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Cellulose and Its Derivatives.

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CELLULOSE AND ITS DERIVATIVES

by

Otis Willard Murray

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Otis Willard Murray

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS
OF
COLLEGE OF WILLIAM AND MARY

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MASTER OF SCIENCE

1937

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CHAPTER I
OCCURRENCE AND PROPERTIES OF CELLULOSE

CHAPTER I

OCCURRENCE AND PROPERTIES OF CELLULOSE

Cellulose, derived from the Latin cellula, meaning "little cell", is perhaps the most abundant organic substance on the earth today. It is supreme among all of our industrial raw materials. It is the basic constituent of all plant life. Cellulose never occurs in nature except with other substances, which require rather severe chemical treatment to remove. It is, however, produced in a relatively pure form, free from almost all of the incrusting impurities, other than the protein cubicle, in the cotton plant. Cotton linters represent the purest form of cellulose from natural sources, but the great tonnage comes from our extensive forests, the northern spruce and the southern pine. Annual crops such as cornstalks, sugar cane, bagasse, peanut shells, and linters from cottonseed may be looked forward to for future supplies should our other sources run low.

In order for us to obtain a fairly pure cellulose we must find methods for purification adequate for the removal of non-cellulosic impurities and which at the same time are sufficiently restrained and controlled to eliminate the possibility of the formation of degradation products. With excess heating or dehydration, cellulose begins to decompose, giving combustible gases, acetone, acetic acid, phenol, furfuraldehyde, and other products. The purity of

any particular sample of cellulose may be determined in six ways: its neutrality, indifference to basic dyestuffs, low ash content, resistance to solution, resistance to solution in caustic alkalis, minimum reducing power, and high viscosity in cuprammonium. Cellulose of high purity may be easily and readily obtained from cotton, the seed hair of gassypium by prolonged boiling of the raw material with a 1% solution of sodium hydroxide and then neutralizing with a slight excess of acetic acid, repeatedly washing with distilled water to remove the acid. On analysis this product on the average gives about 99.8 per cent pure cellulose and .05 per cent ash. This is regarded as standard cellulose. Ordinary chemical filter paper is practically pure cellulose, especially when it has stood exhaustive treatment with hydrochloric and hydrofluoric acids for the removal of ash. These forms of cellulose generally contain water to the extent of six to eight per cent, which may be driven off by drying carefully in an oven at 100°C. The giving off of H₂O appears to take place at a much slower rate than the absorption. A very good and dependable means of purifying cellulose is the preparation of cellulose from raw cotton, as recommended by the Division of Cellulose Chemistry of the American Chemical Society. The process as worked out by Corey and Gray¹ is based upon a prolonged boiling with an alkali with the complete exclusion of air. A sample of approximately 75

1. A. B. Corey and H. L. Gray, *Ind. & Eng. Chem.*, 1924, 16, 853, 1130

grams of raw cotton is extracted in a Soxhlet apparatus for six hours with 95 per cent alcohol and then for six hours with ether. The cotton is placed in a nickel basket and is immersed in 3 liters of 1 per cent NaOH solution which has been previously boiled to expel all the air. This is boiled for 10 hours, during which time 10 more liters of fresh NaOH is added to the original solution. The cotton is then washed with distilled H₂O (air removed) and is immersed for 2 hours in a 1 per cent solution of acetic acid. It is finally dried in air. This cellulose is also standard cellulose, and contains 99.8% cellulose and .05% ash.

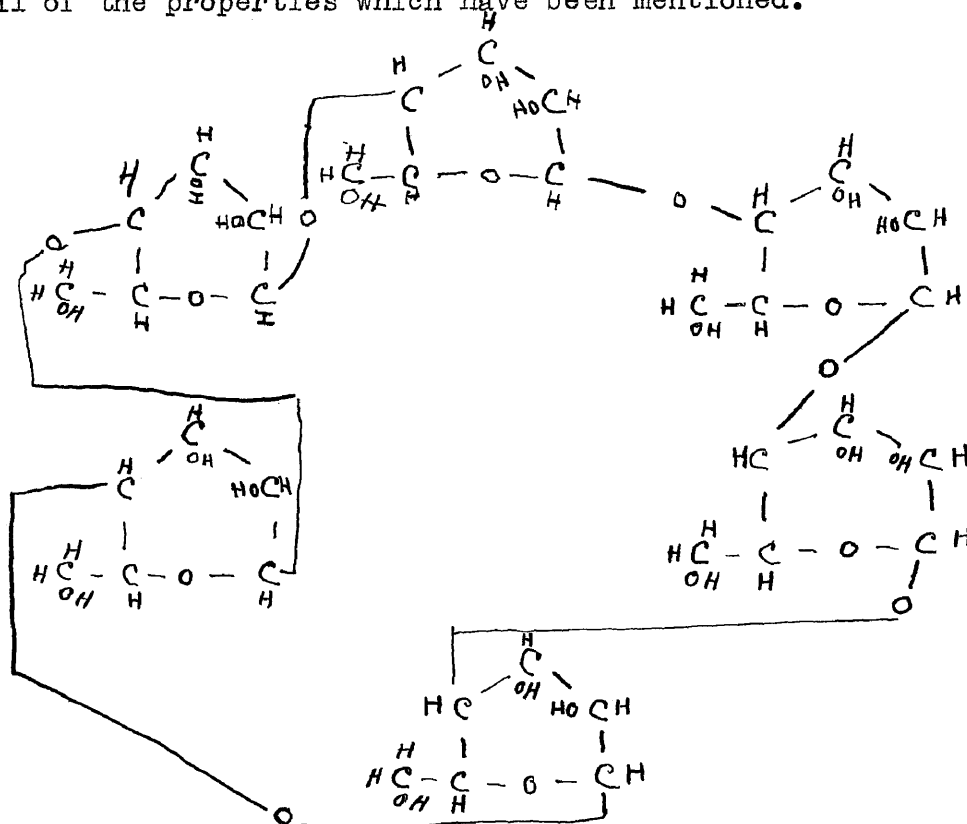
The occurrence of cellulose in the animal world is extremely rare. With a few exceptions in the insect world, true cellulose is not found in animal tissues. Much of it is digested and absorbed by herbivora, but the amount man assimilates is relatively small because as yet no digestive enzyme has been found in the animal body having specific action on cellulose. It is known, however, that the tunicin from *Phallusia mammillaris*¹ furnishes evidence for a structure similar to cellulose. On partial acid hydrolysis, dextrans, cellobiose, atriase, tetrase, and a hexose are all obtained which are identical with the products of partial acid hydrolysis of pure cellulose. Then, too, bacterial cellulose built up from fructose, glycerol and glucose have been examined, and by the comparison of their acetyl and methyl

1. Chemical Society Annual Reports, Vol. XXXI, 1934

derivatives, by x-ray examination, and by examination qualitatively of their degradation products, it was found they possessed a structure similar in nature to that of ordinary cotton cellulose. The membranous material built up by the action of the acetobacter xylinum on glucose behaves in all its observed chemical and physical properties as a true cellulose.

Cellulose, as we know, belongs to the carbohydrate family of organic compounds, and is fundamentally composed of carbon, oxygen and hydrogen, the oxygen and hydrogen being in a two to one ratio as in water. We assign the empirical formula, or what might be termed the unit formula, of $C_6H_{10}O_5$ to it. Its specific gravity is estimated to be 1.58, which, of course, is dependent upon the source or the state of condition of the cellulose. It can be hydrolyzed to the extent of 95 per cent to glucose, which leads us to a formula showing an anhydroglucose structure. Each of the units contains three free hydroxyl groups, the positions of which have been definitely established by the formation of 2, 3, 6 tri-methyl glucose. The hydroxyl groups on the second and third carbon atoms are secondary hydroxyls, while that on the sixth is primary. By the acetolysis of cellulose, thirty-five to sixty per cent cellobiose is obtained, which indicates that the glucose units are united for the most part by cellobiose linkages. The structural glucose units contain the amylose ring; the carbon atoms 1 and 5 are joined by an oxygen bridge. The linkages between the structural glucose

units are through the carbon atoms 1 and 4. There are no reducing groups present because of the failure of cellulose to reduce Fehling 's Solution. With this information we may set up a structural formula for cellulose, taking into account all of the properties which have been mentioned.



As to the actual physical structure of cellulose, we find a diversity of opinion. As far back as 1858, the botanist Nagali¹ fell upon the idea of a very fine organized structure for natural fibrous substances, such as cellulose, from his studies of double refraction, swelling, and mechanical properties. It was from this work that he gave us the micellar theory, that these fibrous materials were built up

1. A. J. Stamm, Colloid Chemistry of Cellulosic Materials, 1936, pp. 3-4

of submicroscopic, water insoluble, birefringent crystallites which he called micelles. The strength and other mechanical properties of the fibers, he considered were due to the orientation of the micelles. He believed that the micelles rather than the molecules were the ultimate dispersion units. His work on the submicroscopic building units of fibrous material received little notice at the time but is now credited with giving the fundamental groundwork upon which the present day colloid chemistry of cellulosic materials is built. Many of the modern investigators of the fine structure of fibrous materials agree in general that these materials are made up of long primary valence chains which exhibit the properties of Nageli's micelles, though they differ somewhat in their opinion as to the grouping of these chains. There is a present day tendency among the investigators of crystal structure to substitute the word "crystallite" for "micel" in order to point out the crystalline nature of this submicroscopic unit group. The dimensions of these crystallites have been the subject of much diversity of opinion. Outstanding work in this direction has been done by Marsh and Hengstenberg¹, who with the equation of Von Laue made measurements on the same fibers and obtained a value of 500A for the minimum length, and 50A for the cross section, all of which indicates that a micelle is made up of chains at least a

1. A. J. Stamm, ibid., p. 8

hundred glucose units long with approximately sixty chains in a bundle.

