Natural Dyes

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Lecture No. # 17

Having learnt about the basic of dyeing, then taking a look at the typical procedures, recipes of dyeing for cotton and silk; we now move on to the technological abbreviations; that were required for commercialization. And some of the work that was done as a developmental work in feat laboratory IIT Kanpur, for dyeing natural with natural dyes. We will talk about this and as we go along, I will emphasize on what was better and what was not so good, and what should be taken up by the industry, because this technological advance.

As advancements are really going in to have an impact on the commercialization aspect; so, therefore, I mean its let us now move on from the laboratory scale dyeing to a more, you know scientific and commercial dyeing procedures, and how the industry should orient itself.

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Natural dyes in India, have been found to be of Indigoid, Anthraquinone, alpha Naphthaquinone, Flavone, Dihydropyrans, Anthocyanidin and Carotenoid; these are the various types of dyes which have been isolated, and used in India very frequently and several several plants have been identified, having Indigoid dyes; similarly, many many plants have been identified, having Anthraquinone dyes in substantial quantity; even alpha Naphthaquinone dyes were found to be present in many dyes, dye dye yielding plants, Flavone dyes, Dihydropyrans, Anthocynidins are full of the entire seasonal flowers; are full of these Anthocynidin dyes. So, they can be good source of natural dyes, and Carotenoid dyes of course, carotene is surely obtained from carrots, but there are other carrots, saffron and annatto, and many other species which yield substantial amount of the carotenoid dyes.

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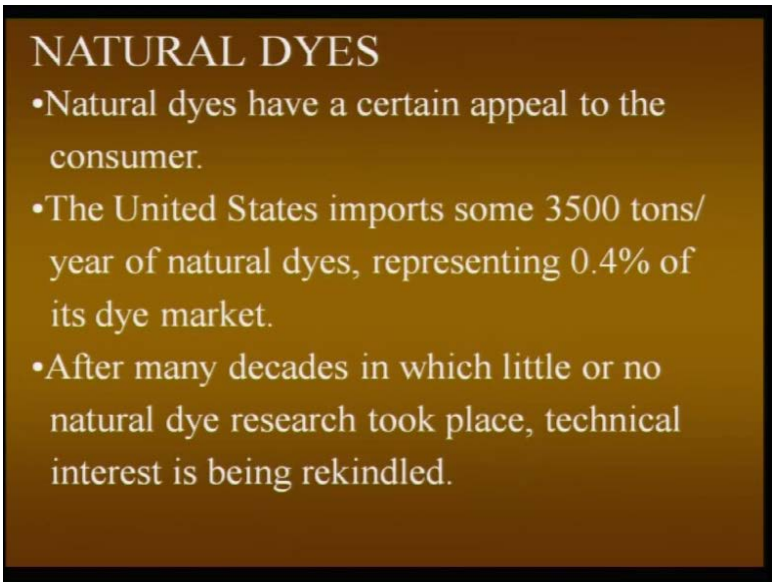

Natural dyes have a certain appeal to the consumer, and that is the reason why it has come up with source revival and resurges. The United States imports, some 3500 tons per year of natural dyes representing only point 4 percent of its dye market. After many decades in which little or no natural dye research took place, technical interest is being rekindle. So, first lot of time when synthetic dyes were in market, the natural dyes went into a shadow. But there is now great revival and resurgence of natural dyes, and this I have been telling repeatedly.

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The list of natural dyes that was screened recently in feat laboratory IIT Kanpur were from Sappan wood, bougainvillea, Lac, Balsm, Tulsi, Canna, Cineraria, Cosmos, Tessu, Pomergrante, Cassia, Tectona, Babool and Eucalyptus and many more. I am just listing a few of them, just to make you understand about 64 or more plants have been screened for natural dye, yielding plant; and they have been shown to have a good industrial application. That kind of technological up gradation on the natural dye front has been done at our laboratory.

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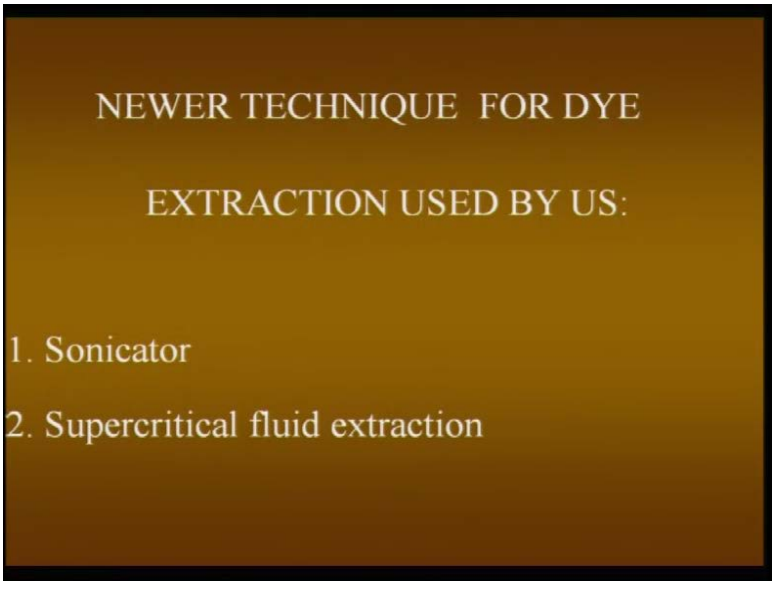

New techniques that we adapted for dye extraction, were mainly based on Sonicator and Supercritical fluid extraction. I will give you a example. Sonicator extraction became imperative, and absolutely necessary and out of this necessity; we used it for a particular case. I give you an example of Sappan wood; you know whenever it is heated, over a prolong heating period, Sappan wood which gives very bright magenta extract.

Actually deteriorated in to dull brown extract; and this process on cooling did not revert back the magenta color. Which means that it has called the extractor has become completely discolor; and this discoloration was responsible that, we try to use a milder method. And so we found that Sonicator was one of the best method for the extraction, at room temperature an at ambient temperature. And pressure. Because the way it works, it is very very effective to extract the dye content, without destroying the nature or the colored structure. Supercritical fluid extraction, we had discussed in great details and this also we used extensively in the case of Eucalyptus bar extract.

When we make an aqueous extract of the Eucalyptus bar - the bar is brown color, as what it could be expected, but when the same bar was put through Supercritical fluid extraction, that is SCFE Yellow- bright Yellow color only appeared, which is a typical falconoid moiety. So that means, that in the aqueous extract, the flavonoid getting mask due these tan in which are brown in color. But as the same time, when SCFE extraction was carried out, the only the falconoid was extracted only preferentially; that means, it did not tough the tangencies, it did not extract. And this is the beauty of the extraction processes called Supercritical fluid extraction; that at a particular critical, at a particular temperature and pressure; just above the critical temperature and pressure of carbon dioxide. If the liquefied carbon dioxide can act as a very good solvent, and can extract preferentially a compound a type of compound; be it essential oil be if dye; so, one has to find out a way, to do the extraction in a manner which can give the desire product.

