Natural Dyes

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Lecture No. # 35

For quite some time, we have been talking about natural dyes and synthetic dyes and then we have seen that how for natural dyes, metals play a very vital role. Similarly, in the synthetic dye series, there is something called metal complex dyes. And we will dedicate some time to understand the chemistry, and then go on to see how dyeing effective dyeing can be carried out with these metal complex dyes.

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So, today's lecture is primarily to make you aware of this new class of synthetic dyes which are called metal complex dyes.

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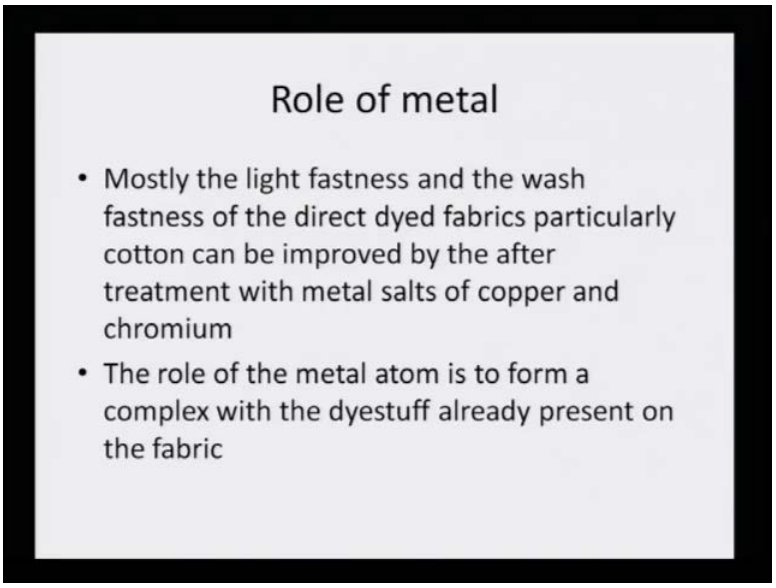

The role of the metal: As the name suggests if it has a metal then what is the role of the metal. Mostly the light fastness and the wash fastness of the direct dyed fabrics particularly cotton can be improve by an after treatment with metal salts of copper and chromium. So, it was observe that if direct dyed fabric particularly cotton, because why we are spending so much of time in talking about cotton, because cotton is the most popular fabric which is used for garment in our country, because of the tropical conditions. And therefore, it has good, you know perspiration absorptive. So, people prefer to wear cotton.

Now nobody will wear white cotton all throughout the year. So, the reason needs to put coloration or dye it. Now, the two ways that we can dye cotton is by means of synthetic dyes or by means of natural dyes. And among synthetic dyes metal complex dyes are one class of dyes which are primarily meant for cellulose, cellulosic fiber and cotton is one of them. So how it is done? First the fabric is dyed with the direct dyes and then an after treatment of metal which is like you know, you can consider it as a mordanting method with copper or chromium is done.

Now, I told you timing again that copper and chromium are you know not very echo friendly metals. So therefore, how can we minimize the use of copper and chromium salts in dyeing procedure at the same time maximize the light and the wash fastness. So, in order to improve the light wash fastness these metal treatments, after treatments were

carried out. The role of the metal atom is to form a complex with the dye stuff already present on the fabric. So, as what we have seen in the case of bio-mordant, as well as in the case of metal salt mordanting in cotton natural dyeing process. Similarly, the role of metal is no different from that, it forms a complex and therefore the name metal-complex dyes.

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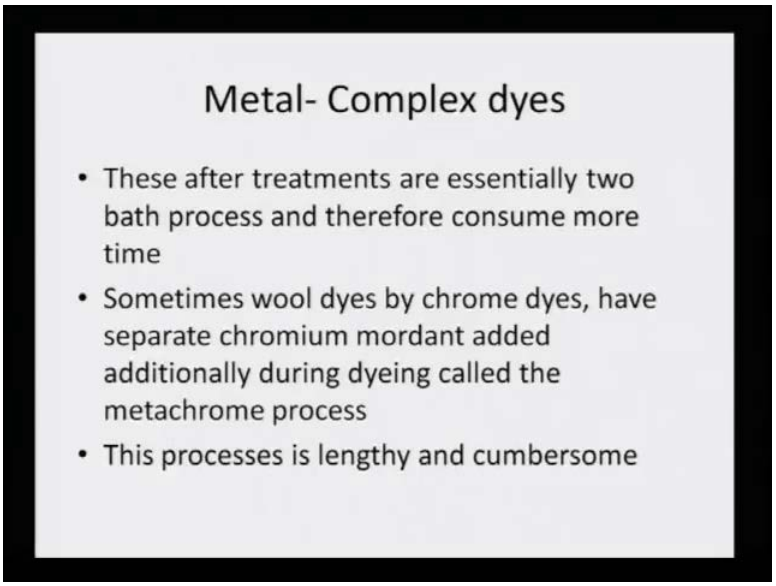

The metal-complex dyes there, these are after treatments are essentially two bath process and therefore consume more time; obviously, once the dying is done with the direct dye, it is the second step where the after treatment is done; it is not a simultaneous process - first thing. Second thing is that after the dying is done the fabric is air dried and then it is put in to the bath of the metal and then allowed to react with that metal solution for sometime at least 2 to 3 hours. And that is foreign industrial process, any extra step will add on to more time in the final product preparation and whether it is time consuming, whether it is energy consuming or whether it is money consuming process will not be regarded as one of the best method for industry.