It is characteristic of all cellulosic materials to possess capillary structure, resulting either from the tubular structure of fibers themselves, as in wood and plants, or from the interstices between unoriented or partially oriented fibers making up the structure of cellulose products such as paper. In connection with this capillary structure, McBain and Kistler¹ have carried on considerable work on the permeability of cellophane membranes which possess an extremely fine capillary structure. They found that cellophane is permeable to water but is almost impermeable to other liquids. They replaced the water in the swollen cellophane by alcohol, and found that the cellophane became permeable to alcohol. This replaced by other organic solutions caused the cellophane to be permeable to each of these in turn.

The mechanical properties of cellulose are most important in the utilization of this raw material in industry. The cellulose fibers are unusually strong in the longitudinal direction. Flax, for example, has a tensile strength of over 100 kilograms per square millimeter. The viscose silk fibers have practically the same strength, particularly if they are well oriented. Cotton, depending upon the type and source, varies from 25 to 75 kilograms per square millimeter. It is interesting to note that the strength of the flax fiber

1. McBain and Kistler, 1930, "Membranes for High Pressure Ultrafiltration", Faraday Society Transactions, 26: 157-162

approaches that of the best steel, which has a tensile strength of approximately 170 kilograms per square millimeter.

The solubility of cellulose in dispersion media has furnished a subject for much controversy. Actually there are no purely physical solvents for cellulose. It is unique among colloidal substances in that it can be dispersed in very few aqueous media, practically all of which are necessarily concentrated solutions. It has long been an unsettled question as to whether cellulose dispersed in these media exists in a native form. Cellulose can be dissolved in an ammoniacal solution of cupric hydroxide (Schweitzer's Reagent), concentrated HCl, H₂SO₄, H₃PO₄ and CH₃COOH. It can be dispersed in hot concentrated zinc chloride solution, but it has been definitely established that degradation products were formed. A hot concentrated solution of calcium thiocyanate is capable of dissolving as much as 7 per cent of cellulose. Very dilute solutions of cellulose can be made by dissolving cellulose in a 4 to 10 per cent solution of sodium hydroxide. Sheppard¹ gives us a process for the mechanical dispersion of cellulose by grinding it in an organic liquid. Actually only a very slight portion of this becomes colloiddally dispersed.

The determination of the molecular weight of cellulose leads to one of the most interesting and most

1. Sheppard, 1930, "The Dispersion of Cellulose and Cellulose Derivatives", Jour. Phys. Chem. 34:1041-1052

evasive fields of cellulose chemistry. The classical methods for the determination of the molecular weights have been of little or no value to us in the determination of the molecular weight of cellulose. The micellar structural building units of cellulose are of large colloidal dimensions. Whether or not these units disintegrate upon being dispersed gives rise to controversy, although most of the physical evidence indicates that the cellulose retains its colloidal dimensions. Differences of opinion exist as to whether these dispersions can rightly be considered as molecules in the chemical sense, or whether they should be considered molecular simply in the physical sense. It is perhaps better to consider the molecular weights as particle weights, although evidence is being collected to prove that cellulosic materials exist as macromolecules in a chemical as well as a physical sense. We know that any attempt to measure the molecular weight by the elevation of the boiling point or the depression of the freezing point, would be uncertain and inconclusive. Whenever the molecular weight exceeds a few thousand, the change in the boiling point, freezing point, or vapor pressure, is too small to be measured with sufficient precision at the low concentrations necessary for a satisfactory molecular weight determination. Every method for the determination of the molecular weight of macromolecules has been applied on cellulose and its derivatives.

Osmotic pressure measurements have been applied in the last few years to the determination of the molecular

weight of cellulose derivatives in organic solvents, but we have yet to establish a classical method for this study. Buchner and Samwel¹ by this method found values for the molecular weight ranging from 18,000 to 60,000.

Herzog and Kruger², using a cuprammonium solution of cellulose, found values for a molecular weight as high as 500,000. They made use of Einstein's diffusion law, which deals with spherical particles in dilute solutions, a state in which the diffusion of the particle is unhindered by the presence of other particles. The cellulose molecule, on the other hand, according to x-ray evidence is shown as a highly elongated structure. Due to the limitations in this method, it is difficult to obtain even a rough estimate of the magnitude of the molecular weight.

Direct evidence of the high molecular weight of cellulose has been obtained by means of the ultracentrifuge. Here too, a solution of cellulose in cuprammonium is used. The measurements are based on the sedimentation velocity method in a high centrifugal field, in which the force of gravity is increased over one hundred thousandfold. By this method the molecular weight of cotton linters was found to be 40,000 \pm 5,000. These measurements furnish no evidence as to the shape of the dispersed cellulosic particles. It is suggested, though, that the particles must be quite

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1. Buchner and Wamwel, 1933, "Molecular Weight of Acetocellulose and Nitrocellulose", *Faraday Soc. Trans.*, pp. 29, 32-40
 2. Stamm, A. J., *ibid.*, p. 28

asymmetrical, due to the fact that such low concentrations are necessary to secure free diffusion. A modification of this method of determining molecular weight is the sedimentation-equilibrium method. Only a sufficient centrifugal force is required to give a measurable concentration change with height in the cell resulting from an equilibrium between the rate of settling of the dispersed particles and their diffusion in the opposite direction. The molecular weights of a number of wood celluloses have been determined by this method, and they were found to agree with the value obtained for cotton linters, that is $40,000 \pm 5,000$.

Mark¹ found a value for the molecular weight of cellulose of 1,000,000. He thought that the dispersion units of cellulose were of the same magnitude as the micellar units found in the solid crystal lattice - 500 A by 50 A. He definitely shows that the spreading of the x-ray diffraction rings of regenerated cellulose is not dependent upon the speed at which cellulose is regenerated from solution. He says that if then the solid crystal lattice micellar units were further disintegrated on solution, the rate of regeneration should affect the extent to which they can rearrange, and, therefore, their size.

Considerable work has been done in order to determine the molecular weight and character of cellulose by simple viscosity measurements. Immediately we run into a difficulty in this method in that the viscosity is dependent upon the state of aggregation of the dispersed

1. Mark, 1930, Über Der Verhalten Der Hochpolmeres in Lösung Kolloid ZTshr 53: 32-46

particles and their shape. Standiger¹ has shown that the empirical relationship $N_{sp} = K_m CM$, or $N_{sp} = K_1 CL$, where N_{sp} is the increase in relative viscosity caused by the addition of the solute, C represents the concentration, M the molecular weight, L the particle length, and K_m and K_1 are constants characteristic of the particular solvent, holds good for long chain polymers whose molecular weights go up as high as 10,000. He worked with this as a basis, and assuming that the amylose ring structure was present in the cellulose molecule, he gave us a molecular weight value of 120,000, and a chain length of 3,900 A., considering the chains as single molecules. Even though his work in this is rather speculative, he proves that there is an indication of a relationship between viscosity and the length of the molecular chains.

Before we pass from cellulose to cellulose products and derivatives, it might be well to give the one positive identification test for cellulose. Although we assign the formula $(C_6H_{10}O_5)_x$ to cellulose, we know little of its absolute structure. There are necessarily structural factors, such as long primary valence chains, micelles of certain size and form, etc. It is easy to see, therefore, that chemical methods for determining whether an unknown preparation was cellulose or not may fail. There is, however, one method of identification which may be relied on. It involves the following steps: Esterify (acetate or nitrate) the unknown and dissolve in acetone or an acetone-alcohol solution.

1. Stamm, A. J., ibid., 31-32

Spin the solution into a fiber under tension. Saponify or regenerate the cellulose, and test the product by an x-ray diffraction pattern. If the original material was cellulose, then the final fiber pattern obtained will be unmistakably characteristic of any native or mercerized cellulose.

CHAPTER II
THE DEGRADATION PRODUCTS OF CELLULOSE

CHAPTER II

THE DEGRADATION PRODUCTS OF CELLULOSE

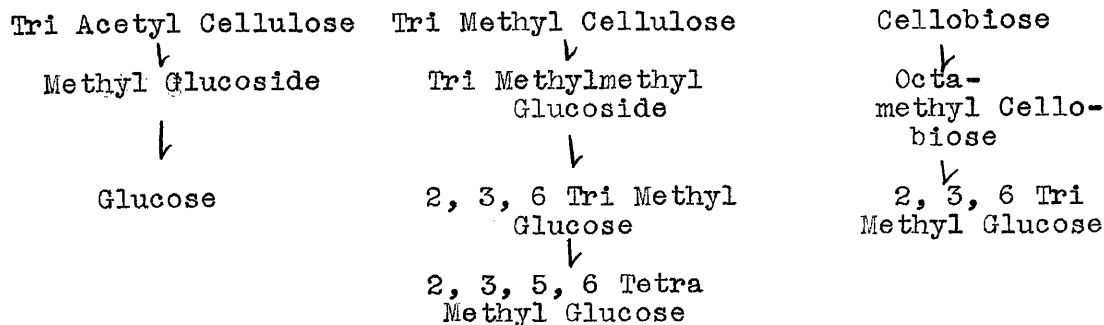
The degradation products of the acetolysis, hydrolysis, or heat decomposition of cellulose are for the most part derivatives of glucose or cellobiose. According to Dorée¹, the more important degradation products may be classified as those formed by:

- A. Action of aqueous acids (HCl, etc.) - glucose, hydroxymethyl-furfural
- B. Action of anhydrous halogen acids: chloro- and bromo-methylfurfural
- C. Action of phosphorus pentabromide (on acetylcellulose) 1-6 dibromo -2: 3: 5 tri acetyl glucose
- D. Action of the reagents that bring about acetolysis: celloglucosan, cellobiose octacetate, aceto-bromocellobiose, iso cellobiose acetate, hexa acetylbiase anhydride, hexa- and tetra- acetyl cellobioseanhydride, and nona-acetyltrihexosan
- E. Action of heat: Glucosan

