Natural Dyes

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Lecture No. # 32

After taking a deep look at the dyeing application of reactive dyes. Today, we will be talking about yet another type of synthetic dye, which is sulphur dyes, and we will see how they are used in dying. Whether we use natural fibers like cotton, silk or wool or we use any kind of synthetic fiber which we have learnt quite great detail, like polyester, polyimide or other types of rayon's and nylons and so on. The reactivity of these dyes are quite different. So, that is why they have been classed or classified into different groups.

So, once we have taken a look at the reactive dyes; now, it is time to talk a bit about the sulphur dyes, because this course deals with all types of dyes. Not only natural dyes, but also synthetic dyes, but of course, more emphasis is being given on natural dyes for the simple reason, that they are the most upcoming dyes that the industry must now adapt. But keeping all that in mind I still feel that, holistic approach towards the course would demand that another very deep over view of the other types of dyes, must also be made available to you people. So, today we will learn about dyeing application on sulphur dyes or with sulphur dyes.

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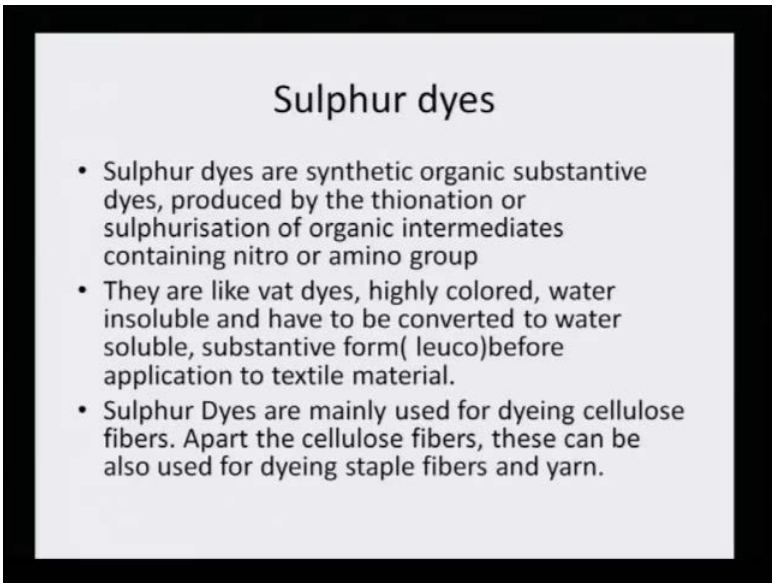

Sulpture dyes are synthetic organic substantive dyes produced by the phonation or sulphurisation of organic intermediates, containing nitro or amino group. So, one thing is clear that the molecule must have either a nitro group or an amino group, and the dye is prepared, it is a synthetic dye as the name suggest and it is prepared by the thionation or suphurasation. They are like vat dyes highly colored, water insoluble and have to be converted to water soluble sustentative form that is the leuco form, before application to textile material.

So, by now you would have recall that vat dyeing, had also gone through similar kind of processing. Where dye per say are insoluble, and then they are solubilized to make it into leuco form which almost like colorless or it has a this color, and then finally, in that solubilize form it penetrates into the fabric, and then it is regenerated into its insoluble form. So, similarly the sulphur dyes also behave in the same manner. Sulphur dyes are mainly used for dyeing cellulose fibers; apart from cellulose fibers they can be also used for dyeing staple fibers and yarns

So, you see that it has also its own range of a material that can be dyed with this a dye. It has what I told in the last few classes, that dye and the dyeing fiber. There there chemistry must be compatible; otherwise, the dye of take will not take place and the fabric cannot be dyed. So, it is important to understand the chemistry of the dye. We already have taken a look at the the chemistry of the fibers that is polyester, nylon,

cellulose, silk, wool and so on and so forth, and poly acrylic fibers, we have already covered all that. So, you now understand that the compatibility factor is very important. The structure of the dye must be compatible to the structure of the fiber or the fabric.

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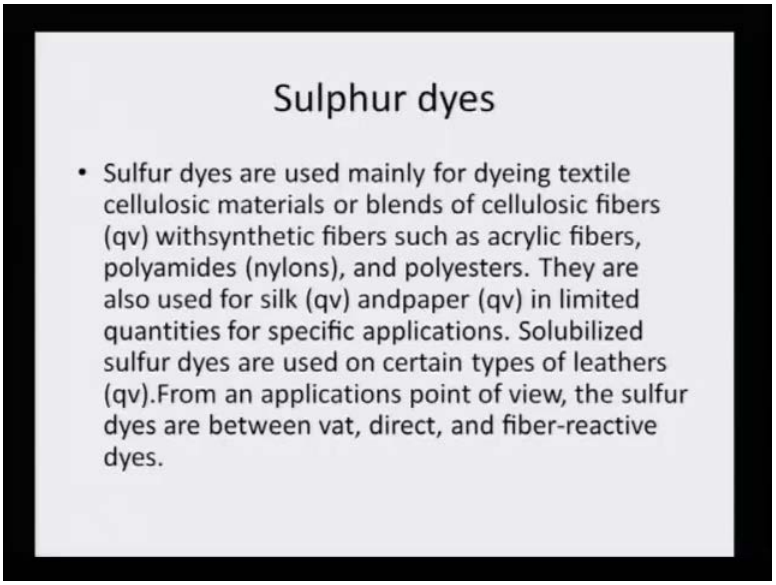

Sulphur dyes are used mainly for dyeing, textiles, cellulosic materials or blends of cellulosic fibers with synthetic fibers such as acrylic fiber, polyamides or and polyesters. So, they are good cellulose not only for cellulose, but also for the blends of cellulose - and the blends could be with polyester with polyamide, and with poly acrylic fibers. They are used for silk and paper in limited quantities for specific application. Solubilize sulphur dyes are used on certain types of level. From an application point of view, the sulphur dyes are between a vat, direct and fiber reactive dyes. So, if one tries to taken overview, as so where are these placed in the industry?

