Natural Dyes
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Lecture No. # 29

The next less lecture that we will be covering now would be related to dyeing of acrylic fiber. We saw we also saw how the dyeing of polyesters were done and its blend, we took a look at the dyeing ability of the polyamide that is the nylon, and the third in the series is another synthetic fiber which is very tough to dye, and that is the acrylic fiber. And because the consumer market of acrylic fiber; obviously, look people are looking for colored acrylic fiber.

And to be able to color the acrylic fiber is what we are going to discuss today in today's lecture. So, therefore this entire lecture would be dedicated to yet another synthetic fiber, which is acrylic fiber, and with the help of synthetic dyes. So, we will take a break from the natural dyes and the natural dyeing for a while, and we will try to learn this new fiber, and new dyeing technique.

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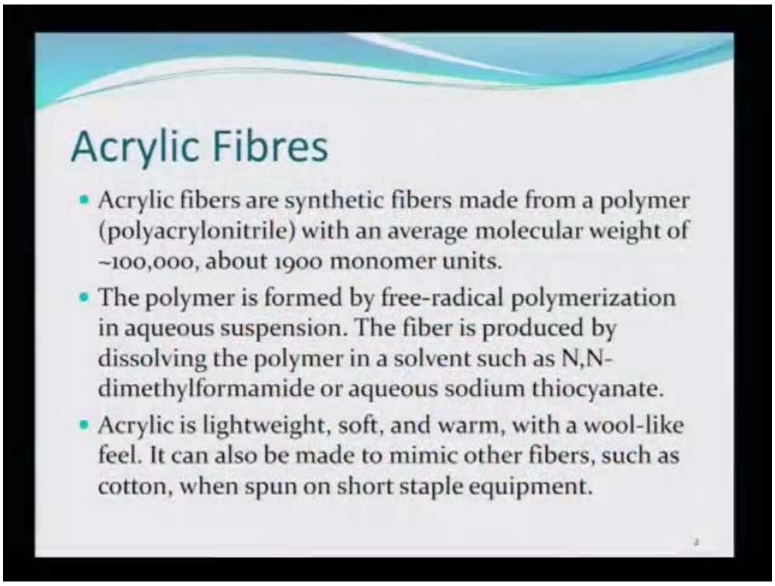

Acrylic fibers: Acrylic fibers are synthetic fibers made from a polymer; that is polyacrylonitrile with an average molecular weight of 100000 about 1900 monomer units being linked up. So, you see it is a macromolecule first thing made out of polyacrylonitrile;

the polymer is formed by free radical polymerization in aqueous suspension. The fiber is produced by dissolving the polymer in a solvent such as N, N- dimethylformamide or aqueous sodium dye thiocyanate.

The acrylic is lightweight soft and warm with a wool-like feel, it can also be made mimic other fibers such as cotton when spun on short staple equipment. So, you see it has all the similarities of cotton and it can be some spun in the same manner, but it is not cotton it is a synthetic fiber. And to be able to produce it in bulk, the monomer that is required is the polyacrylonitrile and as big as 100000 units can be linked up with the molecular weight of 100000 or so on, and 1900 also monomers can be linked up. And the method to prepare this is by the free radical polymerization method.

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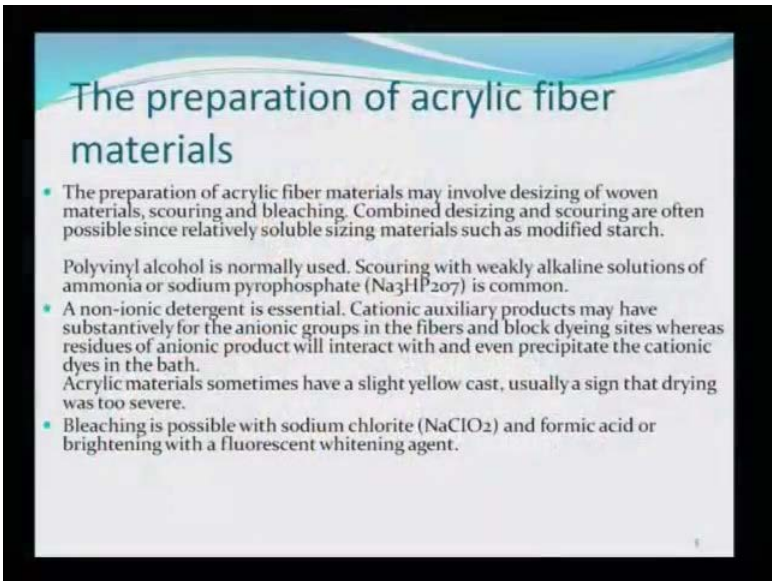

The preparation of acrylic fiber material: The preparation of acrylic fiber materials may involve desizing of the woven material scouring and bleaching. So, by now we know the desizing is required to remove the striations on the surface of the fabric, and scouring is the washing of the waxes on the oils which are actually used at the time of spinning the yarn, and bleaching of course to remove any kind of remaining colorant. The preparation of acrylic fiber material as we all know that fiber whether it is natural or synthetic needs to be prepared. And the usual steps us scouring bleaching and so on before taking it for dyeing.

Similarly, here also acrylic fibers have to be treated before they can be used for dyeing. The preparation of acrylic material may involve desizing of woven materials scouring and bleaching; combine desizing and scouring are often possible, since relatively soluble seizing material such as modified starch have to be removed. So, one can combine the process of scouring and desizing, because the only contaminant that is removed that is required to be removed is the modified starch. Bolyvinyl alcohol is normally used for this purpose; scouring with weakly alkaline solution of ammonia or sodium pyrophosphate is also common.