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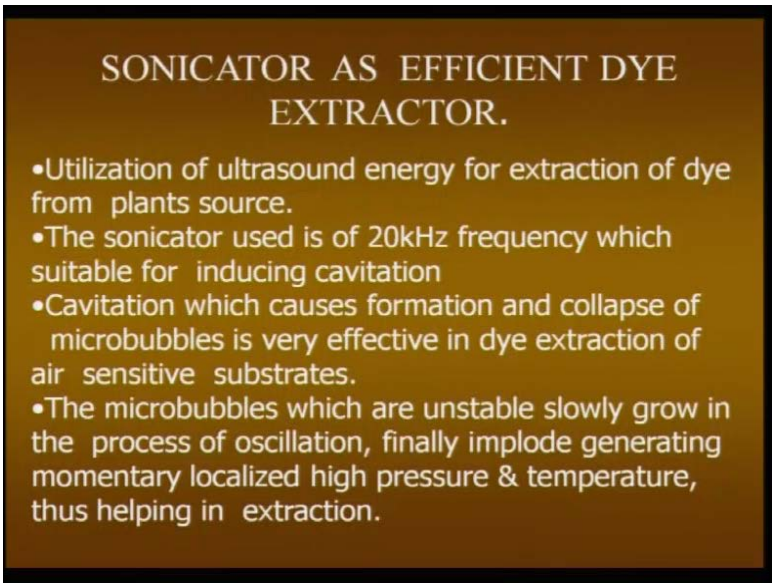

Sonicator as a essential dye extractor. How does it work; and how did we utilize this, how the technological up gradation of using a Sonicator in place of conventional extraction process, came into being what are its positive points how does it work, we will discuss that. Utilization of ultra sound energy, for extraction of dye from plant sources, has been brought into practice. It is for the first time we did it in our laboratory; the Sonicator use is of 20 kilo hertz frequency, which is suitable for inducing Cavitation - the Cavitation which causes formation, and collapse of micro bubbles is very effective in dye extraction of air sensitive, moisture sensitive, substrate. And air sensitive particularly, because under the heating condition; if there is excess oxygen. Then it will get oxidized to undesirable, discolored component.

The micro bubbles which are unstable slowly grow in the process of oscillation; finally, implode. Generally momentary is localized high pressure and temperature are generated, thus help in extraction. So, the way it happens is through cavitations, and because of cavitations these are in, there are micro bubbles that are generated. And, because of the micro bubbles where you know colliding with each other, there is a localized temperature and pressure rise which causes the agitation, along with the agitation to help in the extraction process.

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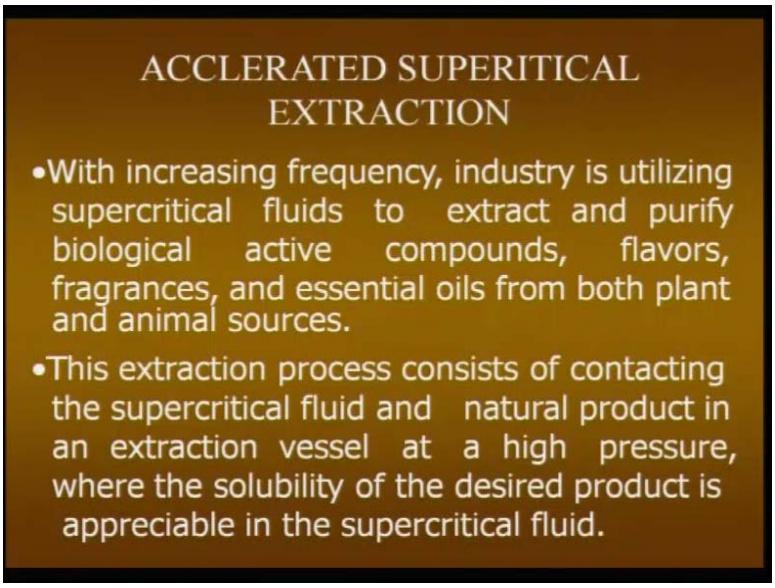

Accelerated supercritical extraction: with the increasing frequency, industry is utilizing Super critical fluids to extract and purify biological and biologically active compounds, flavors, fragrances, and essential oils from both plants and animal sources. This extraction processes consists consists of contacting the Supercritical fluid; that is carbon dioxide. And natural product in an extraction vessel at a high pressure, where the solubility of the desired product is appreciable in the Super critical fluid; and only some time some, ion trainers are added like acetone or methanol or ethyl acetate, but in very small quantity; the beauty of this process is that the liquefied carbon dioxide can be recycled, because as a liquefied carbon dioxide it is a good solvent, but when the gas is rarified when the pressure is released; the carbon dioxide naturally wants to be in the gaseous state; and therefore, it transforms into gases leaving behind the extracting, and that is collected. So, it is the most purified form of extraction, no column chromatography or any other purifying separating devices or procedures are required; and hence we try to utilize this, as I said in the case of Eucalyptus bar. Because it gave beautiful calorie Yellow dye which was completely mask or it did not appear, at least in the aqueous dyeing which gave only Dark brown, tan in colors.

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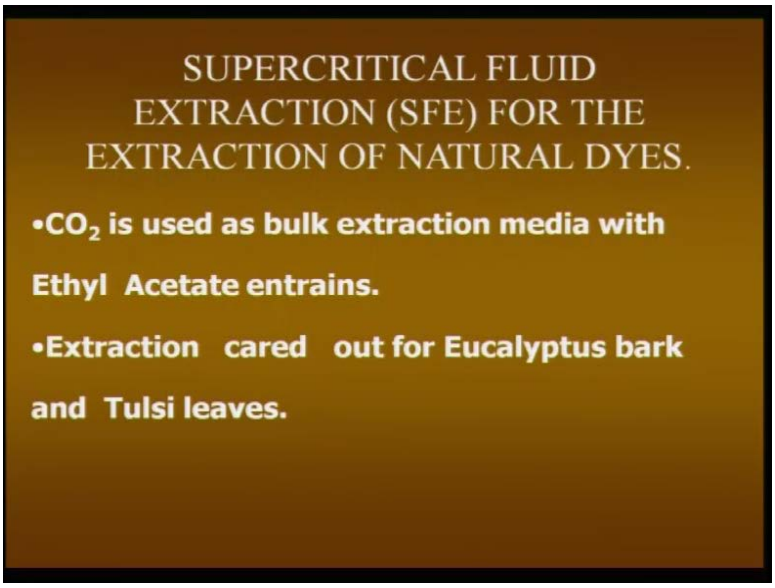

Supercritical fluid extraction that is SF SFE for the extraction; utilizes carbon dioxide as bulk extraction media with Ethyl Acetate and as ion trainer, in the case of our Eucalyptus bar extraction. Extraction carried carried out for Eucalyptus bar and Tulsi leaves also we tried out, and it gave beautiful greenish Yellow dye from Tulsi leave. So, for two cases, we have tried out of course, we did not have the instrumentation in our IIT Kanpur, we had to send it to IIT Bombay, where this is available and one can do it on a payment basis.