The maximum uses of vat dye, direct dyes and fiber reactive dyes which we have learnt in the previous class. And now, comes the class which is the sulfur dyes. So, it is also used for dyeing silk and paper, but in limited quantity. So, what does it come to conclusion from this slide, that it is not only used for cotton, but it also used for cellulosic blends, like polyacrylic blend with cotton or polyamide blend with cotton or poly ester blend with cotton. So that means, it it has the ability. Now, you see when we are talking about blends. One thing has to be kept in mind that the dye chemistry remains the same for both the fibers, but for the dye, the fabric chemistry changes.

So, it has now to deal with two different kinds of material which are compositionally very different or chemically very different. So, how does this dye, then start taking up, because we take a look at the mechanism of dyeing of a a cotton; we have taken a look at the mechanism of the dyeing of polyesters, polyamides and the polyacrylic fibers; so, now you see that there is a computation; if there are two types of fibers, how will this dye now start behaving when its start penetrating into the fiber which is a blend.

So, those things are the intricacies which you should understand, because by now you have already understood, the dyeing of a these different types of synthetic fibers, you have taken a look at other dyes also their chemistry; so, let us try to see how sulphur dyes behave with these cellulosic fibers and blends of cellulosic fibers.

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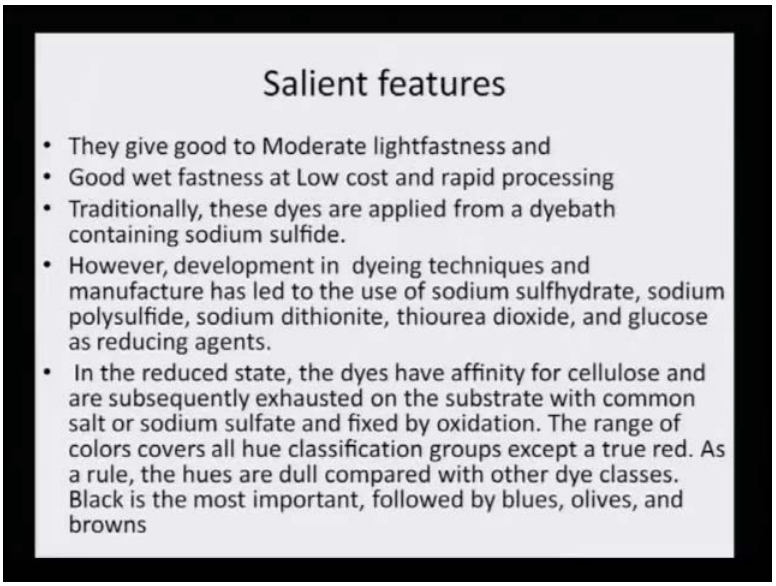

What should a sulphur dye have as a salient features. They give good to moderate fastness, and good wet fastness at low cost, and rapid rapid processing. Traditionally these dyes are applied from a dye bath containing sodium sulphide. However development in dyeing techniques, and manufacture as led to the use of sodium sulfhydrate, sodium polysulphide, sodium dithionite, thiourea dioxide and glucose as reducing agents.

In the reduced state the dyes have affinity for cellulose, and are subsequently exhausted on the substrate with common salt or sodium sulfate that is the glorious salt fixed by oxidation. The range of color covers all hue classification groups except a true red; as a

rule, hues are dull compared with the other dye classes. Black is the most important followed by blues, olives and browns. So, you see that if we try to take a look at the sulphur dyes, and their properties; they are very good when it comes to light fastness. So, one criterion they definitely fulfill as a dye, because they have good fastness.

They also have good wet fastness, and are very low costing and the process of dying is very fast. So, you see even that is very very advantageous for any industrial textile dyeing process. Traditionally these these dyes are applied in the dye bath containing sodium sulphide. Now, this is a chemical which needs to be mandatorily added for the solubilization of sulphur dyes. So, that is something very different from what we had learnt, in when we were doing reactive dyes.

However development in dyeing technique, several other reducing agents have also been used over a period of time. Including glucose, sodium poly sulphide, sodium dithionite, thiourea dioxide, sodium sullfhydrate and so on and so forth; even sodium dithionite is used when vat dyeing is done with the indigo. So, that is there is some more similarity, because the dye has to be solubilized. One thing that vat dyeing and sulphur dyes have an common or indigo, indioid dyes and sulphur dyes have been common; that they have to they are in insoluble state, they have to be solubelized and again insoluble form a must be converted.

So, this process of solubilization to insolubilization on the surface of the fabric is common to vat dyeing or indigoid dyeing, an indigo dyes and sulphur dyes. In the reduced state, the dye has affinity for cellulose. So, once it turns to the solubilize form, it can form bonds with the cellulosic fibers or the blends of the cellolosic fibers, and that is how it gets into the fiber. Otherwise, any insoluble material cannot penetrate into the fiber. So, for that purpose the leuco from is converted. And therefore, it is one of the best source of black dyes.

Many others colors can be obtained; although true red has not been achieved through self dyes through sulphur dyes, but all other colors and preferentially black color has been observed a very well, and has been obtained a pin in great success. But other like blues, olives, and browns also can be obtained from sulphur dyes very readily.

