

**Factors Varying Penetration of Dyes  
on Rayons and Kindred Fibres**

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MICROSCOPIC RESEARCH OF FACTORS VARYING PENETRATION OF  
DYES ON RAYONS AND KINDRED FIBRES.

BY  
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## PREFACE.

During the past few years there has been an enormous increase in the use of Rayon or Artificial Silk. This fibre has sprung into favor not as a competitor of cotton and silk but as a companion fibre used with these other fibres to obtain results much more pleasing than when they are used alone. The price being lower than silk has tended to help its sales.

Twenty years or so ago this artificial fibre was manufactured in such a quality that water had a very detrimental effect on it. Scientific methods have been discovered to overcome this great fault to a large extent, and the discovery of these methods was due to the chemical and physical research that is being continually made in the great artificial silk manufacturing plants.

Changes have also been made in the types of machines used in manufacturing to produce fibres composed of better and finer filaments.

In many ways the textile mill men have benefitted by these wonderful improvements, but there is one fault which still crops out to worry the dyer. Many times after rayon has been dyed, it is found that there are two or more distinct colors in the batch. This will sometimes occur when the entire batch is dyed in the same kettle at the same time. Even with the utmost care, the dyer cannot overcome this trouble because the rayon before dyeing appears exactly the same to the

naked eye. When two or more different types of rayon are being dyed, this trouble can be expected.

As the making of rayon is a chemical process, this fault of non-level dyeing in the same batch has been studied from the chemical side and also from the spinning side. In this thesis attention will be paid to a study by use of the microscope to try to discover factors visible with this instrument which cannot be seen by the eye alone.

The author wishes to express his appreciation to the students in the Textile School who helped with so much of the routine work of dyeing.

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I  
HISTORY AND METHODS OF MANUFACTURING RAYON AND CHEMICAL  
OR ARTIFICIAL SILKS.

The term Rayon is being used to a great extent in the United States to distinguish fibres formerly called artificial silk. However, there are some firms making artificial or chemical fibres who prefer not to use this term. Among these firms' trade names are Bemberg for a fibre of the cupra-ammonium type, Celanese for a fibre of the acetate type and Tubize for a fibre of the nitro type.

Two men are said to have discovered the new fibre; one being Reamur, a French scientist and the other being Chardonnet. It was Chardonnet who secured the first patent.

Real silk is of course an animal fibre, but these others are all vegetable fibres. These are further classified as regenerated cellulose or addition products of cellulose. In the regenerated class we find viscose or xanthate, nitro and cuprammonium types; in the later class is acetate type.

The following history is taken from the writings of Dr. John H. Haerry <sup>1</sup>. " In 1734 Reamur suggested for the first time to replace real silk with artificial silk. But at that time neither chemical nor mechanical knowledge was advanced enough to grasp and develop his ideas,

1. Haerry Dr. John H.- "Artificial Silks"- Textile Library

and for over a century the suggestion was forgotten until 1855, when Audemars, a Swiss patented a process for the production of artificial silk.

He nitrated the bast of branches of mulberry trees to get his nitro-cellulose and so showed that he was trying to imitate the silk worm by using the same raw product; mulberry tree. From his nitro-cellulose product he made a solution by use of ether-alcohol; and dipped a steel rod into this final solution to start a thread which he wound around the rod until the solution was exhausted. Due to the lack of adequate mechanical equipment the process could not attain commercial importance, though it may rightly be considered the starting point of the artificial silk industry.

In 1882-1883 Swan, Wyne, Swinburne, Powell and Weston produced nitrocellulose threads as an intermediate product in the manufacture of carbon filaments for electric bulbs. Swan was the first to press nitro-cellulose dissolved in glacial acetic acid through fine nozzles, and denitrated the filaments by reduction with ammonium sulphide.

Though these inventors had even the very important feature of the denitration of the nitrocellulose patented and though their mechanical proceeding was along lines which were generally adopted in the later commercial manufacturing and though they even exhibited textiles made from their threads, they were not successful



in putting their inventions on a commercial basis, and it was not until 1884-1885 that Chardonnet had the first success of introducing a patented manufacturing process. Nitrocellulose, dissolved in ether-alcohol "collodion" was pressed through fine jets into a precipitating solution, and a certain number of fine filaments were gathered and wound together.

In 1889 Chardonnet showed his artificial silk at the Paris Exposition, but this "Artiseta" as he called the product was not denitrated and hence still highly inflammable and even explosive and therefore at first was little appreciated.

Although Chardonnet followed closely the earlier proceedings of Audemars, Swan and others, he is hailed as the inventor of artificial silk solely because he finally succeeded to "get the money" necessary to put his ideas and lab experiments on a working basis, and because after many years of operating troubles and financial struggles, he was able to make artificial silk a paying commercial proposition.

In 1890 Despaissis had the idea to make solutions from pure cellulose instead of from cellulose derivatives and he tentatively patented a new process by which cellulose was dissolved in an ammoniacal solution of copper. Due to the death of the inventor the process was not worked out any further at the time, but this process has been regarded as the original process for the manu-

facture of copper silk.

In 1891-1892 Cross, Bevan and Beadle discovered that mercerized cotton forms with Carbon disulphide the sodium cellulose xanthate, a product soluble in water. On account of the viscosity of the water solution, which proved very adaptable for the production of filaments, they called the product "Viscose". From this solution pure cellulose could be regenerated by coagulation.

In 1897 Pauly took a patent covering a process in every essential feature identical to the process of Despaissis. "Cuprammonium solution of cellulose."

In 1898-1903 Stearn found in solutions of ammonium salts a very good medium for the precipitation "coagulation" of cellulose from Viscose solutions, "solutions of cellulose xanthate".

The Chardonnet process factories were established in Besancon, France, but were not very successful, this was in 1891.

In 1894 Lehner opened a factory in Switzerland and worked a modified "wet spinning" Chardonnet process.

In Belgium a plant was opened at Tubize.

In 1899 Glanzstoffabriken opened more factories in Germany on the improved patents of Pauly for copper silk. They also opened up two factories in France.

In 1904 Austria entered the game, also England controlled by the Glanzstoffabriken Co.

In 1906 there were 7 factories in Germany, 6 in France, 4 in Switzerland, 3 in Italy and 2 in England. Their products were mainly used by the Swiss hat and braid industry.

The United States started to use artificial silk around 1905, and to manufacture around 1908."

From this brief history, it is shown that the chemical fibres are of comparatively recent origin. Another fact is also shown in that the first products were so coarse that they were used in making braid and not in making the finer fabrics of the present time.

At the present time, the type being manufactured in the largest quantity is the regenerated type called viscose, xanthate, and a few trade names. Dr. Arthur Fath<sup>1</sup> gives a very fine description of the manufacturing of this type and the following is quoted from this authority. " The viscose process is based on a reaction which was discovered by Cross and Bevan in 1892 in England. They found that mercerized cellulose was able to form a definite but unstable compound when treated with a given amount of carbon disulphide. The compound known as xanthate of cellulose, a compound of xanthic acid with the following formula:  $XONa + CS_2 = SC-OX_2SNa$  in which X represents the cellulose group.

1 Fath, Dr. Arthur--"Rayon Making"- 1924-- Industrial Fibre Company.

This compound is soluble in dilute caustic soda solution, from which the cellulose can readily be precipitated by acid. This reaction was first made use of in the manufacture of carbon lamp filaments for the old incandescent lamps, where cellulose with a high degree of purity was required. Some time later, after many attempts, this same reaction was successfully used for the manufacture of artificial silk by Stearn.

The process can be divided into two parts: 1; the spool system and 2, the pot system.

While cotton, in the form of linters, was used as a raw material in the Chardonnet and cuprammonium processes, it was found that the best material for the viscose process was wood cellulose or wood pulp. Not all kinds of wood pulp are satisfactory and only that made by the sulphite process has been found to possess the necessary qualities and uniformity. Great care must be used in selecting a brand, for the pulp is the corner stone of the whole building; a specific defect in the wood pulp cannot be corrected during the process of manufacture. Therefore, upon the wood pulp of proper quality depend the qualities of the finished product and the successful operation of the plant.

Analysis of the wood pulp should show a low percentage of ash and resinous matter, and a small amount of moisture. It must also be free of the chlorine

used for bleaching. The rest should consist of cellulose and cellulose derivatives. These cellulose derivatives are generally grouped under the head of "hemicelluloses" and may be considered as cellulose transformed more or less into hydrocellulose or oxycellulose. Their most interesting property, in connection with the manufacture of artificial silk, is their solubility in a solution of caustic soda; and as the first procedure of the process consists of soaking the wood pulp with caustic soda solution, it would seem at first sight that the lower the hemicellulose content of the pulp, the better the pulp would be.

Experience shows, however, that it is highly desirable that the wood pulp should contain some of these cellulose derivatives to the extent of about 10%. Any excess would be a loss, since it would go into solution in the caustic soda treatment. They are useful as an indicator. Another indicator which is extremely useful is the copper number of the pulp, which is a measure of the amount of bleaching that the pulp has received. An overbleached pulp is difficult to handle and entails great losses in the process, while an underbleached pulp will give a finished product which will never attain to a perfect white bleach.

SOAKING

The sulphite of wood pulp is received at the plant in the form of rectangular sheets 1-1½ mm thick. It

is put in the trough of a hydraulic press, which is then filled with caustic soda solution in order to mercerize the fibres. Strength of solution, its temperature and time of soaking are factors of the utmost importance. These may vary from plant to plant to some extent, the determining factor being the kind of pulp used. It is necessary that the details of this operation be closely watched and that no variations occur.

The wood pulp undergoes a great physical change while soaking; it swells to a large extent by absorption of the liquid. After soaking the required length of time the caustic soda is drained from the ~~trough~~. The piston of the press is set in motion; it slowly presses the wood pulp sheets against the end wall of the press; thus squeezing out the excess of caustic soda solution. The wood pulp must retain a definite amount of caustic soda solution; this is done by setting the pressure of the press, which when set remains constant. Until now the sheets of wood pulp have retained their rectangular form. The pressure is released and the pulp, now called soda-cellulose, is removed from the press and transferred to a machine known as a shredder.

The shredder is a chest enclosing rotating arms, containing teeth operating against a grating, which tear the soda cellulose to very fine shreds. It is necessary that the soda -cellulose be kept at a given temperature during the shredding process. This is accomplished by circulating cold water through the lower part of the shredder to check the heat generated by the mechanical

grinding of the pulp.

Between the shredding and the next operation is the "ageing" of the soda cellulose, which is an interval of the greatest importance. To treat the freshly prepared soda-cellulose without ageing would be disastrous. It is not only the chief factor in the behavior of the soda-cellulose during the next operation, but also determines the viscosity of the solution of the cellulose.

The ageing of soda cellulose has to be kept under perfect control. Time and temperature are two factors which play principal parts. The formula used, the time and temperature once adopted must be strictly adhered to. The temperature of the room must be kept absolutely constant and the operations so timed as to have each batch stay in the room exactly the same number of hours. The room is carefully insulated; the soda-cellulose would overheat if left in bulk, therefore one batch is divided among a number of sheet-iron cans.

#### TUMBLING

The next chemical action or operation is called "tumbling". The soda-cellulose is transferred to large double jacketed tumbling barrels. The airtight door is closed and the tumbling barrel allowed to revolve slowly. At the same time a measured amount of carbon disulphide, carried by a pipe passing through the centre of one of the bearings, is allowed to drip

in the centre of the barrel. A sight glass enables the workman to watch the progress of the reaction. From white the soda-cellulose turns yellow then light orange, and finally to orange. When the desired color is obtained, the tumbling barrel is stopped, the doors opened and the contents allowed to drop down a chute discharging into a mixer.

The reaction is a relatively rapid one and must be closely watched. Temperature plays an important part and any increase in temperature is checked by means of cold water or brine circulating through a double jacket. If the operation is properly carried out, the contents of the tumbling barrel are an agglomeration of more or less dry pulverent balls of various sizes. The color must be uniform throughout the batch, and the ball when broken, must show the same shade inside. They must not be sticky nor gummy. The tint may vary from plant to plant, but once adopted must be strictly followed. If the reaction is allowed to go too far, the contents will form into one large sticky, rubber-like ball, unfit for use and must be thrown away. The color of the over-tumbled batch changes from a dark orange through the various shades of red and some times as far as a dark brown.

This orange compound is the xanthate of cellulose to which Cross and Bevan have given the following formula:  $OX-SC-SNa$  in which X is the cellulose group. This compound of alkali cellulose xanthate, when freshly



prepared, is soluble in water and in dilute caustic soda solution. The solution is made in a mixer provided with revolving paddles for stirring, and a cooling jacket to provide a uniform temperature. The resulting solution is a thick, syrupy, orange colored liquid of extraordinary viscosity, hence the name, Viscose.

#### RIPENING

Preliminary to spinning, the solution must undergo a "ripening or maturing" process, similar to a certain extent to the ageing of soda-cellulose, which is familiar to all workers of cellulose solutions, be it viscose, nitrocellulose or others. Here the reactions are better understood because the xanthate is passing through successive and definite steps of polymerization. The soda cellulose xanthate, when freshly made, has the formula as given above. It is an unstable body and tends to agglomerate in a larger molecular group, containing two, three, four and more cellulose groups, by losing a corresponding amount of sulphur and soda, which are found in viscose as by-products under the form of simple or complex sulphides. The greater the growth of the molecule, the less and less soluble it becomes until finally spontaneous coagulation of the xanthate results.

There is a definite time when viscose is ready for spinning which is in fact a precipitation of the cellulose. This period is not of long duration and during this time the viscose must be spun. Needless to say, the ripening must be carefully controlled. The

ripening of viscose is allowed to take place in iron tanks, located in well insulated rooms where the temperature is kept absolutely constant. The chemist, fortunately, has at his disposal a very quick and accurate test by means of which he is able to follow the maturing of viscose and know that it will be ready at the proper time which has been set for spinning. This is a matter of two carefully controlled factors, time and temperature.

The solution during the spinning process must pass through small openings, about .004 of an inch in diameter. Any minute particles of undissolved matter such as fibre, rust, dirt, etc could readily block one of the small holes causing a defective strand. Hence the necessity of keeping the solution of cellulose thoroughly clean. It is filtered at various stages of the ripening process through layers of absorbent cotton, in order to have it absolutely clean and free from suspended foreign matter. After the series of filtration and proper time have elapsed for ripening or maturing, the viscose is ready for spinning. Up to this point, the various operations are similarly conducted in all artificial silk plants using the viscose process, although the operations may vary to a slight extent. It is in the spinning process that the main differences occur. We have seen that viscose or soda cellulose xanthate is a salt of xanthic acid in an alkaline solution. What is the behavior of such a compound when allowed to come in contact with other

reagents? The earlier workers of the viscose process experimented with numerous salts and acids, and mixtures of both were tried. A number of reactions have been patented, but only a few have been used on a commercial scale. The object is to find a substance that will precipitate cellulose as such, and give the final product all the properties required for a textile material. In the early development of the process, ammonium sulphate was used to precipitate the cellulose, but it is seldom employed today, although there are one or two plants still using this salt for precipitating when a special quality of stiffness is required. Its action on the xanthate of cellulose is peculiar; it does not precipitate the cellulose as such, but transforms the xanthate of cellulose "sodium salt" into xanthate of cellulose "ammonium salt" by displacement, thus

$$2 \text{ CX-SC-SNa} + (\text{NH}_4)_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2 \text{ CX}_2\text{CS-S}(\text{NH}_4)_2$$

The new salt is insoluble in a solution of ammonium sulphate, therefore the xanthate precipitate is a solid form. During the act of precipitating, which is somewhat slow, no dehydrating action takes <sup>place;</sup> and if the viscose is drawn through a round hole into ammonium sulphate solution, it will keep its form. When examined under the microscope, it appears as a perfect glassy cylinder. This form gives the product a certain degree of stiffness; as a matter of fact any material drawn in the form of a rod would be less pliable than the same

material drawn in the form of a ribbon, having the same cross-section area. The precipitation and transformation to the ammonium salt was only the first step in spinning, for ammonium cellulose xanthate was broken up immediately by passing it through an acid bath, usually dilute sulphuric acid, resulting in the formation of ammonium sulphate and cellulose.

#### SPINNING

As stated, ammonium sulphate is now seldom used, for viscose plants are using more stringent and powerful precipitating baths than before. The viscose solution arrives at the spinning machines under constant pressure, which results in a regulated flow and is forced through jets which are perforated with round holes absolutely perfect and having a diameter of about .004 inch. They can be made of either glass or metal, usually glass gold or platinum or their alloys. Formerly glass nozzles were used, but they have now been almost discarded. The number of holes depends entirely upon the count of the thread which is being made, the finer counts having as low as ten holes up to fifty or more for the higher coarser counts.

The jets are dipped into the coagulating bath which is strongly acidulated. As soon as the viscose is forced out of the small holes and comes in contact with the acid, the precipitation takes place instantly, as cellulose and no intermediate product is formed, as is

the case with ammonium sulphate. There is a dehydrating action at the same time, which leaves the thread in a flat ribbon-like form. The flat ribbon-like form is what is desired in the manufacture of artificial silk, for a thread having this form will feel soft and pliable. To make a thread having these qualities, it is necessary that the spinning or precipitating bath be of constant and uniform composition, and be kept at a uniform temperature within a small range. These factors are important at this stage of the process for they determine the quality of the silk.

Each hole in the jet represents a filament which coagulates separately; the conditions during the precipitation must be such as to avoid the adhering of the filaments, for the distance between the holes is small. The viscose solution passes in constant flow out of the small holes of the jet, and after precipitation, it will form a continuous bundle of filaments. Now supposing this bundle is drawn over a revolving spool or drum, one will have a continuous thread consisting of as many filaments as there are holes in the jet.