There is a very marked and distinct relationship between cellulose and one of its most important degradation products, glucose. Should we heat cellulose in a vacuum, we should get a 50 per cent yield of glucosan. Cellulose with 72 per cent sulfuric acid will give a 95 per cent of the theoretical yield of glucose from a known weight of hydrolyzed cellulose. The acetolysis of cellulose forms cellobiose, which is closely related to glucose. Cellulose, methyl- and acetyl cellulose on hydrolysis or acetolysis

1. C. Dorée, "Methods of Cellulose Chemistry", 1933, p.

act thus:



The action of dilute, concentrated, and "super" concentrated acids on cellulose has been widely investigated. The action of dilute sulfuric acid has been thoroughly and successfully investigated by Monier-Williams¹. They were able to isolate glucose in a fine crystalline form and to obtain a yield which was about 95 per cent of the theoretical. Ten grams of cotton wool were dissolved in about 50 c.c. of 72 per cent sulfuric acid, and the dark colored viscous solution which resulted was allowed to stand for a week at about 20-25°C. The sulfuric acid solution was then diluted to 5 liters with distilled water, and boiled under reflux for fifteen hours. A little dark-colored flocculent precipitate is visible in the solution. The liquid, after it has been filtered, is practically colorless. With litmus as an indicator, neutralize it with barium carbonate, filter till clear, and evaporate under a reduced pressure of 40 mm. As alkalinity develops upon the concentration of the product it is well to add a few drops of methyl red to the distilling

1. Monier-Williams, Chem. Soc. Trans., 1921, 119, 803

flash in order to keep the solution neutral. The residue from the distillation is extracted under reflux with acetone free methyl alcohol. It is then filtered and decolorized by a small quantity of animal charcoal, and the solution evaporated in a current of dry air at a low temperature. The crystals form on the sides of the container and are completely crystalline and white. The yield obtained was 9.78 grams, or 97 per cent.

As early as 1819, the French chemist Braconnot dissolved old linen rags in concentrated sulfuric acid. He diluted the solution with water, and boiled it for a period of ten hours. He neutralized it with lime, filtered off the insoluble matter present, and concentrated the syrup by a process of evaporation. The glucose crystallized out from this. Later, sawdust was used to make alcohol by the use of hot dilute sulfuric, sulfurous, or hydrochloric acids, and as much as 16 gallons of 95 per cent alcohol was obtained from each ton of the sawdust. Some treated sawdust with super-concentrated hydrochloric acid, removed most of the acid in a vacuum and spray-dried the resulting syrup. It yielded on the average about 75 per cent of an impure glucose, which was particularly adaptable in its crude form as a nutritious cattle food.

Several laboratory preparations of glucose were made in the following manner from surgical cotton (93-95 per cent cellulose): A super concentrated solution of HCl was used. The surgical cotton, weighing 3.0000 grams, was placed

in a container of concentrated hydrochloric acid which was previously cooled to 0°. Hydrochloric acid gas was passed into it continuously for a period of two hours. The cotton turned first to a gummy, transparent substance, which broke up and finally dissolved, giving a rather viscous solution. The solution was allowed to stand for three hours, and then the acid was evaporated under reduced pressure so as not to char any sugar that might be present. All of the acid did not evaporate, so the sugar solution left had to be spray-dried in order to remove the acid. The final product was a light yellow syrup which refused to crystallize from alcohol and water, regardless of the proportions used. This is due to the contamination with dextrans, cellobiose, etc. Titrated with Benedicts solution, the sample was found to contain .3853 grams of sugar, which represents a 12.84 per cent yield. Larger yields undoubtedly could be obtained by allowing a longer time for hydrolysis to take place. When the solution is evaporated ten minutes after it is formed, a large per cent of sugar will be proved to be present by Fehlings solution; but most of the cotton or degradation products are precipitated on evaporation or addition of a large quantity of water.

After the discovery by Ost and his pupils that when cellulose is treated with a mixture of acetic anhydride, acetic acid, and sulfuric acid, an acetate of cellobiose could be obtained, many experimenters have worked on the numerous products of the acetolysis of cellulose. Hess and Friese¹ maintain

1. K. Hess and H. Friese, Annalen, 1926, 450, 40

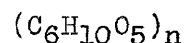
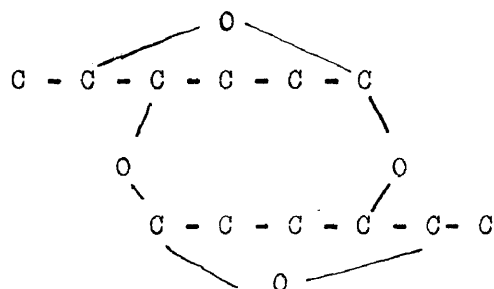
that acetolysis leads to the formation of the same chemical individuals; namely, acetyl cellulose, acetylbiosan, iso-cellobiose acetate, and cellobioseacetate. The proportion of any one of these depends upon the conditions of the reaction.

In the laboratory acetylbiosan was prepared after the following procedure: Prepare a mixture of 150 c.c. of acetic anhydride and 150 c.c. of glacial acetic acid. Cool this mixture to -18°C and gradually introduce 4 c.c. of concentrated sulfuric acid and 40 grams of cotton wool. The temperature should not rise about -5° . The mixture is kept at 30° for 60 hours, and the yellow solution is filtered to remove any insoluble matter. The solution is poured directly into cold water, and the precipitate separates out. This may be purified by boiling with methyl alcohol and allowing it to come out upon cooling. A snow-white powder is the product, which, if prepared correctly, possesses a melting point of 247.5°C . This biosan acetate is insoluble in ether, and is with difficulty soluble in hot absolute methyl alcohol and benzene. Its molecular weight is in the neighborhood of 568-700.

Pure biosan may be obtained by saponifying the acetate with a 10 per cent excess 2-N methyl alcoholic sodium hydroxide. After about 12 hours standing at room temperature, the biosan is isolated as a white powder. It is insoluble in all organic solvents as well as in water. It is fairly soluble in a 2-N sodium hydroxide solution. It can be precipitated from alkaline solutions by the addition of acids

or ammonia, and it slightly reduces Fehling's Solution.

The following constitution for biosan is believed possible:



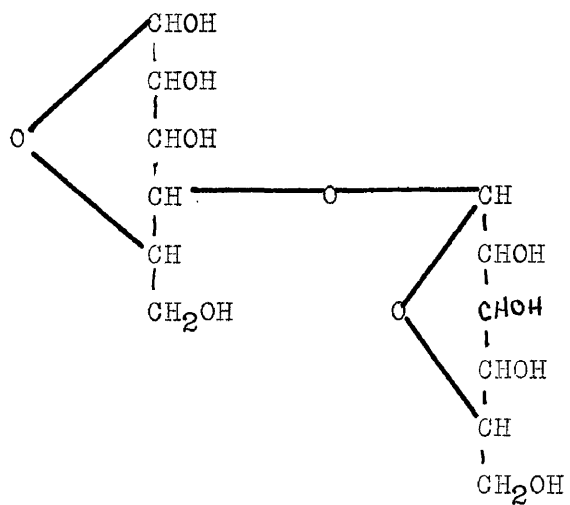
In 1879 Franchimont first isolated the sugar cellobiose which resulted from the acetolysis of cellulose. This sugar was studied closely by Skraup and Koenig¹ and other investigators. A series of experiments on the yield of cellobiose obtained from different types of cellulose The octa-acetate was prepared and 20 grams of the octa-acetate were prepared from 19 grams of standard cellulose.

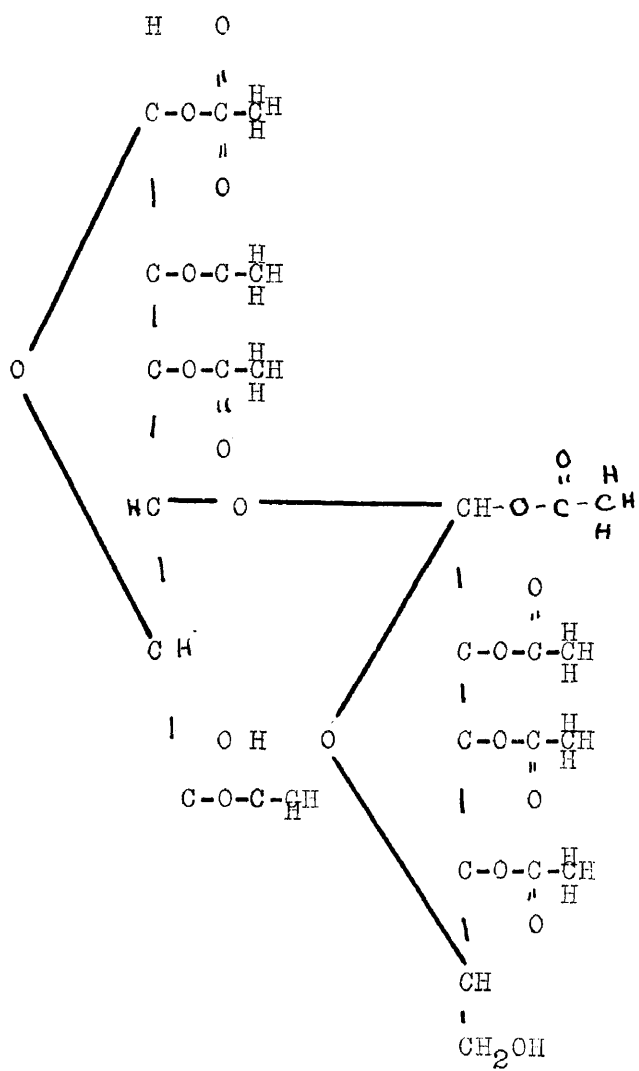
Dorée² gives an excellent method of preparing the octa-acetate, which was followed in my laboratory work. Add 20 grams of cotton wool in small portions to a previously cooled mixture of 75 c.c. of glacial acetic acid and 75 c.c. of acetic anhydride to which at $-15^{\circ} C$, 8 c.c. of concentrated H_2SO_4 has been added. The temperature at which this is done should be kept below 5° . Allow this to stand two hours at about $20^{\circ} C$, and then in a thermostat at 30° . It dissolves in eight hours, and the first crystals form in five or six