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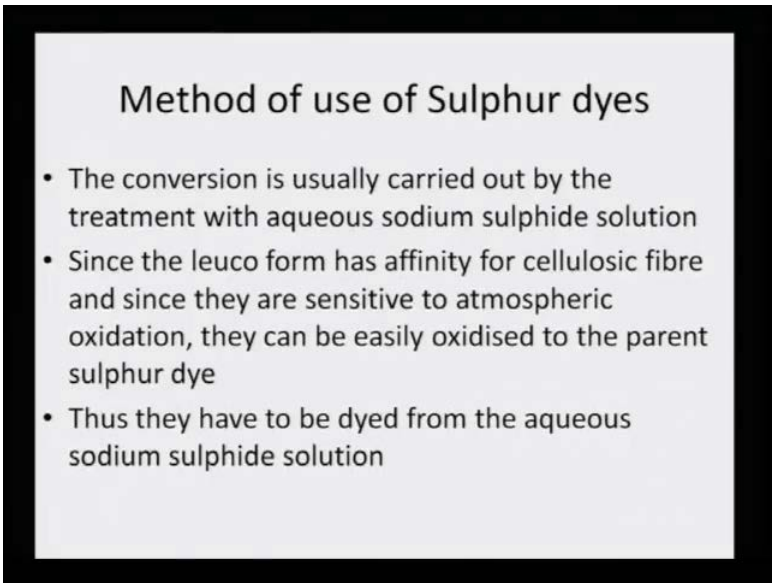

How is the sulphur dye actually used? The conversion is is usually carried out by the treatment with aqueous sodium sulphide solution. I just mentioned a while ago that in the dye bath in order to solubilize sulphur dyes, it is important that sodium sulphide solution be present. Otherwise, solubilization will not take place. Since the leuco form has affinity for cellulosic fiber, and since they are sensitive to atmospheric oxidation; they can be easily oxodised to the parent sulphur dye. So, the first the formation of the leuco, and then the oxidation to the, you know oxidized state of insoluble sulphur dyes.

Thus they have to be dyed from the aqueous sodium sulphide solution. So, one thing that needs to be remembered is that, these dyes cannot be put into the dye bath without adding sodium sulphide solution. So, this is a mandatory chemical when sulphur dyes have to be used for dyeing. Second thing that needs to be remembered, is that is very similar to vat dyes, such as indigoid dyes, because even in the case of indigoid dyes; the dye is in the insoluble form, it has to be solubilized and once it is solubilized it comes to the leuco form, and after it has form the leuco form, it has to be re oxidized on the surface of the fabric.

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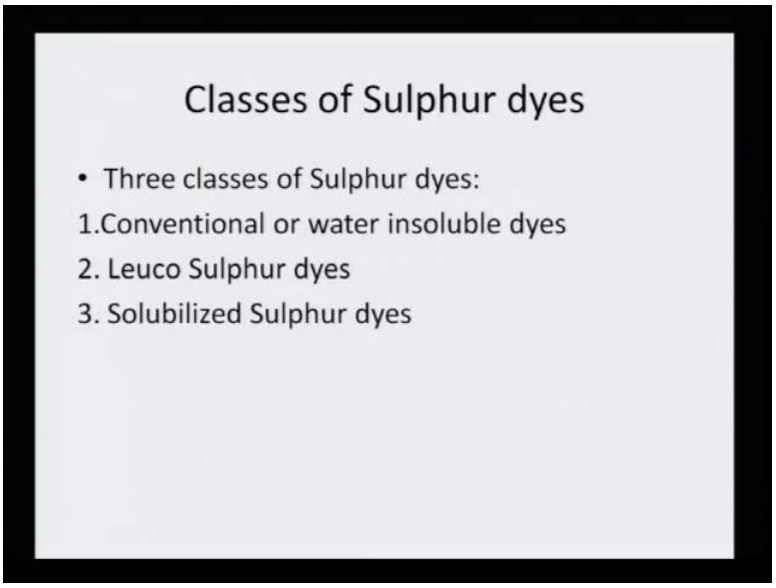

So, this is the chronology of event. So, there is a great deal of similarity. Now, classes of sulphur dyes; let us take a look at how many types of sulphur dyes are available. These classes of sulphur, three classes of sulphur dyes; one conventional or water insoluble dyes, one is the leuco sulphur dyes and the third is the solubilized sulphur dyes.

So, there are three classes of sulphur dyes which can be used in the industry, and they are conventional or water insoluble dyes. The second one is leuco sulphur dyes and the third one is the solubilized sulphur dyes.

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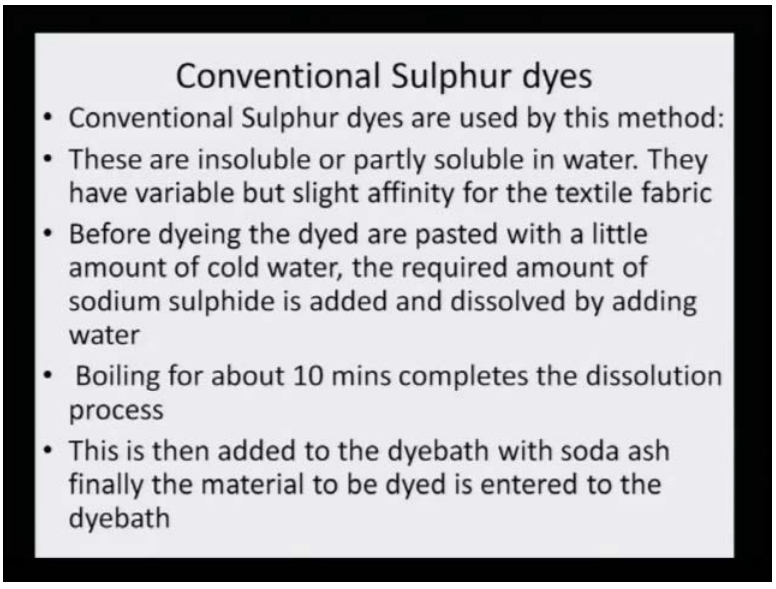