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If we try to look at the global scenario: the Indian textile industry has potential for 25 percent of the total export of the country. Collapse of soviet market has resulted the US and the European union to depend on India. They are demanding ECO friendly textiles; the Indian textile industry has to reorient its activity, to meet the requirement of the importing countries. You see, we just talked about the ECO friendly text, how we can ascertain that all the exports that are sent; whether it is dye or dyed fabric from India is ECO friendly. And we saw that 4 parameters need to be texted, first is the absence of azo dyes where we test the presence of band amines; then the pesticide residues are also analyzed or presence of toxic, heavy metal need to be analyzed; and finally, formaldehyde content in the textile needs to be analyzed.

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So, we have just learnt about that and therefore, you will be able to co relate what I am talking. Technological upgradation effective, and efficient exploitation of new technology will keep us in cumulativeness with the world; why was technological up gradation require - why did not be just help on doing the conventional methods - why was there a necessity to you know do something, new do something more innovative, because we have to keep face with the advancement, that is happening in the developed country.

And since, we are one of the developing countries, we need to keep face with this advancements of technology. And therefore, there was a need for technological up

gradation; utilization of ultrasound energy for dyeing cotton with natural dyes is a definitive improvement even in Dyeing process. So, we saw that in the extraction process, we added two new methods for the ease of the dyers, and similarly Sonicator or ultra sound energy utilization for dyeing was also introduced for natural dyes by us. So, we are trying to bring in technological upgradation, in these dyeing process as well as in the extraction process.

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The limitations with natural dyes: there is a Lack of standardization, and I gave a full lecture related to the standardization process of natural dyes, that also we have developed in our laboratory. Because of High cost of dyeing, we had to now think of processes which can bring down these cost. So, their easy easy and ready ready availability, andt there pastel shade these were some of the limitation. So, can we try to now do an upgradation of technology for either of them or all of them, and the answer is yes; it is possible to do that why, because if we have to bring natural dyes to the market, we have to think of combating all the problems or the limitation, that are associated with natural dyes and dying.

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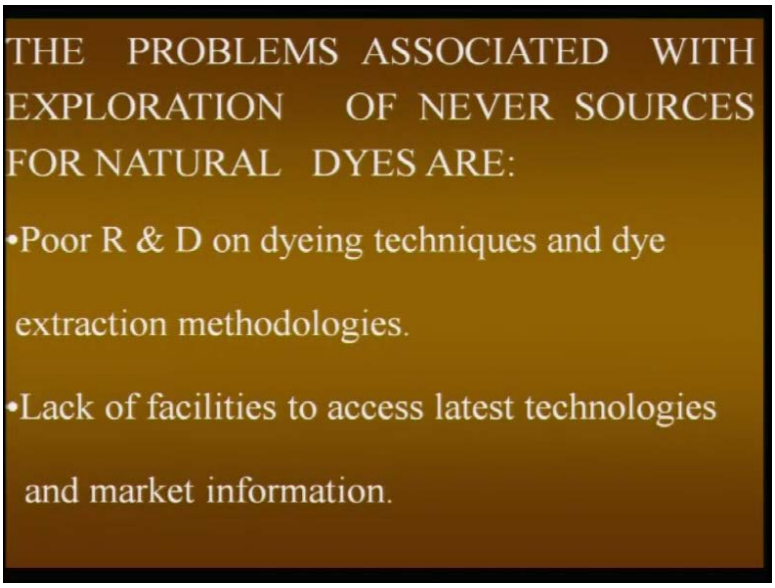

The problem associated with exploration of never sources for natural dyes are - Poor R and D on dyeing techniques, and dye extraction methodology, Lack of facility excess latest technologies, and market information. So, these have two main you know, draw back or I would say hurdles; that was not keeping us have the information as to what is happening in the world ground, and how are these technologies being applied; and can we apply the new technologies on our existing machinery, and so on and so forth. And not many you know, commercial dyeing units were using any kind of R and D. So, there was a very poor R and D on the dyeing techniques and dye extraction methodologies. So, we try to look at these problems, and see whether we can make any substantial contribution towards the technological up gradation.

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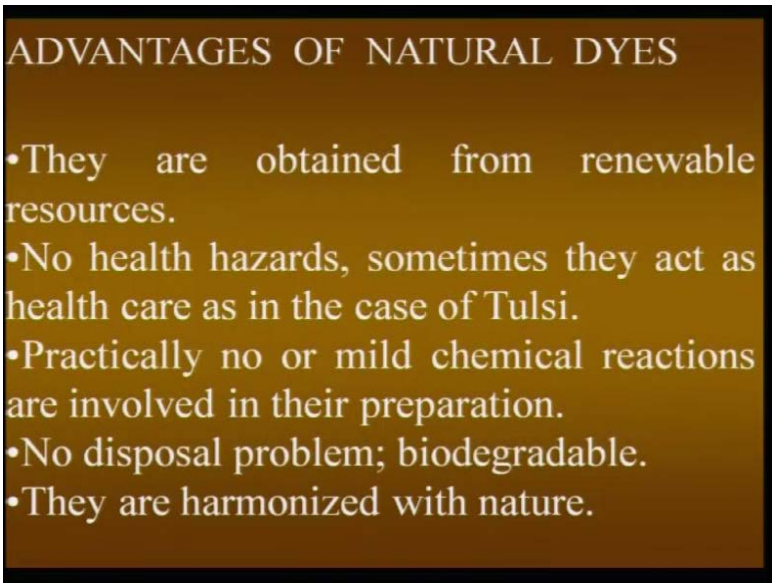

Advantages of natural dyes: they are obtained from renewable sources, no health hazards, sometimes they act as health care as in the case of Tulsi, and we saw in the case of six dyes. I took example of six dyes to show you that, they have immense medicinal properties. Practically no or mild chemical reactions are involved in their preparation, no disposal problem, because they are biodegradable, and they are harmonized with nature. So, these are the things which we are learning repeatedly; why because we want to see that it, it is so; then more and more dyers should be using natural dyes, and to be able to make an easy access of natural dyes to these dyer, what is that we can do facilitate the whole process.

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The spectrum of colours from natural dyes: Red color Dye can be or Red Dye can be obtained from Sappan wood and Lac, just in order to give you an idea has to what yield was of course, we also saw that mordanting and alter completely, the color that the dye actually has, and this plays a very important role. Not only mordent, but even pH can alter the color hue color. Yellow color can be obtained from bougainvillea, Marigold, Eucalyptus extracted by SCFE method, blue dye can be obtained from indigo; black color dye can be obtained with Lac, and some metal mordanting like sulfate, brown color dye can be obtained with Sappan wood and balsam; Green colored dye can be obtained from Canna Red flowers of Canna, under a particular pH will give green color on the fabric. Is in that, you know all most like a miracle.