This is actually what takes place in the spinning operation. The bundle of filament or fibres, which compose the thread, is wound up on a spool revolving at constant speed. The speed of the spool is in a ~~fixed ratio~~ with the flow of the viscose solution, these two factors being constant for a given count and

will vary for different counts. The number of holes in the jet also increases with the count of the thread. A thread of 150 denier is generally made with a jet having twenty holes, making the count of each filament 7.5 denier. One would never attempt to make a thread of 300 denier through the same jet, although this is possible. Each filament would be twice the size of the 150 denier, which would give a heavy fibre and make the thread very stiff. Therefore, 300 denier thread will be made with a jet having a correspondingly greater number of holes, say forty, in order to obtain a thread of the desired softness and pliability, because these qualities depend among other factors, on the count and flatness of each filament.

The reaction between the acid setting bath and the sulphur compounds contained in the viscose solution, gives off a considerable amount of gases, among which are  $H_2S$ , recognizable by its disagreeable odor, and also  $H_2S_2$ , which does not possess an odor and "sui generis", but which is highly irritating to the eyes.

#### WASHING AND DRYING THE FILAMENT.

After the correct yardage has been wound, the spool is removed from the machine and sent to the wash room. Coming from the spinning room, the rayon is wet and saturated with acid. It is absolutely necessary to remove all the acid, otherwise the cellulose would char in the drying operation. The operation of washing consists of placing the spools under a spray of

water which takes away all traces of acids and salts. The spools are tested with methyl orange to determine if the washing has been done properly.

The next step is the thorough drying of the thread on the spools. From here on the treatments, which the rayon receives, are regular textile operations, similar to the operations on other textile fibres. Chemistry has employed an important part up to this point, but from here on the chemical plant changes to a textile plant.

#### TWISTING AND REWELING

Due to the way that the raw thread was made, we know that it is a bundle of many single filaments running parallel to one another. This condition is extremely unfavorable for any weaving or knitting operation, the filament being too easily separated and broken. Therefore the strand receives what is called a "twist" of so many turns per inch, which imparts to the thread at the same time a higher tensile strength.

The twist thus imparted to the thread is unstable. If it were to be reeled into skeins now, the rayon would curl so as to make subsequent winding impossible. To avoid this, the thread is submitted to a steaming and drying operation which gives the twist the desired stability.

The rayon is still far from being a finished product. It contains many impurities, especially

sulphur which gives it a somewhat harsh and stiff feeling and diminishes the lustre. It is very essential to remove the sulphur to give the thread a high lustre and good wearing and dyeing qualities. This is done by the bleaching operation, similar in many respects to cotton bleaching, the chief difference being the handling which must be done with the utmost care, because artificial silk loses strength when wet. The sulphur in the silk is quite soluble in a solution of sodium sulphide and caustic soda, and this solution is used for this purpose. The skeins are placed on two glass rods and dipped into this bath, allowed to soak thoroughly and turned a few times by hand.

A number of reactions occur here, all of which are not quite thoroughly understood. Among the more interesting are the following, the first being the most important:  $6 \text{ NaOH} + 3 \text{ S} \text{ equals } 2 \text{ Na}_2\text{S} + \text{Na}_2\text{SO}_3 + 3 \text{ H}_2\text{O}$ ;  $\text{Na}_2\text{S} + 4 \text{ S} \text{ equals } \text{Na}_2\text{S}_5$ .

In fact analysis of a working bath shows a high percentage of  $\text{Na}_2\text{SO}_3$ . The silk is now washed thoroughly in water; then dipped in chlorine solution, followed by a rinsing with water; then an acid dip and further washing with water to remove all chemicals. When removed from the last tank, the skeins are wrapped in bundles, which are placed in a centrifuge to remove excess water previous to drying. The skeins are now shaken out on wooden poles and placed in a conveyor dryer.



## POT SPINNING SYSTEM

Instead of winding the thread on a spool, it is passed over a smooth or corrugated glass roller, which delivers it into a small centrifuge running at approximately 4,000 RPM. Taking the last point of contact on the roller as a fixed point, and knowing that the thread as it enters the whirling pot ~~is~~ is turning at the same speed as the pot, one readily understands that the thread receives a definite torsion which depends on the speed of the glass roller, the speed of the centrifuge and the distance between them.

The thread is delivered in the pot through a narrow glass funnel, placed exactly in the center. It is made to travel up and down. The centrifugal force throws the thread against the walls; this combined with the up and down movement, builds a cake inside the pot. When about 2,000 yards have been collected, the centrifuge is stopped and the cake taken out. This method of spinning requires quite a different coagulation bath than the spool system, and what would give the desired results for one would be a failure for the other, owing to specific factors which are too long to be explained here.

Although these two, the pot and the spool systems of spinning vary from chemical and mechanical points of view, the ultimate product is almost identical. The thread when taken from the pot has an excess of the coagulating bath extracted from it, but it contains about

22% of cellulose, the rest being largely water, several acid and salts. But it is twisted and is strong enough to withstand loading. The skein is washed under a spray of water, and in order to give the silk some lustre, the skeins are stretched between metal rods on specially constructed trucks, which are placed in the dryer. The shrinkage of the silk, already under tension, adds to the original lustre. After drying, the remainder of the operations such as bleaching and grading, are similar to those of the other spinning processed yarn."

Dr. W.O. Mitscherling<sup>1</sup> writes, "It is well known that particularly in spinning viscose silk on bobbins, that very troublesome white spots occur, which tend to weaken the silk and reduce the stretch and tenacity considerably. This is due to firmly adhering carbon disulphide and sulphur which can only be removed by prolonged washing. But the customary prolonged washing as used in many plants slides up the threads and makes subsequent unwinding difficult; that is the fine filaments break to a greater or lesser extent. Of course the same thing occurs in the pot-spinning system."

Much has been written in regard to cellulose as used as a basis for the making of rayons or artificial silk. Various authorities differ as to the structure of the cellulose molecule. Dr. Harold Hibbert<sup>2</sup> has made an extension. Dr. Mitscherling, W.O.- MaxAms Co.- personal letter.  
2. Hibbert, Dr. Harold-"Artificial Silks"- Dyestuff Reporter- January 26, 1925,

sive study of cellulose and at the present time is the Head of the Cellulose Department at McGill University. "Bear in mind two or three facts: firstly that we are dealing with cellulose which is a product in which we have three hydroxyl groups to each C6 unit; of these two are secondary and one is primary in character; secondly we have a LATENT aldehyde group, and thirdly, we are dealing with a natural plant product which is a colloid.

Accepting all these facts, let us see what deductions and commercial applications can be drawn from them. First of all, consider the fact that the cellulose molecule contains three hydroxyl groups. We know that these three groups are there because we can make a triacetate which is Celanese, and we can obtain a variety of other trialkylated and acetylated derivatives.

Cellulose thus shows all the properties of a trihydroxy alcohol. Furthermore it behaves as any ordinary alcohol does. Another point is the fact that cellulose reacts with alkalis. Any alcohol will react with caustic soda to give us an equilibrium mixture of what we term an alcoholate and water. Excess of water would decompose it; excess of caustic soda, on the other hand, would give us a larger amount of alcoholate. In the same way, cellulose can replace the radical, and we get a caustic soda derivative of an alcohol, namely, cellulose alcohol.

Sodium ethylate, written  $C_2H_5ONa$ , has the re-

markable property of at once entering into reaction when brought into contact with carbon disulphide, giving us sodium xanthate.

Soda cellulose reacts in the same manner, giving sodium cellulose xanthate, a product readily soluble in dilute alkalies.

These reactions represent the changes involved in the viscose process for the manufacture of artificial silk. The alkaline solution of the cellulose is forced through the spinneret and then decomposed by contact with the "acid setting bath", thus regenerating cellulose.

There is thus a thoroughgoing analogy between the properties of cellulose and those of ordinary alcohol.<sup>1</sup>

As the viscose process of manufacturing artificial silk is of such importance, a few words will be quoted from an article by Dr. W. O. Mitscherling, who is one of the authorities of the United States on rayon.

"It will be appreciated that we have to deal chemically with a highly complex compound, and physically with a structure typically colloidal in character, capable of undergoing decomposition into products of varying complexity, so that an analytical investigation involves exceptionally difficult work. Scientifically, we know only one cellulose. Regardless of whether it is ex-

<sup>1</sup> Mitscherling, Dr. W. O.- "The Viscose Process"-- A meri-  
can Dyestuff Reporter- January 26, 1925.

tracted from cotton, wood or other cellulose-containing material, we have a definite knowledge of, and can produce definite derivatives from, cellulose, but we do not know anything about the magnitude of the molecule. Of course, the altered physical condition associated with the ultimate fibres and cells, and the **elimination** of impurities and incrusting matters, changes somewhat the complex soluble, particularly when we subject the compound, cellulose, to the extreme action of acids and alkalies.

It would of course be impossible to go into a discussion of cellulose proper, its peculiarities, and the influence of impurities contained in the material as used for the manufacture of artificial silk.

The latter has won an unassailable position in the textile industry, and the most important process is undoubtedly the viscose process. The demands made upon the manufacturer of artificial silk, both **in** respect to uniformity and fineness, are increasing every day. It is unfortunate that much of the technical research work carried out by the manufacturers remains for obvious reasons unpublished, but work dealing with the more general aspect of cellulose would only help the industry if made available.

To produce artificial silk requires experience and capital. It is impossible to manufacture according to a certain formula. Practically every phase of the process offers difficulties, which can only be

overcome by continuous scientific research.

As raw material, both cotton cellulose and wood pulp are being used. At the present time partially bleached sulphite pulp is preferred. The pulp must be free from lignin. Naturally it makes a vast difference whether cotton or wood pulp is used.

Control of viscosity is of immense importance, but uniform viscosity can only be maintained when the raw material is previously standardized so that it is always the same. Therefore, the utmost care must be exercised in the pretreatment of the raw material.

The raw cellulose is immersed in aqueous caustic soda solution at 20 degrees C and of a concentration ranging from 17.5 to 23 per cent NaOH, depending upon the character of the cellulose used. The excess of caustic soda is pressed out or extracted (either hydraulic presses or centrifuges are used commercially) to a point where the cellulose ratio to that of sodium hydrate stands in the following molecular ratio:

$C_6H_{10}O_5 : 2 NaOH$  or 162 : 80

This would represent theoretical proportions, but since 100 per cent cellulose is not being used in the manufacture of viscose silk, theoretical proportions cannot be maintained. The analysis of the soda cellulose (depending upon the type of cellulose used) is about as follows: 25 to 32 per cent cellulose; 12.5 to 16 per cent

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NaOH; 62 to 51 per cent of H<sub>2</sub>O.

Viscose prepared efficiently from a very good commercial wood pulp would contain about 13 to 13.5 per cent NaOH. It is not necessary to say that the caustic soda must be practically free from carbonate. Mercerization temperature is 20 to 21 degrees C.

The only relation between the concentration of the caustic soda solution and the temperature is that considerably less concentrated caustic soda solutions can be used if the temperature is decreased, but this would make the soda cellulose too wet for xanthation.

The soaked and pressed pulp, now an alcoholate is disintegrated, after which it has the appearance of bread crumbs. The soda cellulose is "aged" from 24 to 48 hours, during which depolymerization and subsequent lowering of viscosity occur.

More complicated is the formation of the xanthate. Rotating drums are used for this operation. Theoretically, for each molecule cellulose one molecule CS<sub>2</sub> is required. Practically, however, considerably less CS<sub>2</sub> is used. As a matter of fact, if the molecular ratio is followed throughout the process, the viscose becomes very dark and the subsequent thread is also dark, or darker than usual. It becomes cream to light brown, rather than a light yellowish white, and it is very difficult to remove all sulphur compounds without subjecting same to very vigorous treatment. Frequently bleached viscose

silk will not dye level, particularly the light shades. This is due primarily to improper desulphurization. Even if traces of sulphur compounds, not easily traceable by analysis, will cause this unlevel dyeing.

Xanthation is carried out at 20 degrees C and is completed in 30 to 35 minutes. The excess of carbon bisulphide must be removed. The xanthate is soluble in water, but more readily in caustic soda solution. Excess caustic soda preserves viscose to a certain extent, and also insures normal and uniform maturing. It retards the speed of decomposition.

The next step is to mature viscose. The decomposition process proceeds in four distinct stages. If we distinguish these steps by the ratios of Na: S : Cellulose, we find that the steps may be indicated by the ratios: First step, 1:2:1; second step, 1:2:2; third step, 1:2:4; fourth step, cellulose.

For the setting bath, acids and acid salts are commonly used with or without the addition of sugars. The concentration of acid, usually sulphuric acid, is about from 9 to 15 per cent, and sodium sulphate of about the same concentration.

It is well to add to the bath glucose or another type of sugar, or hydroxyl compound, to retard the setting of the thread, or rather to effect selective setting. Some plants use a double setting bath; that is,



they finish the setting by a weak bath of sulphuric acid.

The acid is washed out, preferably by a vacuum rotary washer. With the latter it takes about one and a half to two hours to wash a spool having 2,500 to 2,700 meters of silk of 150 denier. The consumption of water is 40 to 50 liters per pound. With the newer type of washing machine the spools remain in a horizontal position, which is claimed to be an advantage, since the upper layer of silk does not become tangled, as is usually the case when the spools are washed vertically.

There are other means of washing spools, namely the spray system, but this requires a very large amount of water and takes a long time. Approximately from 600 to 700 litres of water is required per pound of silk washed on spools by the spray system. Furthermore, fast washing has the advantage that the cellulose thread does not become slimy and the efficiency of the subsequent unwinding is much higher.

The spools are dried at about 50 to 60 degrees C for two to three hours. Also here the vacuum washing process offers many advantages, in that considerably more water can be removed from the individual spool, thus shortening the drying time.

After the spools are dried they are placed on spindles and the thread directly twisted. The spools must not revolve faster than 3,200 r.p.m. The usual twist is about 2.5 to 2.7 turns per inch.

To remove the sulphur and sulphur compounds, the skeins are treated with hot sodium sulphide solution containing about .1 per cent sodium sulphide at a temperature of 60 to 80 degrees C. The skeins are then washed with water, finally bleached by the usual methods, and dried."

As viscose is used to a much greater extent than any of the other types, more space has been given to the manufacture of this type. However, the other types are also important, and a brief description of the manufacturing process of nitro type will now be given.

This type is also known as Chardonnet, Colloidion, Besancon, Tubize, Frankfurter, Hungarian, Lehner, Vivier and Nitro silk. In the United States at this time, the only manufacturers of this type are the Tubize Company with a plant at Hopewell, Virginia.

Cotton linters are used in making this type, and these linters must be thoroughly cleaned before the first process of nitration takes place. The nitration forms the substance known as gun cotton and is very explosive if dry. To avoid these explosive quantities, the operations are "wet" processes. Chemically the results of nitration are called "cellulose nitric acid esters". In order to obtain best results, these esters must be completely soluble in ether-alcohol mixture which is used as a solvent. Dr. Haerry<sup>1</sup> says, "Too much nitration impairs the solubility and renders the fibre weaker after denitration due to too advanced decomposition."

1. Haerry, Dr. John H. - "Artificial Silks" - Vol. 1.

After securing the cellulose trinitrate of the proper qualities, it is washed to remove the excess of the acid. The next step is to make the spinning solution; this consists of dissolving the nitrated material in a solution of ethyl alcohol- ether solvent or in acetone free methyl alcohol mixed with a small amount of ethyl alcohol and ether. This forms a solution called collodion which is familiar to us in the "New Skin" used for cuts. Before spinning can take place, all air and impurities must be removed from this viscous solution.

There are two methods used in spinning; Chardonnet used the dry method in which the solution was forced through capillary openings of very small diameter into a current of warm air. As ether and alcohol are both volatile, they are removed by evaporation in this warm air. Lehner invented the wet process where the solution is forced out of the holes into a precipitating bath, which is usually water. With the wet process, a twist can be placed in the thread as formed; this is not possible in the dry process.

At this point the silk is wound on spools in same manner as with viscose and well washed, then made up into skeins.

Right here, great care is needed in handling if the skeins are dry, due to the inflammability and explosive quality. Treatment with ammonium sulphide or

sodium hydrosulphide solution causes this dangerous nitrate quality to be removed. Too long an immersion in this denitrating bath will cause a weakening of the thread.

In his book on artificial silk, Dr. Haerry<sup>1</sup> says, "If the silk is not denitrated evenly throughout the fibre, it will dye uneven later on, as cellulose hydrate and partly nitrated cellulose have entirely different absorption abilities for dyestuffs. Sulphur, which if denitration is not carefully carried out, may precipitate in the bath and go on the fibre forming a crust, can also be a source of much trouble to the dyer and printer. If calcium and magnesium sulphhydrates are used for denitration, calcium and magnesium hydroxides can be deposited on the silk, causing the well known "lime spots"."

The skeins are now well washed with warm water, and then treated with diluted hydrochloric acid to remove traces of iron sulphides; washed again; bleached and dried

Another type of artificial silk is the Copper-ammonium known also as Glanzstoff, Bamberg, Pauly, Despaissis, Cuprammonium and so forth. In the United States, we have a large plant at Elizabethton, Tennessee called the American Bamberg Co.

Raw cotton is used for this type; the cotton is well scoured, bleached, hydroextracted and dried, and it then is treated with a solution of copper dissolved in ammonia. This is the familiar test solution used under the name of "Schweitzer's reagent", or "ammoniacal copperox-

ide."

The cotton is dissolved in this solution with great care being given to the concentration, temperature and length of time. The qualities of a good thread such as lustre, strength, elasticity and silkiness depend largely on the care given in making and keeping the solution. In proportion as decomposition and liquifaction advance, the good qualities of the thread disappear. In order to have uniformity, it is best to spin the solution as soon as possible. Mr. A.M. Tenney, Vice President of the American Benberg Company said in talk given at the North Carolina State College Textile School that his firm was now making this type of rayon that was perfectly uniform and far superior in uniformity to the real silk as made by the silk worm. Not only was the artificial product more uniform, but they were also making filaments of a size one half as large as the silk worm produced; that is of approximately .6 denier.