Sometimes wool dyes by a dyed by chrome dyes, have separate chromium mordant added additionally during dying called the metachrome process. Sometimes of course, the meta that is the simultaneous chroming also can be done and that is called metachrome process, but these processes are very lengthy and cumbersome. Why because first the wool is dyed with chromo dye, already chromium is present in that and

plus additional chromium salt is added and therefore, the whole dye bath becomes extremely hazarders. You see, hazarders from the point of view of its disposal, but these processes were nevertheless developed particularly for wool dyeing.

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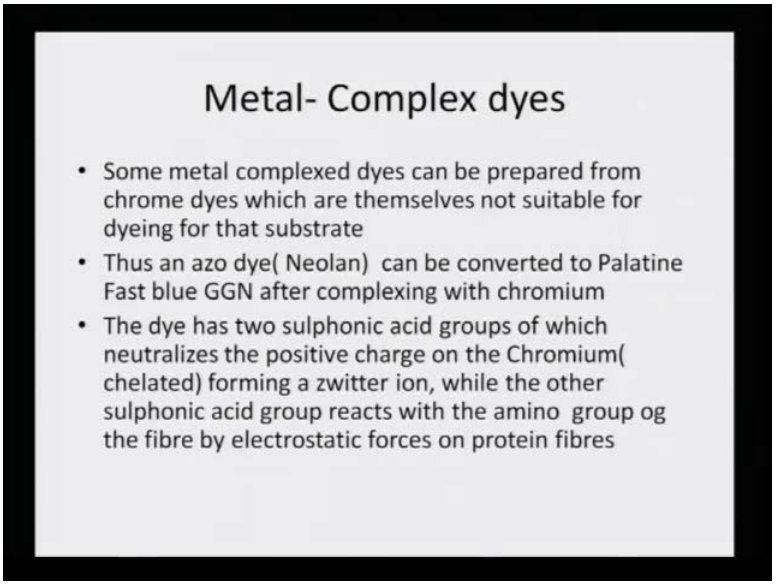

Some metal-complex dyes can be prepared from chrome dyes which are themselves not suitable for dyeing for that substrate. Suppose, if chrome dye is not able to provide the metal complexing metal atom then in that case this additional a metal is added. Thus an azo that is the Neolan can be converted to palatine fast blue GGN after complexing with chromium. The dye has two sulphonic acid groups of which one neutralizes the positive charge on the chromium chelated forming a zwitter ion, while the other sulphonic acid group acts with the amino group of the fiber by electrostatic forces on protein fibers.

So you see, the way it acts at least this metal complexing dye which is an azo dye must have two sulphonic acid groups. One will one sulphonic acid azo 3H minus will try to electrostatically neutralize the positive charge on the chromium metal which is you know co-ordinated, and the other sulphonic acid then reacts with the amino group of the fiber. Because you know that protein fibers, proteinaceous fibers like silk and wool have amide linkages. So, it is the amino group of the amide which is then you know, linked up with the sulphonic acid group.

So, acid base ionic interaction and the acid and metal co-ordinate linkage. These are the two different types of co-ordination and ionic bond formation during the complexation of

the metal which is additionally added to the dying process for meta complex dye formation or metal complex dye formation.

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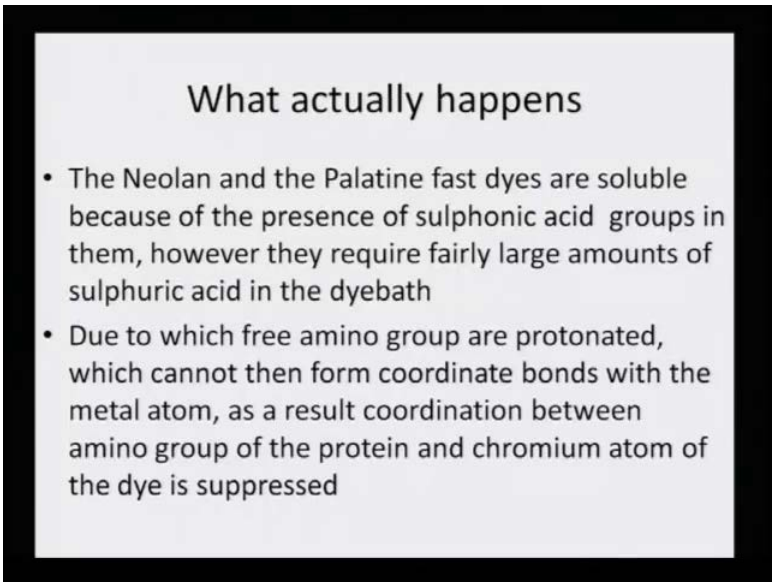

What actually happens, the Neolan and the palatine fast dyes are soluble because of the presence of sulphonic acid groups in them, however they require fairly large amount of sulphuric acid in the dye bath. Now, both the precursor which is the Neolan, and metal added palatine which is also having the same structure. See because the main structure of the azo dye is not changing, it must have azo linkage and must have two sulphonic acid. That is the Neolan and that Neolan after reaction with the metal either copper, chromium, nickel, cobalt can then be transferred into a palatine dye which is nothing but metilated dye or metal complex dye, although both are soluble and the solubalization is primarily because of the auxochrome azo three h minus.