Now, we try to take a look at conventional insoluble sulphur dyes. Let us see what how is the method carried out; conventional sulphur dyes are used in this method, they are insoluble or partly soluble in water; they have variable, but slight affinity for textile fabric before dyeing, the dye are pasted with the little amount of cold water, the required amount of sodium sulphide is added, and dissolved by adding water; boiling for about 10 minutes completes the dissolution process; this is then added to the dye bath with soda ash finally, the material to be dyed is entered into the dye bath.

So, if as you know a regular insoluble sulphur dyes is used, this is the procedure that needs to be followed in order to prepare the dye bath. The first thing that one has to do is to make a paste of the dye with the help of water. But, it is insoluble in water. So, it is just going to be a kind of a physical mixture, to that sodium sulphide is added; so that, the dissolution takes place. And this is almost going to take 10 to 15 minutes, after which the whole solution is poured into the dye bath, and then can now we used for the dyeing of the fabric; and fabric can be entered into it.

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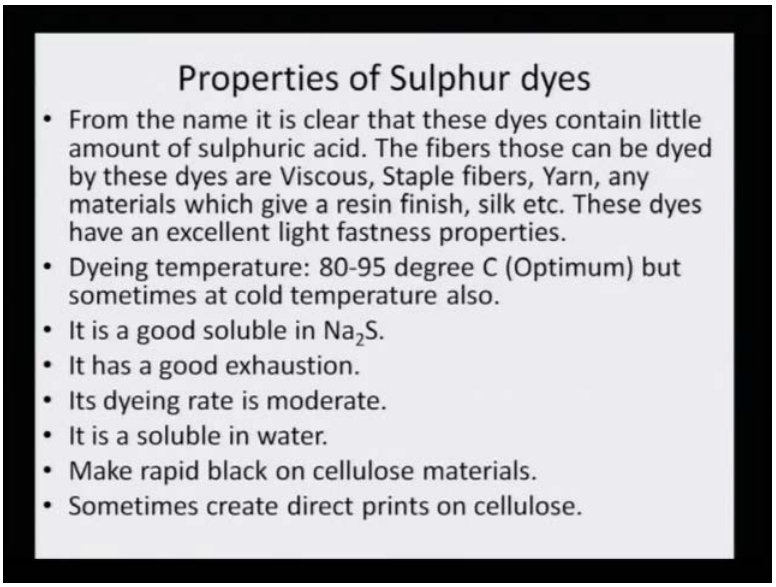

What Let us take a look at the properties of the sulphur dyes; from the name itself it is clear that these dyes contain little amount of sulpuric acid. The fiber those can be dyed by these materials are viscose, staple fibers, yarn, any material which give a resin finish or silk finish, etcetera. These dyes have an excellent light fastness. So, that is very big

advantageous property that sulphur dye has. Dyeing temperature is between 80 to 95 degrees, optimum, but sometimes at cold temperature also dyeing can be carried out.

It is good soluble in sodium disulphide, it has a good exhaustion, its dyeing rate is moderate, it is soluble in water only when it is dissolved in sodium sulphide and make a rapid black on cellulose materials, sometimes create direct prints on cellulose. So, it has several several advantageous situations which the other classes of dyes lacked. And therefore, if one has to obtain black; one has to preferably use the sulphur dyes. And you have seen, that it has a very good fastness, lights light fastness property. So, that makes it a very good candidate as a dye, in the dyeing industry. Plus it has good exhaustion; that means, the dye is not wasted.

The dye affluent left behind in the dye bath is has very minimum amount of dye left behind. So, that is and the dyeing rate is moderate is, it is not slow, it is not very high and at the same time you know, you see that the temperature at which the dyeing is being done is only 80 to 95 degrees, which is slightly below the boiling point of water. And such a dyeing procedure is not very energy intensive. So, even there it has an advantage.

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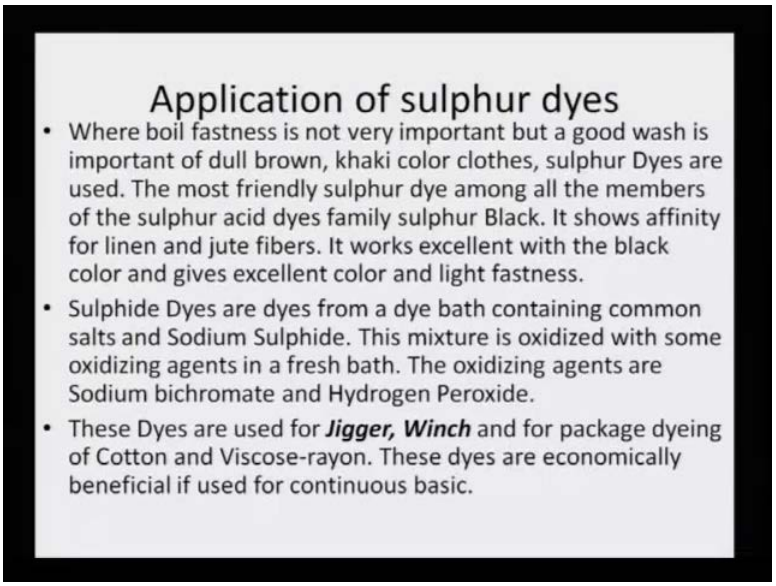