The solution is pressed through filter presses to remove the very smallest impurities such as dust which may be present and which would plug up the minute holes in the spinnerets. In the old days, instead of spinnerets, glass tubes were drawn out and then cut in two to obtain two pieces with very fine holes. The glass is bent in a hook shape and the solution forced out through these tiny holes into the coagulating bath.

The viscose solution is blue<sup>due</sup> to the presence

of copper, but if an acid coagulating bath is used, this blue color is lost. If an alkaline coagulating bath is used, a precipitate of copper cellulose (blue in color) takes place; this is washed in acidified water to remove the copper. Washing and other processes are similar to those used with viscose.

Dr. Haerry<sup>1</sup> states: "It is claimed that cellulose first precipitated with caustic soda and afterwards with acids is less decomposed and therefore gives a stronger fibre, than cellulose precipitated directly with acids. It is very important to wash the fibres absolutely free from acids and alkalies, otherwise they would be damaged in the drying and rot when stored."

Another important type of artificial fibre is cellulose acetate which comes in the trade as Celanese, Acetate and Acetyl. Up to a few years ago, this type was made in this country by one firm only, American Cellulose and Chemical Company. But at this time several other firms are producing or are going to produce this type. Professor Charles Mullin<sup>2</sup> writes, "Cellulose acetate may be prepared from cotton, wood or other cellulosic material, acetic anhydride, acetic acid and a catalyst such as sulphuric acid, phosphoric acid, zinc chloride, anhydrous acetates of zinc and manganese, chloroacetic acid, dimethyl sulphate and so forth."

1. Haerry, John H.-- "Artificial Silks"- Volume 1.
2. Mullin, Professor Charles E.-- "Acetate Silk and Its Dyes".

Acetate silks differ from the other types so far described in that they are all regenerated cellulose; that is to say that the final product is cellulose which differs from the original wood or cotton cellulose in the structure only. These types contain the same quantity of elements carbon, hydrogen and oxygen as the cellulose from which they were derived; this is not the case with acetate types. This type contains besides the cellulose molecule, two or three acetate groups which have replaced hydrogen or hydroxyl groups in the original cellulose. As to where and which elements are replaced, the authorities disagree. For use in this paper, it is sufficient to know that these acetate groups are present either as replacement or additional groups with the cellulose molecule. It is quickly seen that the acetate type will have many properties which differ with all the other types.

Mullin<sup>1</sup> gives in his book under later methods, a short account of present processes divided into five steps in preparing cellulose acetate. "(1) The acetylation of the air-dry cellulose by acetic acid and acetic anhydride in the presence of sulphuric acid (or other chemical compounds), which acts as a "catalyst". (2) Hydrolysis, by adding water and acetic acid, taking care to avoid precipitation of the acetate. (3) Ripening, during

1. Mullin, Professor Charles E.-- "Acetate Silk and Its Dyes".

which the product is left for a period of time, usually for at least 12 hours, at a fixed temperature, which varies in different processes and patents. The reaction thus continues regularly until the desired stage is reached. The duration and temperature of this ripening process have an important effect on the solubility and other properties of the resulting product. (4) Precipitation of the acetylated cellulose as a white flaky mass by the addition of a large excess of cold water containing sufficient alkali carbonate to neutralize the sulfuric acid. (5) Washing, centrifuging, and drying at 20 to 30 degrees C in well-ventilated rooms."

The next processes are not so well known as are the viscose processes. This dry flaky mass is dissolved in a solvent, usually acetone. In the spinning, the coagulation of the thread occurs in warm air, and the solvent is recovered.

With this brief account of the manufacture of the artificial silks, we will continue the work with an equally brief account of the dyeing of the various types.



## II

### VARIOUS CLASSES OF DYES USED AND METHODS OF USING THEM.

All of the artificial silks excepting the acetates can be dyed with dyes such as are used on cotton. On the acetate type, a special series of dyes has been invented.

These classes of dyestuffs will be briefly described under the classification of Direct, Basic, Sulfur, Vat and Dispersol or SRA.

Direct dyes received this name because of their ability to dye cotton directly without the use of a mordant. They are also called "substantive" dyes. Most of them are derived from benzidine, ( $\text{NH}_2 \cdot \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 \cdot \text{NH}_2$ ), and contain the N-N group twice thus being "tetrazol" compounds. As benzidine as shown above contains two amido groups, the directs are sometimes called "diamines".

In Green's classification, there are five classes: disazo, trisazo, tetrakisazo, stilbene and thiazole. These direct dyes have the property of being readily soluble in water.

Some of the direct colors contain a free amino group and after being dyed on the fibre, this dye can be diazotized and developed to change its color or in most cases to produce a faster dye. This section of the direct dyes is called developed dyeing and can be used on the artificial silks excepting the acetates.

The basic dyes, sometimes called the tannin dyes, are mostly color bases with hydrochloric acid or

zinc chloride. On cotton, they require tannic acid or some such mordant in order to produce a real dyeing instead of staining, but on the rayons they dye quite readily. Some of them will dye the acetate types.

Chemically the basic dyes are derived from triphenylmethane, azine, acridine and azo compounds.

Sulphur dyes can be classed with the direct dyes from the fact that they can be applied to cotton without previous mordanting. However, we will place them in a separate class due to the fact that they cannot be dissolved without the use of sodium sulphide. This chemical is so strongly alkaline that it would tend to dissolve the acetate silks if they were being dyed with sulphur dyes in hot solutions. The acetate silks as will be seen later cannot resist the action of strong alkalies.

These dyes are all sulphur compounds and in many cases are cheap in price. They give a dull color and ordinarily would not be used on rayons, but if the cloth contained a large amount of cotton, then sulphur dyes used to dye the cotton could also be used to dye the rayon in the cloth.

The vat dyes within the past few years have come into great favor due to the fact that they have the greatest fastness as a class of all the dyestuffs. As they are applied in a bath that is strongly alkaline, their use on the acetate type is limited. In order to dye on this type, a retarding agent such as glue must be used.

Matthews<sup>1</sup> classes the vats as follows: (a) indigo, including both natural and synthetic; (b) thio-indigo dyes, containing sulphur; (c) indigo derivatives, such as brom-indigos; usually not derived from indigo itself, but built up synthetically; (d) anthraquinone derivatives, including the various Indanthrene, Cibacron, Algoldyes, some Helindone and others; (e) carbazol derivatives, of which Hydron blue is representative."

Some use just the three classes; indigoids, anthraquinones and carbazols. All vat dyes must first be reduced to the soluble leuco compound as the dyes themselves are not soluble in water. After being reduced, they are applied to the fibre and then oxidized either by the oxygen in the air or by solutions of such chemicals as sodium perborate.

As the SRA or dispersol type of dyes are the most recently discovered and used dyes, we will explain them more fully than the preceding classes. When the acetate silks came on the market, the dyers were much opposed to dyeing them due to the fact that they resisted almost all types of dyes. The British company making the largest amount of this type of artificial silk did a tremendous amount of research and finally put on the market, a class of dyestuffs made just for their own acetate product (Celanese) and called these dyes SRA dyes. This

Matthews, J. Merritt-- "Application of Dyestuffs".

name was given to them as sulpho-ricinoleic-acid was used in making the dispersion solution of the dyes. The first dyes put out were the Ionamines; but now we have the class of dispersol dyes including those called SRA, Celatine, Duranol, Celanol and Dispersol. Mullin<sup>1</sup> says, "The affinity of acetate silk for a large number of dyes and bases, containing certain specific chemical groups or characteristics, is well known. Many, in fact, most of these compounds are not soluble in water, and a wide variety of methods to overcome this insolubility have been worked out. The dispersol dyes are merely another attempt to overcome this insolubility of compounds having an affinity for acetate silk, but the modus operandi is entirely new, in that they are solubilized by physical methods and not by chemical methods.

It is a heretofore unexpected fact, possibly not at all characteristic of dyeing acetate silk only, that certain compounds (dyestuffs) have a much greater affinity for acetate silk when in colloidal solution, possibly in even rather coarse dispersion, than when they are in true solution. This is particularly the case where the compound is solubilized by means of chemical combination with some solubilizing reagent, such as the solubilization of certain bases by means of hydrochloric acid to form their hydrochlorides."

Mullin, Professor Charles E.-- "Acetate Silk and Its Dyes".

With most of the dyes used in dyeing artificial silk with the exception of the acetates, the method of dyeing is quite similar to that of dyeing cotton. It might be noted, however, that basic dyes will dye some of the rayons without the use of tannic acid. Some of the methods as recommended by a few American dyestuff manufacturers will be given here.

National Aniline and Chemical Company give the following data with their "Solantine" dyes, which belong in the direct or substantive class. "Prepare the bath with the requisite amount of dyestuff and from 20 to 30% Common Salt. Dye at a boil for one hour. Rayon is dyed the same strength as cotton at a low temperature; somewhat heavier at the boil. Acetate silks are very slightly stained."

With their developed colors, they give the following data: "Dye in a neutral or slightly alkaline bath with addition of 15 to 30% Common Salt for one hour at a boil. Wash well and diazotize in a cold fresh bath containing  $1\frac{1}{2}$  to 3% Sodium Nitrite and 3 to 5% Sulfuric acid 168 degree Twaddle. Rinse lightly and develop at once with  $\frac{1}{2}$  to 1% Developer B dissolved in  $\frac{1}{4}$  to  $\frac{1}{2}$  Caustic Soda 77 degree Twaddle. Rayon is dyed the same as cotton at a low temperature, somewhat heavier at the boil. Acetate Silks are appreciably stained."

The Sandoz Chemical Works, Inc. give the following data with their "Pyrazol Fast Colors", which belong

to the direct group. "  $\frac{1}{2}$  to 3% color; 20 to 40% Glauber Salt; 1 to 2% Turkey Red Oil. The goods should be entered into the dyebath at 120 degrees F, brought up slowly to 160 to 175 degrees F and run at this temperature for 30 to 45 minutes according to the depth of shade." This firm mentions only Viscose in these directions.

John Campbell and Company give the following dyeing directions for their Sol-Amidine and Amidine Colors "The Viscose Silk which has previously been wetted out, is entered into the dyebath with the requisite amount of color and 5 to 10% Glauber Salt ( Anhydrous) for light and medium shades, or 10 to 20% for heavier shades, 1% Sulphonated Castor Oil or "Camasol" and 1% Soda Ash, at 40 degrees C, brought slowly up to 65 degrees C for light and medium shades, and 80 to 90 degrees C for heavier shades; and continued at this temperature for  $\frac{1}{2}$  hour; then rinsed and dried. In preparing the dyebath for the dyeing of Viscose Silk, the dye-liquor for light shades should not exceed twenty-five times the weight of the material. For heavier shades a more concentrated bath is recommended."

Newport Chemical Works, Incorporated, have the following to say in regard to their direct colors: "The dyebath, to which the dissolved color is added, is made up to a volume of 40 times the weight of the material. The material is then entered into the luke warm bath which is gradually raised to a temperature of 160

degrees F. and the dyeing continued for 45 minutes. The use of 10% to 30% of calcined Glauber's salt, depending upon the quantity of dyestuffs, is required."

The Ciba Company give the following directions for use with their Chlorantine Fast Colors on Viscose:

"The material is dyed in 20 to 25 times its weight of water with 5-40% Galubersalt crystals. Commence lukewarm, raise slowly to 30 degrees C. and dye at this temperature for 1 hour. Pale shades are preferably dyed with Soap, Borax or Phosphate."

E. I. du Pont de Nemours and Company, Inc., give these directions for direct colors with artificial silk: "The dye bath should contain the necessary amount of color, 15 to 20% common salt, 1% soda ash; dye at 140 to 160 degrees F for one hour."

For Basic colors, just a few methods will be given, first the method of John Campbell and Company: "For light shades Viscose silk is not mordanted. For medium and heavy shades, Viscose silk is first mordanted by working at 50 degrees C for two hours in a bath consisting of 2 to 4% Tannic acid and  $\frac{1}{2}$  to 1% Hydrochloric acid. After hydroextracting, the mordant is fixed by working cold for 20 minutes in a fresh bath charged with 1% to 2% of Tartar Emetic. Enter the material into the dyebath at 30 degrees C.: work for five to ten minutes and bring the temperature up slowly to 50 to 60 degrees C

and continue dyeing until the required depth of shade is obtained. The dissolved dyestuff may be added to the dye-bath in small portions during the dyeing operation, to prevent too rapid exhaustion.

The dyebath should contain from 2% to 5% of Acetic Acid. It should not exceed forty times the weight of the material for light shades. For heavier shades a more concentrated dyebath is recommended."

Newport Chemical Works, Incorporated give these directions for basic colors: "The material is entered into the cold bath and the temperature gradually raised to 140 degrees F., the dyeing then continued for 45 minutes. In the case of Newport Auramine O the temperature should not exceed 120 degrees F. No mordant is necessary although the use of a small amount of acetic acid retards the exhaustion of these colors and will aid in the securing of level dyeings."

NOTE: Although basic dyes are made by these different firms and put on the market as being duplicates of dyes described in Rowe's Colour Index; these two firms do not agree in their directions as to mordanting, one states that mordants are needed and the other takes the opposite stand.

Next to be discussed are the Sulphur Colors; John Campbell and Company give these dyeing directions for their "Amalthion" ( sulphur) colors. "The dyestuff is first separately dissolved in Sodium Sulphide Concentrated. The



Viscose Silk which has previously been wetted out is entered into the dyebath containing the requisite amount of color and 10% to 15% Glauber Salt (Anhydrous), 2% Sulphonated Castor Oil or "Camasol", 2% Soda Ash at 60 degrees C., brought slowly up to 75 degrees Centigrade and continued at this temperature for one-half to one hour; then wrung out and oxidized; washed in a warm soap solution; rinsed and dried. The dye - liquor should not exceed twenty times the weight of the Viscose Silk."

E. I. du Pont de Nemours and Company, Inc., say for their "Sulfogene" (sulphur) colors: "The dyestuff is dyed in the same manner as most sulphur dyes: made into a smooth paste with cold water and one-half as much soda ash as color. For each pound of the dyestuff used about a gallon of boiling water is added together with the necessary amount of sodium sulphide concentrated, usually the same amount as the dyestuff. This solution is gently boiled and when the color is dissolved it is strained into the dyebath in which 30 to 50 pounds of common salt has been dissolved. Artificial silk should be dyed at 130 degrees to 150 degrees F."

An interesting class of dyes sometimes used on rayons is the Vat colors; these dyes are very fast to light and washing as compared with some of the other classes, and are used where such fastness is needed. However, they are much more difficult to apply and to secure

level dyeings than are the directs and basics. Due to the fact that each vat dye must be dyed at its own particular proper temperature, it is almost impossible to dye a mixture of two or more vat colors when trying to obtain some desired shade. This is not generally understood by the layman and causes the dyer much trouble in trying to obtain a single dyestuff that will give the desired shade by itself.

Sandoz Chemical Works give directions for making up 10 gallons of Dye Vat with separate notes for each dye: "Caustic soda 64 degree Twaddle,  $\frac{1}{2}$  to  $1\frac{1}{2}$  pints; Hydrosulphite T2 $\frac{1}{2}$  to 16 ounces; Glauber or Common Salt, 2 to 8 pounds; reduction temperature varies from 125 to 190 degrees F.; dyeing temperature varies from 70 to 140 degrees F."

National Aniline and Chemical Company, Inc., give these directions for their "Carbanthrene Blue BCS" "100 pounds of rayon yarn; 1 to 10 pounds of dye; 4 to 8 pints Caustic Soda 76 degree Twaddle;  $1\frac{1}{2}$  to  $3\frac{1}{2}$  pounds of Hydrosulphite Conc. Powder; make up to 200 to 225 gallons. Reduce and dissolve the dyestuff at 120 degrees F. in a stock vat, containing from 30 to 40 gallons, with the required amount of Caustic Soda and Hydrosulphite. Add this to this dyebath, which previously has been sharpened with a small amount of Caustic Soda and Hydrosulphite. Dye for one hour at 120 degrees F., squeeze or allow to drain and

rinse in cold and then in hot water. The removal of the caustic soda is facilitated by souring with Hydrochloric or Sulphuric Acid, and then thoroughly rinsing in cold water. Yarn and piece goods are usually given a final boiling soap treatment."

Newport Chemical Works, Incorporated say of their vat colors: "The Anthrene and Thianthrene Colors are the fastest dyestuffs now obtainable. They are dyed from hydrosulphite vats at various temperatures, depending upon the color." This firm uses the color in paste, Hydrosulphite Conc. Powder, dry Caustic soda.

E.I. Du Pont de Nemours and Company, Inc. say of their vats of which Sulfanthrene Pink FF Paste will be used here for an example: "The required amount of Paste should be mixed with caustic soda which has previously been dissolved in water. This mixture should then be poured into the dye vat which contains the total volume of water to be used, and then sufficient Hydrosulfite Conc should be added.

The quantities of dry caustic soda and hydrosulfite which are necessary in the preparation of the dye-vat should vary approximately from one-half to twice the amount of color used. The vat should be heated nearly to a boil, at which temperature the dyestuff should be completely reduced. As soon as reduction is complete the heating is discontinued and the vat allowed to cool to about 140 degrees F. and 10 pounds of soap added if necessary, before the dyeing is started.

The yarn which has been previously boiled out hydro-extracted and suspended on bent sticks, is entered into the dyebath. The yarn is dyed in the cooling bath for one hour and is then lifted, allowed to drain and rinsed in cold water. After the cold water rinse it is given a wash in hot water, soured with sulphuric acid, again washed and soaped at a boil for twenty minutes in a bath containing 3 pounds of soap. A thorough rinsing should follow."