So you see that, you know this particular sulphonic acid group is responsible for its solubility. When we were talking about other dyes like reactive dyes and many other dyes, sulphur dyes and so on. One thing, that dyes we were talking about the solubalization that is a primary effect and is cannot be ignored, because only when the dye is solubilize, it will penetrate in to the fiber that is how the chemistry or the compatibility that we are talking about is brought about.

If we do not have a dye which is soluble, then the dye will only sit on the surface of the fabric and it will not a penetrate and unless and until the dye penetrates in to the core of

the fiber. We do not say that even dying has occurred, because it will get stripped off in the first washing if it is just a matter of surface action, because surface action will not have any bonding, it will just be electrostatically held up and that can be washed up with the water and the detergent and so on.

So, no dye will pass through this test of being a good dye unless and until it has penetrated and for penet good dye penetration solubilization is a prime factor. Due to which pre amino group are protonated, which cannot then form co-ordinate bond with the metal atom, as a result coordination between the amino group of the protein and chromium atom of the dye is suppressed.

So, because the dye bath has to be kept at a very low PH with the help of additional sulphuric acid which is a very strong acid. There are many things that happen in a competitive manner now because of excess of sulphuric acid, there is a huge amount of H plus which is available in the dye bath. So what happens, the amino group of the protein fiber gets protonated with that, and therefore, it is not available for coordination with the metal bond, metal atom and therefore, the amino group of the protein, and the chromium atom of the dye are then not coordinating and they are that this effective suppressed.

So, that is in order to keep that effect suppress dye bath must be highly acidic and this acidic condition is brought about by the addition of sulphuric acid. The properties of metal complex dyes; obviously, we have to look at the features and properties of metal complex dyes because so far, you have learned about reactive dyes, you have learnt about fiber reactive dyes, you have learnt about sulphur dyes, you have learnt about vat dyes. So, what is so different about this particular dye let us try to understand.

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No pre or post after treatment with metal salt is required, because already it is an after treatment. So, any no other additional step is required. Some of them are brighter than the chrome dyes. However their fastness is slightly lower than the chrome dyes, but still it is good enough. Due to their ease of application and fastness properties, they are use for dyeing high class dress materials, hosieries, ladies wear and so on.

So you see, they have an advantageous situation because they are able to dye the finest of the fine material and the hosiery which is a nickel fabric is also able to take up these dyes metal dyes in a very efficient manner. Now, the efficiency of any dye is actually evaluated by two factors, time and again I am trying to emphasize one is the fastness property and the other one is the penetration which is due to the solubility.

So, according to that, this dye definitely has an edge over many of the chrome dyes which do not have these properties. So, they are also sometimes brighter than the chrome dyes and they can be used for brighter shades as well as lighter shades both. And they are use for very fine materials which are used for ladies wear, hosiery, dress material, high class dress material and so on, and so forth.

These metal complex dyes that are otherwise known as pre metallized dyes shows great affinity towards protein fibers.

So, as we saw, that because of the sulphonic acid group interacting with the protein amino group of the protein rather the amide of the protein fiber. It is a very compatible dye for these particular proteinaceous fibers, and under that category we have silk and wool. Generally it has been seen that metal complex dyes are chromium or cobalt complexes. So, if we take a look at the various types of metal complex dyes that are available in the market most of them are chromium or cobalt complexes.

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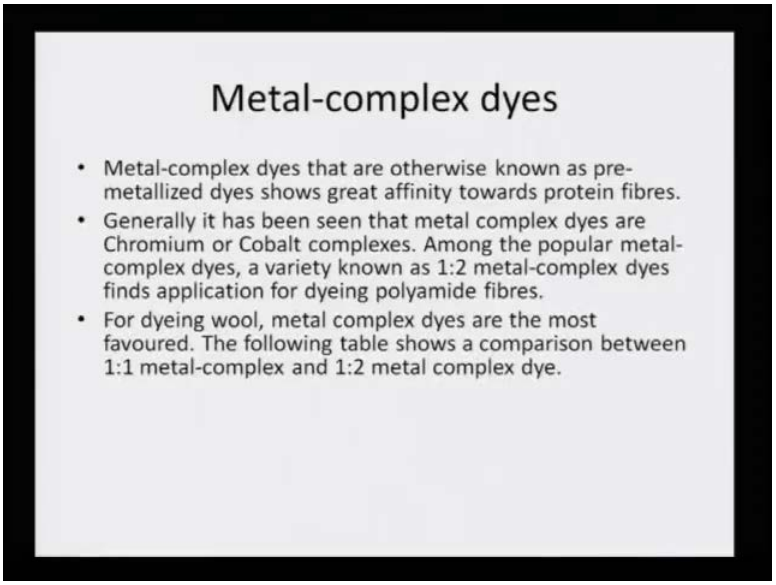

Among the popular metal complex dyes a variety known as 1 is to 2 metal complex dyes finds application for dyeing polyamide fibers. Now, there are, as you would know, that every broad class of dyes have different sub class of dye. So, 1 is to 2 metal complex dye is a class of metal complex dye. For dying wool, metal complex dyes are most favored. The following table shows the comparison between 1 is to 1 metal complex and 1 is to 2 metal complex dyes. So far wool, this is an ideal metal complex dye is very good. For cotton also, it we have been explored and it has been found to be very good for polyamide fibers also.