That you see a Red extract, but when the Fabric is dyed it is Green in color. Tulsi is also, because Tulsi leaves its self give Green color. So, that is also a source of Green Dye; Orange Peach color can be obtained from balsam flower or bougainvillea. So, by using proper mordent, and by maintaining the proper pH, the shade can be manipulated. And you will see that there is a huge spectrum of color, that can be obtained from the same dye.

Lac dye can range from gray to red to maroon to purple to violet. So, this is from just one dye, and just by proper manipulation of the mordent and by treating with the modifiers or by manipulating the pH, one can get a huge spectrum of colors. And various

various shades can be developed - shade cards are developed; so that, vone can no which recipe will give what kind of color.

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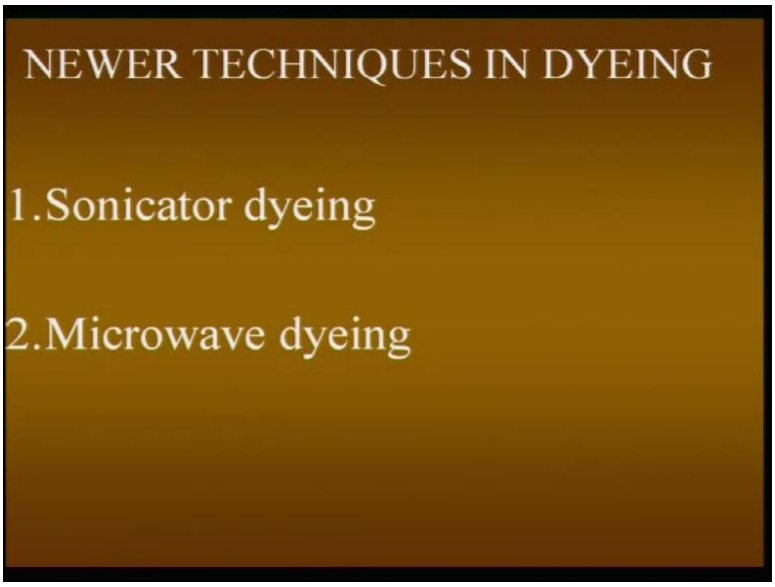

The newer techniques in dyeing that were tried out in the laboratory was Sonicator dyeing; that is use of ultra sound energy for the dyeing purpose, and we also tried out Microwave dyeing. But here, this the regular house hold domestic micro waves also can be used, because you know that in micro wave the basic principle is the agitation or excitation of water molecule; and all the dye solution are in water. So, even in open micro wave vessel, one can do micro wave dyeing; and it is a process which facilitates dye up take in a much faster manner, as compared to conventional dyeing.

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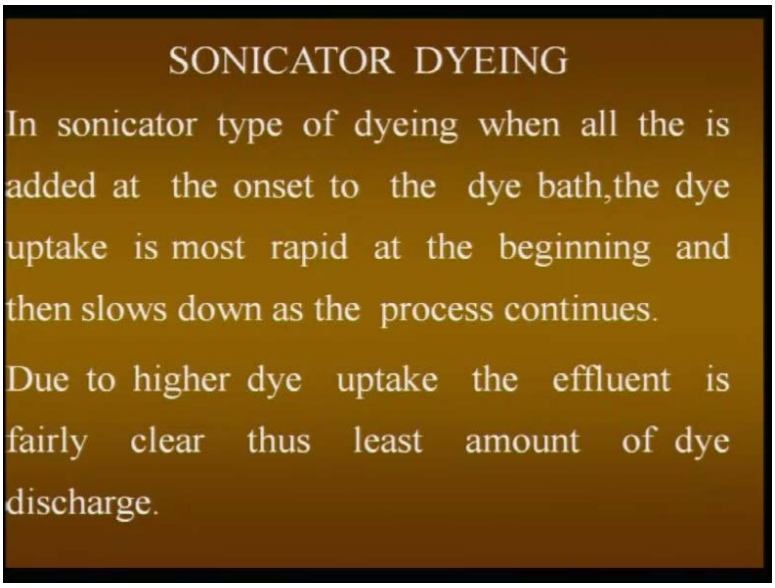

Sonicator dyeing, in Sonicator type of dyeing when all the dye added to the onset of dye bath, the dye up take is most rapid at the beginning and then slows down as the process continues. Due to higher dye uptake the effluent is fairly clear, thus least amount of dye is discharged. So, there are two major advantages of Sonicator dyeing. One is that it is much faster than the conventional dyeing sources. And the second is that, because the dye are uptake due to ultra sound energy agitation is much higher; the dye bath shows a good exhaustion. An if it, if the dye bath dye is taken up by the fabric; obviously, the dye bath will have lesser quantity of the dye content; and therefore, least quantity will be discharged in the effluent.

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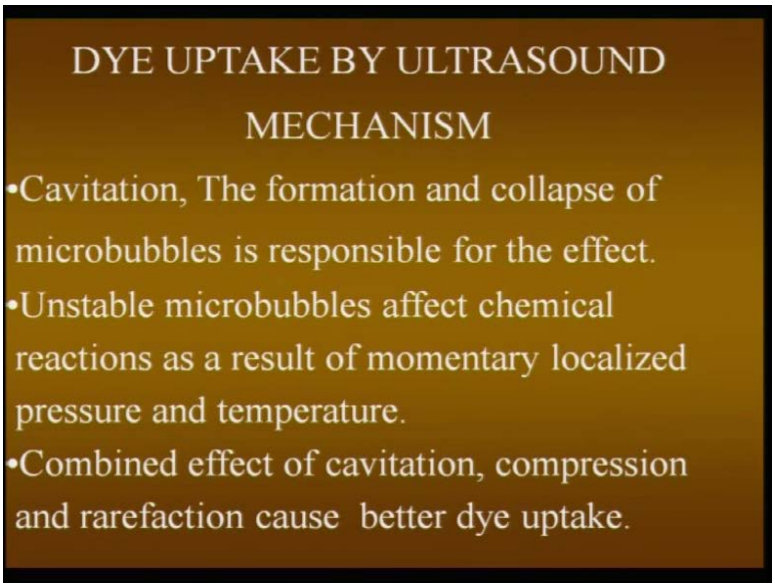

Dye uptake by ultrasound mechanism: The same Cavitation, the formation and collapse of the micro bubbles is responsible for the effect. Unstable micro bubbles affect chemical reactions as a result of momentary localized pressure and temperature. Combined effect of Cavitation, compression and rarefaction cause better dye up take. So, there is total you know, concerted effort of the Cavitation, of the micro bubbles, of the implosion of the micro bubbles, and they cause momentarily localized pressure, and temperature. And that enhances the dye up take process, and really facilitating the dying process.