For acetate silk dyeing, the makers of the Celanese type have put on the market a set of dyes called S.R.A. colors. In the directions for dyeing with these dyes, the makers say: "the assistants to be employed for these colors are Olive Oil Soap, Turkey Red Oil, Common Salt, Ammonia. These colors are paste colors ( usually 10% strengths) which are dissolved in boiling water or better in boiling soap ~~sap~~ solution. They dye Celanese direct from mildly alkaline ( ammoniacal) or soap baths. They may be mixed together indiscriminately in any or all proportions for the production of compound shades. The general method is simple being similar to the dyeing of cotton or other artificial silk in a direct manner. For heavy or tightly twisted goods difficult of penetration to be dyed in pale shades it is advisable to dye an extended period in the cold, and to make increased addition of soap or Turkey Red Oil to the bath. It will be found that most of the S.R.A. colors have good af-

finitly in the cold. The level dyeing qualities are very good provided due regard is paid to the ratios of affinity to temperature. Pale shades generally may be dyed cool or even cold without much sacrifice in the matter of subsequent fastness to washing.

In dyeing deep shades there is little advantage in the use of inorganic salts such as common salt or Glauber Salt. In any case excesses of these tend to throw the colors or Turkey Red Oil out of solution.

The Celanese is scoured and bleached when necessary before dyeing. Soft water is essential for successful dyeing with S.R.A. colors. The volume ratio is usually about 25:1 to 30:1 depending upon the type of machine used. The bath is set with about .5 to 1.5 grams per litre of Olive Oil soap. Where the amount of color in the bath is very small as in pale shades, the addition of a little Turkey Red Oil up to 1 to 2 cc per litre has a beneficial effect. Temperature should not go over 80 degrees C."

The above was copied from a small pamphlet put out by the British Celanese Company. The American Cellulose and Chemical Manufacturing Company, Ltd., also use the same writeup but have added another preparation called "Celascour" which is used as an assistant and also as a scour. They say this for it: "This product is a new colloidal liquid preparation specially devised for

use in scouring and dyeing goods containing Celanese yarns. It has proved not to affect Celanese at all deleteriously and to have many useful properties in respect to scouring, particularly very oily or greasy goods, and notably as an addition to dyebaths containing S.R.A. Colors for level dyeing and penetration."

The Ciba Company also make a special series of dyes called "Cibacet" which are to be used on acetate silks. Their dyeing instructions are as follows: " A previous cleansing or even bleaching is necessary, particularly for pale shades. WETTING OUT, work the material in a bath containing 2 grams of Soap and 1 cc of Ammonia per litre for  $\frac{1}{2}$  hour at 50 degrees C. Instead of Soap 1.5 grams Solapol Oil and 1.5 cc Ammonia may be used to avoid formation of Lime Soaps in hard water.

Dyeing is carried out with addition of 2-4 grams Soap per litre dyebath, Turkey Red Oil may also be used. The calculated quantity of Soap or Oil is dissolved in 20 times the amount of water at 50-60 degrees C, poured over the requisite amount of dyestuff paste and stirred until a fine state of dispersal is attained. This Emulsion is added slowly to the dyebath and the whole well raked up. Enter the material and dye for  $\frac{1}{2}$  - 1 hour from 20 to 30 degrees C. After dyeing rinse well and brighten if necessary."

So much is being studied in the colloidal field as regards dyeing, that a short resumé will be made of

this important dyeing subject.

One of the best articles was given in a paper read in England to the Foreman Dyers' Guild by E. Greenhalgh<sup>1</sup>. The title of this paper was "Artificial Silk Dyeing From a Colloidal Standpoint", and a few of the most important parts will be quoted now: " Colloids are substances which generally consist of two phases in the same way that solutions do, namely one phase being called the disperse, and the other the dispersion medium. To give you an example of this take the case of thickened starch; this, being a colloid, has starch for its disperse phase and water for its dispersion medium, Similarly in this case all solutions of dyestuffs may be regarded as colloids, the dyestuff being dispersed through the medium phase of the solvent whatever it may be. Now the disperse phase may be of a coarse nature as in the case of starch, or it may be, on the other hand, very fine as in the case of the dyestuff, and we therefore get two kinds of phases, namely, one of what is known as a phase of low dispersion and the other as a phase of high dispersion.

The high dispersion phases are akin to solutions and the low phases partake of the nature of gels or even in some case partial solids, so that it can be clearly determined that although far different though

<sup>1</sup> Greenhalgh, E.- "Artificial Silk Dyeing From A Colloidal Standpoint"--The Dyer and Calico Printer- May 15, 1927.

they appear to be, silks or fibres are to a certain degree correlated to dyestuff solutions in that they both are of a similar physical structure. All artificial fibres are excellent examples of colloids, particularly Celanese and viscose and partaking of that class which appertains to low dispersion gives us substances which partake of the solid nature yet possessing in themselves the physical structure of solution.

Liquids are more mobile than solids for the simple reason that they contain more ionic activity and it must not be concluded that solids are absolutely inert, for the latest advances in science have shown that everything is capable of ionic movement in some degree or other. Acceptance of these facts shows also that accordingly colloids of high dispersion must necessarily be more mobile than those of a lower order of dispersity so that solution must possess a superlativeness over colloids and likewise colloids over solids. As an example, the action of direct colors on cotton and viscose show an increase of color on the viscose, this being due not to increased activity of the dye solution, but of increased activity, if it thus may be termed, of the higher dispersion phase, namely viscose, over the cotton. Dyeing is not only the action of the dyestuff in solution but the combination of actions of the color and the substance to be dyed.

Having thus gained some little insight as to



what the colloidal and physical aspect of dyeing is, we must now consider what it is that causes certain colors to be taken up by certain fibres and why in other cases resistance of combination ensues as is the case with Celanese and certain direct cotton colors. Although two substances may be instanced as being colloidal, yet it is not wholly a corollary that they possess similarity of action; on the contrary, they may each be so distinctly antagonistic as to be absolutely repellant in their combined action, so much so that in certain cases a break up of one or both colloidal phases takes place. This is analogous to precipitation. In cases such as these where ionic action is not so drastic, but where no clear mutual action is discernable, the colloidal phases are said to be unsympathetic to each other and as such have no common function between them. This explains why no dyeing will take place by immersion of Celanese in a bath of Sky Blue FF, neither the dyestuff solution nor disperse phase, nor the acetyl cellulose disperse phase having anything in common between them, but each being of an unsympathetic nature as regards each other.

It is therefore plain to see that dyeing can only be carried out effectively if the dyestuff and the substance to <sup>be</sup> dyed are in absolute sympathy, and this after all is an explanation of what is meant by a statement that a certain fibre has an affinity for certain dyestuffs. This

term affinity is rather misleading as it may imply anything from a physical mixture to a chemical combination taking place between the two bodies and has been previously stated it is only by an acceptance of the principles of colloidal chemistry that a definite and true understanding of the function of dyeing can be appreciated.

The first principle therefore to be learnt is that for production of perfect dyeing, the function must be one of perfect accord in respect to the fibre and the dyestuff. It is at this junction that another question arises, namely, that of variation in degree of dispersion as represented by different dyestuffs in solution and the resultant action on a stable colloid such as artificial silk. For instance, solutions of Direct Yellow G and Direct Brown are very diverse, the yellow being as it were many more degrees "in solution" than the brown, or in colloidal language, the yellow possesses a higher degree of dispersion than the brown.

This is exactly what one finds in the dyeing of viscose, namely, that certain colors are absorbed or taken up more rapidly than others of the same class, and this factor alone is one which must be reckoned with in the production of secondary or tertiary shades. Arising from this argument we realize that a second principle of perfect dyeing is that in which the degrees of dispersion of members comprising the dyebath should be practically analogous and somewhere about the same plane. This means

that for mixed shades, the indiscriminate use of dyestuffs should be avoided and only definite colors whose solution properties are definitely known utilised.

Considering these various functions there is a period where an explanation of certain erratic factors becomes necessary, particularly with regard to that state known as barriness or unevenness of depth or tone between two or more samples of a supposedly stable fibre. For instance, two hanks or cops of viscose either single or woven in the piece, each subjected to the same tinctorial treatment may on examination be found to exhibit two distinct shades of the same color, this color being too a pure organic compound. Here is a metamorphosis which seems inexplicable in that there are present two definite sympathetic stable colloids whose actions mutually should always produce the same result yet variation has arisen.

This leads us to a further consideration of of this colloidal functioning and on examination of the process factors, it will be found that there has been reached a point where the dispersion of the dyeing phase has become too low and hence its activity has been likewise lessened, causing in part a breaking up or partial precipitation of the dyestuff solule, and functions of this kind are practically uncontrollable, so that any amount of variation may easily be expected. From this point, therefore, we are led to the conclusion that the best dyestuffs to be employed in dyeing colloidal bodies

such as artificial silk are those which possess high degree of dispersion in solution, or if we may put it so, colors which in themselves are exceptionally soluble and give clear solutions. This factor applies more to viscose than to Celanese.

Referring to the activity of substances when dyed on silk, there is an excellent example to be found in what is known as phototropism. Certain azo dyestuffs are sympathetic to Celanese, but after dyeing function has finished and the goods are dried, it is found that exposures to light and darkness have the property of giving a difference of shade. Portions of the fabric which have been shielded from light possess an entirely different shade from the exposed portions, and these former on exposure to light readily assume a normal tone again, reverting to the abnormal when covered again. This is due to the action of the light causing a wandering of a certain atom in the dyestuff molecule, which movement is capable of producing two definite chemical compounds each possessing the same empirical formula, yet being totally diverse through different orientation of their molecules.

Considering the dyeing of Celanese from this standpoint, particularly as regards the use of S.R.A. and kindred dyestuffs, the degrees of dispersion of the dyeingphases are very much lower than those obtained in the case of processing of viscose with direct dyestuffs,

and under this consideration it must be realized that the Celanese silk itself must be of a more sympathetic nature towards these low dispersion media than what viscose is, in that it is easier to obtain uniformity in shade on Celanese than on viscose particularly when dyeing media of low dispersion are utilised. Evidence of this can be seen by the fact that Celanese will give practically level results when processed in a dyeing solution that is not only muddy, but has specks of undissolved color present, whereas with viscose, treatment under similar conditions would be distinctly chaotic.

Dyeing takes place in this manner: the dyestuff phase being more mobile than the lower disperse phase of the silk employs this latter phase as a field for activity. This activity results, however, in the transference of the dyestuff from the original phase to the silk phase, the colour thus being absorbed in a specific manner and becoming an integral part of the silk phase thus producing another colloidal state. In fact the dyestuff becomes dissolved in the silk thus forming a color phase or solution wherein the color is the dispersion phase and the silk the dispersion medium.

Dry Dyeing: it may be doubted whether this is possible, that is, whether one solid may be dissolved in another, yet if perfectly dry S.R.A. dyestuff be placed adjacent to a sample of perfectly dry Celanese and the two kept together in a dry atmosphere such as that provided by a desiccator, it will be found, after some time, that a union has taken place and the silk has been dyed with the color. Here is an instance of a defi-

nite and integral function having been performed without the aid of any auxiliaries such as water or Turkey Red oil and only goes to prove that after all the silk being colloidal possesses some of those properties which are analogous to liquids and that also solid bodies do possess ionic power.

It is in this manner then that dyeing takes place on artificial silk; that is, the disperse phase of the dye solution is transferred so that it becomes the disperse phase of the color-silk colloid. Reasoning further it will be readily understood that the dyeing of silks whether viscose, Cellulose or other varieties, is not as has been very often supposed, a chemical combination, but is purely a physico-colloidal function wherein there obtains each specific and integral factor in its original state, namely, as disperse phase and dispersion medium.

It must not be forgotten that colloids are not always sympathetic to any agency but are in many cases otherwise, and must themselves exert a repellent action. In this way they become protectors of their contents, and they seek to shield those phases they have absorbed even to the point of their own destruction. In this way a high dispersion phase obtains much more protection from external agencies than does a phase of low dispersion, and hence it is that colors on viscose ex-

hibit faster properties than when dyed on cotton. "

In dyeing viscose you can use the same type of dyes as are used on cotton. Care in the dyeing of the temperature will make it possible to dye unions of viscose and cotton of the same depth of shade. The assistants used with cotton are also used with viscose in the same manner. For a number of years it was not deemed advisable to kier boil goods containing viscose but with the improvements which have constantly been made in the manufacture of this fibre, kier boiling of viscose cotton goods is now commonly performed. However, if the material is entirely of viscose, this strong scouring is not needed, and a milder scouring in the open jigs or continuous washers using soap or soap and alkali is usually sufficient to remove impurities. These impurities consist mostly of oils and dirt picked up during processing. The neps and wax and other impurities common to cotton are not present in the viscose. The oils come from the treatment given during the manufacture of fibre and from that applied as a lubricant to the fibre as an aid in knitting. There may also be some used in a sizing compound if the viscose is used as the warp. The lubricating oils in many cases are of a mineral oil base combined with some emulsifying agent to make them more easily removed in the scouring process.

The assistants used are as for cotton dyeing

and are common salt, Glauber Salt, soluble oils such as sulphonated castor oil and similar compounds, soda ash, various penetrating assistants and wetting out compounds.

Thomas M. Harris<sup>1</sup> writes a few pertinent remarks in one of his articles in regard to dyeing viscose. "Viscose has higher receptivity for dye (direct) than cotton has." Another good point is brought out in the following: "Application of Vat colors to Viscose is attended with considerable difficulty. This is attributed to the great affinity of the Viscose for the dye." Whether or not this affinity is chemical or physical will remain to be seen.

Formulae have been given for dyeing Celanese which formulae and dyes can of course be used for acetate silk as made by other firms. Just a few words from an article by H. Platt<sup>2</sup> in regard to Celanese dyeing: "the SRA dyes are not dyed by reducing; they are simply dyed direct on the fibre from a soap bath." Here we find a use of soap as an assistant rather than as a cleansing agent. If the water is hard, we must be careful to use something to previously soften it or we will find that there is a precipitate of lime soap on the Celanese fibre.

Another care must also be taken with Celanese in dyeing to avoid the use of alkalies as far as possible

1. Harris Thomas M.--"Some Points in Dyeing Viscose"--  
Textile Colorist-- September 1927.
2. Platt H.--"Cellulose Acetate Silk"--Dyestuff Reporter--  
January 26, 1925



because strong alkalies will saponify acetate types of artificial silk. With dilute acids, this is not the case, in fact, acids such as formic and acetic are used to give certain effects such as "scoop".

The temperature must be controlled so that higher than 185 degrees F will be avoided. The high heat of boiling causes the acetate types to lose their lustre, and is known as "blinding".

Acetate silk does not swell in hot nor in cold water nor in pure alcohol ( absolute), but does swell in mixtures of water and some organic solvents such as alcohol,; it is also soluble in acetone, pyridine, acetic acid glacial etc.

Tubize will take dyes as will Viscose, in some cases some of the basic dyes are deeper on this nitro type than on the xanthate type. The temperature can also be raised higher than it can with Celanese.

Cupra ammonium types of rayon work along the same lines as do the other regenerated types. A short account of the dyeing of this yarn will be quoted from a special contribution to the Textile Colorist of December 1927, page 833. This deals with one special make of cupra ammonium rayon, "Bemberg".

"Before that type of rayon known as Bemberg is dyed and subjected to any of the technical operations involved in the dyeing process, no matter what they might be, it must first be treated with a hot fatty soap li-

quor, being allowed to remain in this bath at its boiling point for a period of approximately one hour. The fibre is then washed with luke-warm water, and the dyeing process begins.

Dyeing with substantive dyes: the shallow vats, in which the dyeing process is carried out, are filled with water and soda, so that the liquor has a slightly alkaline reaction. Dyeing is begun at a temperature of 95 degrees F., and this is then raised until it reaches the boiling point. The liquor is boiled for a minute or two; then the goods are washed and subjected to a brightening treatment. It is advisable to add a fatty soap solution to obtain more level dyeing. Brighten by treating with acetic, lactic or formic acid in a liquor to which a little oil emulsion has been added.

Dyeing with a tannin mordant: vary from  $\frac{1}{2}$  to  $3\frac{1}{2}\%$ , in accordance with the depth of shade that is being produced on the fibre, the mordanting taking place in a bath which has been acidified with a little acetic acid. Cool and treat fibre with  $\frac{1}{2}$  to  $1\frac{1}{2}\%$  tartar emetic solution. Wash the fibre and dye with the basic dyestuff with addition of acetic or formic acid.

Sulphur dyestuffs: these dyestuffs are dissolved as usual, in sodium sulphide solution, and the solution is then added to the soda liquor, the dyeing being carried out at the boiling temperature. Wash and brighten; sodium acetate is used in this bath to prevent formation of sulphuric acid."

R.P.Dicks<sup>1</sup> states: "The dyer knows and we all know that cuprammonium silk has a greater attraction for dyestuffs than viscose silk. Naturally it requires a little more resist in its application, but if handled in the right manner it will give you the same results with possibly a shade deeper color."

After studying the previous pages, it will be possible to form some idea of the problem as picked out for this thesis.

Dicks R.P.<sup>2</sup>- "Cuprammonium Silk Industry"--Dyestuff Reporter-- January 26, 1925.

## III

PROBLEM: TO TRY TO DETERMINE BY USE OF THE MICROSCOPE REASONS FOR UNEVEN DYEING OF VARIOUS TYPES OF RAYONS.

If the preceding sections have been read and studied, there is no doubt but that chemistry plays a most important part in the making and in the dyeing of rayon and kindred fibres. Therefore, many of the changes are without a doubt of chemical nature. However, there may be some changes which are physical and which by use of proper apparatus and correct methods can be shown with the microscope. Such, if any can be solved, problems will be the work in this thesis.

Cellulose whether in form of linters or wood pulp undergoes many chemical changes and also various physical changes before it is made into the artificial finished fibre. These changes have their effect on the subsequent dyeing. Many times, the dyer has found that his dyed rayons, although dyed in the same bath with everything under identical conditions, have two or more shades or tones.