So, there are two class of metal dyes one is 1 is to 1 metal complex dye, the other one is 1 is to 2 metal complex dye. And let us see a comparative analysis of what is there in our performance according to their reactivity.

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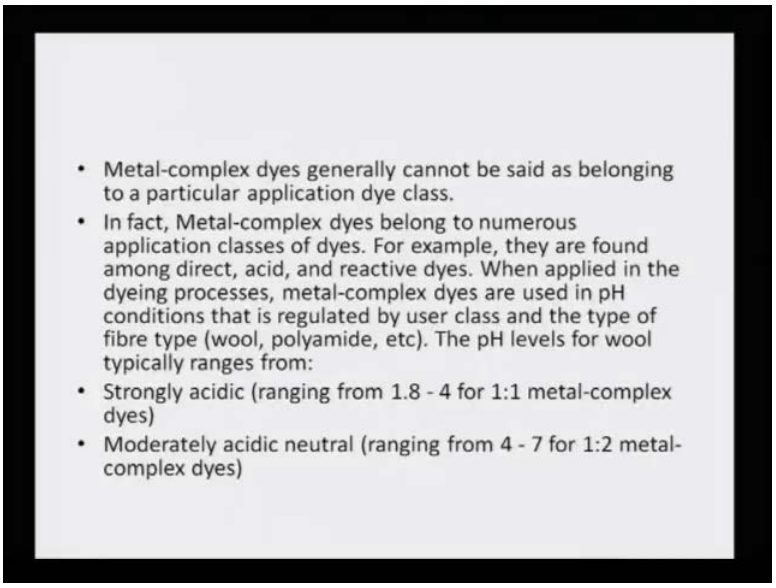

The metal complex dyes generally cannot be said to be belonging to a particular application dye class. Why because they can be use for various purposes and the only amendment that one does is to make a pre or post treatment or an after treatment with metal salt.

In fact, metal complex dyes belong to numerous application classes of dyes. For example, they are found among direct, acid, and reactive dyes. So, the starting dye can be either a direct dye or an acid dye or a reactive dye. After the dyeing has been done with these respective dyes separately of course, the metal after treatment can be done to all three of them. So, one cannot say that metal complex dyes are belonging to only direct class of dyes or acid class of dyes or reactive class of dyes, because this methylation process can be carried out, as an after treatment in all the three classes of application. When applied in the dyeing process, metal complex dyes are used in PH condition that is regulated by user class and by the type of fiber that is to be dyed, it may be wool, polyamide, cotton etcetera.

The PH levels for wool typically ranges from strongly acidic ranging from 1.8 to four for 1 is to 1 metal complex dyes and moderately is acidic neutral ranging from four to seven for 1 is to 2 metal complex dyes.

Now you see, it is common sense that one cannot use very high acidic solutions for cotton and cotton blends. Why because it will completely decompose the cotton material

and therefore, strongly acidic conditions are only meant for more you know, fiber which has more tensile strength which is stronger like polyamides and wools, but mild or moderately acidic or neutral solutions of dye bath can be used, because they are in the range of four to seven.

Now, PH four to seven can be with which stood by cotton and cotton blends. So it is this which is ideally suited for cotton and cotton blends and for having 1 is to 1 metal complex type of sub class of dye one has to use very strongly acidic dye bath, but for 1 is to 2 metal complex dyes, it is possible to do it and a moderately acidic or neutral condition.

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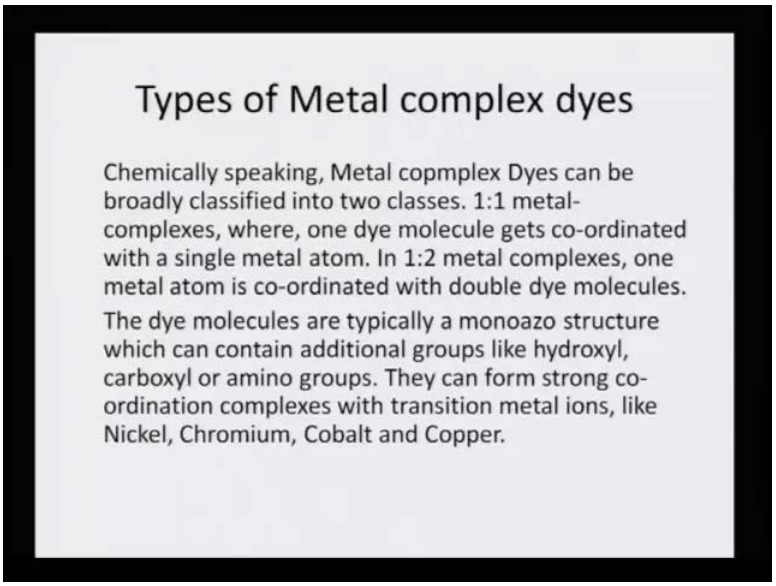

Types of metal complex dyes, we have just spoken about the two varieties 1 is to 1 and 1 is to 2 metal complexes, but still we will take as more closer look at it.

Chemically speaking, metal complex dyes can be broadly classified into two classes. 1 is to 1 metal complexes, where, one dye molecule gets co-ordinated with the single metal. In 1 is to 2 metal complexes, one metal atom is co-ordinated to two double dye molecules. The dye molecules are typically a monoazo structure which can contain additional groups like hydroxyl, carboxyl or amino groups. They can form strong co ordination complexes with transition metal, like nickel, chromium, cobalt and copper.