Application of sulphur dyes. Where all it can be applied; where boiling fastness is not very important, but a good wash is important of dull brown, khaki color clothes, sulphur dyes are used. The most friendly sulphur dye among all the members of the sulphur acid dye family is sulphur black. It shows affinity for Lenin, and Jute fiber is well. It works

excellent with with the black color and gives excellent color and light fastness. So, you see when boiling any material, it is not going to create any problem for the fiber, from the fiber point of view, if it can withstand 80 to 90 to 100 degree centigrade.

There using a sulphur dye is very very good. And particularly if one wants to get that get black, it is not possible to get black color in natural dyes or in reactive dyes or in any other series of dyes that we have done, as you know uniformly and as deep a color of the black as what can be obtained through the sulphur dyes. So, that is where it has an edge over the other series of dyes. Sulphide dyes are dyes from a dye bath containing common salt, and sodium sulphide. This mixture is oxidized with some oxidizing agent in a fresh bath. The oxidizing agents are sodium bichromate or hydrogen peroxide.

So, when the leuco form has to be reoxidized; these are the two most common oxidizing agent. One is hydrogen peroxide, and the other one is sodium bichromate, but preferably sodium peroxide is more advantageous, because it does not liberate any harmful element or material. When hydrogen peroxide dissociates, it gives water and nascent oxygen. And that nascent oxygen is instrumental in the oxidation of the leuco form. But in the case of sodium bichromate; the chromium metal itself is a hazardous. So, therefore, it is preferable to avoid using strong oxidizing agents like, sodium bichromate.

These dyes are used for jigger or winch and for package dyeing and cotton and viscose-rayon. By now you know, what the jigger machine looks like, by now you know what a winch machine looks likes, and in several several types fiber dyeing, we have been talking about winch, and jigger again and again, why because for the simple reason that every dye house will definitely have a jigger and a winch machine. Then is a possibility that the hang dyeing may be there, may not be there; other types of sophisticated dyeing machines may be present, may not be present.

But these two dyeing machines are definitely available with most of the dye-houses, and that it is why I have impractically told about that, if the sulphur dye can be used on jigger and winch very easily; you have learnt about package dyeing, and even it can be used in the form of package dyeing. These dyes are economically beneficial, if you use for continuous basic dyeing. So, as we already known that they are low cost. Therefore, it is economical plus it has good exhaustion. So, that also adjoined to the economics. It, you know is an it it takes lesser time to the rate of dyeing is moderate. So, even there it is, in

the energy saving. So, all these points go to prove that sulphur dyes are very good for industrial processes.

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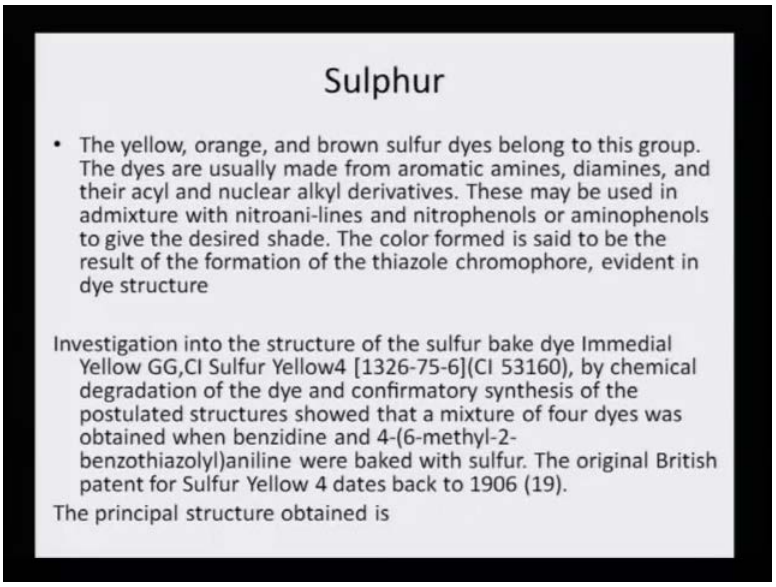

Sulphur dyes can give the yellow, orange, brown, sulphur dyes belong to this class; that dyes are usually made from aromatic amines dye amines, and their acyle and nuclear alkyl derivatives; these may be used in a admixture with nitroani-lines or nitrophenols or aminophenols to give the desired shape, shade; the color form is said to be the result of formation of thiazole, chromophore, evident in the dyes structure. So, what happens is that, we can have a variety of sulphur dyes, and the shade we can be altered from the yellow to orange to brown, simply if the structure is altered. And for alteration of the structure, the reaction of aromatic amines or dye amines or their or acyl derivatives could be done with nitroani-lines or nitro phenols or amino phenols.

So, as I told you right in the beginning. That is sulphur dye must desirably contain a nitro group and an amino group; apart from having a a sulphur in its moiety. Obviously, it as to have and sulphur in the molecule otherwise, it will not fall into the category of sulfur dyes.

Investigation into the structure of sulphur big dye, immedial yellow GG, sulphur yellow 4 by chemical degradation of the dye, and confirmatory synthesis of the postulated structures showed that a mixture of four dyes were obtained, when benzidine and four-six-methyle-two-benzothiazolyl, aniline were baked with sulphur. The original british

patent of sulphur yellow four dates that to1906. So, you see that it it is that old dye. In 1906 the dye- first sulphur dye was made with the help of Benzedrine and 6 4 methyl 2 benzothialyl, aniline.

