May 9, 1933. W. H. BRADSHAW 1,907,726

RAYON, ARTIFICIAL HORSEHAIR, FILMS, AND THE LIKE AND PROCESS OF MAKING THE SAME

Filed May 21, 1926 2 Sheets-Sheet 1

Fig. 1.

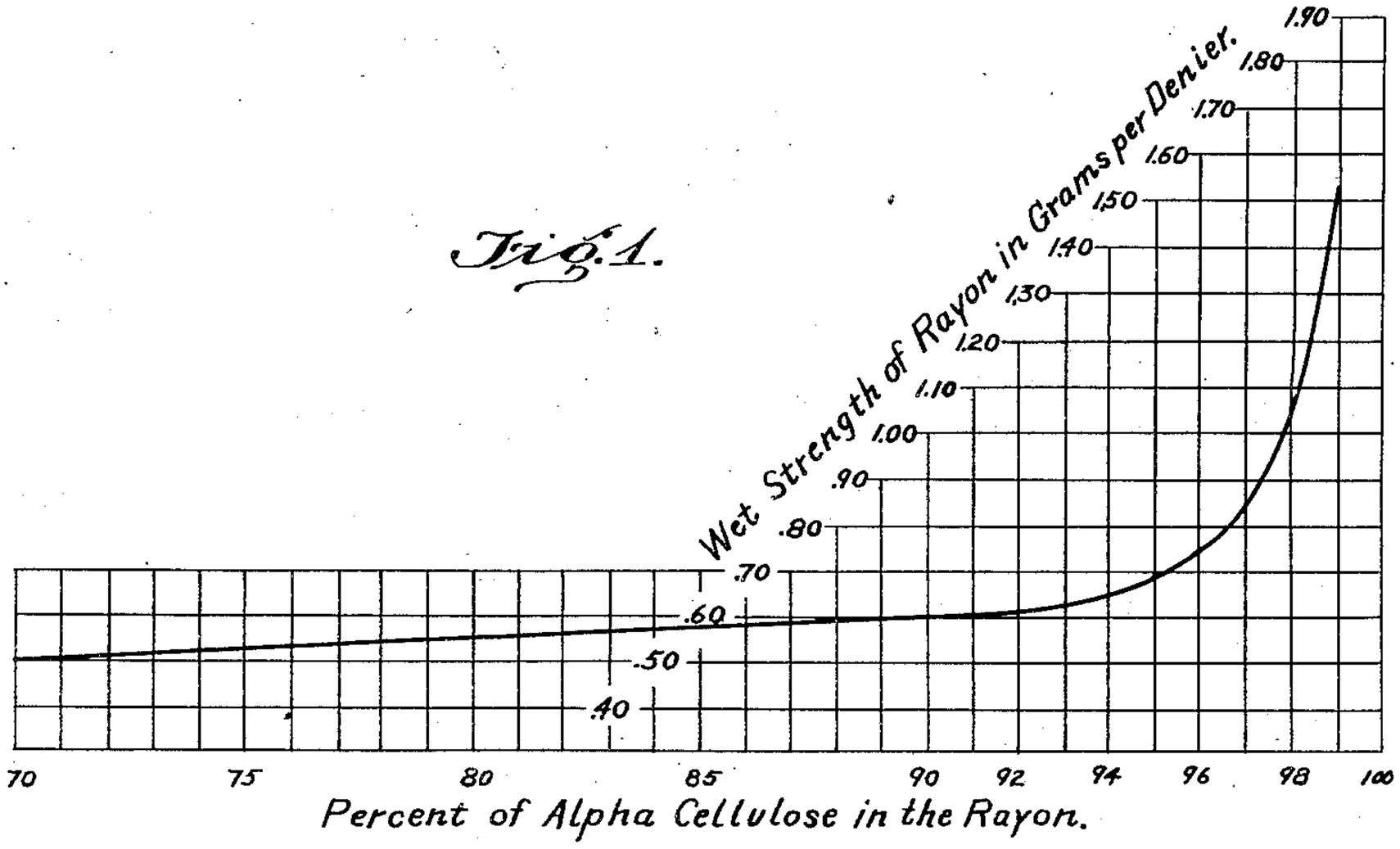
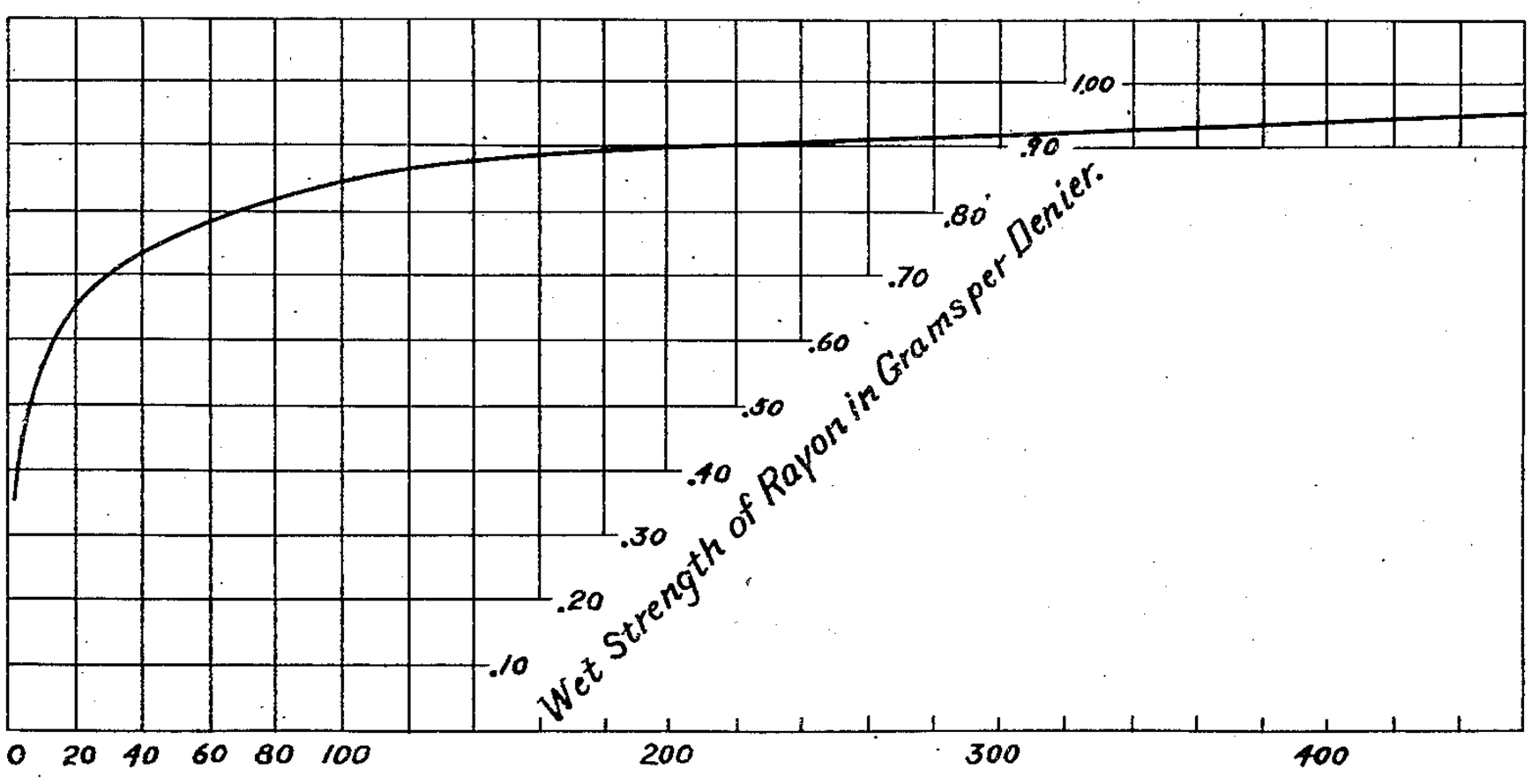


Fig. 2.