So, there are various possibilities, as I told you, from the Nolan which is a non metalized monoazo structure to a palatine which is a metalized structure of the same. It can have a 1 is to 1 ratio; that means, one metal atom, one dye atom or one dye molecule where as in the case of 1 is to 2, it is one metal atom and two dye molecule which are co-ordinated to that and the metal atom can have variance, it can be a nickel metal or chromium or a cobalt or copper, so that many varieties of dyes are possible.

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Now, when we try to take a closer look at the features of the metal Complex dyes, they are excellent to handle and have good light-fastness, excellent light fastness, medium washing fastness. Show very good level dyeing and penetration characteristic can cover up for the irregularities in the substrates. They are water soluble dyes, because see for a dye to be good dye a falling in to a good dye category; light fastness, washing fastness, solubility which is related to penetration all must be from good to excellent category, otherwise the dye is of no use for the industrial application.

One can use it in the laboratory, but that is not the final aim because these dyes have been designed primarily to cater to the textile industry and the textile industry has various kinds of natural fibers and synthetic fibers. So, it is a competitive market where newer and newer dyes are required to be able to successfully dye these you know, sometimes it is even blends of the natural and synthetic fibers. So, the main challenge is to be able to die.

And the next then issue is level dyeing unless and until the penetration is good the evenness in the dyeing will not come. So, all this is interrelated and adds on to the category of good dyeing properties.

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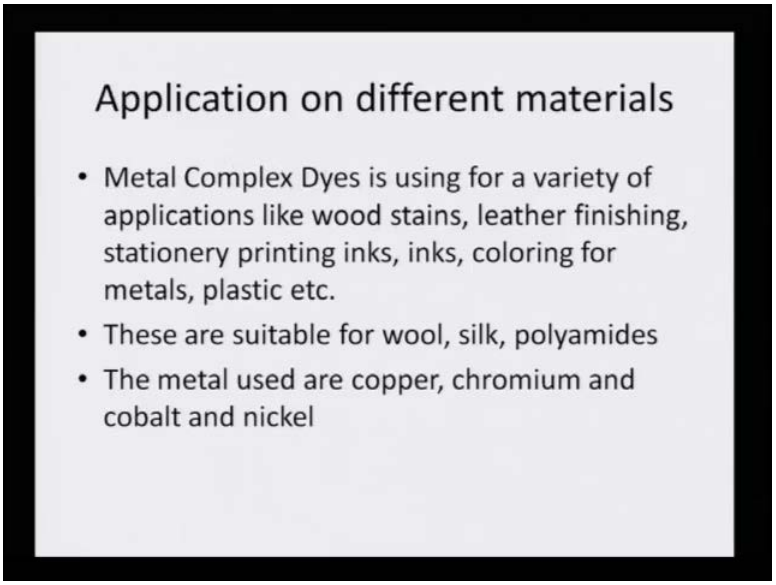

Application on different materials, because if we are talking, if a dye has a more versatile feature of being able to handle or being able to use for natural as well as synthetic dyes, then nothing can be better than that. Metal complex dye is used for a variety of applications like wood stains, leather finishing, stationary printing inks, inks, coloring for metals, plastic and etcetera.

So you see, from the non textile point of view also, it is a very good dye. At the same time, it is very suitable for wool, silk and polyamide and the metals that can be used are copper, chromium, cobalt and nickel, as what I said just told you a while ago.

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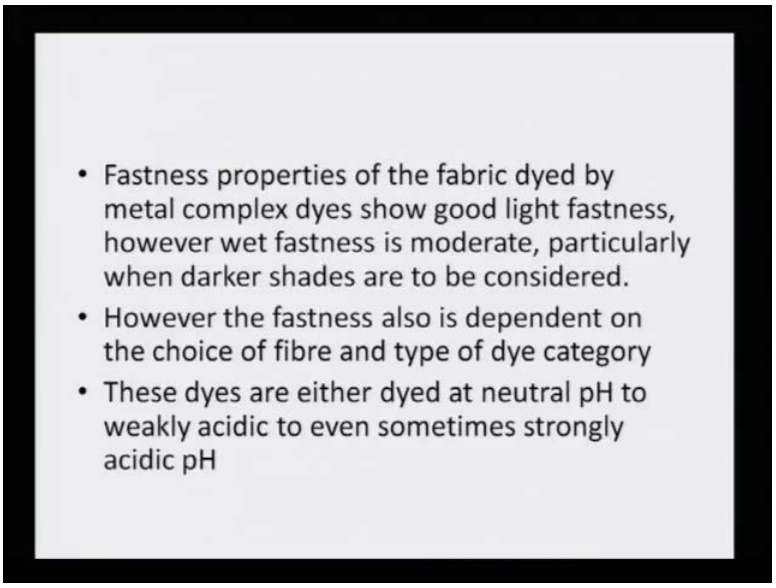

Then comes the fastness properties of the fabric dye by the metal complex dyes show good light fastness, however the wet fastness is moderate. This we have seen that when we were looking at the features of this. So now, one has to way has to what are the main properties and if the main properties are from good to excellent, if one or two property is not so good, it is from fare to good a category. We will still accept that dye to be a good dye.