1. H. Skraup and J. Koenig, *Monatsh.*, 1901, 22, 1016
 2. C. Dorée, "Methods of Cellulose Chemistry", 1933, p. 201

days. The yield is about 10 grams. To change the cellobiose octa-acetate to pure cellobiose, the method of Peterson and Spencer¹ can be followed. A 10 per cent solution of sodium ethylate is prepared in 95 per cent alcohol. Finely pulverize 10 grams of cellobiose octa-acetate, and add it to 85 c.c. of this solution during an hour, keeping the mixture constantly stirred. The reaction is very rapid and is completed in less than an hour. The sodium salt formed is collected, washed with absolute alcohol, and dissolved in a minimum amount of ice water, and filtered. To this add glacial acetic acid very slowly until a precipitate begins to form. The cellobiose is completely crystallized at the end of fifteen or twenty minutes after sufficient glacial acetic acid has been added. The crude cellobiose is purified by dissolving in water, filtering, and adding acetone until reprecipitation begins. The formula for cellobiose octa-acetate and cellobiose may be written thus:

1. F. C. Peterson and C. C. Spencer, J. Amer. Chem. Soc., 1927, 49, 2822





CHAPTER III
CELLULOSE ACETATE

CHAPTER III
CELLULOSE ACETATE

The reaction between cellulose and acetic anhydride should theoretically produce a tri-acetate of the general formula $C_6H_7O_2(OCOCH_3)_3$. When the product is examined, however, part, at least, shows what we believe to be di- and mono-acetates. The tri-acetate is probably formed first, and this hydrolyzes to form the di- and mono-acetates. Recently it has been shown by x-ray analysis that only the tri-acetate is formed, but this has been disputed.

In the acetylation of cellulose the product first formed is an acetate which is soluble in chloroform and insoluble in acetone. This is known as a primary acetate. After a "ripening" period, the di- and tri-acetates which are soluble in acetone are obtained. These are known as the secondary acetates. Various catalysts are employed in this reaction, most of which are dehydrating agents. Sulfuric acid, phosphoric acid, the chlorides and oxychlorides of sulfur and phosphorus, zinc chloride, dimethyl sulfate, chloracetic acid are some of the catalysts used. Sulfuric acid is generally used in the laboratory, but actually it is a poor catalyst. Due to its degrading action upon cellulose and its formation of sulpho-acetates which cannot be separated from the product, dark solutions giving brittle films are obtained. Sulfuryl chloride is considered the best catalyst, even though it is seldom used.

Modern methods for the preparation of the acetate involve five steps:¹

1. Acetylation of air dry cellulose by acetic-anhydride and acetic acid in the presence of sulfuric acid or other catalysts
2. The addition of water and acetic acid to produce hydrolysis, precipitation of the acetate being avoided
3. A ripening period at a fixed temperature. This conditions the solubility and physical properties of the final product
4. The addition of a large excess of cold water, which precipitates the product in white flakes
5. Washing, centrifuging, and drying at 20 - 30° C.

Cellulose tri-acetate may be prepared on a small scale by carrying out the following procedure:² Cool a mixture of five parts of acetic acid to three parts of acetic anhydride to 5°C. Introduce one part of cotton to this, constantly shaking and stirring. After all the cotton has been added, you may increase the temperature to 20 - 25°C. Stir until the cotton has all dissolved, and allow the solution to stand. The acetate may be precipitated out of solution by adding the solution to a large quantity of water. Filter, wash, and dry in air (the drying must be complete or the product will be insoluble in acetone).

I prepared a sample of cellulose acetate in this manner: Ten grams of cotton were moistened with five grams of water. This was placed in a solution of 60 grams of acetic

1. Dorée, "Methods of Cellulose Chemistry", p. 260
2. Dorée, ibid., p. 268

anhydride in 180 grams of benzene to which $1\frac{1}{2}$ grams of H_2SO_4 has been added. This was heated to 60 - 70°C for five hours. An acetate was formed which was soluble in chloroform. The formula $C_6H_7O_2(OCOCH_3)_3$ has been assigned to this product.

In working with cellulose acetate, nitrate, or other esters, it is often found necessary in factory routine and research work to determine the best solvent. This solvent may be a single liquid or a mixture of liquids, depending upon its nature. An indirect way of accomplishing this is to find the solvent which will give solutions that will bear the greatest dilution with an indifferent miscible non-solvent; e.g., petroleum ether before the cellulose in the solution is precipitated out.¹ In order to find the best solvent for one of these cellulose esters, we make use of the solvent power number. The solvent power by definition is the "number of cubic centimeters of a miscible non-solvent required to start precipitation of a cellulose ester from 1 gram of a 5 per cent solution at 20°C".²

In addition to the cellulose ester of acetic acid, it might be well to mention cellulose esters of other organic acids. In the presence of proper catalysts, such as sulfuric acid, zinc, chloride, gaseous hydrochloric acid, or phosphorus pentoxide, formic acid is able to esterify cellulose to cellulose mono- and di-formates. If the cellulose was

1. J. Mardles, J. Soc. Chem. Ind., 1923, 52, 127
2. Doree, "Methods of Cellulose Chemistry", 1933, 278

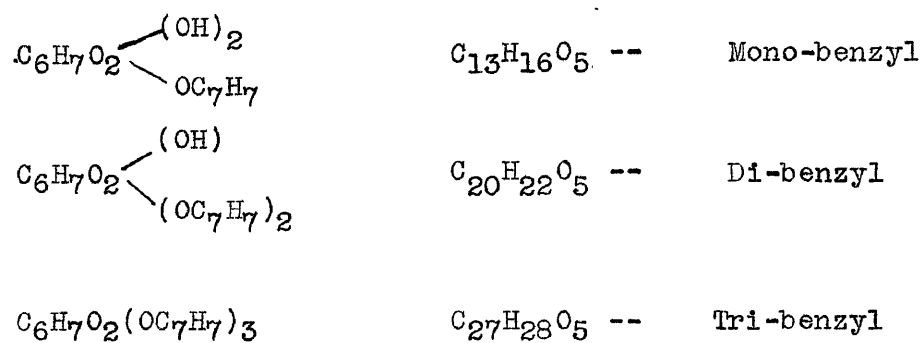
previously modified, that is, made reactive by regenerating either from a 70 per cent solution of sulfuric acid or from viscose, the esterification can proceed without the aid of a catalyst. The formyl esters are insoluble in most organic solvents with the possible exception of pyridene and formic acid. They are, however, soluble in aqueous solutions of acids, such as lactic, acetic, hydrochloric; and of zinc chloride and most thiocyanates. If the formic acid content of these esters amounts to as much as 50 per cent or more, they furnish a material which is particularly satisfactory for making a fine grade rayon with a high tensile strength.

In making rayon from cellulose formate, the formate is dissolved in formic acid and is then coagulated by means of water or sodium formate solution. Cellulose butyrate can be prepared in a manner very similar to that of the acetate. Many methods are employed - the use of catalysts, modified cellulose, and organic diluents to retard or modify the reaction. The cellulose butyrate has one decided advantage over the acetate in that it is soluble in inexpensive solvents such as mixtures of alcohol and benzene. The mono-, di-, and tri-cellulose esters of lauric, stearic, and palmitic acids are believed to have been prepared. These mono esters are grains composed of broken fibers, which are insoluble in ordinary solvents, in some of which they swell. The di esters exist both as grain or fibers which are soluble in many organic liquids, particularly benzene, chlorinated

hydrocarbons, fatty acids, and oils. The tri esters exist as masses or pellicules which are soluble in the same substances as the di esters. These esters of the higher fatty acids are of little practical importance and are of little importance except to the chemist.

Along with the cellulose esters we have a number of cellulose ethers that deserve to be mentioned. Cellulose ethers have been found to be of great importance in the last few years in making films and threads of artificial silk. The films or threads of cellulose ethers in organic liquids are of great tenacity and flexibility. Besides these two qualities, they are non-inflammable and are of low specific gravity. By the action of benzyl chloride on soda-cellulose or hydrocellulose in the presence of an alkali, a substance is produced which is insoluble in all the usual solvents and in Schweitzer's reagent. Its composition suggests the formula of a mono benzyl ether of cellulose ($C_{12}H_{19}O_{10}C_7H_7$). A repetition of the treatment leads to products which possess definite melting points and which dissolve in organic solvents. In the endeavor of C. Dorée¹ to obtain a fully benzylated product along the lines of Gomberg and Buckler², he found that nothing higher than the dibenzyl derivative was obtained. The following formulas show the theoretical composition of all the ethers possible:

-
1. C. Dorée, unpublished investigation
 2. J. Amer. Chem. Soc., 1921, 43, 1904



In addition to these products, nitro-benzyl cellulose, allylcelluloses, cellulose ethers of polyhydric alcohols, and cellulose ether-esters have been prepared.