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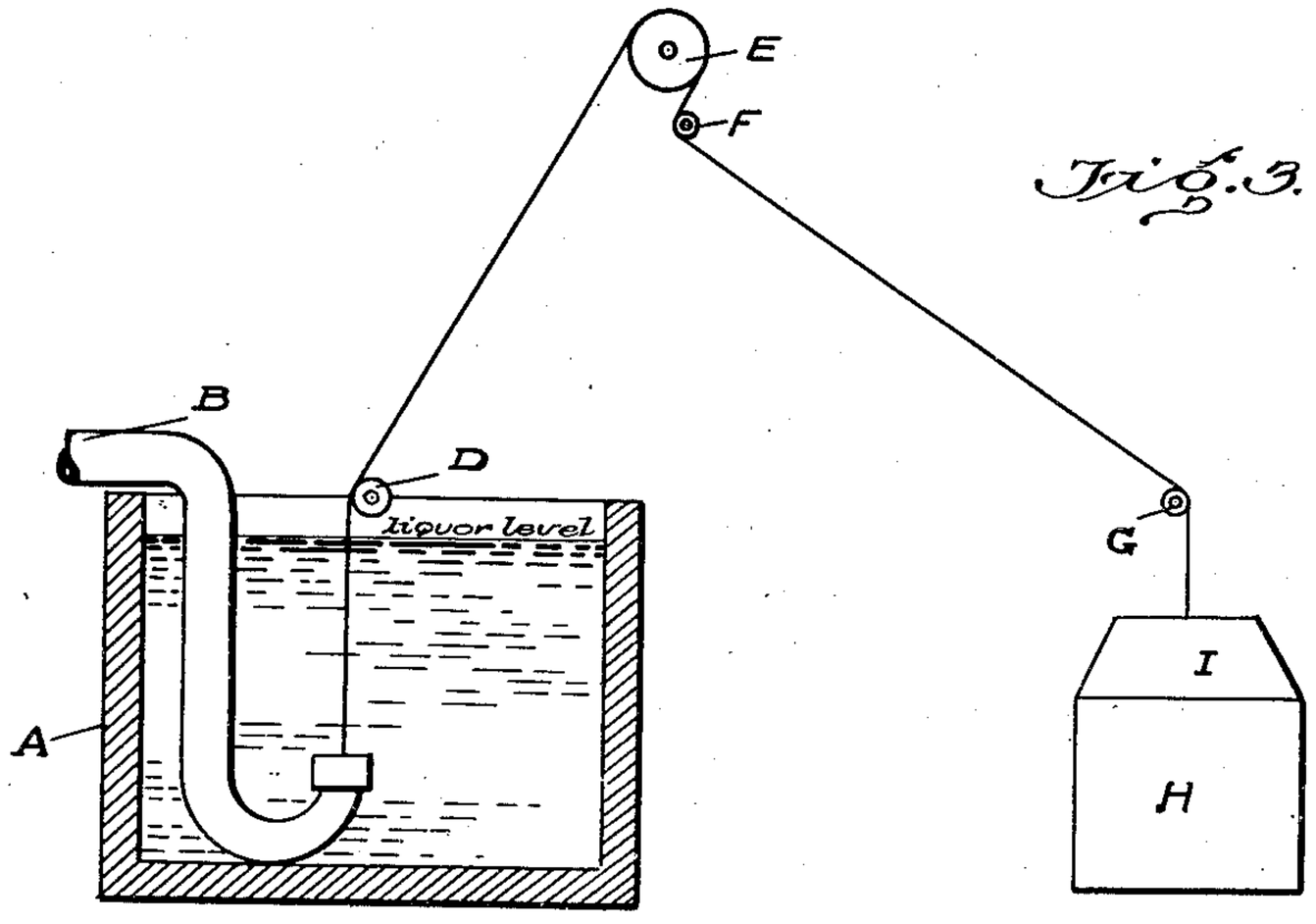

Fig. 3.