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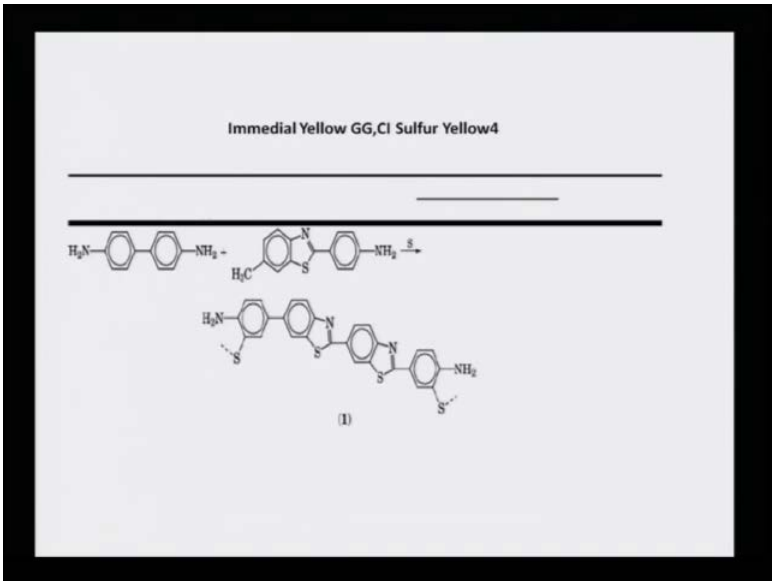

This is the structure and so, this Benzedrine when reacted with this kind of benzothiozolyl gave this very conjugated system, you see there are four aromatic rings, and you know four sulfurs two terminal amines and so on and so forth.

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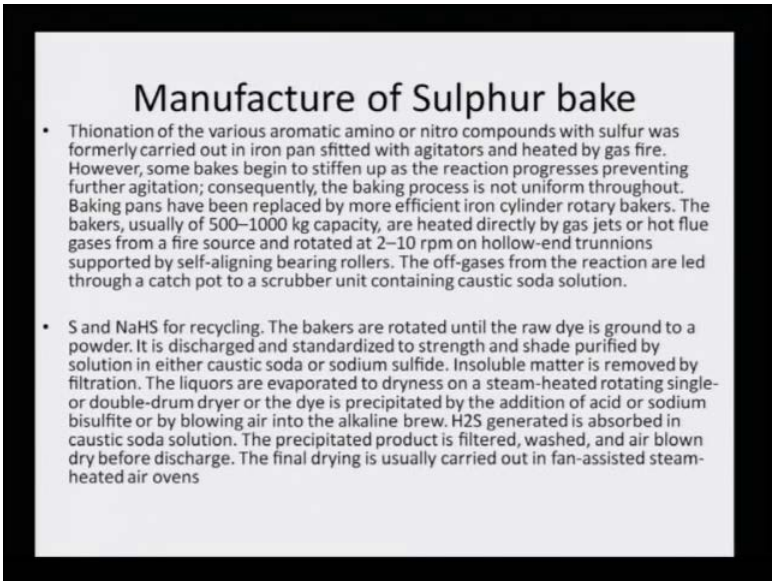

Manufacture of the sulphur bake, because you see these are so important dyes, and as I told you low cost, good light fastness, very good a rate of dyeing. And so they fall in a better category of the dyes. Thionation of various aromatic amino or nitro compounds, this sulfur was formerly carried out in iron pans shifted with agitators and fitted with agitators and heated by gas fire. However some bakes begin to stiffen up as the reaction progresses, preventing further agitation.

Consequently the baking process is not uniform throughout. Baking pans have been replaced by more efficient iron cylinders rotating bakers. The bakers usually of 500 to 1000 kilogram capacity are heated directly by gas jets or hot flue gases from a fire source and rotated at an RPM of 2 to 10, on hollow end trunnions supported by self aligning bearing rollers; the off gases from the reaction are led through a catch pot to a scrubber unit containing caustic soda solution. So, now you see, the whole process was first done in a baking machine. But that baking machine was making the whole thing settle. Now, if it's a the hole process settles up there would not be any mixing of the reactance.

As a result the thionation will not take place properly of the amino phenols and the nitro phenols. So, in order to you know, have more mechanized machine; these, because were replaced by rotatory bakers. And in that rotatory bakers is one could stiffen as much as 500 kilogram to 1000 kilogram material, and they were rotated at a 2 to 10 RPM. So, very slow rotation, but yet the mixing of this sulfur for the process of thionation can be carried out. And then, you know it was kind of warmed up by flue gases and then these gases were kind of trapped into the caustic soda ash solution, because you know any harmful sulphurous compound should not escape, it can cause a hazard for the factory workers.

So, that is how they were the scrubber unit containing caustic soda solution, would have trapped these escaping gases. Sulphur and sodium hydrogen sulfide for recycling were then process; the bakers are rotated until the raw dye is ground to a powder, it is discharged and standardized to strength and shade purified by solution in either caustic soda or sodium sulfide, insoluble material is removed by filtration, the leuco are evaporated to dryness on a esteem heated rotating a single or double-drum dryer of the dye is precipitated by the addition of acid or sodium bisulfate or by blowing air into the alkaline brew.