CHAPTER IV
CELLULOSE NITRATE

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CELLULOSE NITRATE

The nitrate process of making artificial silk was discovered by Count Hilaire de Chardonnet while he was connected with the Polytechnic School of Paris. He devoted both his life and his fortune in the effort to perfect it. At the Paris exhibition in 1889 samples of artificial silk were exhibited, and two years later he started a factory at Besancon. Chardonnet tried spinning the filaments from collodion, which is a solution of the nitric acid esters of cellulose in alcohol and ether. He forced the collodion through very fine capillaries, and as the alcohol ether solvent evaporated, he obtained thin fibers of artificial silk, which he spun into thread. Even though this silk was not explosive, it was found to be very inflammable. In order to make this silk safe, means were found to denitrate it by means of FeCl_2 , HCHO or ammonium hydrogen sulfide. The denitrated product is believed to be a hydrocellulose very similar in nature to that obtained from mercerized cotton, and it possesses the same silk-like properties.

The actual nitration of cellulose can be brought about by treatment of the cellulose with concentrated nitric acid alone. Actually in practice, however, nitration is brought about by the use of a mixture of concentrated nitric and sulfuric acids. The amount of nitrogen present in the cellulose ester is dependent upon the amount of water present. The greatest nitrogen content is brought about when the

sulfuric acid acts as the hydrate; e.g., $\text{HNO}_3 + n(\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O})$ and the lowest nitrogen content is brought about when the nitric acid is present as the hydrate, as $\text{HNO}_3 \cdot \text{H}_2\text{O}$. It follows from this, therefore, that the sulfuric acid dehydrates the nitric acid.

According to Dorée¹, the following table should cover all the nitro celluloses that are theoretically possible, provided, of course, that we assume a C_{24} unit formula for cellulose instead of the customary ($\text{C}_6\text{H}_{10}\text{O}_5$):

CELLULOSE	FORMULA	NITROGEN PER CENT
Dodecanitrate	$\text{C}_{24}\text{H}_{28}\text{O}_{20}(\text{NO}_2)_{12}$	14.16
Endecanitrate	$\text{C}_{24}\text{H}_{29}\text{O}_{20}(\text{NO}_2)_{11}$	13.50
Decanitrate	$\text{C}_{24}\text{H}_{30}\text{O}_{20}(\text{NO}_2)_{10}$	12.78
Enneanitrate	$\text{C}_{24}\text{H}_{31}\text{O}_{20}(\text{NO}_2)_9$	11.98
Octanitrate	$\text{C}_{24}\text{H}_{32}\text{O}_{20}(\text{NO}_2)_8$	11.13
Heptanitrate	$\text{C}_{24}\text{H}_{33}\text{O}_{20}(\text{NO}_2)_7$	10.19
Hexanitrate	$\text{C}_{24}\text{H}_{34}\text{O}_{20}(\text{NO}_2)_6$	9.17
Pentanitrate	$\text{C}_{24}\text{H}_{35}\text{O}_{20}(\text{NO}_2)_5$	8.05
Tetranitrate	$\text{C}_{24}\text{H}_{36}\text{O}_{20}(\text{NO}_2)_4$	6.77

Because of the extremely high nitrogen content of the endecanitrate and the dodecanitrate, from a manufacturing point of view they have no commercial value because they are

1. C. Dorée, "Methods of Cellulose Chemistry", 1933, 221

too unstable. Nitrate esters with a nitrogen content of 10.7 - 11.2 per cent are soluble in alcohol. They are used in conjunction with tricresyl phosphate, camphor, and tri-phenyl phosphate in the celluloid plastics industries. The lower nitrates of cellulose are known as pyroxylin, and are less explosive than the higher nitrates. The nitrate esters containing 11.2 - 11.7 per cent nitrogen are soluble in both ethyl and methyl alcohols, ethyl acetate, acetone, and numerous other solvents. They are used for photographic films, but the cellulose acetate is replacing the nitrates because it is less brittle, cheaper, and less inflammable. It is also used in nitro-cotton lacquers and artificial silk. The esters containing 11.8 - 12.3 per cent nitrogen are soluble in ethyl, butyl, and amyl acetates, methyl alcohol, and acetone. They are soluble in ether-alcohol but are practically insoluble in ethyl alcohol. These are used in our gelatinous explosives, cellulose lacquers, and in the artificial leather industry. Finally, the esters containing 12.4 - 13.0 per cent nitrogen are for the most part insoluble in all usual solvents with the exception of acetone. Due to the high nitrogen content they are used for explosives.

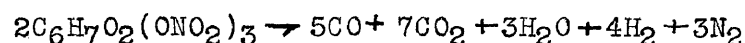
A good sample of cellulose nitrate was prepared in the laboratory from filter paper in the following manner:¹ It is essential that the water content of the paper should not exceed one per cent. A nitrating mixture is prepared containing 71.03 per cent sulfuric acid, 28.11 per cent nitric

1. K. Hess, "Chemie der Zellulose", Leipzig, 1928, p. 391

acid and .86 per cent water. One hundred grams of this acid solution should be used for each gram of filter paper. Immerse the paper in the acid, and allow it to stand for three-quarters of an hour at 25° C. At the end of this time, remove the paper and squeeze out the excess acid. Then with thorough cooling, bring the fibrous mass gradually into glacial acetic acid. After the removal of the acid, remove the product to a 1 : 1 solution of acetic acid, and stir rapidly. Boil with acetic acid of the same concentration for one hour, and wash with water until it is neutral. Dry the product in an oven at 60 - 70° C. in order not to char or decompose, and then in a vacuum over phosphorus pentoxide. This sample should have a nitrogen content of approximately 13.6 - 13.9 per cent.

A common procedure for the preparation of gun cotton from ordinary absorbent cotton is as follows: Place the cotton on a nitrating acid bath for about two hours. Cold water is allowed then to flow into the top of the bath while the acid is withdrawn at the same rate from the bottom. Finally, when all of the acid has been removed and replaced by water, remove the nitrated cotton, centrifuge, and boil. It is then drained of all but 25 per cent of the water. For use in mine cartridges and torpedoes, the moist gun cotton is compressed. This tends to make it safer yet more powerful in its actual explosive force. It is an exceptionally strong and shattering non-propelling explosive, and when moist or compressed, is easily set off by a detonator of dry gun cotton which in

turn is ignited by a fulminating cap. When gun cotton is burned unconfined, it does so rapidly without explosion, as follows:



One kilogram of gun cotton yields approximately 740 liters of gas when it is burned. This same gun cotton, even though it is insoluble in nitroglycerin, can be mixed with it, and treated with acetone and vaseline to form a gelatinous paste which is known as cordite. While this is a smokeless powder, most of the smokeless powders are made from the lower nitrates and not from gun cotton. Alfred Nobel, the Swedish chemist, dissolving some gun cotton in an alcohol-ether mixture to cover his cut finger, discovered that this sticky mass might be used for an absorbent and solidifier for nitroglycerin. He found that this superior and safe blasting gelatin, which is very similar to cordite, was insensitive to shock and could be safely transported or fired from a cannon. Nitrocellulose is used for explosives in the natural fibrous condition and in the gelatinized form produced by the plasticisers. The value of the gelatinization lies in the fact that it slows down the explosive action of the compound, and allows the gelatinized product to burn progressively. The fibrous raw gun cotton, on the other hand, detonates with enormous velocity, and possesses great shattering and destructive power. It has been found that the progressive burning gelatinous gun cotton is much

superior to the fibrous variety as a propellant in gunnery for driving a projectile from the gun.

It is interesting to note the influence of the water content of the nitrating mixture upon the degree of esterification of cellulose nitrates, and the solubility of each of the products in an ether-alcohol mixture.¹ From this table, if we use a set procedure in each case, we can always prepare with ease an ester with the desired nitrogen content.

NITRATION MIXTURE IN PER CENT			PER CENT NITROGEN	SOLUBILITY IN ALC-ETHER PER CENT
H ₂ SO ₄	HNO ₃	H ₂ O		
45.31	49.07	5.62	13.65	1.5
42.61	46.01	11.38	13.21	5.4
41.03	44.45	14.52	12.76	22.
40.66	43.85	15.49	12.58	60.
40.14	43.25	16.61	12.31	99.14
39.45	42.73	17.82	12.05	99.84
38.95	42.15	18.90	11.59	100.
38.43	41.31	20.26	10.93	99.82
37.20	40.30	22.50	9.76	74.22
36.72	39.73	23.50	9.31	1.15
35.87	38.83	25.30	8.40	.61
34.41	37.17	28.42	6.50	1.73

The solubility of cellulose nitrates varies considerably. They are practically all soluble in cuprammonium solution. Acetone ethyl acetate and amylacetate are the best general solvents. Only esters with extremely low nitrogen content (3 - 7 per cent) are insoluble in acetone. It has been found that if the acetone is moistened just a little with water, it increases its solvent power.