So, scouring can be done by several methods either by polyvinyl alcohol or with the weakly alkaline solution of ammonia or sodium pyrophosphate. So, these are the various alternatives for scouring, a non-ionic detergent is essential. Cationic auxiliary products may have substantively for the anionic group in the fibers, and block dyeing sites whereas residues of anionic product will interact with and even precipitate the cationic dyes in the bath. So, that is why a non-ionic detergent needs to be used. If the detergent is anionic or cationic it will interfere with the dye chemistry; and therefore, a non-ionic detergent needs to be used.

Acrylic materials sometimes have a slight yellow cast usually a sign that drying was too severe. So, sometimes while drawing this process the acrylic fiber takes a yellowish sting, which is because of the process not being done in a proper manner. Bleaching is possible with sodium chlorite, and formic acid or brightening with a fluorescent whitening agent. So, there are possibilities that this yellow coloration can be removed. So, scouring, bleaching, desizing; all this needs to be done before the fabric can be used for dyeing.

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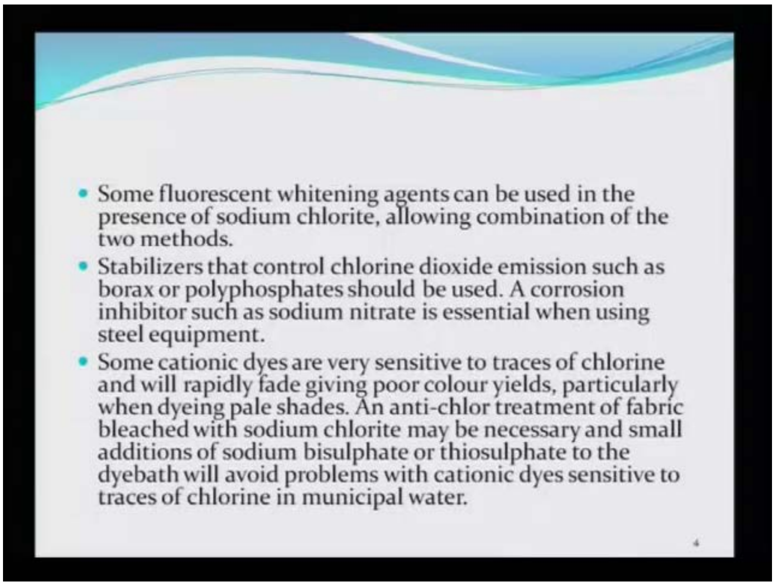

Some fluorescent whitening agents can be used in the presence of sodium chlorite, allowing combination of the two methods. So, it is possible to use fluorescent, whitening agent and bleaching agent together, but may be not an all types of combination. So, one has to carefully choose the different re-agents as what I mentioned a while ago, the anionic and the cationic detergents cannot be used. So, a non ionic detergent is used for washing.

Stabilizers that control chlorine dioxide emission, such as borax a polyphosphates should be used, because as we all know chlorine dioxide is not eco friendly chemical; and therefore, they needs to be a method or a measure to rectify the process, and if it is being used the the these emissions can be controlled by the use of borax or polyphosphates. A corrosion inhibitor such as sodium nitrate is essential when using steel equipment. So, because of these you know very harsh chemicals that are used, there has to be a non corrosive materials sodium nitrate, if steel equip ments are used. And we know that most of the dyeing machines that we took a look a while we were doing the chapter on dyeing machines were made out of steel of different qualities of steel that is alright.

But they were stainless steel. So, in order to prevent this equipment from getting corroded with the, because of the use of these auxiliaries; one needs to rectify the material and a only method rather. And this is done by the use of using the sodium nitrate chemical. Some cationic dyes are very sensitive to traces of chlorine, and will rapidly fade giving poor color yields particularly when dyeing pale shades.

An anti-chlor treatment of fabric bleached with sodium nit chlorite may be necessary, and small additions of sodium bisulphate or thiosulphate to the dye bath will avoid problems with cationic dyes sensitive to traces of chlorine in municipal water. So, if we have to look at a long term type of dyeing process. We have to take into account what would be the outcome of this water? What would be the situation when it the affluent goes and joins the municipal water. And therefore, several modifications and several dosing of safe chemicals are done. So, that the affluent is safe.

So, an anti-chlor treatment to the fabric bleached with sodium chlorite is also necessary from the fabric point of view as well as from the affluent point of view. The dye bath preparation now once the fabric is ready, after the desizing the scouring and the bleaching. How does one go about preparing for dyeing, and the first in the foremost thing that one has to do is to prepare the dye bath.

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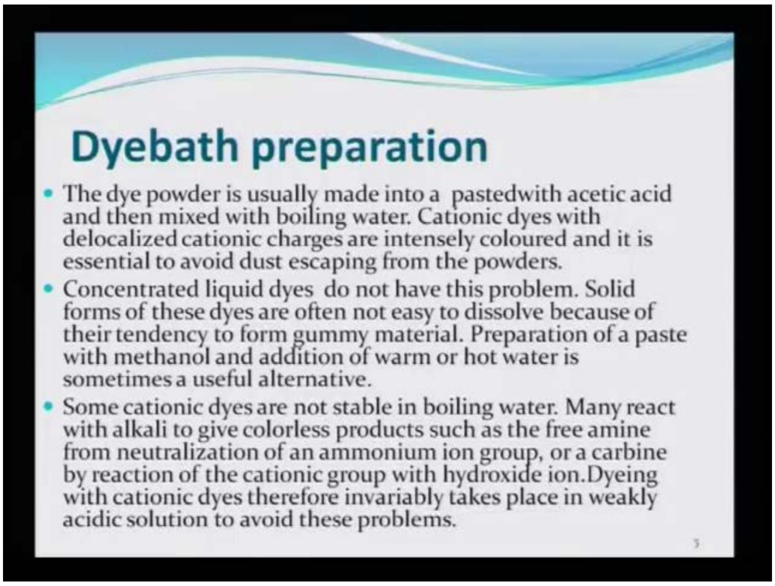

The dye powder is usually made into a paste with acetic acid, and then mixed with boiling water, cationic dyes with delocalized cationic charges are intensely colored, and it is essential to avoid dust escaping from the powders. So, in order for the dye powder which is in the powdery form and the dusty form; a paste is first prepared with the help of acetic acid. And then only it is mixed with hot boil or boiling water; otherwise what will happen? If the dye is directly put into the hot water, a lot of dust particles from the dye powder will escape.