The author has on his desk at present two skeins of xanthate rayon which he saw dyed commercially in the same bath, and these two skeins have different depth of color. The skeins were taken from the same box as it came from the artificial silk manufacturer and were given identical treatment throughout every process, but even with this care, they are different in color. This

has happened many times at this and other mills even though the utmost care is taken with the dyeing. Possibly this fault is entirely chemical, but investigation may prove some physical fault.

In Black and White of January 1928, the following article appeared: "A great deal of trouble is being caused now-a-days, by streaks appearing in piece-dyed fabrics, made wholly or in part, of rayon, which trouble is caused entirely by physical strain so changing certain rayon yarns in the fabric that they do not dye up the same as yarns which have not be subjected to excessive physical strain. The use of the microscope is of great assistance in this matter."

<sup>1</sup>  
J.W Walsh h's this to say : "The light and dark stain nuisance so familiar to the dyer, has been reduced to a minimum by the rayon manufacturers, and we think by this time that all know that it is impossible for the dyer to remedy this trouble. It is <sup>as</sup> impossible to stop it as it is for a person to make two different growths of the same kind of wood identical, so that when it is varnished it will have the same appearance. The dyers formerly bleached the yarn in order to do away with this trouble, but it was of no avail. The light and dark skein horror was much the same as the uneven dyeing of skein yarn after the mercerizing process.

Walsh J. William--"Dyeing Fast and Uniform Shades"---  
Textile World-- September 29, 1928.

Rayon that leaves the dyehouse damp or not bone-dry will always give trouble. One reason is that it is not uniformly damp and the damp places in the thread will produce what are known as shiners, due to the yarn stretching in the damp places, thereby producing a different tone of color than the rest of the thread. A rayon thread will lengthen out on becoming damp or wet, without even being stretched, and unlike other fibres, it will never come back to its normal length. This causes rayon goods to pucker in some places, which makes them appear a different color than the rest."

The above refers mostly to piece goods, and the microscope, especially the binocular type equipped with special lenses and stages has been of great aid in determining these unevenly dyed yarns, but this thesis is mainly to determine unevenness throughout the whole skein and difference in color in skeins dyed in the same bath.

James W. Cox Jr.<sup>1</sup> writes: " The maintaining of an even, or definite degree of bleach in rayon yarns by manufacturers and afterwards in textile plants, still seems to be a more difficult proposition than with cotton yarns, but the progress has been great. The knowledge of the proper degree of bleach necessary in the textile plants has been gradually becoming better. The general

Cox, James W. Jr.--" A Year's Progress in Rayon"--  
Textile World-- September 29, 1928.

average trend in most materials in the cotton and silk branches of the industry to be piece-dyed and printed, or both, has been of great assistance in lessening bleach troubles, as a large part of all troubles caused by bleached and over-bleached rayon have been with YARN-DYED materials. Fortunately, the average textile mill man, as well as the cotton goods and silk fabric converter, has at last wakened up to the fact that the degree of bleach in the yarn as received from the cotton manufacturer is a very vital factor in the final quality of the goods, made wholly, or in part, from rayon yarns."

The above was a purely chemical theory as given by a non-manufacturer, so here is a theory for this uneven dyeing placing the fault on the dyer. R.P.Dicks, formerly President of Cupra, Inc., states as follows: "The manufacturer of real silk or other silk is familiar with the change in color or reflection of light due to the height of lustre, and if you have in your drying two different tensions, you will get two different appearances of color in the dyed product."

Mr. Dicks gave the following theory also for uniform dyeing. " Those are things that are , after all, mechanical and are problems which are familiar to all silk manufacturers. I venture the opinion that all artificial silk made by the various groups would dye uniform-  
Dicks, R.P.--"Cuprammonium Silk and the Artificial Silk Industry"-- Dyestuff Reporter-- January 26, 1925.

ly if the following procedure were rigidly adhered to, namely: first clean the silk properly of all foreign matters. Step number 2 is to dry that silk under uniform tension before it leaves your hands. Step number 3 is for the dyer: in his manipulation, to be exact as to his dye-bath in every particular; and finally, it is necessary for him to be exact in his **DRYING.**"



## IV

## DATA AVAILABLE CONCERNING THE PROBLEM.

Data in regard to the use of the microscope with rayon was not available in any quantity. A search through many of the Journals failed to produce but very few articles on this subject, and none that really were exactly on the subject or problem.

<sup>1</sup>  
Professor E. R. Schwarz of M.I.T. wrote the following: " Rayon fibre, which appears to the naked eye as a filament of cobweb fineness--- so fine as to be invisible in certain light--- is seen under the microscope as a broad strand of unique conformation. By use of proper accessories, almost any desired measurement may be made upon it. In brief, the microscope and its accessories equipment open up a most fruitful field of investigation."

<sup>2</sup>  
Arthur K. Johnson, formerly professor at Lowell Textile Institute says in one of his articles: "Progress and diversification in the manufacture of rayon ( whether taking place in the spinning solution, in the coagulating bath, in the reeling conditions, or after completion of the original yarns) has brought the types not groups of rayons closer and closer together

Schwarz, Edward R.--"Rayon Research Problems"--Textile World-- September 29, 1928.

Johnson, Arthur K.--"Methods of Identifying Rayons"--Textile World-- September 29, 1928.

in their similarity of physical and chemical properties used for testing.

These changes in process, made for the purpose of producing an improved and more pleasing product with respect to such properties as subdued lustre, feel, softness, water resistance, covering power, weighting, sizing and dyeing properties, have caused a reasonably progressive change in the sizes ( diameter), shapes, surface and internal conditions of the fibres and of the yarns. The result is that physical facts and appearances used as a basis for identification ( as cross-sectional appearance) must be continually altered and brought up to date."

The German author, G. Heink says: "Especially in Viscose artificial silk a consistent cross section form in respect to the structure is indeed rare, and this ( in the entire manufacturing, which the viscose silk undergoes ) lies in the first line in the composition of the precipitating bath. By higher salt additions to the acid bath, the true smooth edged shape of the cross-section is indented; the more or less rounded shape disappears, and a different kind of structure appears.

Also the kind and amount of the individual salt additions in the precipitating bath imprint their

Heink, G.--"Mikroskopie an Kunstseide"---Melliand Textil-Berichte-- January 1928. American translation by A.H. Grimshaw in N.C.S.C. Library.

characteristics in the cross-sections. The cross-section picture is a more valuable means of distinguishing between the various kinds of artificial silk than the chemical."

Professor Harold Hibbert,<sup>1</sup> formerly of Yale, but now of McGill told a little about the X-ray examination of cellulose in one of his talks to the Textile Chemists and Colorists. He spoke as follows: "It might be well to discuss the results which have been obtained in the Kaiserstoff Institute, Berlin, with regard to the structure of cellulose and other fibres as shown by X-ray analysis. This is not the place to go into the detail of the work, except to say that by taking X-ray photographs of cotton fibres it has been possible to show that cellulose probably has a "building unit" of quite small molecular proportions, probably of the order of  $(C_6 H_{10} O_5)_4$ , and that such a product is capable of combining with itself to give a derivative of much higher molecular weight, which we know as ordinary cotton cellulose. This is not in conformity with Irvine's results, in which we have three units, nor is it in conformity with other researches, so that the question must be left open.

Nevertheless, this work has already given us quite an important insight into the properties of Hibbert, Harold--"Composition and Properties of Various Artificial Silks"--Dyestuff Reporter-- January 26, 1925

the cotton molecule. In the first place, it teaches us that cotton cellulose is not, as we have previously assumed, a simple colloid substance; it is what we term a crystallite, and judging from the evidence available cotton cellulose would seem to consist of these crystalline aggregates of cellulose, which form the skeleton of the fibre, seated in a magma of amorphous material produced from a previously liquid body. In other words, you must look at your fibre as a series of these crystalline aggregates in this magma, and this has many advantages. It allows, for instance, reactions to occur between these crystallites and many reagents. If all these crystallites are arranged parallel to the axis, as seems to be the case in cotton, this accounts for the strength of the cotton fibre.

These results are borne out by an examination of the various types of ARTIFICIAL SILK. For instance, in Viscose silk after precipitation of the cotton (hydrated cotton), these crystallites, instead of all being arranged parallel to the axis, are arranged in topsyturvy fashion as contrasted with, say, cellulose which we obtain by the Chardonnet process.

You can see that such a method of analysis offers considerable promise."

## V

## PREPARATION OF THE SAMPLES.

In the preceding pages, mention has been made of many chemicals used in scouring and as assistants in the dyeing of the different types of rayons or artificial silks with the various classes of dyestuffs. As there were too many for a short thesis of this kind, only the more important were used in the preparation of the samples.

The yarn used was obtained from the various manufacturers in skein form. ~~Through~~ <sup>Through</sup> ~~the~~ <sup>the</sup> kindness of Dean Thomas Nelson of the Textile School of North Carolina State College, who solicited these samples, the following firms contributed their product in the 150 denier size: DuPont; American Bemberg Corporation; Tubize Artificial Silk Company of America; American Cellulose and Chemical Company; and the Viscose Company. The DuPont Company furnished their xanthate and also their acetate product; Bemberg furnished the cuprammonium type; American Cellulose, the acetate type; Tubize the nitro type; and Viscose the xanthate type.

The skeins were wound onto spools and then smaller skeins of 120 yards in length were wound for the samples to be treated.

In treating the samples with the various solutions, it was necessary to have some identifying mark as the six different samples were treated in the same bath at

the same time in order to have identical conditions. The method of identifying was real simple, as cotton, silk and wool thread with one or two knots was tied onto the fibre each time.

On page 73, on the top row, are samples of the six yarns as they came from the manufacturers without having been treated in any way. Bemberg had the least lustre of all.

In the middle row of page 73 are mounted the samples obtained by treating the samples with plain water at the boiling point. If this boiling were to be continued for some time, the acetate silks would be blinded, but a short submersion does not harm them to a marked degree.

The names of the different types appear at the top of the page and refer to that type in the three sets all the way to the bottom group.

In set # 6 in the bottom row, the samples or rather the skeins were subjected to a solution of soap made up 1 part to 1000 at 190 degrees F. For the acetate types, this is of course, beyond the safety point of 185 degrees F. The soap was neutral olive oil soap. This method of scouring was used to show effects of a dilute soap solution such as could be used on any fibre without danger of alkaline action dissolving them, as would be the case of an alkaline soap solution on wool or silk.

DYEING

Acetate  
DuPont

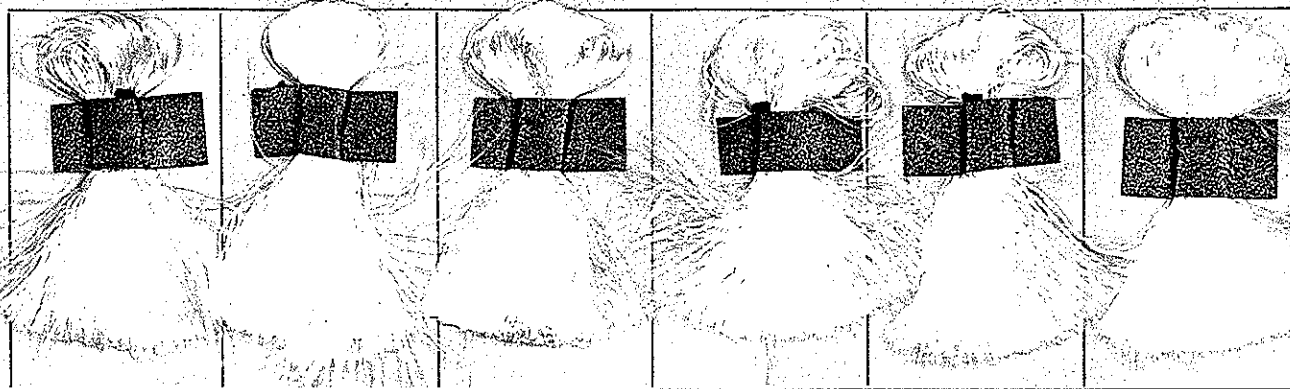
Bemberg

Celanese

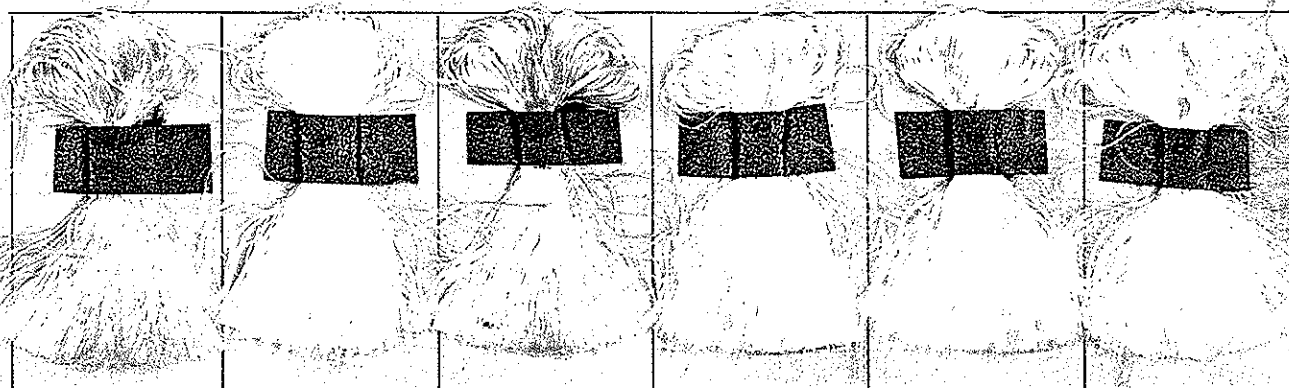
Tubize

Viscose

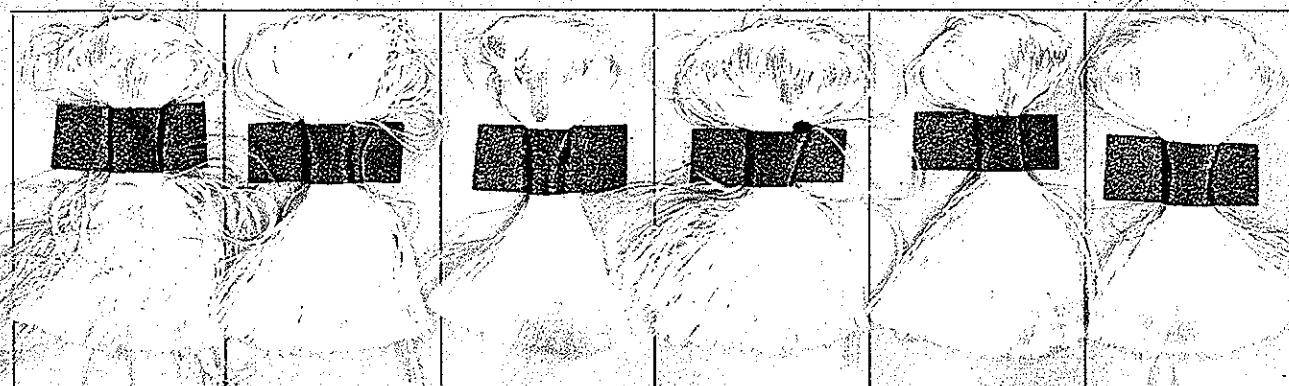
Xanthate  
DuPont



" AS IS"



Set # 7. Treated with water at a boil.



Set # 6. Treated with soap solution made 1 to 1000 at 190 F.

On page 75 are mounted the results of the treating of the skeins with various temperatures of 1 to 100 soap solution.

This soap was also a neutral olive soap, but the solution was made ten times stronger than in the previous case. In scouring with soap in practice, the percentage will vary according to the fibre and the amount of dirt and oil in the fibre. In a mixture containing cotton and rayon or artificial silk, the amount would be based on the quantity of each fibre present. With a larger amount of cotton ( especially in the grey), a larger amount of soap would be necessary to remove as much ~~impurities~~ impurities as possible. Cotton can stand stronger and rougher treatment than any of the rayons as cotton is stronger when wet, whereas the rayons are weaker.

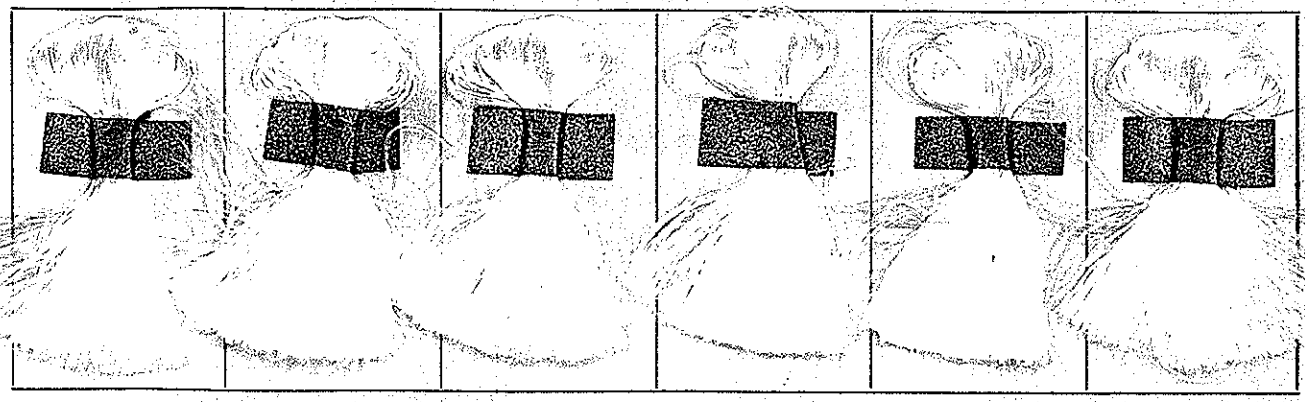
It should have been stated that porcelain dye cups were used for these tests and all of the following tests. The dyecups were heated in the large iron baths fitted with holes in which the cups were placed, the cups were submerged to within two inches of the top and the solutions in the cups were kept at this level inside the cups. For boiling tests, direct heat was used as the dyebaths run usually at 190 to 205 which would not reach the boiling point of 212 F.