1. G. Lunge and J. Bebie, Z. angew. Chem., 1901, 14, 486

The solubility of cellulose nitrates would run as follows:¹

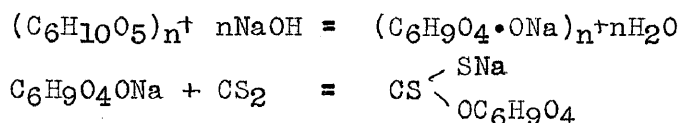
NITROGEN PER CENT	SOLUBILITY IN		
	ACETONE, ETHYL ACETATE AMYL ACETATE PER CENT	ETHER-ALCOHOL 2:1 PER CENT	ABSOLUTE ALCOHOL PER CENT
13.1 -			
13.4	95 - 100	Insoluble	Insoluble
12.75 -			
13.1	95 - 100	30	Insoluble
12.5 -			
12.75	95 - 100	50 - 100	10
12.0 -			
12.5	95 - 100	95 - 100	50
11 - 12	95 - 100	90 - 100	50 - 100
10 - 11	95 - 100	80 - 100	50
9 - 10	30 - 90	3 - 90	Insoluble
7 - 9	30	30	Insoluble
3 - 7	Insoluble	Insoluble	Insoluble

1. Ullmann, "Enzyk", 1917, 5, 96

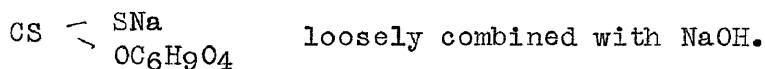
CHAPTER V
CELLULOSE XANTHATE

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CELLULOSE XANTHATE

It is to Cross and Bevan¹ that we owe the discovery of cellulose xanthate, in 1891. They found that if they impregnated cellulose with sodium hydroxide of mercerising strength, and allowed it to react with carbon disulfide, they obtained a sodium cellulose xanthate which, according to the discoverers, was formed in the following manner:



A very dilute alkaline solution of this product is known as viscose, and it contains units of the type



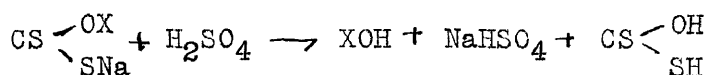
Today it is believed that alkali cellulose has the formula $(C_6H_{10}O_5)_2 \cdot NaOH$. T. Liesner² in his work on the viscose reaction prepared a pure sodium cellulose di-theo-carbonate with the formula

$$CS \begin{cases} OC_6H_9O_4 \cdot C_6H_{10}O_5 \\ SNa \end{cases}$$

which would seem to suggest even more complicated structures in viscose. Liesner also found evidence that it is the hydroxyl group in the unit cellulose formula $(C_6H_{10}O_5)$ in the number two position that is important in the formation of the xanthate.

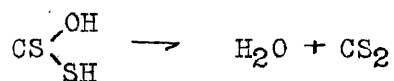
1. C. F. Cross, E. J. Bevan & C. Beadle, Eng. Pub., 8700 (1892)
2. T. Liesner, "Cellulosechem", 1929, 10, 156

Sodium cellulose xanthate is decomposed by the mineral acids in general to give cellulose and carbon disulfide, as follows:

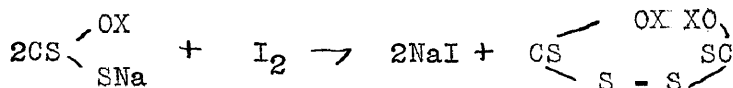


X represents the cellulose residue.

The di-thiocarbonic acid breaks down further

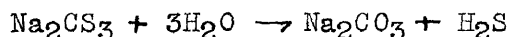


Sodium cellulose xanthate reacts with iodine to bring about a condensation as follows:

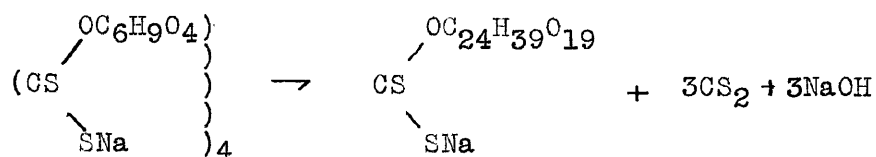


This reaction is important in the determination of cellulose xanthate present in viscose.

Probably the most important by-product formed during the viscose reaction is sodium thiocarbonate, which gives the solution its characteristic yellow color. In an alkaline solution the thiocarbonate is attacked by the water, thus:



The hydrogen sulfide formed by this reaction accounts for the odor of a viscose solution which has stood for some time. In the ripening process of the viscose, sodium hydroxide and carbon disulfide are also formed, according to the equation:



After having established the formula $\begin{array}{l} \text{OX} \\ \text{SC} \\ \text{SNa} \end{array}$

for the viscose in which the X lies between C_6 and C_{12} , we can look at the changes taking place in a viscose solution. When the solution has stood less than a day, the X is nearer C_6 as a unit formula, and the compound cannot be precipitated by dehydrating agents. After having stood a day, however, the viscose approaches a unit C_{12} formula. At this point the substance may be precipitated by such reagents as alcohol and brine. After standing a period of six days in an alkaline solution, the viscose reaches C_{24} dimensions and the compound can be completely precipitated by acetic acid into a water insoluble substance. Eventually, on standing, X approximates to cellulose itself, and coagulation takes place spontaneously. A possible explanation is that the unripe viscose contains xanthate compounds which are gradually decomposed into cellulose. As ripening proceeds, the amount of cellulose increases in proportion to the suspending medium which brings about spontaneous coagulation. The cellulose formed comes out as a stiff coagulum which shrinks and takes the shape of the containing vessel. The author found that by preparing a viscose solution and allowing it to stand in the

presence of air for a period of several weeks, a plastic was formed which had undoubtedly a large percentage of cellulose. As the substance shrank and the surrounding liquid was removed, the product began to harden slightly and become thoroughly elastic. It was extremely soluble in water and had a characteristic yellow-green color, which was due to the sulfur present.

Besides the spontaneous coagulation just described, there are three methods of bringing about coagulation¹

(1) The addition of certain salt solutions; (2) by the changing of the sodium cellulose xanthate into a much less soluble compound by the zinc or ammonium salt; (3) by the direct decomposition of the xanthate into cellulose by the action of a mineral acid, generally sulfuric. The last method is the one employed generally today for the spinning of the viscose in our large industrial plants.

After working on the preparation of a viscose solution and its subsequent coagulation to form cellophane, the author found the following method suitable for the laboratory: Shred four grams of surgical cotton (95 per cent cellulose) into fine bits, and warm carefully in 62 c.c. of 17.5% sodium hydroxide solution for approximately 15 minutes. Remove the cotton from the alkali and press between two glass plates to remove excess liquid, until it weighs 17 grams. Place the cotton in a test tube and add 10 c.c. of carbon disulfide, and allow to stand several days. The carbon di-

1. Dorée, "Methods of Cellulose Chemistry", 1933, 242

sulfide must be in contact with all of the cotton, and this can be brought about by shaking the shredded cotton in the carbon disulfide for an hour and one-half. Stopper the container so as to keep out as much air as possible. Bring the substance formed into solution by adding 14 c.c. of 5 per cent sodium hydroxide and 4 c.c. of 10 per cent sodium sulfite solution. Add more sodium hydroxide, if necessary, until a clear solution is obtained. The product is known as viscose solution. Stopper the viscose solution and allow it to ripen for 48 hours. In ripening, the solution tends to become more homogeneous in nature. If the solution appears to be lumpy or if it contains any air bubbles, filter it through a spun glass filter. Take a little of the ripened viscose, and pour a small portion of it on a smooth glass plate. Spread it by means of a spatula into a thin even layer. Now immerse this glass plate in a solution of 40 per cent ammonium sulfate for ten minutes. Remove the thin yellow-white transparent film from the plate and immerse it in a sodium chloride solution for ten minutes. Next place it in a 10 per cent sulfuric acid solution until all the white spots disappear. Dry over a beaker, and a thin transparent film without white spots or holes should be the product.

The commercial preparation of viscose is somewhat different from the above process in the laboratory. A sulfite pulp is used as the starting substance. One hundred kilograms of this pulp are steeped in 1600 liters of 17 - 18

per cent sodium hydroxide at ordinary temperature for two to four hours. Next, the soda cellulose is pressed by means of hydraulic pressure to 3 to 3.5 times its original weight, e. g., 300 - 350 kilograms; and then it is kneaded in a water and cork jacketed machine which converts the soda pulp into a crumb-like mass. This takes about two to three hours at 18° C. The crumbs contain about 15 per cent sodium hydroxide and 26 per cent alpha cellulose. They are placed in covered bins for a period of two or three days at 20-25° C, until they have "matured". Three hundred and twenty-five kilograms of this alkali cellulose are placed in a sulfide drum which has temperature regulation. Thirty kilograms of carbon disulfide are allowed to run into the drum slowly. The drum is rotated for a period of two to four hours at a temperature below 30° C. The churning must be stopped before the xanthate commences to cake together in large masses. The xanthate is mixed with sufficient alkali and water to produce a viscose containing from 7 to 8 per cent cellulose and 6 to 7 per cent sodium hydroxide. From three to six hours are required for the reaction to be completed. The viscose is kept in a room at 15 - 20° C. until it is ready for use. In making cellophane, the viscose is forced from a narrow slitted opening into an acid bath, where it immediately coagulates. It is run through a number of these baths, and then through a water bath. Next, it passes through a sul-

fite bath to remove the sulfur, and then through glycerin to soften it. It is finally dried and waterproofed by a lacquer.

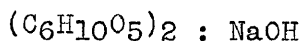
CHAPTER VI
DISPERSED CELLULOSE

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DISPERSED CELLULOSE

It has long been known that the treatment of cellulose fibers with water and aqueous solutions of certain acids, bases and salts causes swelling. In 1844 John Mercer, a Lancastershire calico printer, discovered that by passing cotton cloth or yarn through a 30 per cent solution of sodium hydroxide at about 25° C., the fiber was shortened and strengthened. For over forty years very little attention was paid to this discovery, until it was found that if the material was stretched so that it could not shrink on drying, the twisted cotton fibers were changed into smooth walled cylinders very much like silk. Today the process is used to make one well known "mercerised" cotton. This "mercerising" action of solutions of caustic alkalis on cotton has been the subject of considerable investigation. The effect of solutions of sodium hydroxide of 27 to 32 per cent concentration is to bring about the untwisting of the fiber. The cold alkali converts the cellulose into a sodium cellulose compound, and this on washing with water is converted into a hydrocellulose. The general fibrous form remains unchanged, but the fibers which were originally flat become cylindrical, thicken, and at the same time show an eight to ten per cent increase in weight. On drying, the fiber shrinks to approximately 75 to 80 per cent of its original length, and it increases as much as 68 per cent in strength.