Concentrative liquid dyes do not have this problem. Solid forms of these dyes are often not easy to dissolve, because of their tendency to form gummy material; preparation of a paste with methanol and addition of warm or hot water is sometimes a useful alternative. So, one can either use acetic acid for making the space or one can use methanol also, because the whole idea is to convert the dye powder into the pate form. So, there are two alternatives either one can use acetic acid or methanol.

Some cationic dyes are not stable in boiling water. Many react with alkali to give colorless products such as free amine from neutralization of an ammonium ion group or a carbine by reaction of the cationic group with hydroxide ion. Dyeing with cationic dyes; therefore, invariably takes place in weakly acidic solution to avoid these problems. So, while using cationic dyes for acrylic fiber, many precautions need to be taken; and these precautions are that sometimes this cationic dyes are rendered colorless.

Now that would be a futile exercise, because you are also dipping, but no color is coming on the fabric. So, the whole exercise would be a waste. Instead of that the cationic dyes you know should be handled only under acidic conditions. So, that one can avoid this kind of discrepancy or any kind of non coloration or discoloration.

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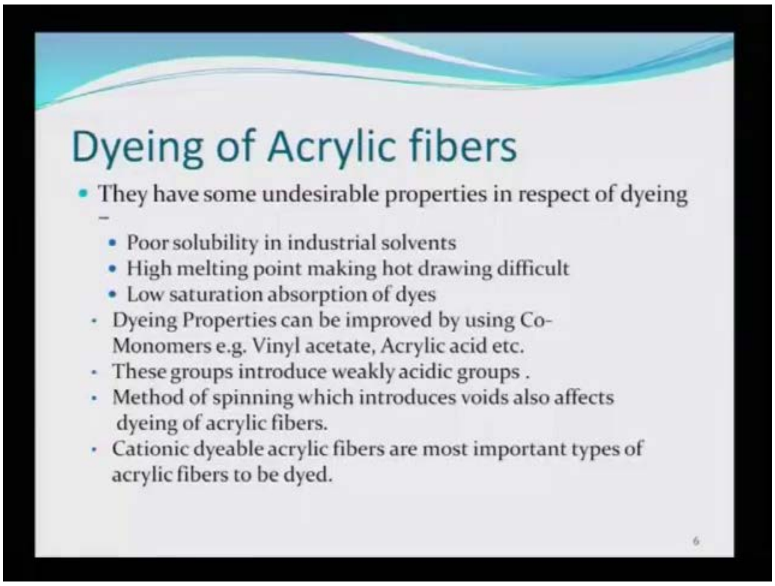

Dyeing of acrylic fiber: They have some these undesirable properties in respect of dyeing, and those need to be taken in into account what is the problem? That needs to be addressed while dyeing an acrylic fiber. They have poor solubility in industrial solvents, high melting point making hot drawing difficult, low saturation absorption of dyes; dyeing properties can be improved by using co-monomers like vinyl acetate acrylic acid.

These groups introduce weakly acidic groups; methods of spinning which introduces voids also affect dyeing of acrylic fibers. Cationic dye able acrylic fibers are most important types of acrylic fibers to be dyed. So, now you see that several several undesirable, you know properties need to be tackled while taking care of dyeing of acrylic fiber. Now, because these dyes which are used for acrylic fibers they have poor solubility in industrial solvents.

They the choice of the solvent must be very, very correct, then because of the high melting point making the you know the fiber cannot be melted. So, they also have a problem with that, then they have poor or low saturation absorption of the dye. Although very high concentrated solutions of the dye is taken while acrylic fibers have to be dyed. The problem with that is the the diffusion of the dye into the fiber takes very slowly. And therefore, they have low saturation in terms of absorption of dyes.

Then even the dyeing properties are not very good, but however there are methods of improving the dyeing property, and that is by using co-monomers such as vinyl acetate and acrylic acid. The the improvement that these bring about is because they add on some acidic groups. And because of the introduction of weakly acidic groups from vinyl acetate or the acrylic acid, this particular acrylic fiber then becomes good enough to take up the dye in a more facile manner. The cationic dyes are the best suited dyes for acrylic fiber.

