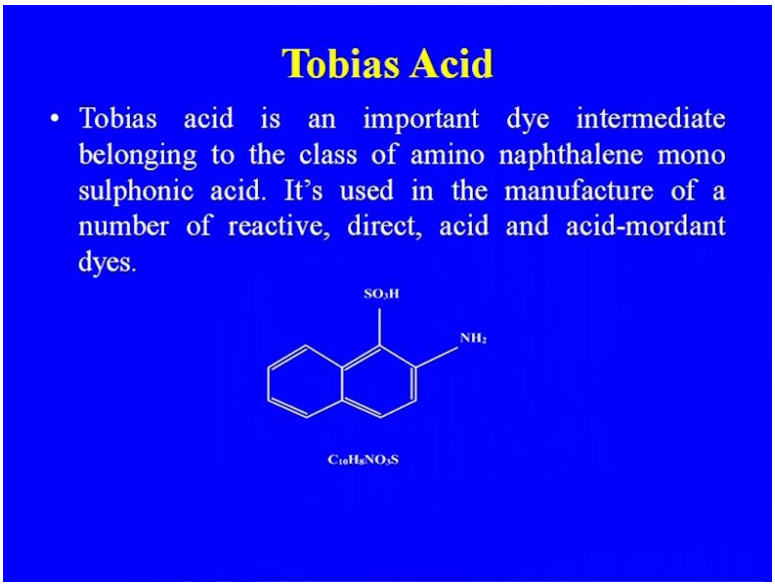

Tobias acid; tobias acid is an important dye intermediate belonging to the class of ammonia naphthalene mono sulphonic acid, it is used for in the manufacture of a number of reactive, direct, acid and acid-mordant dyes.

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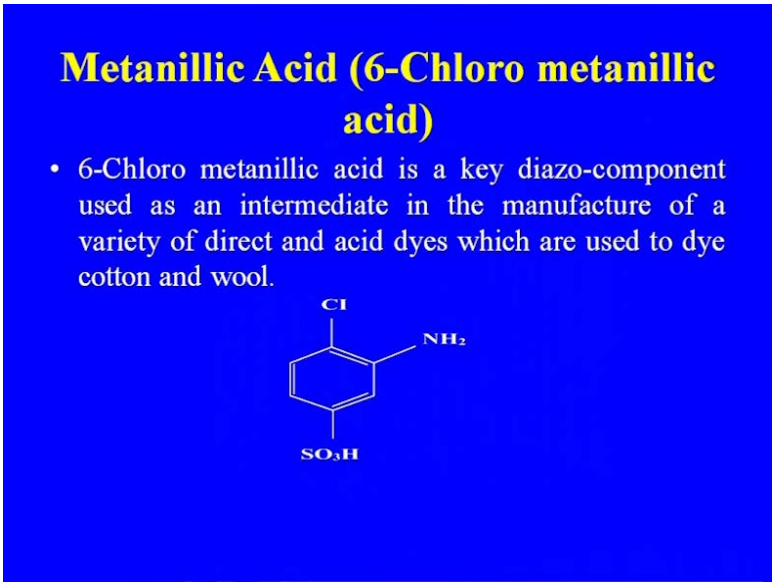

Metallic acid 6-chloro metanillic acid is a key diazo-component used as an intermediate in the manufacture of a variety of direct and acid dyes, which are used to dye cotton and wool, and one it is called the metanillic yellow.

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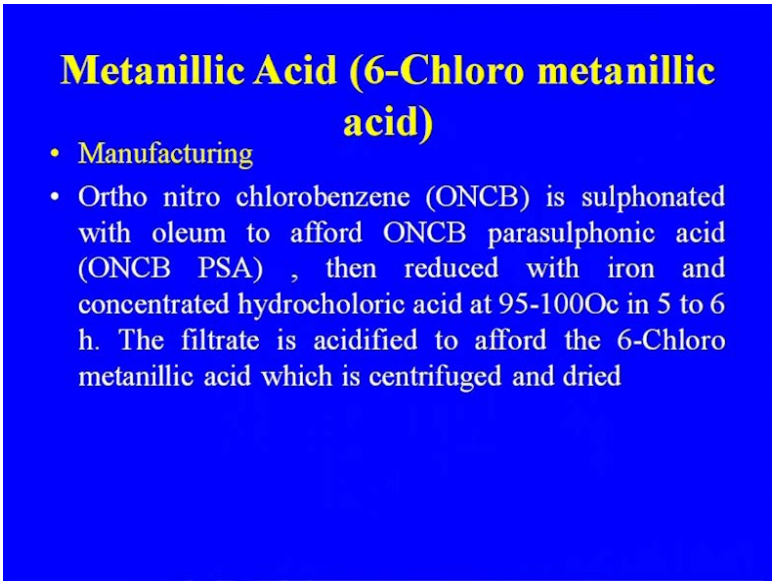

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This is the manufacturing process for the metanillic acid ortho nitro chloro benzene is sulphonated with oleum to afford ONCB ONCB para-sulphonic acid, then reduces with iron and concentrated hydrochloric acid at 95 to 100 degree centigrade in 5 to 6 hour.