Particularly, when darker shades are to be considered, so the goodness is only you know at par when we are talking in terms of darker shades, but for lighter shades, there is no problem. However the fastness is also dependent on the choice of fiber and the type of dye category. I have told you that the entire processing of dyeing or the process of dyeing is basically related to the chemistry of the fiber and the dye. So, that is what makes whether it is going to make the light fastness better or not so good or whether it will make the wet fastness better or not so good. All that will be dependent on what fiber is being used and which of the metal complex dye has been used along with it.

These dyes are either dyed at neutral PH to weakly acidic to even sometimes strongly acidic PH and we discussed this point a while ago, because this dye also has a big role when we talk about the PH of the dye bath. Because these dyes are again very, very PH sensitive and therefore, these dyes must be understood that they can be either worked with on neutral to mildly acidic or at strongly acidic PH as well, 1 is to1 metal complex

dyes. Let us try to look at this sub class, these dyes have good leveling and good penetration into the carbonized wool. They worked at very low PH that is 1.8 to 2.5 with sulphuric acid or three to four with formic acid, hence are not at all suitable for cotton or blends of cotton. We have talked about this while ago, but still we should understand that, what are the do's and what are the do not.

You know, you cannot use a very acidic dye bath for cotton or cotton blends, because what will happen, that the cotton will get completely eaten up by the acid. Because it reacts with the acid and it is highly corrosive for the cotton fabric.

So, sulphuric acid which is present in the dye bath and we discussed why sulphuric acid needs to be use, because it is a big source of first thing is that the acid PH of the dye bath has to be between 1.8 to four that is the range and in order to obtain that range a very you know, strong acid is required. Therefore, the use of sulphuric acid is required plus the sulphonic acids that are participating or also replenished in some way by the sulphuric acid and so on.

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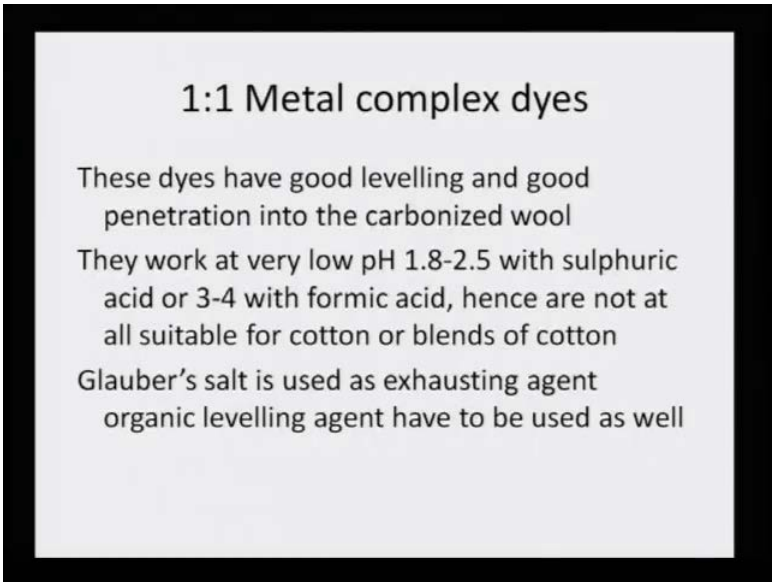

Glauber's salt is used as exhausting agent organic levelling agents have to be used as well. So just a way, we saw that in many of these dyes exhausting agents have to be used some electrolytes sodium sulphate, which is Glauber's salt is to be used for this purpose. So, that more and more dye can penetrate that is call the exhaustion of the dye and leveling, because it should not accumulate it should help the dye to migrate into the other

parts of the fiber in a very facile manner. That is the role of the levelling agent and that also has to be added in even we are dealing with 1 is to1 metal complex dyes.

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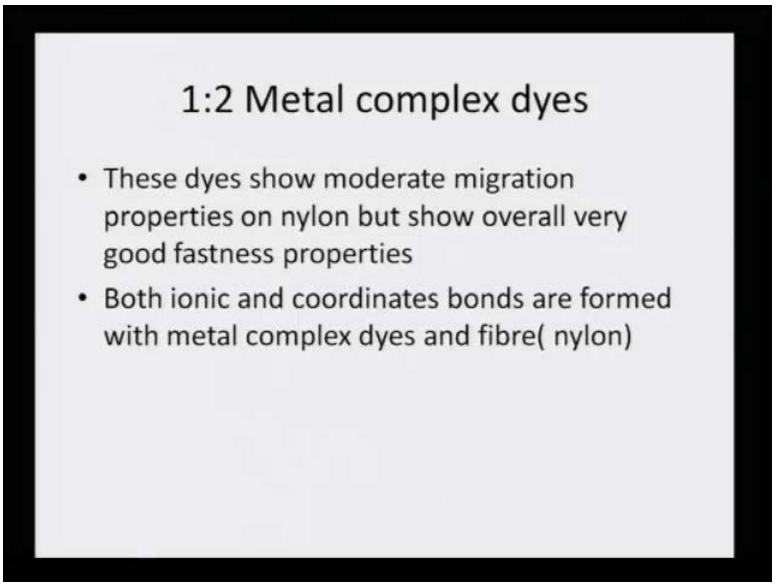

Now, let us take a look at the 1 is to 2 metal complex dyes. These dyes show moderate migration properties on nylon, but show overall very good fastness properties. Both ionic and co-ordinate bonds are formed with metal complex dyes and fiber that is the nylon.