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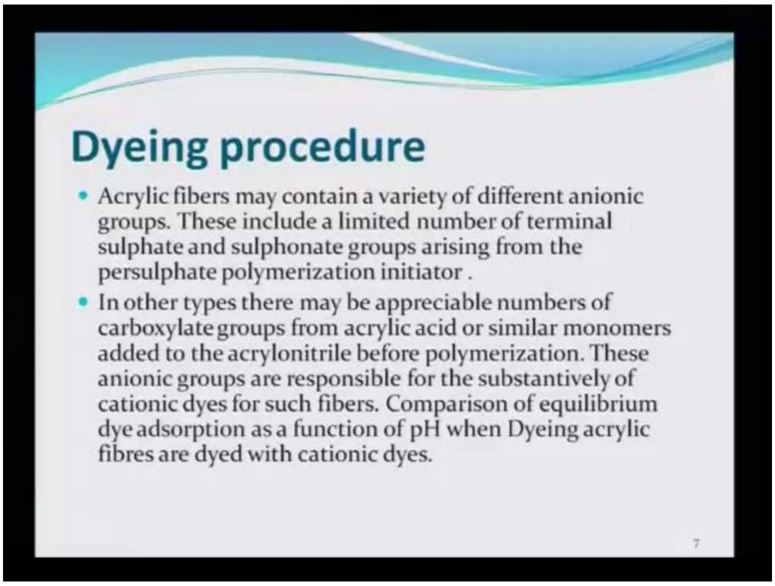

Dyeing procedure: If we try to look into the actual procedure of dyeing, acrylic fibers may contain a variety of different anionic groups. These include a limited number of terminal sulphate and sulphonate groups arising from the persulphate polymerization initiator. So, now you see that is the reason, why cationic dyes have to be used, because the acrylic fiber by itself is anionic in nature, and the anionic nature comes from the fact that at every end, it has anionic groups like sulphate and sulphonate.

And these have actually come from the fact that they were polymerized by an initiator called persulphate. So, persulphate is actually given at the end groups these anionic groups, and they have attached to the polymer making it more anionic it nature, and because of its anionic being an anionic nature; the cationic dyes are best suited. Because then there will be an enactor static attraction between the anionic fiber, and the cationic dye.

In other types there may be appreciable numbers of carboxylate groups from acrylic acid or similar monomers added to the acrylonitrile before polymerization. So, just a while ago we were saying that the property are the absorption property, which is low in the case of acrylic fiber per say can be improved by the introduction of co-monomers that is vinyl acetate or acrylic acid. Now, this acrylic a actually provides a carboxylate an ion, and while if it is introduced in acrylonitrile at the time of polymerization; there will be some acrylic acid ends also apart from the nitrile groups. These anionic groups are responsible for the substantively of cationic dyes to be adhered on the fiber, comparison of equilibrium dye absorption as a function of pH when dyeing acrylic fibers are dyed with cationic dyes. So, you see that again here even in this case; the dye is absorbed and it is just a function of the PH; that means, if it is acidic, it will be better; if it is basic, it will be desorbed, because the cation anion the cationic dye and the anionic fiber. Their equilibrium will be lost if pH is altered.

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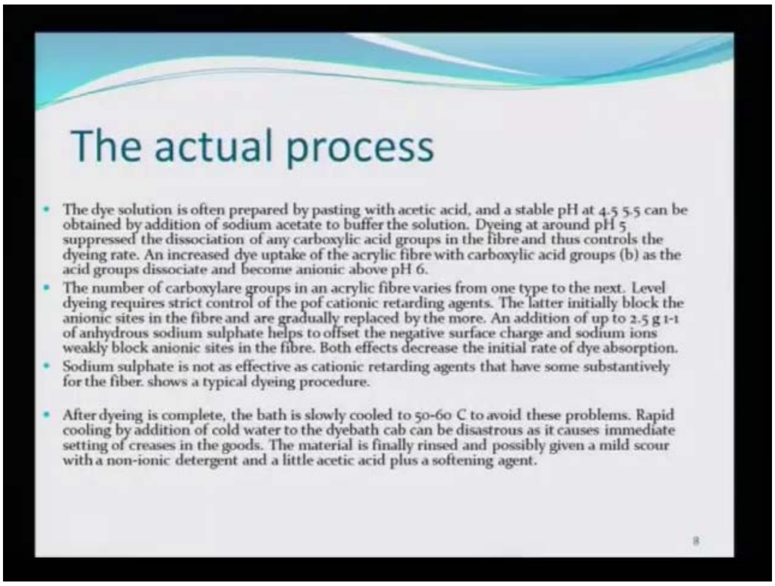

The actual process the dye solution is often prepared by pasting with acetic acid as what we learned a while ago. And a stable pH at 4.5 to 5.5 can be obtained by adding sodium acetate to buffer the solution. When we have to maintain a certain pH it is always better to use a buffer and sodium acetate is a buffer, and to be able to maintain a pH between 4.5 to 5.5, we cannot use very strong solutions of sodium hydroxide or HCL. Because what will happen one drop will make a drastic difference in the pH value, but in order to keep the pH under control buffers are used and sodium acetate is one buffer, through which this pH is maintained. So, The dye is pay made into a paste with the help of acidic acid, and the pH is maintained at 4.5 to 5.5. Dyeing at around pH 5 suppressed the dissociation of any carboxylic acid group in the fiber and thus controls the dyeing rate, and increase dye uptake of the acrylic fiber with carboxylic acid group; as the acid group dissociate and becomes anionic above pH 6.

So, you see in order to keep the carboxylic group in its acidic form it is necessary to carry out the reaction below 5 or at 5 or between 4.5 to 5.5 and not at 6. So, this is this must be very clearly understood that it plays a major role with the pH alteration. The number of carboxylate carboxyl are groups are in the acrylic fiber varies from one type to the next type. Level dyeing requires strict control of the pH of the cationic retarding agents, the later initially block the anionic sites in the fiber and are generally replaced by the more of it. An addition up to 2.5 grams per liter of anhydrous sodium sulphate helps to offset the negative surface charge, and sodium ions of anhydrous sodium sulphate help, block the weakly anionic site of the fiber.

So, you see both effects decrease the initial rate of dye absorption. So, there is a necessity to use either a globate salt, in order to maintain the salt very if the anion and the cation balance, and this can only be done with the help of sodium sulpate anhydrous. So, any time when acrylic dyeing is done apart from the dye powder, apart from the pH maintenance, an another leveling agent or should or the other name for sodium sulphate is globate salt should be added.