After being treated, the skeins were washed in warm water.

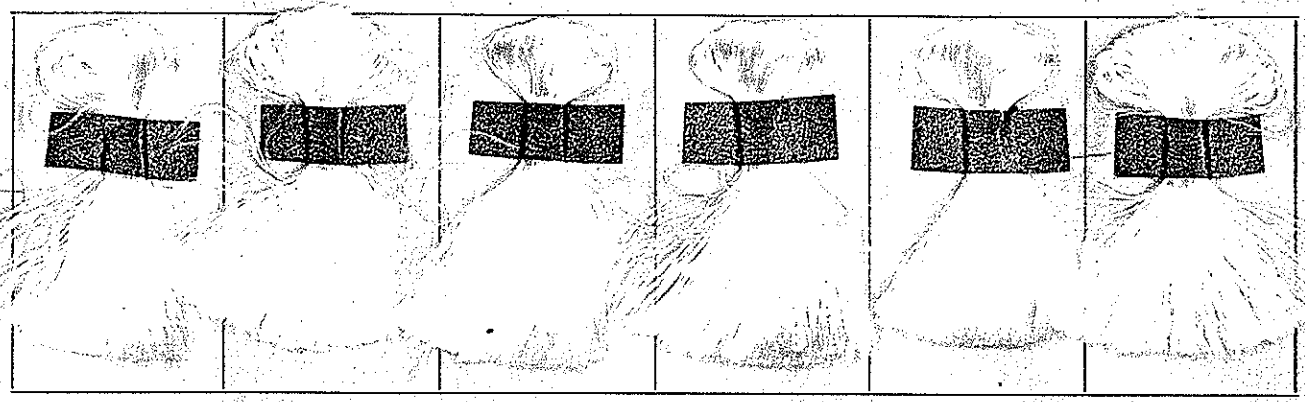


DYEING

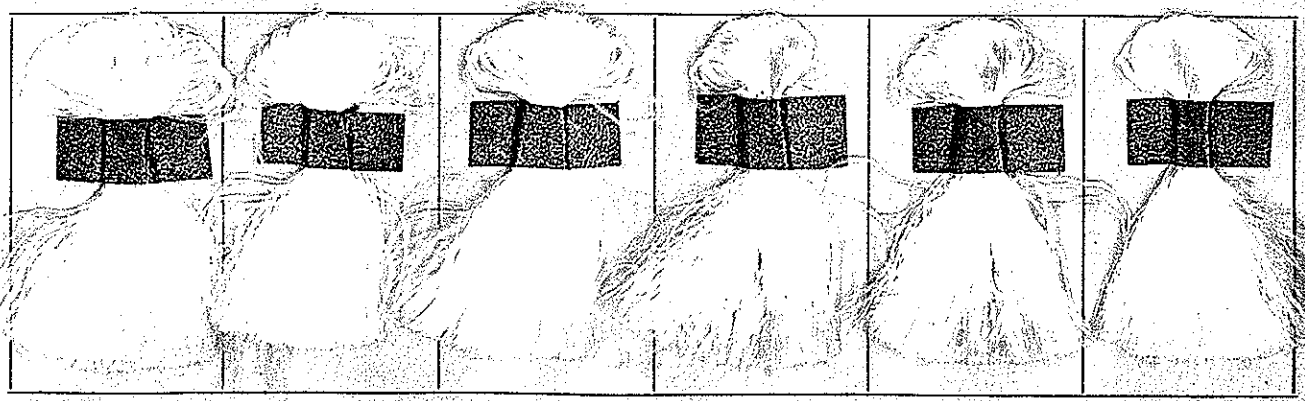
Acetate DuPont	Bemberg	Celanese	Tubize	Viscose	Xanthate DuPont
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Set # 3. Soap 1 to 100 at 140 degrees F



Set #4. Soap 1 to 100 at 180 degrees F.



Set #5. Soap 1 to 100 at a boil.

The soap solution was made one to a hundred in each case but set #3 was treated at 140 F; set #4 at 180 F; and set #5 at a boil.

So many assistants are used in dyeing that all of them could not be used in these tests, therefore, a few of the more important were used. The temperature of 190 F was used as an average between the boiling point at which many dyes are treated and the low temperature at which some of the others are dyed.

In many of the formulae given by the makers of dyestuffs, two chemicals much used as assistants were most mentioned. They were common salt and Glauber salt or sodium sulphate. The common salt contains no water of crystallization but sodium sulphate comes to us both ways; in these tests the sodium sulphate crystals was used.

On page 77; set # 8 shows the results of treating with a dilute solution, 1 to 1000, of common salt, NaCl. Set #9 gives results of treatment with a 1 to 1000 solution of sodium sulphate, Na<sub>2</sub>SO<sub>4</sub>.

Soda ash, Na<sub>2</sub>CO<sub>3</sub>, is used with some direct dyes and also used as a scouring agent. Because of its alkaline properties, its use is avoided on the acetate types to avoid "blinding". This chemical also occurs in several forms containing various amounts of water of crystallization. The calcined salt was used in set #10.

TEXTILE DEPARTMENT  
NORTH CAROLINA STATE COLLEGE

DYEING

Acetate  
DuPont

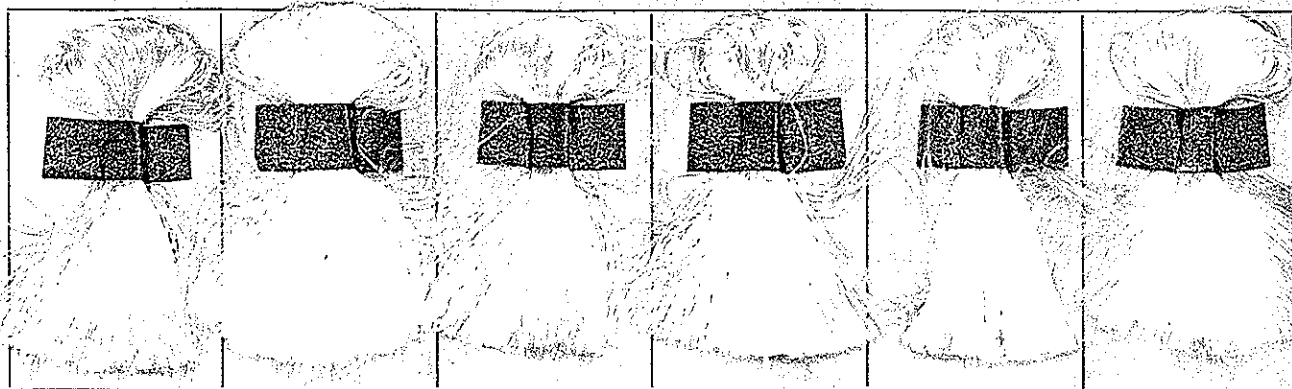
Bemberg

Celanese

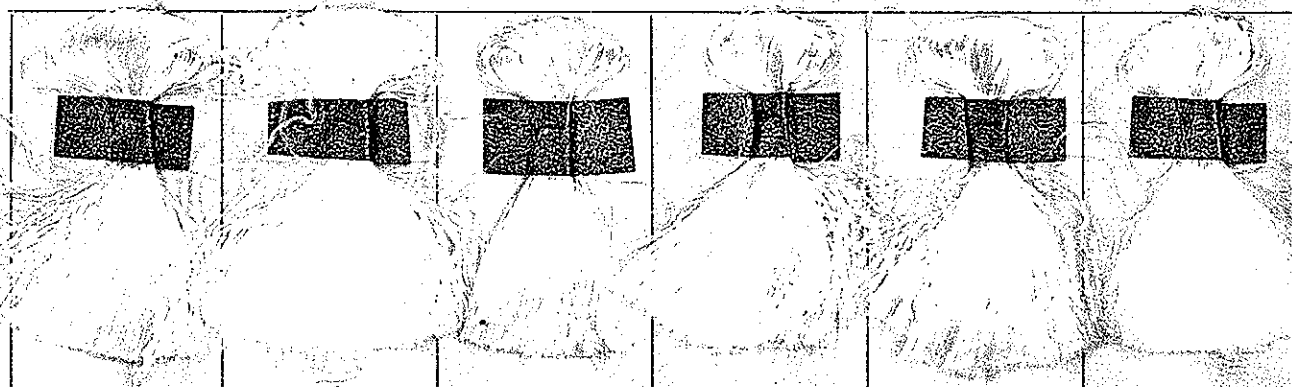
Tubize

Viscose

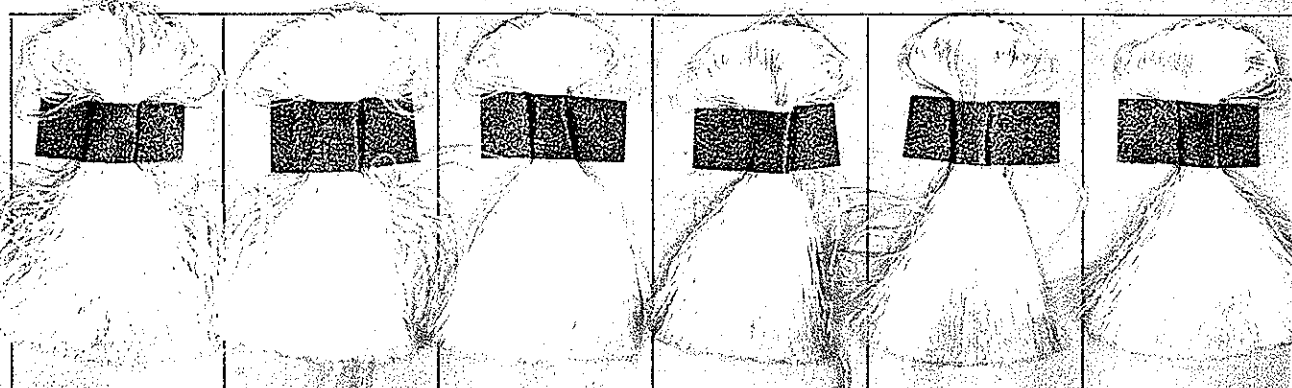
Xanthate  
DuPont



Set # 8. Sodium Chloride 1 to 1000 at 190 degrees F.



Set # 9. Sodium Sulphate 1 to 1000 at 190 degrees F.



Set # 10. Sodium Carbonate 1 to 1000 at 190 degrees F.

On page 79 are the samples obtained from the use of direct dyes. To show the affect of the dyes alone, no assistants were used.

Set # 1 was dyed with Niagara Blue made by the National Aniline Company. This dye has the Colour Index number, 406, and is thus described by Rowe. The sodium salt of diphenyl-disazo-bis-8-amino-1-naphthol-3:6-disulphonic acid. From this formula, it is quickly seen that it contains two each of the amino, naphthol, azo and sulphonic groups, thus being a good representative of the direct dyes as described in previous part of the thesis.

Set #2 was dyed with the same dye in the same manner, but on scoured material. The yarns had been scoured with 1 to 1000 soap at 150 F to avoid the possible "blindine" of the acetate silks which might have taken place at the higher temperatures.

The yarns were washed after dyeing, but were not subjected to as strenuous treatment as would have taken place in commercial work. It was done in this way to try to save effects which might be present from the dye-stuff if not washed off too soon.

Set # 11 was dyed with Solantine red which is listed as Colour Index # 353: sodium salt of 3:3-disulphodiphenyl-urea-4-4-disazo-bis-2-amino-8-naphthol-6-sulphonic acid. Quite similar to the previous dye.

DYEING

Acetate  
DuPont

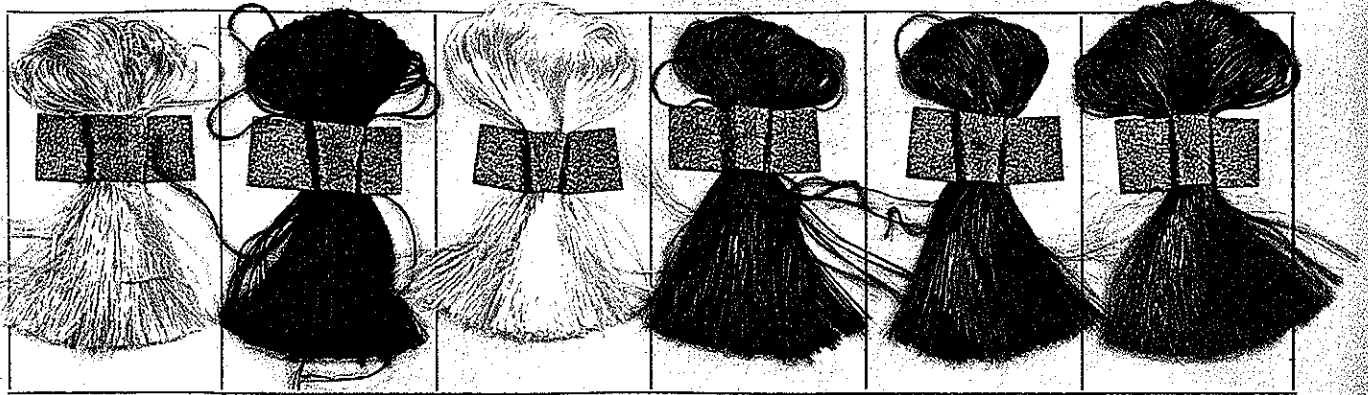
Bemberg

Belanese

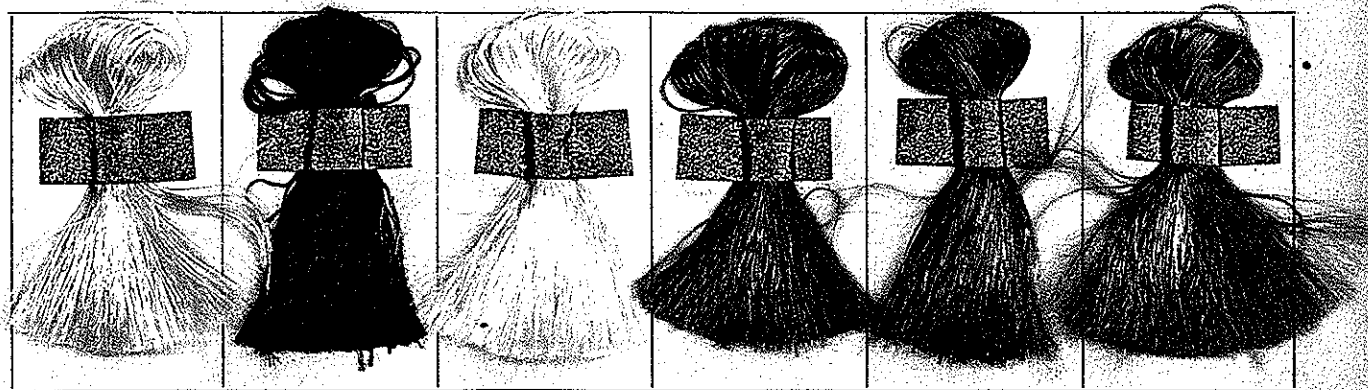
Tubize

Viscose

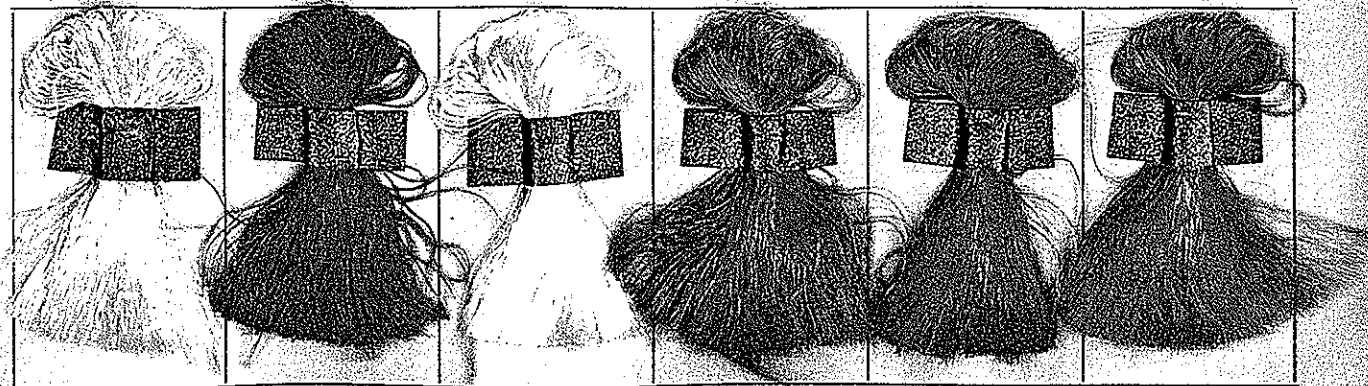
Xanthate  
DuPont



Set #1. Dyed with Niagara Blue Direct Dye on Unscoured material.



Set #2. Dyed with Niagara Blue Direct Dye on Scoured material.



Set # 11. Dyed with Direct Red

The basic dyes were among the earlier of the artificial dyes discovered and one of the older dyes of the group is the well known Methylene blue with a Colour Index number of 922. Sets #12 and 13 were dyed with this basic dye. On cotton, it is necessary to use a mordant such as tannic acid in order to get a dye and not a stain, but with these chemical fibres, the tannic acid is not needed as in most all cases dyeing takes place and not a staining. This may seem odd since both cotton and four of these rayons are plain cellulose, the acetates alone containing an additional radical.

The Colour Index says of Methylene blue: tetramethyldiamino-diphenazthionium chloride usually the corresponding zinc double chloride.

Although acetic acid is used in dyeing of basic colors, none was used with these dyeings even to dissolve the dyestuffs. Dyed at 175 F.

Set # 14 was dyed with Rhodamine B, Colour Index number 749, and described as hydrochloride of diethyl-m-amino-phenol-phthalein, or tetraethyldiamino-0-carboxy-phenyl-xanthenyl-chloride. No acetic acid was used in this case as an assistant.

Only a light washing was given to these basic dyes, consequently they will be more liable to crock than some of the other dyed samples.