So, we have seen that for dying nylon 1 is to 2 metal complex dyes need to be used, why because they can form ionic and co-ordinate bond together with the metal of this metal complex dyes.

And nylon fiber is best suited when 1 is to 2 metal complex dyes have to be used. So therefore, you know already there are information that has been established the acidic can be done very or fabrics which can we withstand very high acidic dye bath solution they can be died by 1 is to1 metal complex dyes where as moderate or mildly acidic to neutral solutions of dye bath can take only 1 is to 2 metal complex dyes. So, that is the kind of sub classing that has been done for the main class metal complex dyes.

So, that the ease of you know, choice is dependent on the nature of the fiber and therefore, not everything can be dyed with every metal complex dyes that is absolutely clear and categorically they have been separated out, because of the high acidity and moderate acidity of the dye bath. Now, one such dye which is called Delosol S type of

dye we will discuss a little bit about the chemistry and why is it so popular among the metal complex dyes.

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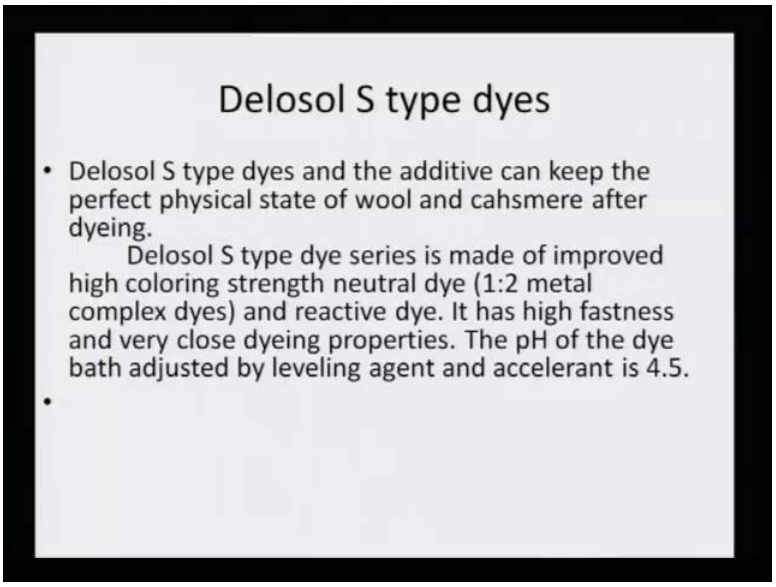

Delosol S type dyes and the additive can keep the perfect physical state of wool and cashmere after dyeing; that means, you know there is very fine wool and this wool needs to be dyed in a very tender manner and for this, because we already know that metal complex dyes for wool actually acts at a very high PH. So, Delosol S or rather low PH when we talk in terms of the scale of the PH, but high acidic solution. Delosol S type dye series is made of improved high coloring strength neutral dye that is 1 is to 2 metal complex dyes.

So, this has been improved; see, wool under normal condition or cashmere wool under normal condition cannot sometimes with stand very acidic solutions which are ideally required for 1 is to1 metal complex. Now this Delosol has been improved version where high coloring strength can be important at a neutral PH and 1 is to 2 metal complex dyes are used along with it, along with reactive dye. It has high fastness and very close dyeing properties. The PH of the dye bath adjusted by leveling agent and accelerant is just kept at 4.5 which was not possible if one was using 1 is to1 metal complex dyes.

So this way, you know Delosol has been really improved to take care of dyeing of wool. This dye system is characterized by high dyeing exhaustion rate and excellent dyeing

reproducibility. Delosol S type dye series has only 15 colors but complete chromatogram that can blend almost all the trend colors.

You see, you know with the 15 colors or gamete of colors can be prepared by permutation combination. So, because of that and because they have very high dyeing exhaustion rate and excellent dyeing reproducibility because see, that is what the kind of dye industry deals, that how many colors can be generated, what is the reproducibility can the same shade be reproduced again and again and again in different batches.

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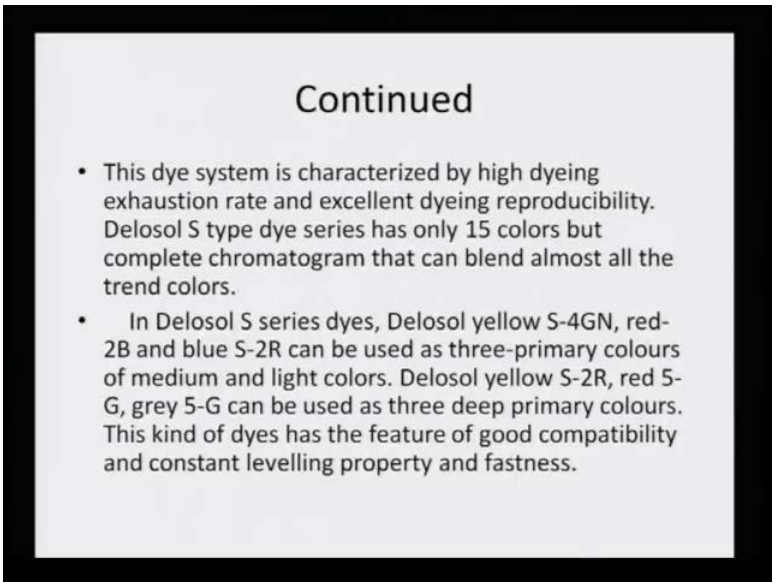

And the third thing is that it should have good exhaustion if it has good exhaustion the dyebath has very little to be disposed and the fluent problem is taken care of. In Delosol S series dyes Delosol yellow S- 4GN, red -2B and blue S-2R can be used as three primary colors of medium light colors. Delosol yellow S-2R, red-5G, gray-5G can be used as three deep primary colors. This kind of dye has the feature of good compatibility and constant levelling property and fastness.