The extent to which the mercerising has proceeded is measurable in three different ways: by the contraction produced; by the amount of sodium hydroxide taken up by the cotton; and by the increased affinity of the cotton for alkaline hydroxides and for dyestuffs. The degree of mercerisation varies with the temperature and concentration of the alkaline solution and the time of immersion.

The absorption of alkali hydroxides and water during mercerisation has led to numerous researches. Gladstone¹ in 1853 treated cotton with sodium hydroxide solution, washed out the excess solution with absolute alcohol, and then estimated the amount of sodium hydroxide remaining in the cotton after drying. The chief trouble with his method, however, is that he assumes that the alcohol acts as an indifferent solvent, removing only the uncombined alkali, and this is not true. Vieweg² avoided this difficulty simply by estimating the amount of caustic alkali in the solution before and after the mercerising treatment. He assumed in this method that no water was removed from the solution by the cotton. He found that the absorption of sodium hydroxide was fairly constant and that the amount absorbed indicated the formation of a compound with the formula



More recent work by Vieweg confirms the formation of this compound which exists in solutions containing 16 - 24 per cent

1. J. Gladstone, Chem. Soc. Trans., 1853, 5, 17
2. W. Vieweg, Z. angew. Chem., 1924, 37, 1008

of the hydroxide. The other alkali hydroxides also react with cellulose in a similar manner to give $(C_6H_{10}O_5)_2 : MOH$

Neale¹ has explained the mercerisation effects upon cotton in the following manner. In the cotton hair the micelles are arranged roughly parallel to the axis. When water is taken up by the cotton, the hydroxyl groups of the long carbon chains attract water molecules, breaking up some of the secondary valence forces, and at the same time being replaced by water hydroxyl linkages, causing the structure to expand transversely. With alkali the sodium ions tend to replace some of the hydroxyl hydrogen atoms, and a system of high ionic concentration is set up. Water enters the system by the process of osmosis, and more of the secondary linkages are broken and replaced by linkages with alkali or water. When water is used to wash the alkali cellulose, the sodium and hydroxyl ions diffuse away, and the osmotic pressure decreases, causing the substance to contract.

In carrying out an experiment on the mercerisation of cotton, the author found the following method very satisfactory. Immerse a yard or more of cotton yarn in a solution of sodium hydroxide containing three-fourths as much sodium hydroxide by weight as the yard used. Keep at a temperature of 25° C. for three minutes, and remove. Tie a small weight on the end of the yard to produce enough tension so that it will retain its original length. Wash

1. Loc. cit., 1929, 20, 398 T

while the tension is being applied and allow to dry under tension. The yarn shortens slightly, becomes lustrous in appearance, and increases in strength. The action of sodium hydroxide on cellulose does not endow it with new properties, but results in an activation of the properties which it already possesses. After further experimentation, it was found that the cellulose-sodium hydroxide compound dissolved readily in an ammoniacal copper oxide solution (Schweitzer's reagent). If this solution is poured into H_2SO_4 after the alkali cellulose has been dissolved in it, the cellulose is reprecipitated as an almost transparent oxidized hydro-cellulose. In practice, cotton waste after purification is treated with sodium hydroxide, copper sulfate, and ammonium hydroxide, and is allowed to dissolve to a stringy mass. Then it is filtered under pressure, and the cellulose solution is forced through a fine set of capillary tubes into a coagulating solution. The coagulating solution may either be dilute sulfuric acid or a 5 per cent solution of sodium hydroxide followed by a dilute sulfuric acid bath to remove the copper hydroxide. The resulting coagulated cellulose is in fine filaments, which are spun into thread and are then woven into other desired forms.

CHAPTER VII
HYDROCELLULOSE

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HYDROCELLULOSE

As early as 1875 Girard recognised the fact that cellulose was very sensitive to the action of acids. He began a series of investigations on the properties of this modified type of cellulose, and introduced the term "hydrocellulose". He found that by drying small quantities of dilute acids into the cellulose, he could produce the type of hydrocellulose which is commonly spoken of as Girard's Hydrocellulose. Hydrocelluloses prepared in this manner are for the most part friable powders, generally white in color. They give a blue-violet color with zinc chloride-iodine reagent, and by potassium, iodide-iodine. They reduce ammoniacal silver nitrate solutions and Fehling's solution. They do not react with Schiff's reagent. They dissolve to the extent of 52 per cent on boiling for ten minutes with a 15 per cent sodium hydroxide solution. In a laboratory experiment, hydrocellulose was prepared by the action of a 5 per cent oxalic acid solution on cellulose, and this hydrocellulose was heated for an hour with a dilute hydrochloric acid solution, and^I obtained an extremely heavy test for sugar. This would suggest that the hydrocellulose is more easily hydrolyzed to sugar than ordinary cellulose. Hydrocellulose is far more reactive toward esterifying agents than cellulose, and in industrial processes the

cellulose is often modified by acid treatment before esterification.

To prepare a very fine grade of hydrocellulose we have the method suggested by Hess¹. Treat 75 grams of viscose silk with carbon dioxide to remove air, and saturate with hydrochloric acid gas, making sure that all moisture has been excluded. Allow the material to stand for 15 hours at 20° C. Put it into ice water, and neutralize with bicarbonate to remove acid. Thoroughly wash the product, and dry. Take the yellow fibrous mass obtained and immerse in 400 c.c. of 10 per cent sodium hydroxide solution, and centrifuge. Ammonia gas is then passed into the solution until saturation is reached. A fine white precipitate is easily separated by the centrifuge from the liquid. Remove the ammonia, and then the residue. Carefully wash the residue with alcohol, and dry in a vacuum.

There is often difficulty in determining whether an unknown is an oxy- or hydrocellulose, and which of the two it is. We have several qualitative tests which denote their presence: (1) Cellulose in the presence of iodine gives a yellow color which is changed to blue by the addition of sulfuric acid. Oxycellulose, on the other hand, gives an immediate blue color which is destroyed by sulfuric acid; (2) A piece of cotton and the piece to be tested are

1. K. Hess, Ann., 1923, 435, 142

dyed in benzopurpurin 4B, rinsed in dilute sulfuric acid, and washed in water until the red color of the normal cotton reappears. Any of the oxidized portion will be colored a bluish black. (3) The presence of red copper oxide after boiling with Fehling's solution shows the presence of modified cellulose.

To differentiate between oxy- and hydrocellulose we have two outstanding distinctions: (1) On the hydrolysis of oxycellulose in the presence of hydrochloric acid, we have the evolution of carbon dioxide, which is not true of the hydrocelluloses. (2) A suspension of oxycellulose in water will give an orange red color in the presence of methyl orange which changes to red on the addition of sodium chloride solution. Hydrocellulose does not give this test.

There are numerous acid degraded products of cellulose which are of the cellulose dextrin type. They are colloidal in nature and for the most part are relatively unimportant. Among these we have:

Guignet Cellulose¹. In a mortar, knead 5 grams of air-dry cotton for 15 minutes with 85 c.c. of 62.5 per cent sulfuric acid, and allow to stand for five hours with frequent working. Add 170 c.c. of water, stir thoroughly and filter through a linen filter. Wash the residue with water and then alcohol.

Flechsigs Amyloid². Mix 5 grams of cotton which

1. C. Guignet, C. R., 1889, 108, 1255
2. Zeit. Physiol. Chem., 1882, 7, 524

is air dry, with sulfuric acid in a mortar. The acid is prepared by the mixing of 30 grams of 92 per cent sulfuric acid with 10 grams of water. Do not let the temperature rise above 30° C. This may require continuous cooling, and several hours may be necessary to complete the addition. A somewhat grey syrup-like liquid results, which, when added to water, changes into white flecks and a milky liquid. On filtering this, a great deal of the product is lost in colloidal solution. The residue on the filter paper is washed by decantation until it is free from acid. A salt solution might be used for the wash in order to avoid loss and to remove the sulfuric acid more readily. Flechsigs amyloid should be dried below 90° C., in order to avoid decomposition. It is colloidal in nature and forms colloidal solutions which are readily coagulated by salts.

Cellulose Parchment. The nature of this substance is dependent upon the type of cellulose used, whether filter paper or cotton wool. Parchment paper was made from filter paper in the laboratory by dipping it for a period of twenty seconds into a sulfuric acid solution containing as a maximum 78 per cent sulfuric acid. It was rapidly removed and allowed to drain for ten more seconds; then it was washed thoroughly until it was completely free of any trace of acid. In order to obtain parchment cellulose from cotton wool, one gram of the wool was brought into contact with 9 c.c. of sulfuric acid of similar strength of that used in the production of parchment paper, for ten seconds. It was then removed and

mixed with 200 - 300 c.c. of distilled water.

In preparing these two cellulose parchments, the solvent action of the concentrated sulfuric acid is not allowed to progress to complete disintegration of the cellulose fibers. The acid transforms the superficial layer of cellulose into amyloid. The product obtained is a hard, tough, durable, semi-transparent substance, which is unaffected by grease, and colors potassium iodide-iodine solution blue.

Ekstrom's Acid Cellulose¹. Five grams of air dry cotton wool were gradually immersed in 18 grams of 78 per cent sulfuric acid during the course of forty-five minutes. It was next removed and diluted with 29 c.c. of distilled water, and pressed between linen. The mass was shaken with a rather small amount of water, and a grey-white sticky mass was formed. When shaken with a large amount of water, however, a product very similar to cellulose parchment was obtained. This product, when ground up in a mortar with water, forms a colloidal solution. Like cellulose parchment, the acid cellulose colors potassium iodide-iodine reagent blue without the addition of sulfuric acid. It must be dried in an oven at a temperature below 95° C., in order to avoid decomposition. It has no claim to acidic properties.