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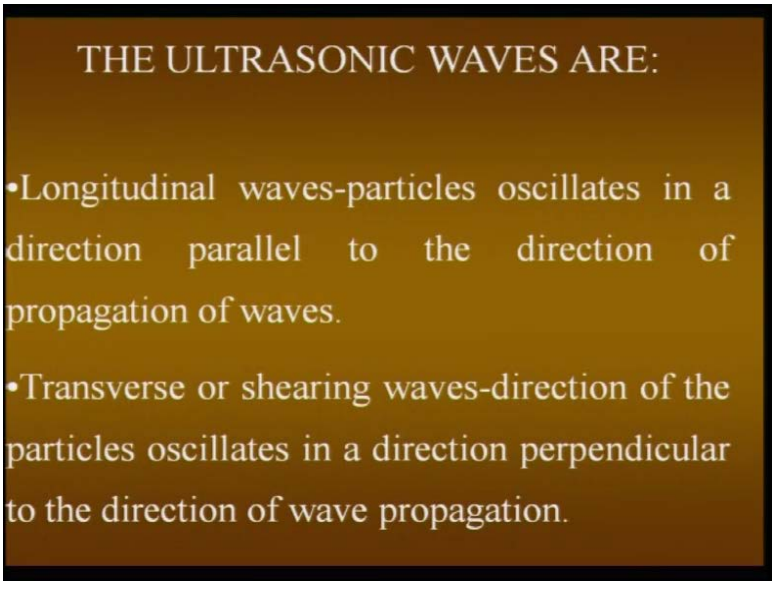

Ultra sound waves: Longitudinal waves-particles oscillates in a direction parallel to the direction of the propagation of the waves. And transverse or shearing waves direction of the particle, oscillates in a direction perpendicular to the direction of the wave propagation. So, the various of the ultra sound waves move; they move longitudinally also, and they move traversing on the vertical or horizontal scale also. And therefore, there is a complete you know, oscillation, agitation which causes the dye uptake to be further facilitated.

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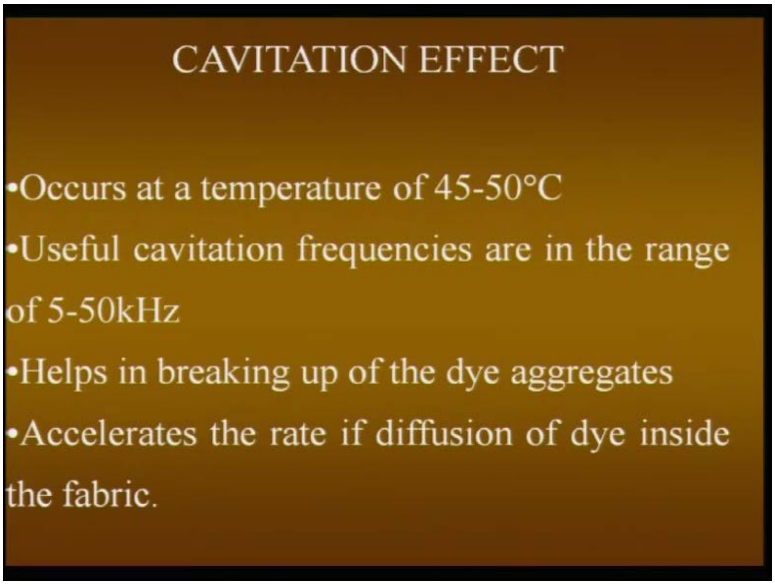

The Cavitation effect: Occurs at temperature between 45-50 degrees, useful Cavitation frequencies are in the range of 5-50 kilo hertz, helps in breaking up of the dye aggregates, and accelerates the rate if diffusion of the dye inside the fabric. So, it you know Cavitation effect is actually divided into its 4 functionality. First thing is it happens at very not so very high temperature; normally, we just saw that typical dyeing, conventional dyeing processes required; 80 degree heating; whereas, here we are only maintaining a temperature between 45-50 degrees. So, there is one had advantage that unnecessary heat is not required; there is an energy saving factor.

And the useful Cavitation frequencies are between 5 to 50 kilo hertz. So, a machine of 20 kilo hertz does the need full; helps in breaking the dye aggregates. Because these dyes have the tendency to come together and coagulate, this agitation process actually are the frequency or oscillation helps the dye molecules to move away from each other. And

thus it accelerates the rate of diffusion of the dye inside the fabric. And therefore, if there are only smaller molecules, the diffusion into the fabric by capillary action can take place very easily. Now, let us try to look at how the micro wave dying takes place, because this is also a new technological advancement in the field of dyeing.

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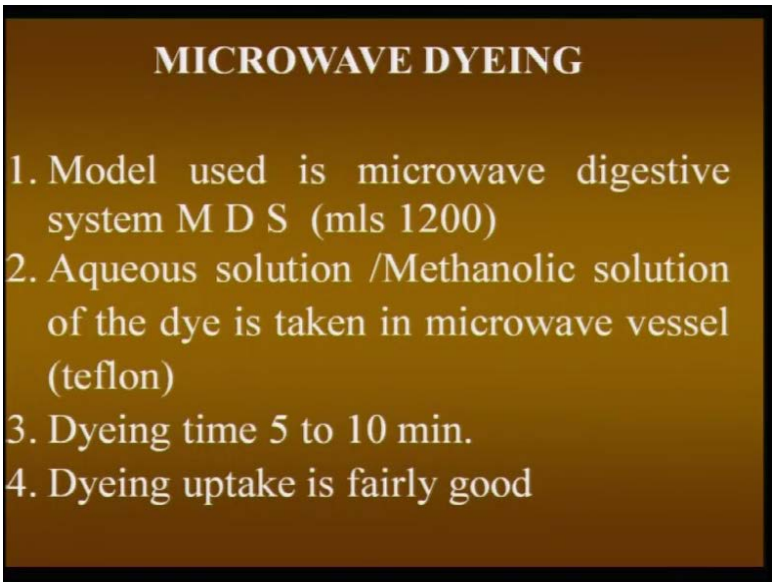

Model use is micro wave digestive system and M D S, because that was available in the laboratory aqueous solution or even Methanolic solution of the dye is taken up in micro wave vessel, which is made up out of Teflon; Dyeing time is required only 5-10 minutes dye up take is fairly good. But there are certain disadvantages that we found. That you know, although it is very fast, but the entire dye is not taken up; and therefore, there are some draw backs with micro wave dying.

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Pre Mordanting: Fabric treated mordant before dyeing. Post morddanting: we just learnt about this when the Fabric is treated with mordant after dyeing or Simultaneous Mordanting when they are added the mordant and the dye is added together. All three Mordanting processes can be done even in the micro wave dying, but microwave dyeing as I said is not very practical, for a you know a big scale reaction; for smaller fabrics one can carry out micro wave dyeing.