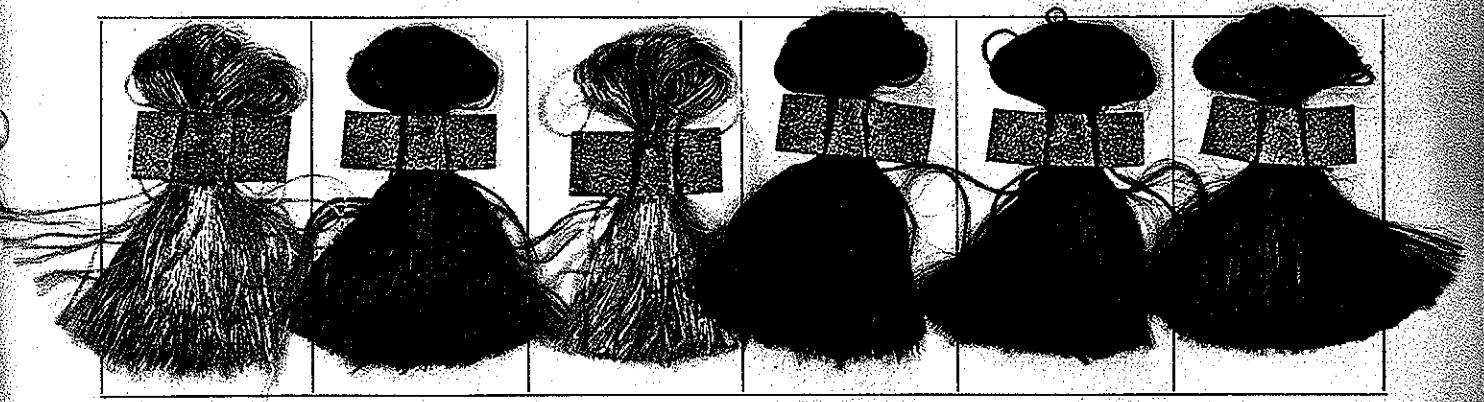
These dyed samples are shown on page 81.

DYEING

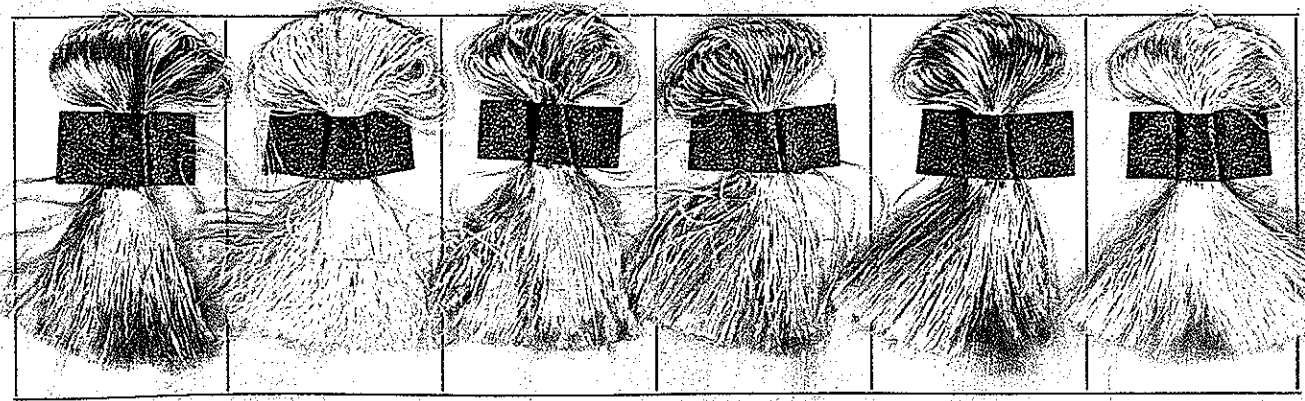
Acetate DuPont	Bemberg	Celanese	Tubize	Viscose	Xanthate DuPont
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Set #12. Dyed with Methylene Blue Basic Dye on Scoured material.



Set #13. Dyed with Methylene Blue Basic Dye on Unscoured material.



Set # 14. Dyed with Basic Red Dye on Unscoured material.

In section two , the vat dyes were discussed and it was stated that they are of comparatively recent origin, and their manufacture in the United States has come within twenty years.

These dyes are not soluble in water alone and also require a reducing agent such as hydrosulphite of soda. In these dyeings, Lykopen, a sodium hydrosulphite was used for reducing and sodium hydroxide to form the alkali solution needed to keep the dye in solution. The effect on the fibres is more likely to occur from these reagents than from the dyestuff but as they must be used, the results can be laid to the class of vat dyeing.

Sets # 15 and 16 were dyed with Ponsol Blue likely the Colour Index number 1109 and thus described: possibly a hydroxy-derivative of N-dihydro-1:2:1:2-anthraquinoneazine. This agrees with the remarks on vat dyes of the anthraquinone group.

These sets and set # 17 appear mounted on page 83.

Set # 17 was dyed with a popular dyestuff, Sulfanthrene Pink FF, but a search of Rowe's and also of Schulz fails to discover any number or any reading matter to show in which class of vat dyes this particular dye should be placed. It would be interesting to have its formula because of its dyeing, not staining, of the two acetate samples.



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DYEING

Acetate  
DuPont

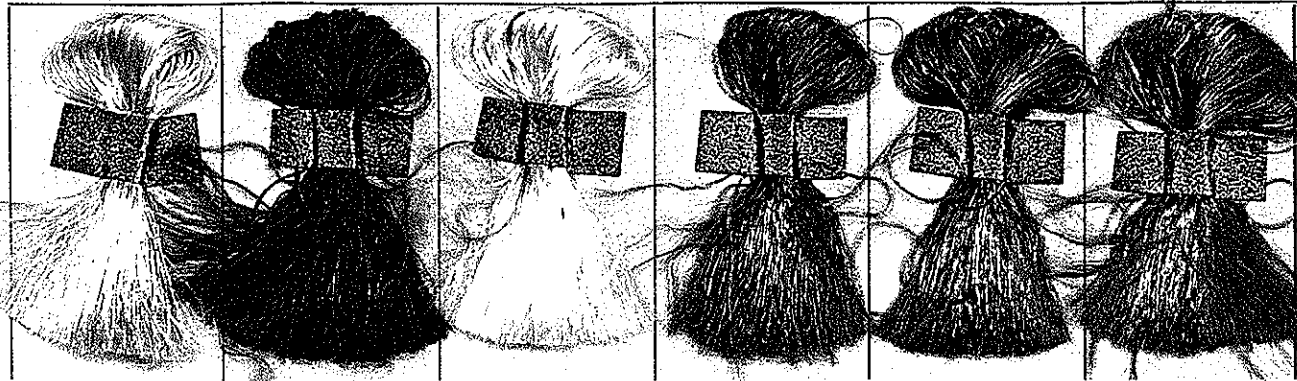
Bemberg

Celanese

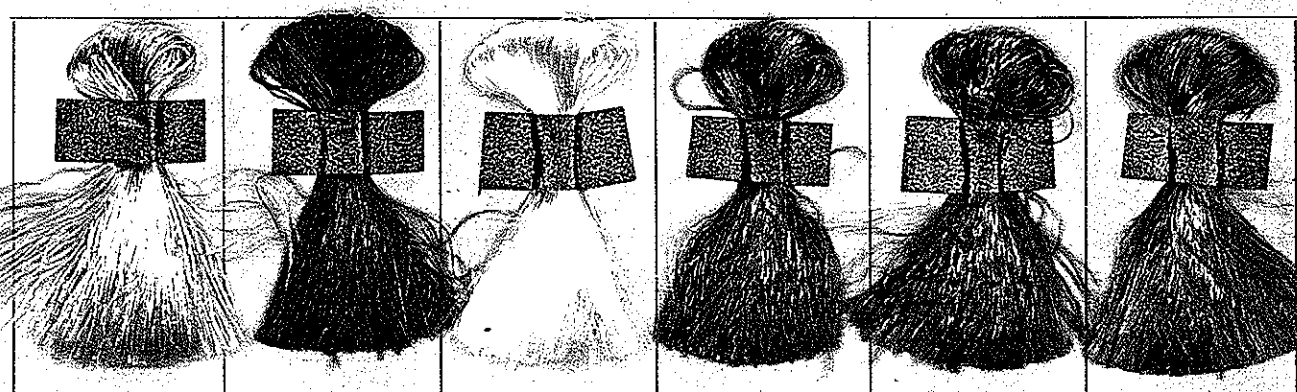
Tubize

Viscose

Xanthate  
DuPont



Set #15. Vat Blue on Scoured material.



Set # 16. Vat blue on Unscoured material.



Set # 17. Vat Red on Unscoured material.

Sets number 18, 19 and 20 were dyed with the SRA dyes as put out by the American Cellulose and Chemical Company. These samples appear on page 85.

The dyes were rubbed up with a very small amount of sulphonated castor oil and dyed at 160 F. After dyeing the skeins were washed in a dilute soap solution at 160 F. A more severe treatment at a higher temperature would remove much of the dye that has remained to stain the fibres that are not of acetate composition.

The acid dyes are not usually mentioned when dyeing the rayons or artificial silks by themselves, but as these dyes are used in dyeing of wool and silk which are also combined with rayon, it was decided to try out a couple of them. As the acid dyes vary greatly in composition, a much greater variety should be used before fixed opinions should be formed as to their effect or value.

On page 87 are sets# 21 and 22. Set 21 was dyed with Fast Acid blue appearing in Colour Index as # 208 and thus described. Sodium salt of 3:6-disulpho-8-hydroxy-gamma-naphthalene-azo-phenyl-gamma-naphthylamine sulphonic acid. Usually dyed with aid of Glauber salt and acetic acid, but in this case both of these assistants were omitted.

Set 22 was dyed with Fast Red likely of

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DYEING

Acetate  
DuPont

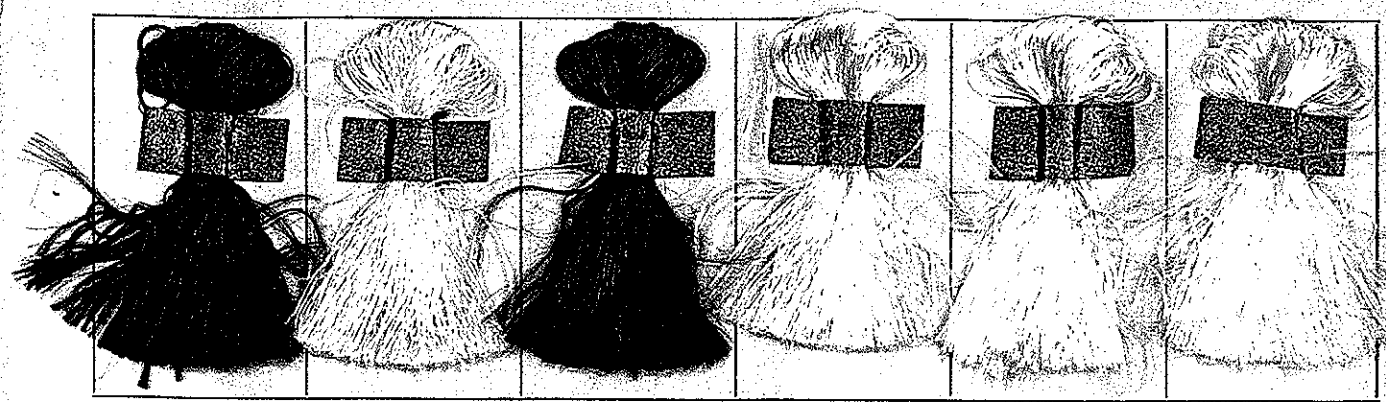
Bemberg

Celanese

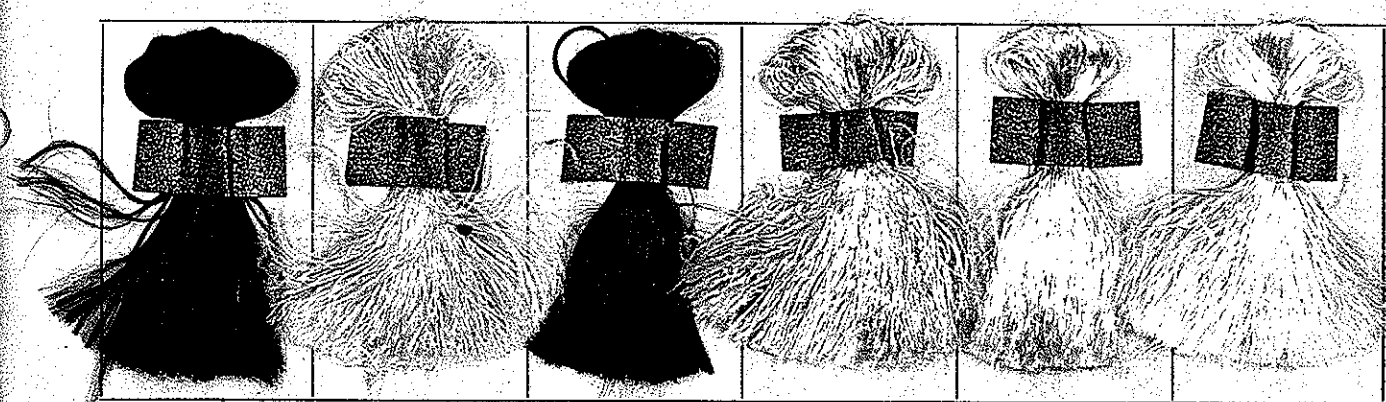
Tubize

Viscose

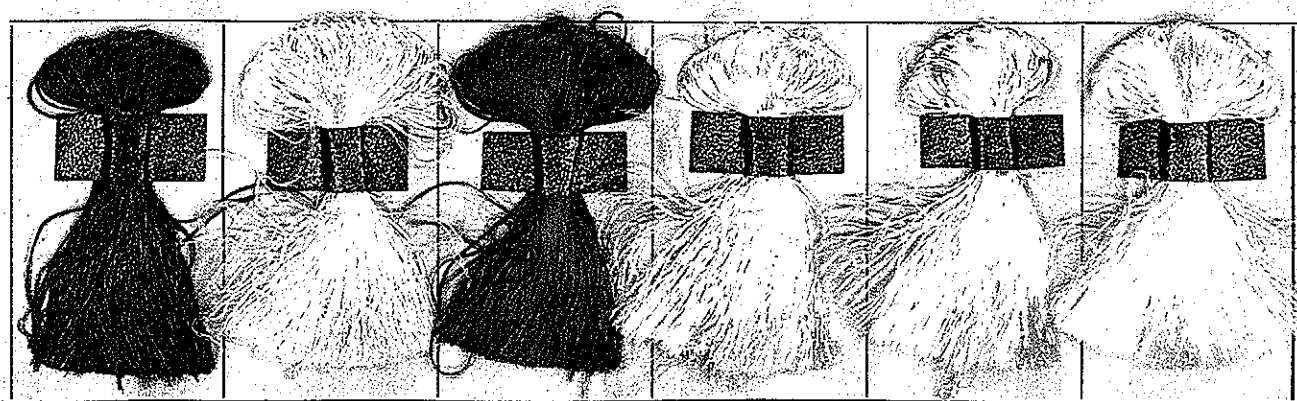
Xanthate  
DuPont



Set # 18. SRA Blue on Scoured material.



Set # 19. SRA Blue on Unscoured material.



Set # 20. SRA Red on Unscoured material.

Colour Index number 88 and thus described. Sodium salt of gamma-naphthalene-azo-beta-naphthol-3:6-disulphonic acid. Dyed from an acid bath, but acid omitted in this test.

When all samples had been dyed, they were mounted as shown on these pages. The reason for leaving the end cut was to make it easier to see the amount of penetration, also evenness.

DYEING

Acetate  
DuPont

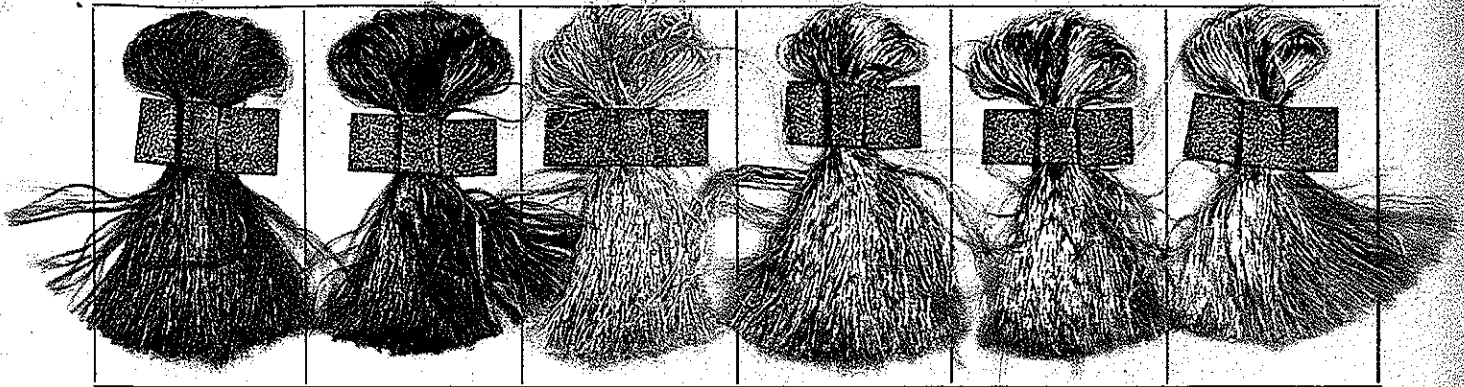
Bemberg

Celanese

Tubize

Viscose

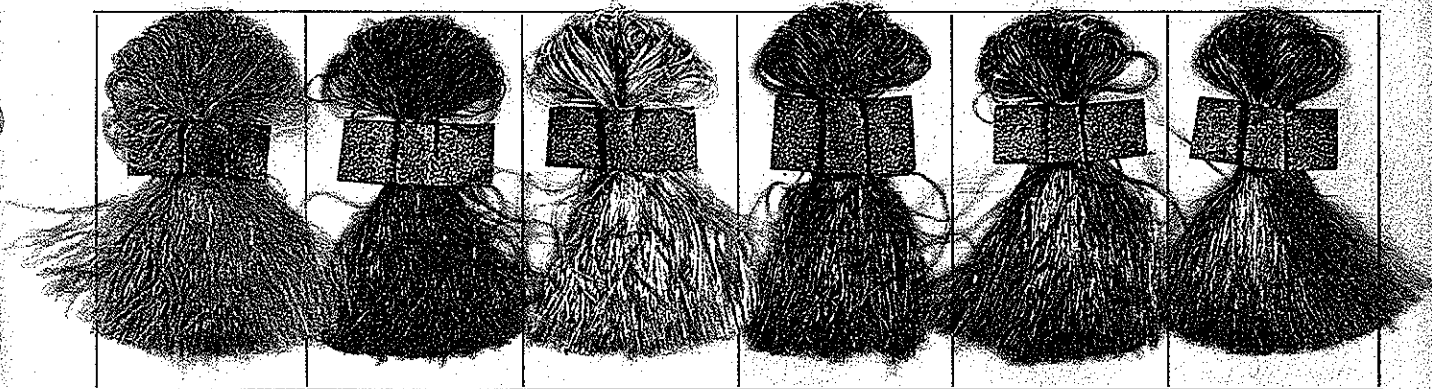
Xanthate  
DuPont



Set 21.