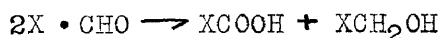
1. Ger. Pat., 207354 (1906)

CHAPTER VIII
OXYCELLULOSE

CHAPTER VIII

OXYCELLULOSE

Oxycelluloses are products formed by the action of oxydizing agents on cellulose in acid, alkaline, or neutral solutions. They dissolve in dilute sodium hydroxide solutions, yielding a yellow-gold solution. They have fairly strong reducing properties, and seem to possess reactive carbonyl groups. There are investigators who consider cellulose composed of anhydro-cellobiose units, and consider that the oxidation which takes place converts some of these units into a cellobionic acid which remains linked to the anhydro-cellobiose units by secondary valence forces. An alkali would dissolve the acidic units and leave behind a modified cellulose which would account for the solubility of oxidized cellulose in alkaline solutions. It is possible that the alkali acts on the aldehyde, giving an acid and an alcohol (cellulose):



Oxycellulose may be prepared in a number of ways. Some of the earlier ways were by the action of bromine water on cellulose, permanganate on cellulose, nitric acid on cellulose, and chromic acid on cellulose. Hess¹ worked upon these four methods, and prepared a chart to give a few of the properties of the oxycelluloses prepared:

1. K. Hess and G. Katona, Ann. 1927, 455, 221

METHOD OF PREPARATION	YIELD PER CENT	ANALYSIS	COOH PERCENT	SOLUBILITY IN NaOH * PER CENT
Bromine Water	79	C = 43.5 H = 6.1	1.2	26.8
Perman-ganate	78	C = 44.0 H = 5.6	.9	33.8
Nitric Acid	77	C = 43.7 H = 5.7	.67	22.7
Chromic Acid	84	C = 43 H = 5.2	1.06	40.5
Original Linters	--	C = 44.4 H = 6.2	.43	--

A highly oxidized cellulose with about one atom of oxygen per $C_6H_{10}O_5$ unit was prepared in the laboratory in the following manner: A pulp was made of 30 grams of filter paper in 600 - 900 c.c. of sodium hydroxide at 15° . The pulp was removed and mixed with a slight excess of dilute sulfuric acid. It was refiltered, washed, and while still moist, suspended in 600 - 900 c.c. of sulfuric acid at 10° , and stirred by an electric stirrer. Twelve grams of potassium permanganate were dissolved in the same sulfuric acid. After several hours the solution became decolorized and the pulp disintegrated, falling to a finely divided brown mass. This was filtered off and decolorized by hydrogen peroxide. These oxycelluloses reacted with phenyl hydrazine to give a red coloration with aniline, and were less stable and far more reactive than the celluloses proper. When they were boiled with hydrochloric acid, they yielded furfuraldehyde, which can be estimated with

phloroglucinol.

Oxycelluloses are widely distributed in nature, and occur generally in the form of compound celluloses. They are, therefore, present in the cellulose from woods and lignified tissues, and are the chief constituents of the celluloses from cereal straws.

It is worth noting that the substances which are termed cellulose hydrates, oxycelluloses, and hydrocelluloses are not chemical entities but are mixtures of different products.

CHAPTER IX
CELLULOSE AND CUPRAMMONIUM

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CELLULOSE AND CUPRAMMONIUM

Probably one of the oldest and most important discoveries of cellulose chemistry, which is now considered as colloidal, is the discovery by Mercer and Schweitzer of the solvent power of ammoniacal copper oxide for cellulose. It was found that if the sodium cellulose produced in mercerising cotton is dissolved in this cuprammonium solution, and the solution poured into sulfuric acid, the cellulose is reprecipitated as an oxidized hydrocellulose.

A solution of cuprammonium was made from a fairly strong solution of copper sulfate. To this was added ammonium chloride and finally a slight excess of a sodium hydroxide solution. The blue precipitate was collected and washed thoroughly on a cloth filter. The precipitate was redissolved in a solution of ammonium hydroxide d.o.92. Instead of dissolving the precipitate directly in the ammonia, it could have been drained and preserved with a 10 per cent solution of glycerol. The glycerol in contact with the precipitate preserves it from change until such a time as it is needed.

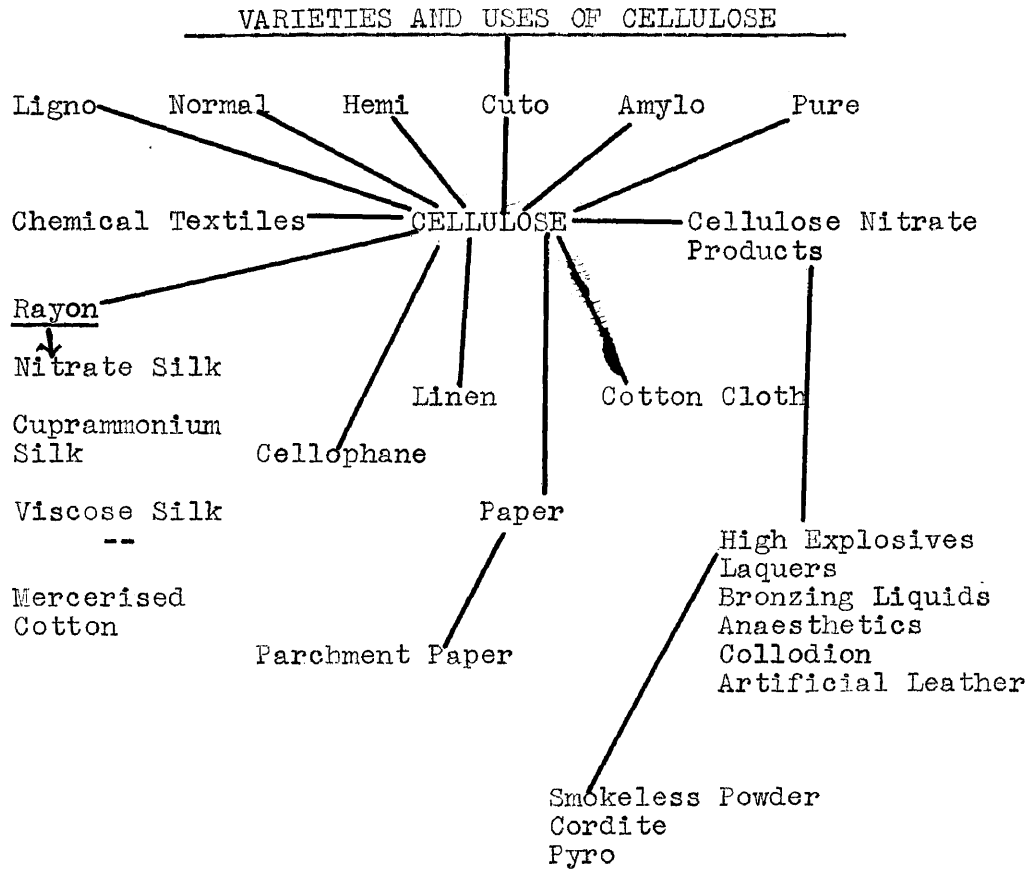
While we know that there are no true physical solvents for cellulose, cuprammonium comes the closest to being one. The higher the concentration of the copper in the cuprammonium, the greater is its solvent power for cellulose. Cellulose has been dissolved in it up to 4.5 per cent. In

making rayon, in order to obtain a product of the highest possible quality, the cellulose micelles must be broken down and degraded as little as possible. The fact that cuprammonium silk has always been esteemed for its very high quality would lead us to believe that the reagent is able to swell and even disperse cellulose with relatively little diminution of the micelle size. As to why this is so, we may only hazard a guess, but it is reasonable to believe it allows much of the water present in the solution to be imbibed with only a few of the hydroxyl groups reacting. There seems to be a difference of opinion as to whether cellulose combines chemically with the copper-ammonia complex, or whether it is merely absorbed. Hess¹ by means of optical rotation shows that the combination 1 Cu : 1 C₆H₁₀O₅ unit is formed. Bauer², on the other hand, after analyzing the work of Hess, was able to obtain a characteristic adsorption curve from his data.

Traube³ in his work on cellulose found that if amines were substituted for ammonia, he obtained a greater solvent power. This may open an entirely new field in cellulose chemistry, if we are able to use organic amines with cellulose, provided, of course, that we can understand the relationship between the two.

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1. A. J. Stamm, "Colloid Chemistry of Cellulosic Materials, 1936, p. 26
 2. Ibid.
 3. Ibid.

VARIETIES AND USES OF CELLULOSE



SUMMARY

The work that was carried out in the laboratory by the author covers only a small part of the chemistry of cellulosic materials. Modifications of the commercial processes for the preparation of the esters of cellulose and the acid hydrolysis of cellulose furnished the basis for most of the work discussed in this paper. Our knowledge of cellulose chemistry is increasing day by day. We are on the verge of what may be termed a "cellulose era". Explosives, plastics, paints, sponges, cellophane, silks, cosmetics, synthetic leathers, building materials, synthetic glass, fuels, sugars, and alcohols all may be derived from cellulose. In our future wars, cellulose compounds will be used to drive projectiles, and cellulose (wool, adhesives, etc.) will be used to heal the wounds. The great abundance of raw cellulose in the world today furnishes a substance that will rival and even surpass the coal and coal tar industries. When our supply runs low, we may easily replenish it so that we should never have a lack of raw materials. In this age of synthesis, cellulose leads the field as a source of raw materials, and it has promise of being the most valuable as it is now the most abundant substance available for the industries of modern civilization.

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