So, if you look at the various you know different types of Delosol dyes, you know they can be used for light dyeing, for dark shade dyeing as well as because of these three combination of these three primary colors many, many other colors can be generated from these three primary colors and of course there are 15 main colors that have come up in the Delosol series and many permutation, combination and a gamete of colors can be made out of it.

Delosol S type which is a primarily meant for wool and specially the very delicate cashmere wool dyeing system can provide the following features and benefits.

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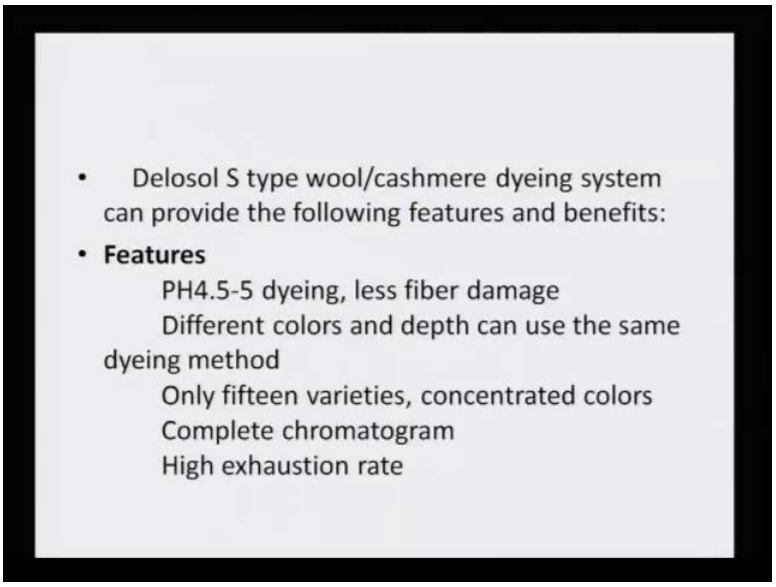

So, what are the features the dying can be done at PH4.5 to 5 and less fiber damage occurs, different colors and deep depth can be use, can use the same dying bath, only fifteen varieties concentrated colors are available, complete chromatogram can be actually generated from these 15 varieties and they have high exhaust rate.

Now, exhaustion rate when it is very, very high, as I told you a fluent disposal problem automatically comes down. So, that makes it a very good dye, because we are using do not forget, that we are using metal here. And so this metal can create a worked if it is remains in the dye bath and if the exhaustion is poor. So, because the dye update is enough and the dye bath is left with less amount of the metal. It is the disposal is not so crucial.

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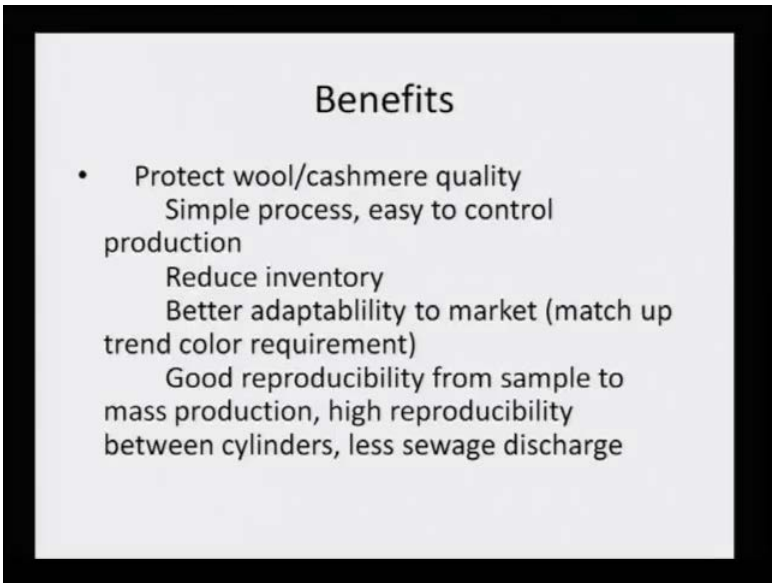

There are several benefits of using Delosol. It is protective towards wool and cashmere quality of wool which is very, very fine; simple process, easy to control production, reduces inventory, better adaptability to market match up the trend color requirement, good reproducibility from sample to mass production, high reproducibility between cylinders, less sewage discharge.

So you see that, it has most of the dye quality which an ideal dye must have and therefore, this class of dye although one would think that, they fall in the category of hazardous dyes, but because of it is good you know exhaustion, because of it is good fastness property, because of it is good you know reproducibility, because of it is good shade variation that is possible and less sewage discharge. All these put together this metal complex series of dyes as one of the best in the synthetic dye series.