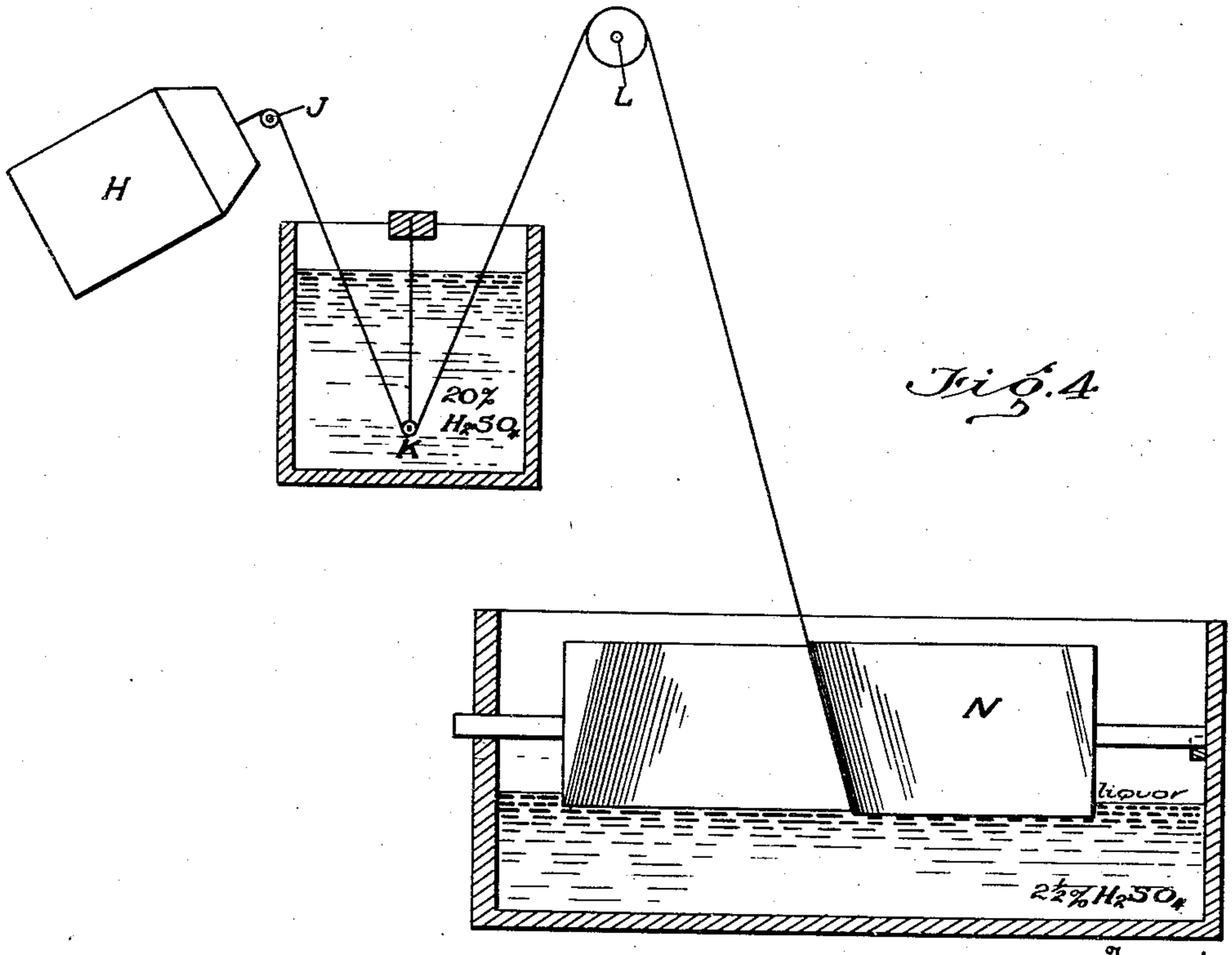

Fig. 4

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Patented May 9, 1933

1,907,726

UNITED STATES PATENT OFFICE

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RAYON, ARTIFICIAL HORSEHAIR, FILMS, AND THE LIKE AND PROCESS OF MAKING THE SAME

Application filed May 21, 1926. Serial No. 110,774.

This invention relates to rayon, artificial horsehair, films, sheets, and the like, and a process of making the same.

One of the objects of the present invention is to produce rayon, horsehair, films, and the like, which shall have a high tensile strength when wet. A further object is to produce rayon which can be woven or knitted into fabrics without exact control of humidity in the weaving room. A further object is to produce rayon which shall have a high tensile strength. A further object is to produce rayon which shall have a high true elasticity as well as a high distensibility. A further object is to produce rayon which when wet can be handled more readily by the dyer. A further object is to provide a process for making rayon whereby a higher percent of perfect skeins can be produced. A further object is to produce rayon which will dye evenly. A further object is to produce rayon which will have a soft lustre. A further object is to produce rayon which can be used in many ways, hitherto impossible, due to its improved strength and toughness when wet. A further object is to provide a process whereby such rayon, horsehair, and the like, can be made which will be relatively inexpensive.

Other objects will be in part obvious from the annexed drawings and in part indicated, in connection therewith, by the following analysis of this invention.

This invention accordingly consists in the several steps and their various relations to one another, as well as the composition of matter and their relations to it.

To enable others skilled in the art so fully to comprehend the underlying features that they can embody the same with the numerous modifications contemplated by this invention, the following analysis is given of what I consider the preferred embodiment of my invention.