And the role of the globate salt is that the anhydrous sodium sodium sulphate helps to offset the negative surface charge, and sodium ions weakly block the anionic sites of the fiber. So, because then only the cationic dyes can go and do the dyeing part. After dyeing is complete, the dye bath is slowly cooled to 50 to 60 degrees to avoid these problem. Rapid cooling by adding by addition of cold water to the dye bath can be disastrous as it cause immediate setting of creases in the goods.

The material is finally rinsed and possibly given a mild scour with a non–ionic detergent, and a little acetic acid plus a softening agent. So, you see now this procedure is so different from the once which we had learnt while we were doing dyeing of polyester, and particularly when we were also doing dyeing of polyamides this morning. It is entirely a different ball game and the step the methodology, the emphasis, the chemicals they are all very different, but yet they come into the category of synthetic dyes and synthetic dyeing. So, you see even they there is so much of variation, because every fabric be its synthetic or natural has its own dynamics to take up the dye. And this dynamic is very, very related to the structure of the fiber, and to the structure of the dye that is used. So, by now you must be able to understand and appreciate that it is just the role of the chemistry of the dye fiber. And the chemistry of the dye that needs to be first understood. Sodium sulphate is not an effective as catinonic retard in agent; that has some sustentative t for the fiber, and it shows in that it plays a role, but it has a very small role, yet that small role is very important when it comes to dye absorption.

So, that is where a small chemical. It does not alter the pH drastically it is not a chemical that is going to you know be acting like leveling agent or something, but it mildly allows this kind of electrostatic forces to move towards neutrality, so that the dye can get impregnated on to the fiber.

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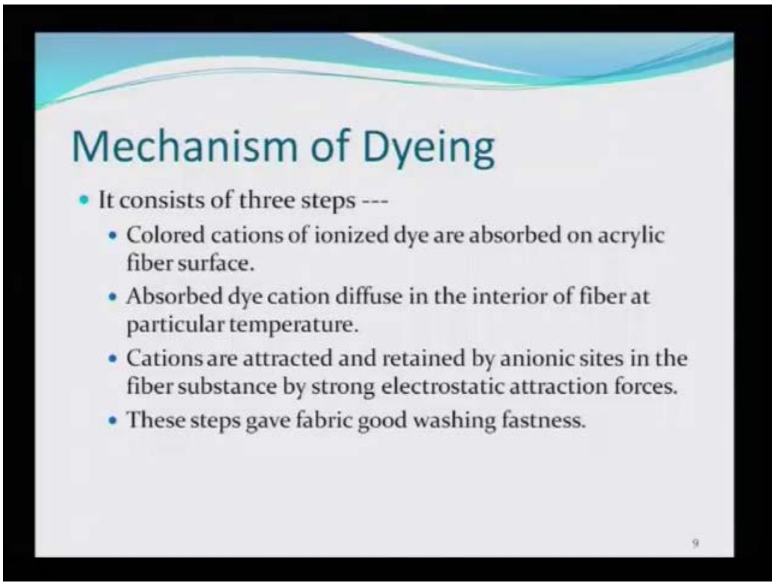

Mechanism of dyeing: It consists of three major steps; colored cayions of ionized dye are absorbed on acrylic fiber surface, absorbed dye cation diffuse in the interior of fiber at particular temperature.

Cations are attracted and retained by anionic sites in the fiber substance by strong electrostatic attraction forces. These steps gave fabric good washing fastness. So, it is all a role of electrostatic attraction, that’s why tetionic dyes and anionic sites on the fiber. If this is not maintained properly with the help of maintaining the proper pH these colored cations will not get on to the surface of the acrylic fiber, because they will have no reason to get attracted, and will be washed off, similarly when they get absorbed that these dyes then start diffusing invertly in to the interior of the fiber, and interior of the fiber at a particular temperature.

So, the temperature also plays a very big role otherwise there will be creases, there will be if there is too much of heat or if there is too much of cold as what we discussed a while ago that is if suddenly cold water is put in to the dye bath. What will be the situation it will create a creases and these creases will not be able to be removed later on. So, each methodology has its own great importance, and these have been devised over experiences of several years.

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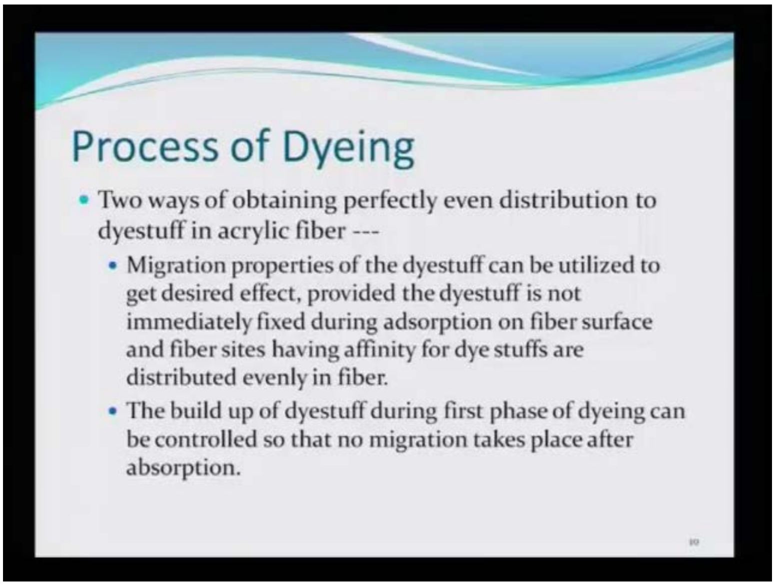

The process of dyeing: Two ways of obtaining perfectly even distribution to dyes of dyestuff in acrylic fiber. Now, you see that there are possibilities the dye aggregates may form. So, how can one attain a very perfect method of dyeing. Migration properties of the dyestuff can be utilized to get desired effect provided the dyestuff is not immediately fixed during adsorption on surface, fiber surface and the fiber sites having affinity for dye stuffs are distributed evenly in the fiber.