The filtrate is acidified to afford the 6-chlorometanillic acid which is centrifuged and dried.

Anthraquinone sulphonic acid sodium salt, this is the all it is derivatives are important building block for a variety of dyestuffs in particular for disperse solvent and acid dyes. Here we using the for the anthraquinone sulphonic acid sodium salt, we are using again as I told you earlier also the two routes are available; one is from ortho xylene and other is from the naphthalene route. Now the most of the ethylic manufacture by the ortho xylene.

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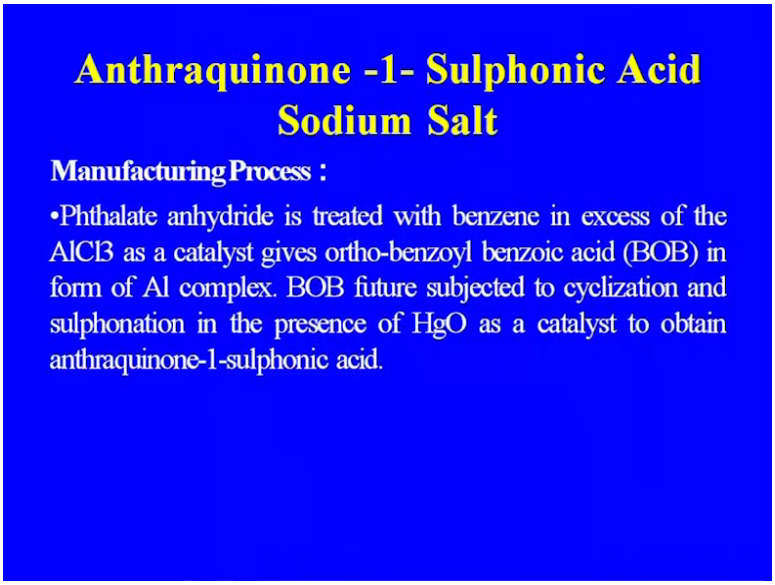

So, the phthalate anhydride is treated with benzene in excess of the aluminium chloride as a catalyst gives ortho-benzoyl benzoic acid inform of a aluminium complex. B OB future subjected to cyclization and sulphonation in the presence of the mercury's salt as a catalyst to obtain anthraquinone 1-sulphonic acid.

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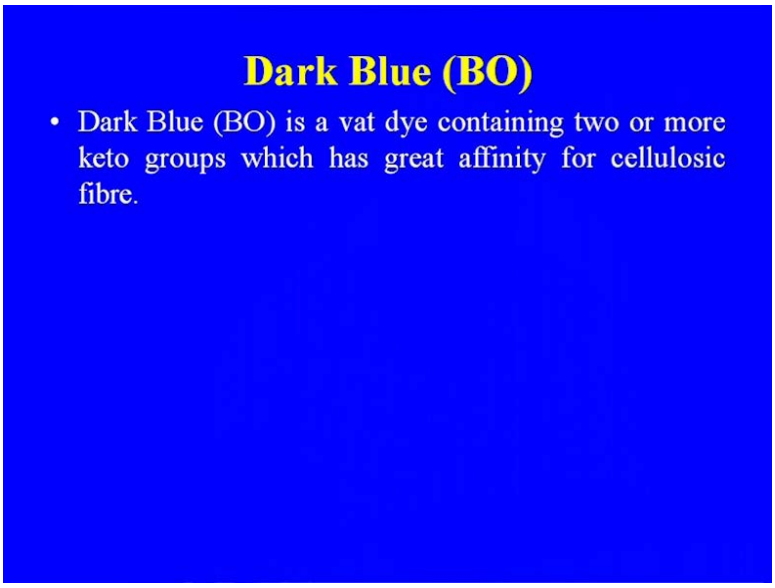

Dark blue; dark blue is a vat dye containing two or more keto group which has great affinity for cellulosic fibre.