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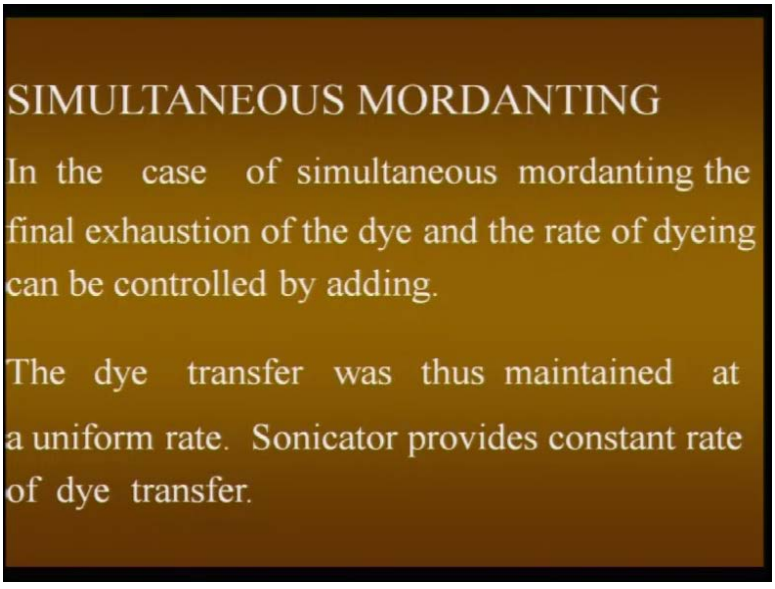

So, it has its own limitation; however, Simulataneous Mordanting was one more method, that we tried to promote for the technological technological up upgradation. Simultaneous Mordanting: In the case of Simultaneous Mordanting, the final exhaustion of the dye, and the rate of dyeing can be controlled by adding. The dye transfer was thus maintained at a uniform rate; Sonicator provides constant rate of dye transfer. So, in this particular see, what we were trying to aim. That if we can simplify the process of dyeing of natural dyeing, it will be of utility for more and more people in the dyeing industry, to take up these technologies or to apply.

So, one thing that we promoted was that Sonicator should be used for extraction, of particularly heat sensitive plant material. The second thing that we promoted was the use of Sonicator for dyeing, because even big dye baths can be fabricated, where any amount of fabric can be dye; just by introducing transducers at the base of the dye bath, one can create the same oscillation, and the same frequency waves sound waves can be generated. So, that fabrication is just a matter of getting these transducers, fitted at the bottom of the dye bath. So, that was second up gradation that we suggested; however, we realized that micro wave dyeing cannot be suggested to big industrial dyers, because it is not a practical solution; that big micro waves are not available.

So, those who are into thousands of meters of dyeing, cannot find micro wave dyeing has a useful useful method. The third thing that we tried to promote as a technological upgradation process was to promote Simultaneous Mordating in Sonicator. And that was precisely, why we started working on this, that one full step of Modranting, and then waiting pre Modenting, and then waiting, and then dyeing could be you know mixed with the dyeing process. And if that can be done, then definitely industry there is saving of energy, saving of time, and there is saving of money. And so therefore, this process would definitely be well coming change for the dyers for using conventional dyeing.

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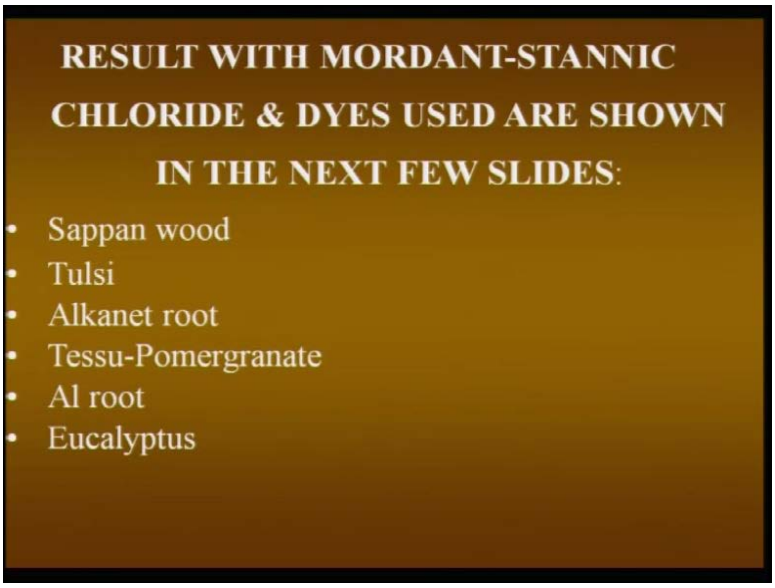

Some of the result with morant-stannic chloride, and dyes used are shown in the next slide; Sappan wood, Tulsi, Alkanet root, Tessu-Pomergranate, al root, Eucalyptus these are few dyes where you know certain, simultaneously mordanted fabrics and there results have been shown. The structures of the dyes that were isolated were Alkanin,m and this Alkanin you know on oscillation gave different products.

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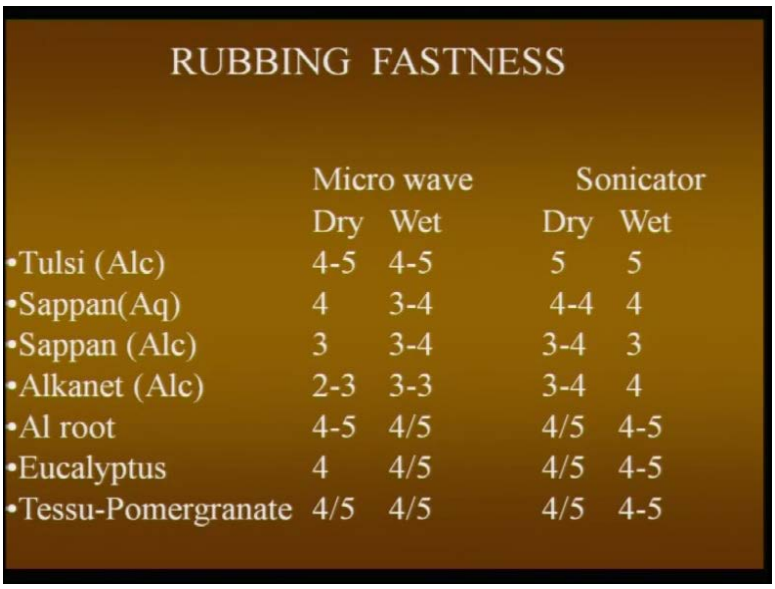

So, these are some of the structures of the dye's fustian, Morin were the dyes and Laccaic acid from the, these are Fastness properties, as what we were mentioning. So, if

we have to make comparative study of micro wave, and Sonicator dyeing; you will see that the Tulsi which was carried out with alcoholic solution dyeing, shows Rubbing Fastness of 4 to 5 in both dry, and wet microwave; that the same dye shows 5 and 5 in Sonicator. So, it is an obvious choice that for Tulsi dying Sonicator is the choice. Similarly, you will see that Sappan wood alcoholic, Sappan wood aqueous also has lower values of Rubbing Fastness, as compared to the… I mean if one makes a comparison between micro wave and Sonicator; the values for Sonicators are always high. So, that goes to prove that in some way or the other micro wave is little inferior than the Sonicator dyed fabric.