Now, when we were talking about addition of the co-polymer vinyl acetate, and as acrylic acid, they should be evenly distributed on the acrylic fiber. If there are too many groups on one end, and none on the other there will be an uneven migration of the dye, because you remember that its all the cationic dyes moving towards the anionic sites, and these co-monomers are actually creating more anionic sites on the acrylic fiber.

So, therefore the adsorption is also related, and the migration property of the dye stuff is totally related on this effect. The buildup of dye stuff during the first phase of dyeing can be controlled, so that no migration takes place after absorption. So, first there is migration then there is adsorption, and during this process one should be able to stop the migration when all the adsorption has taken place otherwise dye aggregates will form, because on the same place more dye will come and hold up. Now that should not happen, because that will cause, you know a lot of un evenness in the dyeing.

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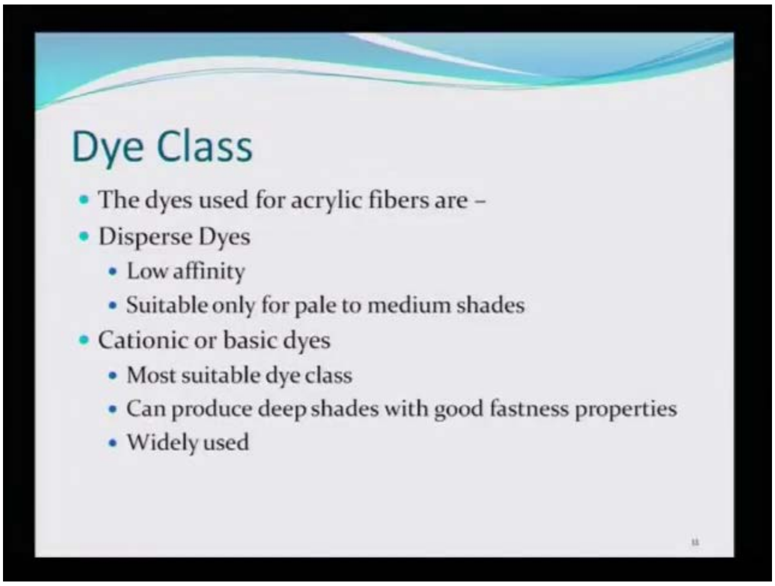

The type of dyes that can be used with acrylic acid or acrylic fiber is very important to be understood. Not every dye can be used, now you understand, because this has to have cationic nature dye, because the fiber is more anionic in nature.

The dyes that are used for acrylic fiber are disperse dyes, because they have low affinity suitable only for pale to medium shades or otherwise one can use cationic or basic dyes most suitably dyep; most suitable class of dye can produce deep shades with good fastness properties and a widely used.

So, there are two options one can either use a disperse dye which has you know low affinity, so you know pale a shades, and not very you know brightly colored dyes can be used or can have an affectivity on the acrylic fiber. But on the other hand cationic of basic dyes are just the appropriate kind of dye, and we have been talking all along, because the cationic dyes are structurally. So, that they have you know a basic center, they are cationic in nature, so that is attracted by the anionic fiber which is the acrylic fibers basic nature.

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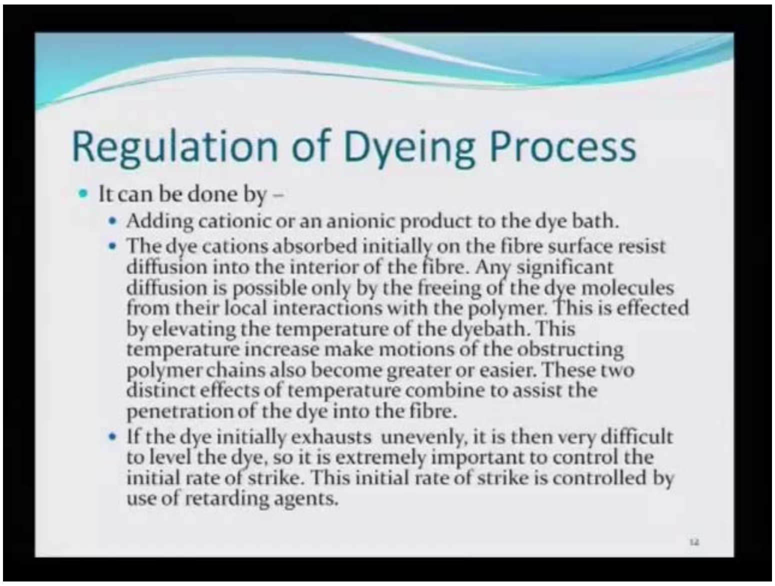

Regulation of dyeing process: It can be done adding cationic or an anionic product to the dye bath the dye cations absorbed, initially on the fiber surface resist, the diffusion into interior of the fiber. Any significant diffusion is possible only by the freeing the dye molecules from the local interactions with the polymer. This is effected by elevating the temperature of the dye bath, this in temperature increase makes motions of the obstructing polymer chain also become greater or easier.

These two distinct effect of temperature combine to assist the penetration of dye into the fiber. Now once it is absorbed, it is the temperature which actually helps and enhances the dye absorption. So, ever thing is very a carefully manipulated or designed, and even giving a temperature has a reason why, because it has a 2 fold reason. Temperature not only helps to for the dye to diffuse properly. So, that local interaction the polymer and sitting in one place making dye aggregates can be avoided.