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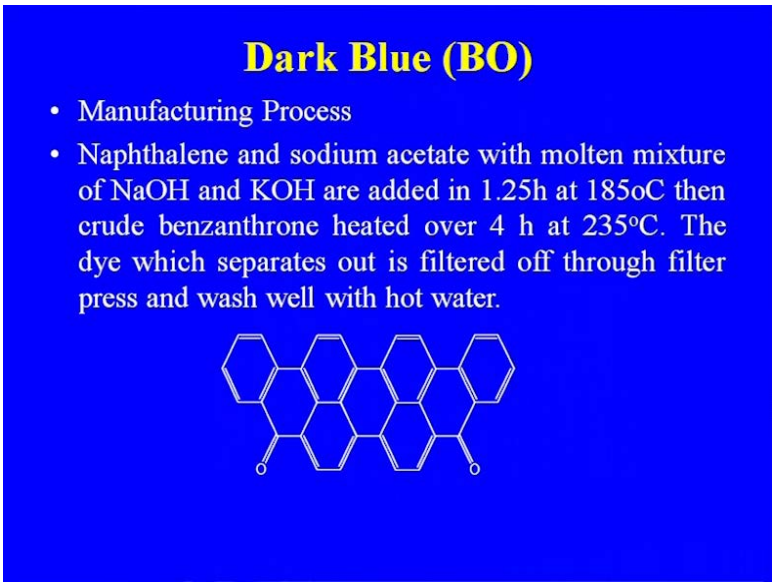

This is the process were we are using naphthalene and sodium acetate for making of the dark blue, naphthalene and sodium acetate with molten mixture of NaOH and KOH are added time 1.25 hours at 185 degree centigrade then crude benzanthrone heated over 4 hour. The dye which separates out is filtered off through filter press and wash well with hot water.

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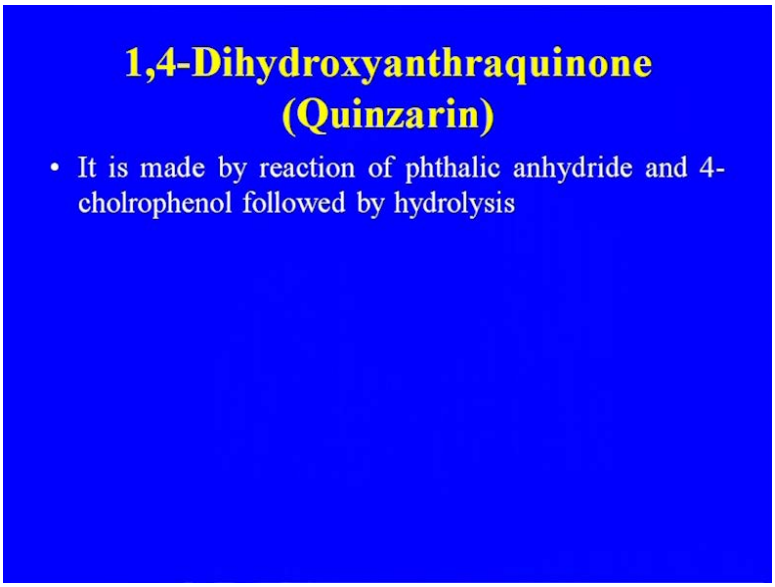

1 4-dihydroanthraquinone that is the quinzarin it is made of phthalic anhydride and 4-chloro phenol followed by hydrolysis. So, this was about the dyes manufacture dyes an intermediate we discuss about the what are the importance of the dyes in our daily life, because most of the material always there is people are going for the colourful material, and so the dyes intermediate there are going to play important role and at the same time ability of the one of the dying force for the dyes industry, that is the development of the synthetic fibre industry coming of the synthetic industry and the development of the textile industry ability of the raw material from the petro chemical route.

So, this was all about the organic chemical industry we discussed from the starting from the introduction, various process, unit process involve in organic chemical what are the raw material for the organic chemical industry, then we discuss about the sum the important sector of the organic sugar alcohol, and then the soup detergent petroleum industry, petro chemical and then the polymer, elastomer, synthetic fibre, and then about the pesticide role of the pesticide and then the dyes and the intermediate.

So, although the some portion of the organic chemical technological course could not be covered, but because it is not possible everything in one actually the course module, and so this was the (( )) discuss about the organic chemical industry, and the thankful to the various actually resources from where the information that is collected and especially to the from the net and from the your this hydrocarbon processing, where the lot of the

information that has being taking in the petroleum pet and the petro chemical chapter, and the your polymer and the elastomer and the your this and one thing I can mention here in this whose because all the beautiful diagram that is been done by or one of the researcher Chandra Kanthta Khor, we acknowledges contribution development of this course making of the various slides and making of the various diagrams for making the your presentation more attractive.