Hydrogen sulfite generated is absorbed in the caustic soda solution. It is this that I was referring to that all the sulfur which is got converted into hydrogen sulfite must be checked, because it not only creates a bad smell, but it is also harmful for inhalation. The precipitated product is filtered, washed and air blown dry before discharge. The final drying is usually carried out in fan-assisted steam heated air ovens. So, you see that the whole process is very simple. So, a that is the reason why sulfur dye production is low. So, the dye cost is also low. And the only effluent in the process or hazardous chemical that comes out is the hydrogen sulfide which is trapped in sodium sulfide.

And even the re crystallization and purification is very easy as what you heard just now. Because they if the process is simple, the cost will automatically be low. If the process of making the dye is very complicated, and requires many ingredients; the cost will automatically go up.

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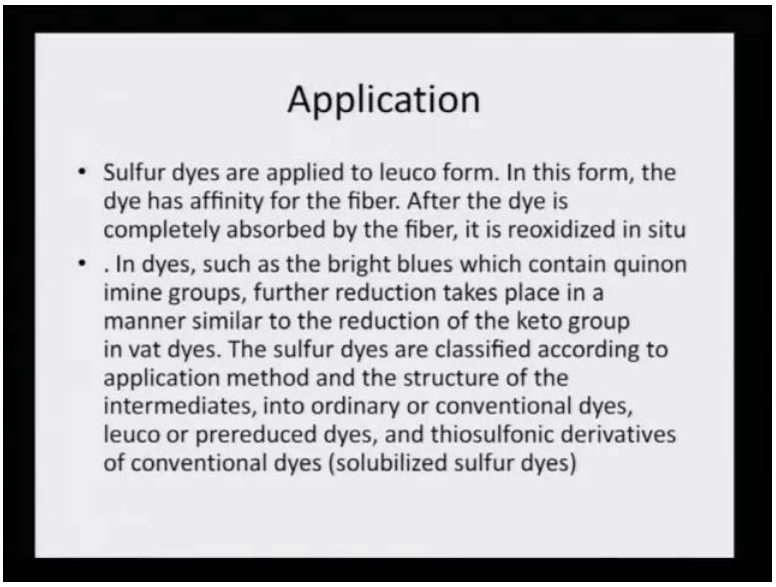

Now, let us take a look at the application part: sulfur dyes are applied to leuco form. In this form, the dye has affinity for the fiber. After the dye is completely absorbed by the fiber it is re oxidized in situ. In dyes such as the bright blues which contain quinon imine (( )), further reduction takes place in a manner, similar to the reduction of the keto group in the vat dyes. The sulfur dyes are classified according to application method, and the structure of the intermediates into ordinary or conventional dyes, leuco or pre reduced dyes and thiosulfonic derivatives of conventional dyes that is the solubilized dyes.

We were already seen this, we were already learnt that there are three types of dyes, sulfur dyes based on their structure. And on their way they can be applied. And one is the conventional insoluble dye, the other one is the soluble leuco dye, and the third one is the solubilized sulfur dyes which can be used in fibers, not only not only reduced the for the purpose of dyne cotton, but also for the blends of cotton.

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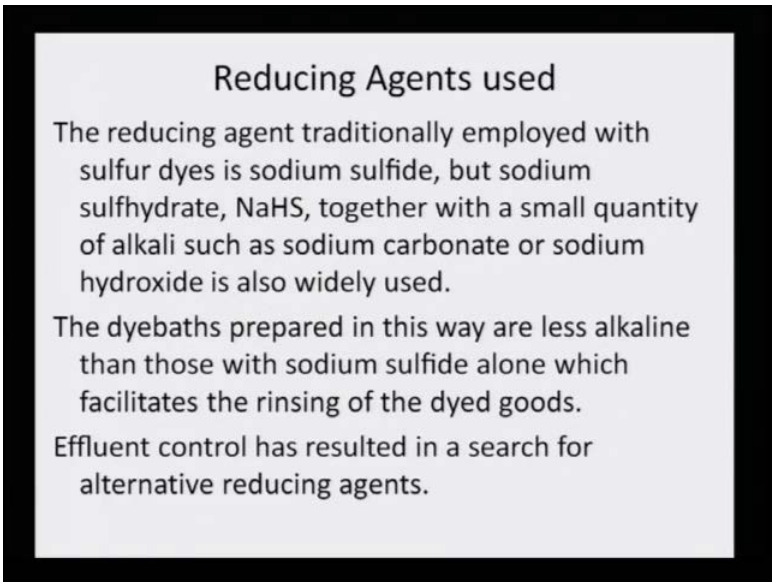

Now, let us take a look at the reducing agents that can be used. The reducing agents traditionally employed with sulfur dyes is of course, sodium sulfide, but sodium sulfhydrate, sodium bisulfide together with small quantities of alkali such as sodium carbonate or sodium hydroxide is of common or wide use. The dye baths prepared in this way are less alkaline than those with sodium sulfide alone. Which facilities the rinsing of the dyed goods; effluent control has resulted in a search for alternative reducing agents. So, commonly the reducing agent is a sodium sulfhydrate or sodium bisulfide, but other in combination with alkali, mild alkali, like sodium carbonate can also be used.

And it is all with the view that the effluent should have minimum amount of any hazardous chemical. And therefore, newer and other alternative reducing agents are also being search for this process. But one cannot, you know replace sodium sulfide. Why, because sodium sulfide is what dissolves the sulfur dyes.