And secondly, the temperature also helps in migration. So, it not only kind of breaks the aggregate, but it also causes migration, and is if low of the dye into the polymeric chain. If the dye initial exhaust unevenly it is then very difficult to level the dye. So, it is extremely important to control the initial rate of strike.

This initial rate of strike is controlled by using retarding agents. So, therefore the dye that is absorb should be done slowly, and for that retarding agents are used. Once the dye uptake is very fast it will be very difficult to control and dye aggregates will keep forming at various places of the polymer. And that will cause uneven dyeing, but for even dyeing the initial rate of dye pickup should be very slow, and that slowing down is done with the help of retarding agent as the name suggest any agent which slows down the process.

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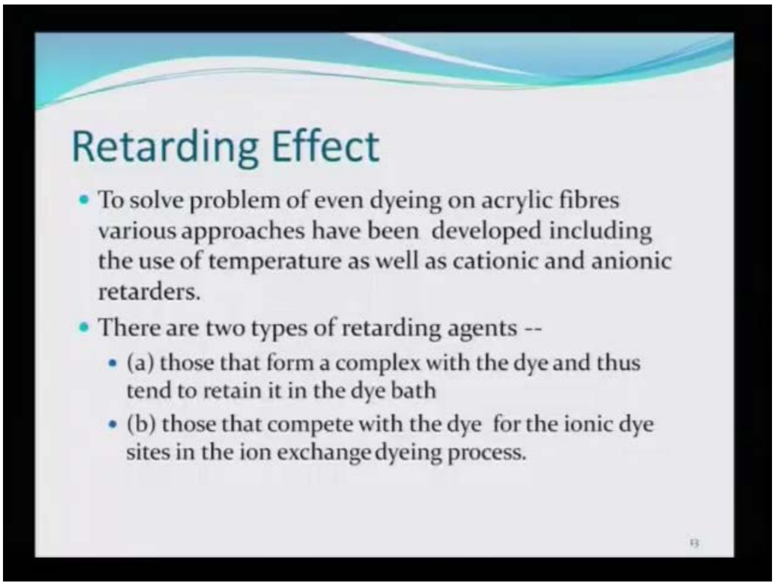

Retarding effect: To solve problem of even dyeing on acrylic fibers. Various approaches have been developed including the use of temperature as well as cationic and anionic retarders. There are two types of retarding agents; those that form a complex with the dye and thus tend to retain it in the dye bath, and those that compete with the dye for the ionic dye sites in the ion exchange dyeing process. So, there there even their retarding agents are could be cationic or anionic, and their sold function is to release the dyes slowly; either by forming a complex and keeping it in dye bath and slowly releasing the dye or by you know creating ionic sites, so that ion exchange dyeing can occur fast.

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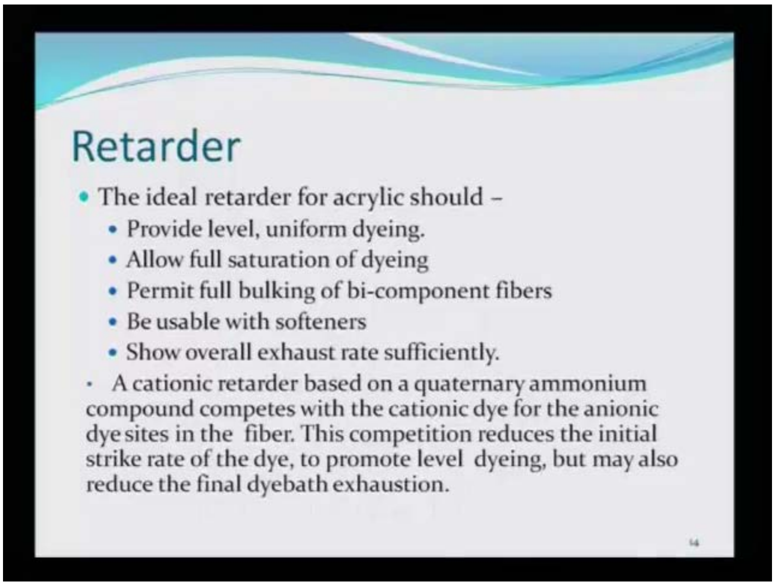

So, these retarders the ideal retarder for acrylics are it should provide level uniform dyeing, allow full saturation of dyeing, permit full bulking of bi-component fibers, be usable with softeners, show overall exhaust rate sufficiently. Because the rate of adsorption, and the rate of penetration should be even. If the rate of adsorption is fast, the dye will aggregate and that much has not penetrated. So, it will cause uneven un that many sites are not available for electrostatic attraction.

A cationic retarder based on quaternary ammonium compound competes with the cationic dye for the anionic dye sites in the fiber. This competition reduces the initial strike rate of the dye. To promote level dyeing, but may also reduce the final dye bath exhaustion. So, there is also a fear that if the retarding agent is added too much, then it will also cause problem, that too much of the dye will be remaining and will not be taken up. So, one has to strike a balance as to how much of the retarding agent should be added, so that the striking rate into the fiber is at an optimal rate, and not very slow and not very fast.