Heretofore it has been thought a viscose or a cuprammonium cellulose solution could not be made sufficiently smooth and uniform to spin unless the viscosity of the solution were reduced to a point where the cellulose became thoroughly hydrated.

In the viscose process this is accomplished by subjecting the cellulose to a prolonged treatment with about 18 percent caustic and by ageing the viscose solution.

In the cuprammonium process it is accomplished by working the cuprammonium cellulose in a mixer in such a way that air is beaten into the mass causing an oxidation of the cellulose with a concurrent drop in viscosity. The oxidation itself lowers the percentage content of alpha cellulose. The hydration is sometimes partly accomplished by a preliminary treatment of the cotton with about 18 percent caustic soda at 20 degrees C. or below, followed by washing before the cuprammonium cellulose is formed.

It has not heretofore been understood that the strength, when wet, of rayon, horsehair and the like, composed of regenerated cellulose, will be high only when the following two conditions are fulfilled: (1) The percent of alpha cellulose must be high, and (2) the viscosity of the cellulose must not be too low, i. e. the degree of hydration of the cellulose must be relatively low.

To obtain a rayon with a high percent of alpha cellulose it is necessary to start with a carefully prepared cellulose containing a high percent of alpha cellulose and then regulate the process so this percent is not materially reduced. The degree of hydration can be kept relatively low if the viscosity of the cellulose in solution is kept high enough, and if the subsequent coagulating and acidifying operations are properly carried out.

I have found it is possible to make a smooth, uniform cellulose solution with a viscosity suitable for spinning rayon without materially reducing the percent of alpha cellulose present, and without hydrating the cellulose to but a relatively small degree when compared with the processes mentioned above, by mechanically working a viscose solution or cuprammonium cellulose mass either in a closed mixer in the absence of air, or in a closed mixer adapted to accomplish a thorough working of the material but at the same time to beat or work into it as little as

possible of what air might be in the mixer above the material.