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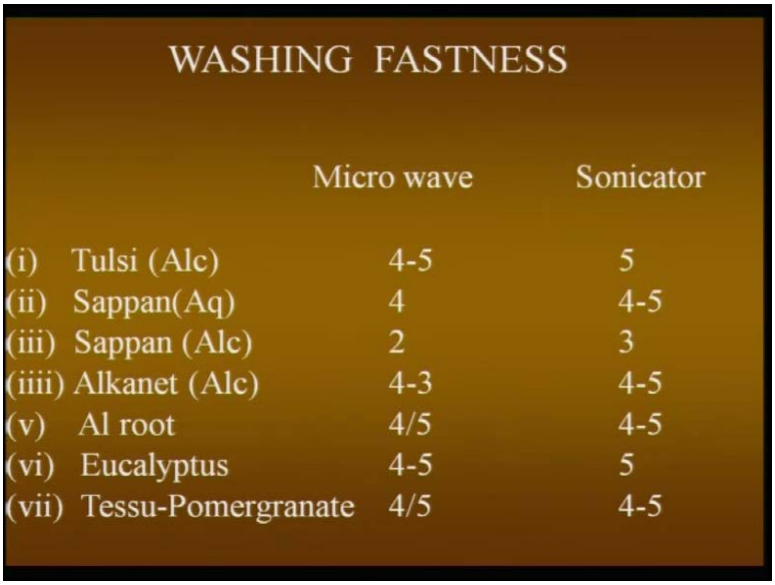

And the same was observed in the case of washing fastness. You will see that Tulsi, Sappan wood, Alkanet, al root, Eucalyptus all show lower values in the case of micro wave dyeing, and in the case of Sonicator dyeing the washing fastness was better to be with the micro wave.

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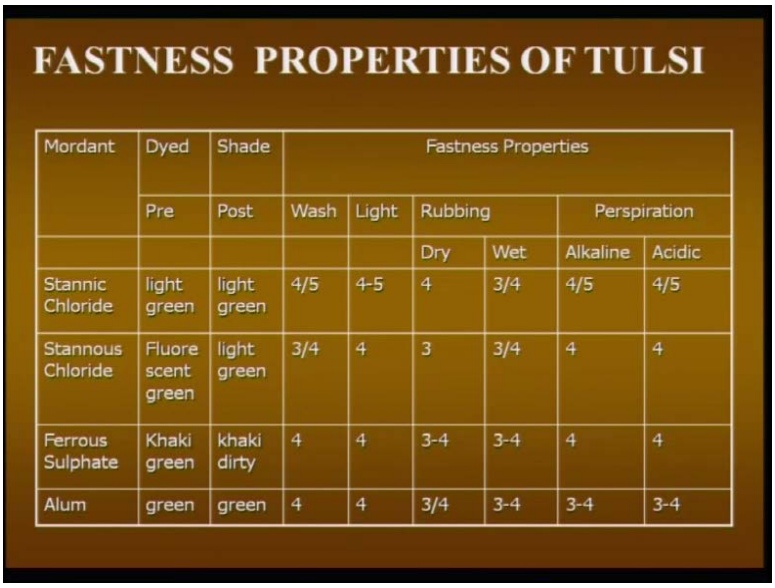

Mordant	Dyed	Shade	Fastness Properties					
	Pre	Post	Wash	Light	Rubbing		Perspiration	
					Dry	Wet	Alkaline	Acidic
Stannic Chloride	light green	light green	4/5	4-5	4	3/4	4/5	4/5
Stannous Chloride	Fluore scent green	light green	3/4	4	3	3/4	4	4
Ferrous Sulphate	Khaki green	khaki dirty	4	4	3-4	3-4	4	4
Alum	green	green	4	4	3/4	3-4	3-4	3-4

Even when we try to look at the Fastness properties of Tulsi: With Stannic, Stannous, Ferrous and Alum. Both pre and pro Mordant; it was found that, these are the values which are fairly acceptable. Because Tulsi was a new dye source; and therefore, we were trying to promote Tulsi. Now, promotion of Tulsi as a natural dye also had two aspects. One of course, it is an easy source of dye; it is a plant that can be grown anywhere the organized forming can be done for Tulsi. And secondly, it has lot of medicinal value. So, for surgical purposes or for hospital use, these Tulsi dye Fabric can be very well accepted. Because it has anti-microbial property, and those who deal with lot of blood stains and all that, can be safely using this Tulsi dyed fabric, because it has a pleasing odor as well as a pleasing Light Green color.

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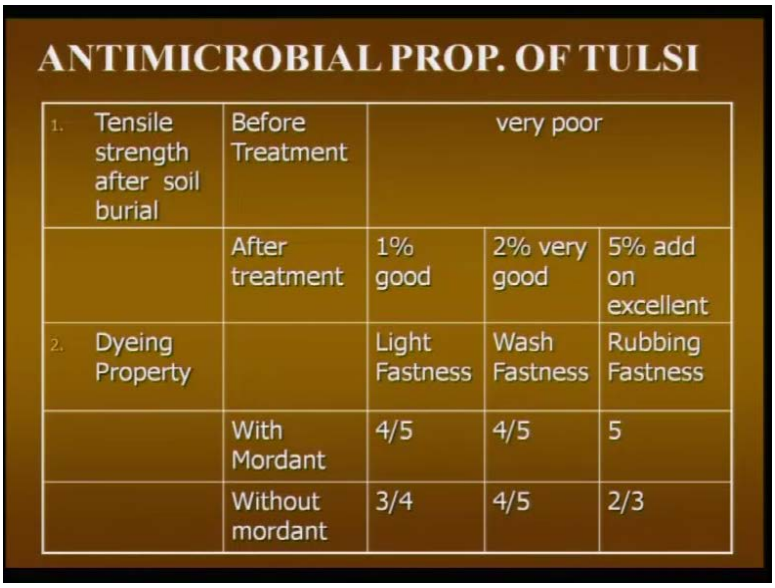

Anti-microbial properties were studied in great detail with Tulsi extract, the Tensile strength after the soil burial test was before Treatment was very poor, after Treatment one percent was good; 2 percent was found to be very very good and 5 percent has showed excellent anti-microbial, you know property. Similarly, Dyeing property also showed that you know, it has very good Light Fastness, wash Fastness and Rubbing Fastness with a mordant of course, the properties were much higher are the dyeing Fastness property showed pronounce effect; whereas, without mordant they were certainly the values were lower.