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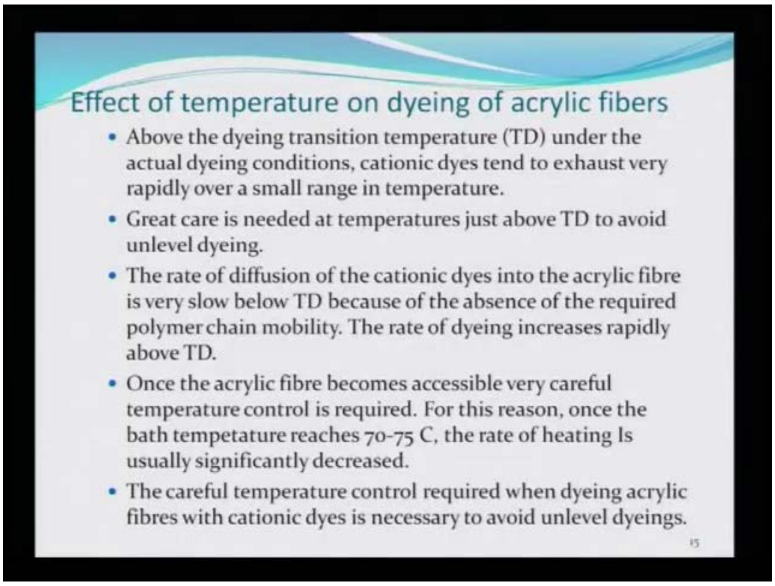

The effect of temperature we have already seen that above the dyeing transition temperature under the actual dyeing condition, cationic dyes tend to exhaust very rapidly. Great care is needed at temperature just above the transition temperature to avoid unlevel dyeing. The rate of diffusion of cationic dyes into the acrylic fiber is very slow below the transition temperature, because of the absence of the required polymer chain mobility.

The rate of dyeing increases rapidly above the transition temperature. So, this is a very crucial temperature above which everything is very good below which everything is very bad. So, one has to find an optimal temperature to be able to have a very good dyeing and even dyeing leveling dyeing. Once the acrylic fiber becomes accessible very careful temperature control is required. For this reason once the temperature bath reaches 70 to 75 degrees, the rate of eating is usually significantly reduced.

So, the most optimum temperature is between 50 to 60, but certainly not beyond 70 to 75. Careful temperature control required when dyeing with acrylic fiber with cationic dye is necessary to avoid unlevel dye. I am repeatedly telling this, because one needs to understand these parameters, and all these parameters are related to structure activity.

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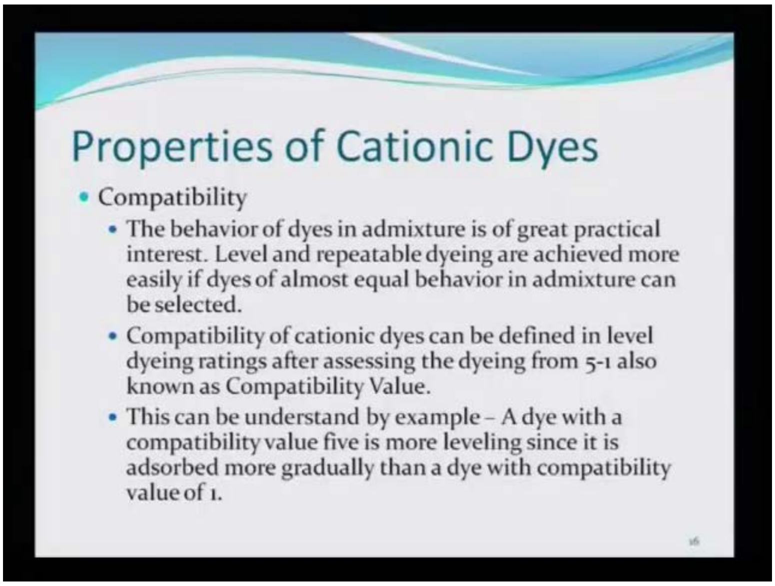

Therefore, properties of cationic dyes: Compatibility - the behavior of dye in admixture of the great practical interest. Level and repeated dyeing are achieved more easily if dyes are almost equal in behavior in admixture, and that can be selected. Compatibility of cationics eye dyes can be defined in level ratings after assessing the dyeing from 5 to 1 also known as compatibility value; that means, that number of dyes can be used. Number of cationics dyes, but they must have similar functioning. So, that those things have to be kept in mind, then this saturation value also should be kept in mind otherwise one would saturate, and the color will come out differently.

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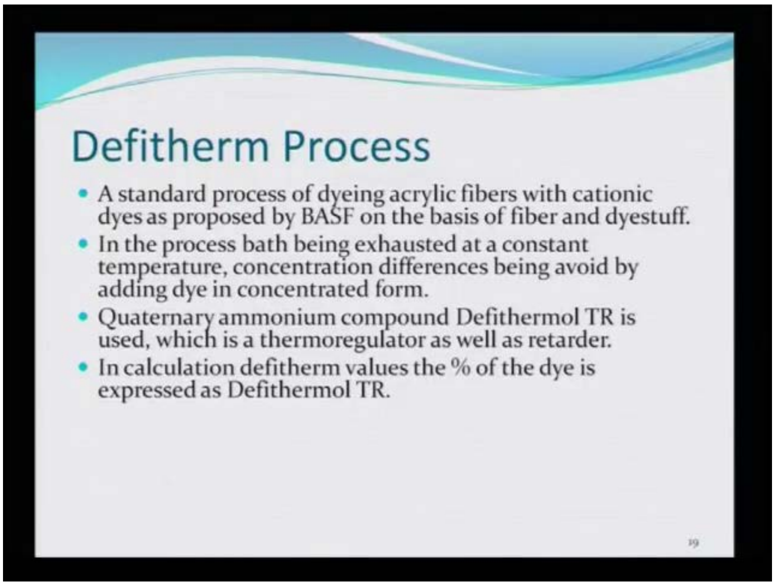

So, that is why there is a the process must be standardized, and a process standardized by BASF called the Defitherm process for dyeing of acrylic fiber has also been established.

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