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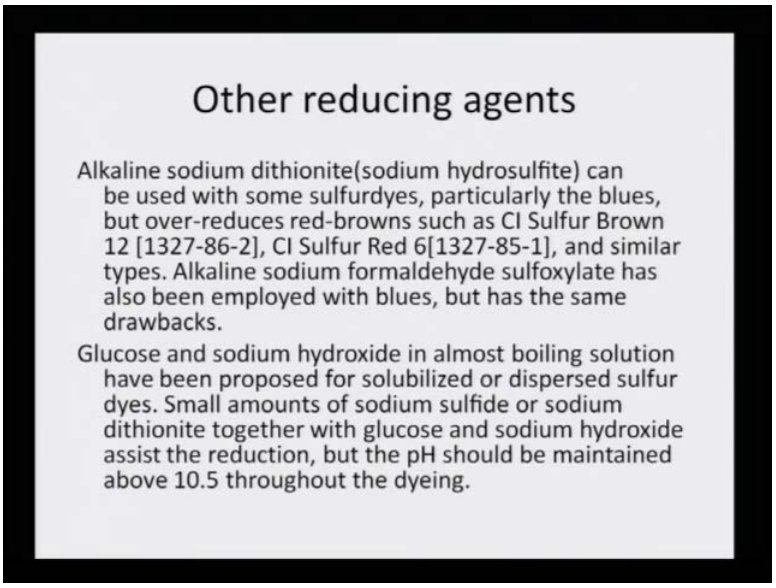

Other reducing agents that have been used alkaline sodium dithionite. This was also use in vat dyes, as I referred sometimes back; sodium hydrosulfite can be used with some sulfur dyes particularly the blues, but over reduces red browns such as sulfur brown 12, sulfur red 6, and similar types. So, one has to make the choice of the reducing agent. So, that it should not interfere with the dye. Alkaline sodium formaldehyde, sulfoxylate has also been employed with blues, but has the same drawback.

So, one has to way which reducing agent is going to work, and will not hamper the dye per say. Glucose and sodium hydroxide in almost boiling solution have been proposed for solubilized or dispersed sulfur dyes. Small amounts of sodium sulfide or sodium dithionite together with glucose and sodium hydroxide assist the reduction. But the pH should be maintained above 10.5 throughout the dyeing. So, there are possibilities of using a combination also; one can use sodium hydroxide along with glucose and with that small amount of dosing of sodium dithionite and sodium sulfite for solubilization is possible, but the main issue is that the Ph should be maintained at 10.5. And therefore, these reducing agent have to be used in permutation, and combination in order to use sulfur dyes very successfully.

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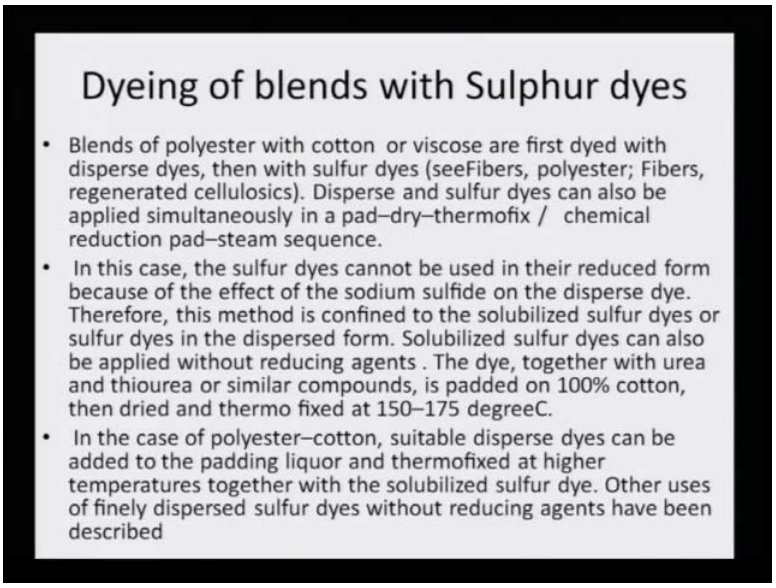

Dyeing the blends with sulphur dyes; that is what is the biggest challenge why, because I clearly made you understand, that now we have two different chemistries happening; one chemistry of the sulfur dye with cellulose and the other chemistry with the blended fiber. Blends of polyester with cotton or viscose are first dyed with disperse dyes and then with sulfur dyes. So, disperse and sulfur dyes can also be applied simultaneously in a pad-dry-thermofix which we learned yesterday, and chemical reduction pad-steam sequence. In this case the sulfur dyes cannot be used in their reduced form, because of the effect of the sodium sulfide on those disperse dyes.

Therefore, this method is confined to the solubilized sulfur dyes or sulfur dyes in the disperse form. Solubilized sulfur dyes can also be applied without reducing agents; the dye together with urea and thiourea or similar compounds is padded directly on hundred percent cotton, then dried and thermo fixed between 150 to 175 degrees. In the case of polyester cotton suitable disperse dye can be added to the padding liquor, and the thermo fixed at high temperatures together with the solubilized sulfur dyes. So, you say that these dyes cannot be used in isolation.

When there are blends, first a disperse dye must be used or in combination, but when dispersed dye and sulfur dye are used together, then sodium sulfide cannot be used. So, there has to be alterations in the process, according to the need of the fiber. If the fiber is pure, there is no problem is using in sulfur dyes and not very high temperature is

required. But when there are blends temperatures like one 50 to 175 degrees have to be brought about, and it is it is far beyond the boiling point of water; and therefore, very high heating is required for these blends when sulfur dyes are used. So, this is what the chemistry of sulfur dyes is all about, and the dyeing process certainly is very different from what we have learnt so far.