Acid Blue

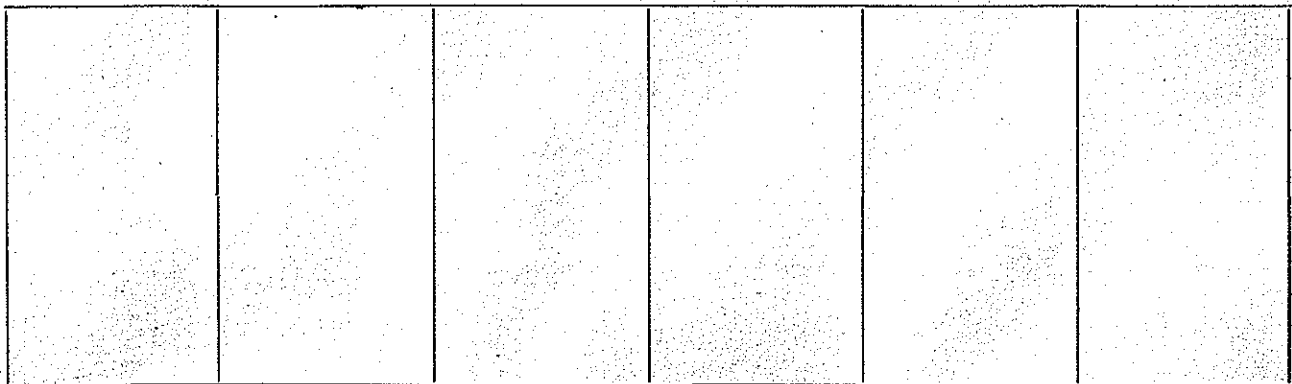
on Unscoured material.



Set 22.

Acid Red

on Unscoured material.



## VI

## PREPARATION AND EXAMINATION WITH THE MICROSCOPE.

A brief outline of methods of preparation and methods of examining samples of the treated yarns as well as description of apparatus will now be given.

G. Heink<sup>1</sup> states in his article: "The simplest microscopic investigation is the so-called longitudinal view, that is to say, the inspection of the individual filament in relation to its fibre breadth, structur, impurities, its flaws etc.

We examine the filament first in air, and indeed here again, the measurement of the filament width is of importance in respect to the thickness of the individual filament. This is different in the different kinds of artificial silk."

It was desired to examine the samples as they appeared after being treated and before they were subject to any change due to application of any agents used in mounting in the ordinary way. For the longitudinal views, four or five of the threads of the various yarns were mounted on the slides and held down by placing labels at either end. In this way, the samples were in air only, not even a cover glass intervening when being examined with the microscope.

One or two of the threads were teased open with a needle in order ~~to secure a~~ good view of the filaments. These also were examined as is in air.

1. Heink, G.--"Mikroskopie an Kuntseide"-- Melliland Textil Berichte-- January 1928. Translated into English by A.H.Grimshaw, Copy in NCSC Library.

Cross-sections were also prepared; two methods being used, the paraffin method and also the brass block method as originated by Professor E. R. Schwarz of M.I.T. This method is very well described in the Textile World of September 29, 1928 in an article written by Arthur K. Johnson.

At our school, we are equipped with a Spencer Rotary microtome and this as well as the safety razor method was used in slicing paraffin samples. A paraffin having a melting point of 56 was used, the paraffin being kept a couple of degrees higher than its melting point. Wire hair pins were used for mounting the samples. The hair pins were unbent to form a straight line and then each end was turned at right angles to leave two inches of the wire as its length. The yarn was wrapped around the bent ends about an inch from the bend. After the samples were wound on the wire, the ends of the wire were bent once more to form a loop. This left the yarn on the lower part of the wire which acted as a spring and kept it tight; also the fact that it was one inch down on the end allowed room for dipping the yarn into the warm paraffin solution. The yarn was dipped and then placed in cold water and then shaken and allowed to dry while other samples were being dipped, then dipped and cooled and the process repeated until a rodlike piece about  $\frac{1}{2}$  inch or more in diameter had been formed.

Care had been taken to place the yarn one inch down on the wire and it was an easy matter to cut off the sample in the form of a pencil.

This pencil was then placed in the holder of the microtome and slices cut of approximately 5 microns. The slices were mounted on slides using a little egg-fixative, and the paraffin dissolved off with xylene. This method gave the thinnest cross-sections, but a set of thicker ones were made also. To make these, the pencil were held in the hand and a Gillette razor blade held in a holder from the 5 and 10 cent store was used for the slicing. Although these slices were thicker, they were useful for quick examination.

However, these methods of course involved the use of paraffin and also xylene as well as heat. These might not affect the dyeing, but it was thought best to use the brass block method of Professor Schwarz in addition to these. This method is as follows: A brass block one inch thick and round has a hole bored through it from top to bottom. The hole is conical to about the middle of the block when it changes to parallel sides. The hole at the top is about one sixteenth to one eighth inch in diameter, at the bottom it is nearly three quarters of an inch. The yarn is threaded in the hole from the bottom and given a quick pull to fill up the small part of the hole. It is then tightened until the complete



space of the top hole is filled. A sharp razor blade is then drawn across the top of the brass block cutting the yarn at right angles. With a little practice this is done with one stroke. Of course, you cannot get every little filament into focus, but you can get many of them. This works well for light colored and bleached yarn, but not so well for the darker colored ones.

Needless to say it is almost compulsory to have an apochromatic objective when working with colored or dyed yarns. It was hoped to have one for this work, but circumstances prohibited it, therefore, the work was done as well as possible using the achromatic lenses in our possession.

The following equipment was used in our research: Leitz microscope and Bausch and Lomb microscope. Many combinations of set-ups including use of achromatic objectives, 4 mm, 8 mm., 16 mm, 32 mm, 48 mm.; 6 X, 10X and 12 X Oculars; Ocular Micrometer Disc; Wratten Filters; Bausch and Lomb Photmicrographic Apparatus; Silverman Illuminator. Many photos were taken and will be shown later; used commercial Ortho 5 by 7 films for this work and Azo paper.

The Ocular Micrometer disc fits into the ocular and was used to get comparative sizes of the samples. Direct measurements were not made.

Many tests were tried and discarded due to non-uniform results, too much reflection; too deep a color of the sample and wrong combinations of oculars and objectives. The main trouble was too much color which could not be cut out when using achromatic instead of apochromatic objectives.

## VII

## TABLES OF RESULTS AND ALSO PHOTOMICROGRAPHS.

This section will show results tabulated in separate charts for each type of yarn.

Charts I,II,III,IV, V and VI on pages 94 to 99 inclusive show the appearance of the yarns when using the brass block cross-sections with Bausch and Lomb microscope at 160 mm, equipped with 8 mm achromatic objective, 12 X eye-piece or ocular and the micrometer disc.

Chart VII on page 100 gives the appearance and comparative size of the six types of yarns with the filaments teased out. This chart concerns the filaments whereas Charts VIII, IX and X are based on the yarns themselves. These were longitudinally mounted in air. The set-up for the filaments was Bausch and Lomb microscope at 160 mm; 8 mm objective; 12 X ocular; and micrometer disc. Reflected light.

With Charts I to VI inclusive which could not use the reflected light, the Silverman Illuminator was used, but in some cases later on this could not be used as it formed too strong a light and too much reflection.

Charts XI to XVI inclusive give results after treatment of the individual types of filaments instead of yarns. Using reflected light.

## CHART I

DUPONT ACETATE: BRASS BLOCK: NO ILLUMINATOR: PENETRATION.

- Set 7; water at a boil. Slight loss of lustre.
- Set 6; soap, 1/1000, at 190 F. No change.
- Set 3; soap, 1/100, at 140F. No change.
- Set 4; soap, 1/100, at 180 F. Slight lustre loss.
- Set 5, soap, 1/100, at boil. Large loss of lustre.
- Set 8, NaCl, 1/1000, at 190 F. Slight lustre loss.
- Set 9, Na<sub>2</sub>SO<sub>4</sub>, 1/1000, at 190 F. Slight loss lustre.
- Set 10, Na<sub>2</sub>CO<sub>3</sub>, 1/1000, at 190 F. Lustre gone.
- Set 1, Direct blue, unscoured. Some staining, light.
- Set 2, Direct blue, scoured. Some staining, light.
- Set 11, Direct red. Very little staining.
- Set 12, Basic blue, scoured. Dyed but less than regenerat  
ed cellulose types.
- Set 13, Basic blue, unscoured. As set 12.
- Set 14, Basic red. Well dyed.
- Set 15, Vat blue, scoured. Light dyeing.
- Set 16, Vat blue, unscoured. Light dyeing.
- Set 17, Vat red. Well dyed.
- Set 18, SRA blue, scoured. Deeply dyed.
- Set 19, SRA blue, unscoured. Deeply dyed.
- Set 20, SRA red. Deeply dyed.
- Set 21, Acid blue. Dyed violet. Fibre affects dye.
- Set 22, acid red. Dyed brownish red. Fibre affects dye

BEMBERG: BRASS BLOCK: NO ILLUMINATOR: PENETRATION.  
ORIGINAL HAS VERY LITTLE LUSTRE.

Set 7; water at a boil.	No change.
Set 6; soap 1 to 1000 at 190 F.	No change.
Set 3; soap 1 to 100 at 140 F.	No change.
Set 4; soap 1 to 100 at 180 F.	No change.
Set 5; soap 1 to 100 at a boil.	No change.
Set 8; NaCl 1 to 1000 at 190 F.	No change.
Set 9; Na <sub>2</sub> SO <sub>4</sub> 1 to 1000 at 190 F.	No change.
Set 10; Na <sub>2</sub> CO <sub>3</sub> 1 to 1000 at 190 F.	No change.
Set 1; Direct blue, unscoured.	Well dyed.
Set 2; Direct blue, scoured.	Well dyed.
Set 11; Direct red.	Well dyed.
Set 12; Basic blue, scoured.	Well dyed.
Set 13; Basic blue, unscoured.	Well dyed.
Set 14; Basic red.	Well dyed.
Set 15; Vat blue, scoured.	Well dyed.
Set 16; Vat blue, unscoured.	Well dyed.
Set 17; Vat blue red.	Well dyed.
Set 18; SRA blue, scoured.	Slight stain.
Set 19; SRA blue, unscoured.	Slight stain.
Set 20; SRA red.	Very little stain.
Set 21; Acid blue.	Medium deep dyeing.
Set 22; Acid red.	Medium deep dyeing.

## CHART III

- CELANESE: BRASS BLOCK: NO ILLUMINATOR: PENETRATION.
- Set 7; water at a boil. Slight loss of lustre.
- Set 6; soap 1 to 1000 at 190 F. No change.
- Set 3; soap 1 to 100 at 140 F. No change.
- Set 4; soap 1 to 100 at 180 F. Slight loss of lustre.
- Set 5; soap 1 to 100 at boil. Large loss of lustre.
- Set 8; NaCl 1 to 1000 at 190 F. Slight loss of lustre.
- Set 9; Na<sub>2</sub>SO<sub>4</sub> 1 to 1000 at 190 F. Slight loss of lustre.
- Set 10; Na<sub>2</sub>CO<sub>3</sub> 1 to 1000 at 190 F. Lustre gone.
- Set 1; Direct blue, unscoured. Some light staining.
- Set 2; Direct blue, scoured. Some light staining.
- Set 11; Direct red. Very little staining.
- Set 12; Basic blue, scoured. Dyed, but less than the re-generated types of cellulose.
- Set 13; Basic blue, unscoured. As set 12.
- Set 14. Basic red. Well dyed.
- Set 15; Vat blue, scoured. Light dyeing.
- Set 16; Vat blue, unscoured. Light dyeing.
- Set 17; Vat red. Well dyed.
- Set 18; SRA blue, scoured. Deeply dyed.
- Set 19; SRA blue, unscoured. Deeply dyed.
- Set 20; SRA red. Deeply dyed.
- Set 21; Acid blue. Dyed violet. Fibre affects the dye.
- Set 22; Acid red. Dyed brownish red. Fibre affects dye.

## CHART IV

TUBIZE:	BRASS BLOCKS:	NO ILLUMINATOR:	PENETRATION.
Set 7;	water at a boil.		No Change.
Set 6;	soap 1 to 1000 at 190 F.		No change.
Set 3;	soap 1 to 100 at 140 F.		No change.
Set 4;	soap 1 to 100 at 180 F.		No change.
Set 5;	soap 1 to 100 at a boil.		No change.
Set 8;	NaCl 1 to 1000 at 190 F.		No change.
Set 9;	Na <sub>2</sub> SO <sub>4</sub> 1 to 1000 at 190 F.		No change.
Set 10;	Na <sub>2</sub> CO <sub>3</sub> 1 to 1000 at 190 F.		No change.
Set 1;	Direct blue, unscoured.		Good dyeing.
Set 2;	Direct blue, scoured.		Good dyeing.
Set 11;	Direct red.		Good dyeing.
Set 12;	Basic blue, scoured.		Deep penetration.
Set 13;	Basic blue, unscoured.		Deep penetration.
Set 14;	Basic red.		Deep penetration.
Set 15;	Vat blue, unscoured.		Good dyeing.
Set 16;	Vat blue, scoured.		Good dyeing.
Set 17;	Vat red.		Good dyeing.
Set 18;	SRA blue, scoured.		Deep stain.
Set 19;	SRA blue, unscoured.		Deep stain.
Set 20;	SRA red.		Deep stain.
Set 21;	Acid blue.		Dyed unevenly.
Set 22;	Acid red.		Dyed unevenly.

## CHART V

VISCOSE : BRASS BLOCKS : NO ILLUMINATOR: PENETRATION.

Set 7; water a boil.	Slightly whiter.
Set 6; soap 1 to 1000 at a boil.	Slightly whiter.
Set 3; soap 1 to 100 at 140 F.	Trifle whiter.
Set 4; soap 1 to 100 at 180 F.	Trifle whiter.
Set 5; soap 1 to 100 at a boil.	Whiter.
Set 8; NaCl 1 to 1000 at 190 F.	No change.
Set 9; Na <sub>2</sub> SO <sub>4</sub> 1 to 1000 at 190 F.	No change.
Set 10; Na <sub>2</sub> CO <sub>3</sub> 1 to 1000 at 190 F.	No change.
Set 1; Direct blue, unscoured.	Well dyed.
Set 2; Direct blue, scoured.	Well dyed.
Set 11; Direct red.	Well dyed.
Set 12; Basic blue, scoured.	Deeply dyed.
Set 13; Basic blue, unscoured.	Deeply dyed.
Set 14; Basic red.	Deeply dyed.
Set 15; Vat blue, unscoured.	Deeply dyed.
Set 16; Vat blue, scoured.	Deeply dyed.
Set 17; Vat red.	Deeply dyed.
Set 18; SRA blue, scoured.	Stained.
Set 19; SRA blue, unscoured.	Stained.
Set 20; SRA red.	Stained.
Set 21; Acid Blue	Deep stain.
Set 22; Acid red.	Deep stain.



## CHART VI

DUPONT XANTHATE: BRASS BLOCKS: NO ILLUMINATOR: PENETRATIO

Set 7; water at a boil.	No change.
Set 6; soap at 1 to 1000 at a boil.	Slightly whiter.
Set 3; soap 1 to 100 at 140 F.	Trifle whiter.
Set 4; soap 1 to 100 at 180 F.	Trifle whiter.
Set 5; soap 1 to 100 at a boil.	Whiter.
Set 8; NaCl 1 to 1000 at 190 F.	No change.
Set 9; Na <sub>2</sub> SO <sub>4</sub> 1 to 1000 at 190 F.	No change.
Set 10; Na <sub>2</sub> CO <sub>3</sub> 1 to 1000 at 190 F.	No change.
Set 1; Direct blue, unscoured.	Well dyed.
Set 2; Direct blue, scoured.	Well dyed.
Set 11; Direct red.	Well dyed.
Set 12; Basic blue, scoured.	Well dyed.
Set 13; Basic blue, unscoured.	Well dyed.
Set 14; Basic red.	Well dyed.
Set 15; Vat blue, scoured.	Well dyed.
Set 16; Vat blue, unscoured.	Well dyed.
Set 17; Vat red.	Well dyed.
Set 18; SRA blue, scoured.	Stained.
Set 19; SRA blue, unscoured.	Stained.
Set 20; SRA red.	Stained.
Set 21; Acid blue.	Deep stain.
Set 22; Acid red.	Deep stain.