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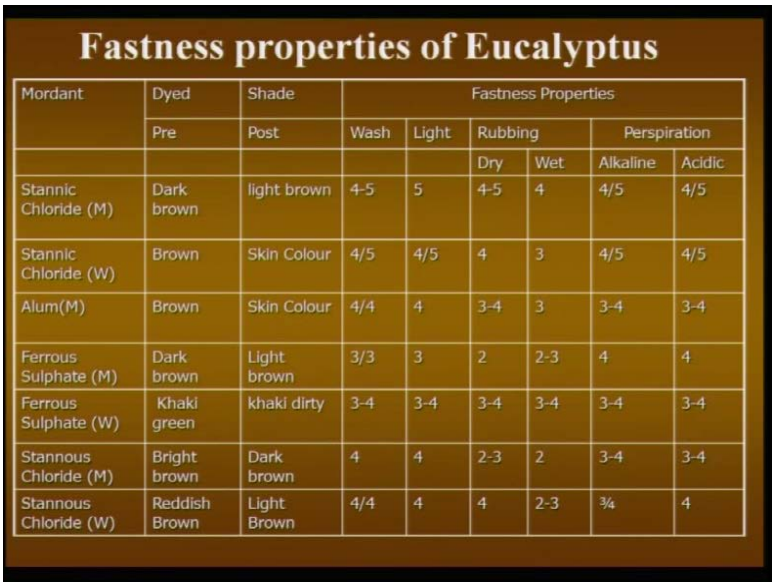

Mordant	Dyed	Shade	Fastness Properties					
	Pre	Post	Wash	Light	Rubbing		Perspiration	
					Dry	Wet	Alkaline	Acidic
Stannic Chloride (M)	Dark brown	light brown	4-5	5	4-5	4	4/5	4/5
Stannic Chloride (W)	Brown	Skin Colour	4/5	4/5	4	3	4/5	4/5
Alum(M)	Brown	Skin Colour	4/4	4	3-4	3	3-4	3-4
Ferrous Sulphate (M)	Dark brown	Light brown	3/3	3	2	2-3	4	4
Ferrous Sulphate (W)	Khaki green	khaki dirty	3-4	3-4	3-4	3-4	3-4	3-4
Stannous Chloride (M)	Bright brown	Dark brown	4	4	2-3	2	3-4	3-4
Stannous Chloride (W)	Reddish Brown	Light Brown	4/4	4	4	2-3	¾	4

Fastness properties of Eucalyptus also shows the similar trend that with stannic chloride, with stannous chloride, with ferrous, and with stannous, different shapes of pre and post mordanting fabrics would be obtained, and the fastness properties like light fastness, wash fastness, rubbing fastness and perspiration fastness was actually evaluated; why I am giving you all these details, because for a dye to be accepted in a commercial market, unless and until, it has good fastness property, it can never come up to the mark for the commercialization process. So, since a eucalyptus, yellow dye and Tulsi were two new sources, we tried to show that they are having the required stipulated and essential fastness properties to be categorized as good dye sources.

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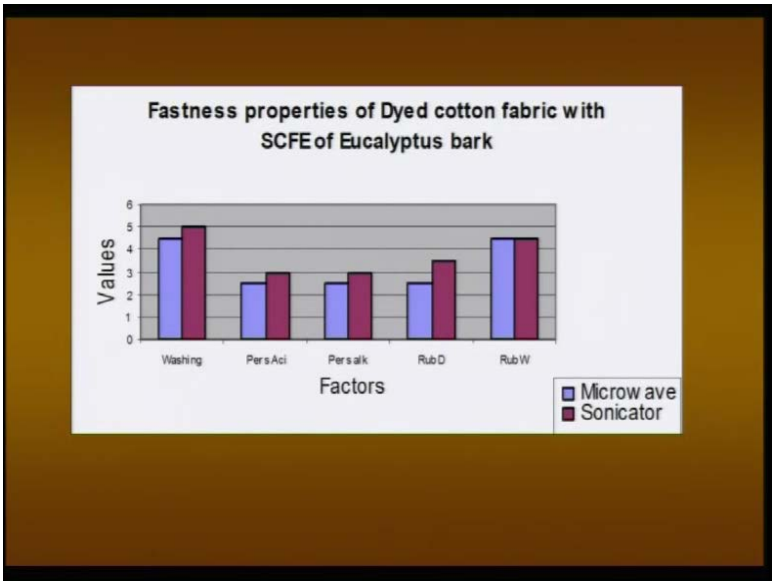

If we try to look at the fastness property of the dyed cotton fabric with the Super Critical Fluid Extracted Eucalyptus bark that is the yellow calorie yellow and if we try to make comparison between micro wave and sonicator, you will see that the sonicator that is the red bar is always longer, then the blue bar which represents the micro wave. So, only in the case of rubbing fastness, that to the wet rubbing fastness, they were found to be at bark with each other; otherwise sonicator was always better, and therefore we came to a conclusion that micro waves are slightly inferior and therefore, sonicator dyeing should be promoted in the industry. Now having done all that, there was a need to find out, whether any of the primary, dyed material or the dye is ECO friendly or not

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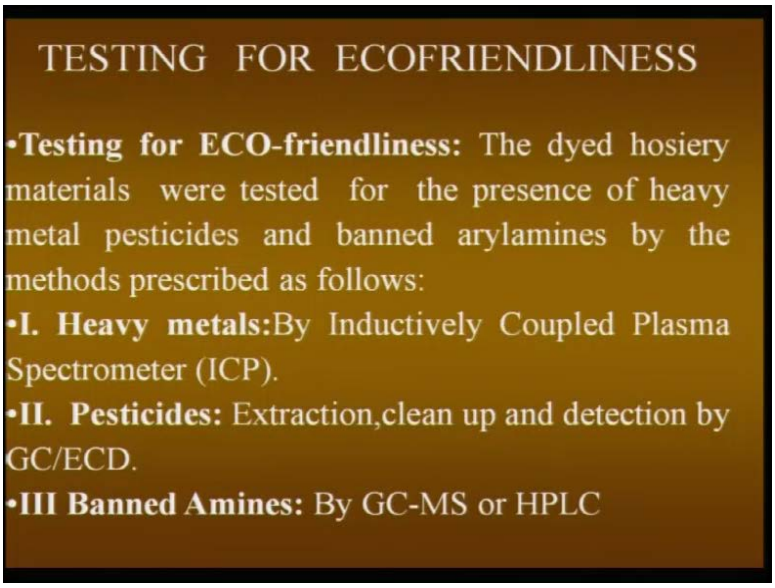

And for testing ECO-friendliness, we just did it the last lecture was dedicated for testing of ECO-friendliness; testing for ECO-friendliness of these material could be done by analyzing the presence of heavy metal pesticides, and banned aryl amines, by methods that are described below; heavy metals were analyzed by inductively coupled plasma spectrometer or atomic absorption spectrometer; pesticides were analyzed by extraction clean up and detection by GC and ECD, and banned amines were analyzed by the help of HPLC and GC-MS. So, you see that all these efforts was mainly to prove that natural dyeing has a great potential and is safe, because it normally passes through the ECO friendly test very well.