For example three sets of tests were run, starting with a prepared cellulose containing over 99 percent alpha cellulose. In all the tests identical conditions were maintained in regard to the materials used and their weights and temperatures. Solutions were made to contain about 6 percent of cellulose by treating the cellulose with cuprammonium solution, and mechanically working the mass until the solution was smooth and uniform and the viscosity had dropped to practically 100 seconds. In this patent specification viscosity values given are for a solution containing 6 percent cellulose, 9 percent ammonia (NH_3), 2.5 percent copper and are the number of seconds required for a steel ball $\frac{3}{32}''$ in diameter to fall 15 centimeters through the solution when the solution is kept at 20 degrees C, in a vertically supported glass tube having an internal diameter of 1 centimeter. The results of these tests are as follows:

(A) When the operation was performed in a mixer designed to beat air into the material, at the end of the operation the cellulose regenerated from the solution contained only 85 percent of alpha cellulose.

(B) When the operation was performed in a closed mixer designed not to beat into the material the air above it, at the end of the operation the cellulose regenerated from the solution contained 97 percent of alpha cellulose.

(C) When the operation was performed in a closed mixer in which the absolute partial pressure of the air present was less than 1" of mercury, at the end of the operation the cellulose regenerated from the solution contained 98.5 percent of alpha cellulose, yet the solution was smooth and uniform, and the viscosity had been reduced to the same value as in the other sets of tests.

The following table shows what effect the preparation of solutions by the above methods has on the tensile strength, when wet, of the rayon made from those solutions. In this Table No. 1 was a standard viscose rayon; No. 2 was spun from a solution made as described under (A), but with the viscosity reduced to 7; No. 3 was spun from a solution made as described under (A); No. 4 was spun from a solution made as described under (B).

	1	2	3	4
Tensile strength, grams per denier	1.40	1.50	1.50	1.90
Percent elongation at breaking	18	28	25	13
Tensile strength wet, grams per denier	.55	.35	.53	.90
Percent of alpha cellulose in the rayon	85	80	85	97.5
Viscosity of solution from which silk was spun	about 100	7	100	100

Referring now to the drawings, "Fig 1" shows to better advantage the relationship existing between the percent of alpha cellulose in the rayon and its wet strength. "Fig. 2" shows the relationship between the viscosity of a solution and the wet strength of the rayon spun from it. The values plotted for "Fig. 1" are for rayon spun from cuprammonium cellulose solutions containing 6 percent cellulose, 9 percent ammonia and 2.5 percent copper, and having a viscosity of 100. The values plotted for "Fig. 2" are for rayon containing close to 97 percent alpha cellulose and spun from cuprammonium cellulose solutions containing 6 per cent cellulose, 9 percent ammonia and 2.5 percent copper.

"Fig. 1" shows plainly that the wet strength begins to increase rapidly when the percent of alpha cellulose is around 96 and that the rate of this increase rises tremendously as the percent of alpha cellulose approaches 100. "Fig. 2" shows that the wet strength decreases gradually with falling viscosity until the viscosity is reduced to around 100, when the wet strength decreases more rapidly, and that the rate of this decrease increases very rapidly as the viscosity is further reduced.

The treatment of cellulose with 17.5 percent caustic soda solutions for a short time will not hydrate it sufficiently to reduce its wet strength seriously. It is the extreme dispersion, occurring when the viscosity of the cellulose in solution is greatly reduced, which results in a profound hydration or swelling of the cellulose, thereby reducing the wet strength of the rayon spun from the solution.

It may have been known that it is desirable to have a high percent alpha cellulose in rayon, and it may have been known that regenerated cellulose rayon is a highly hydrated cellulose. However it has not heretofore been understood that the tensile strength of wet rayon is determined by these two factors in combination. It has not been understood that the excessive hydration which seriously affects the wet strength is a result of lowering the viscosity of the solution below a certain region which in the case of the solutions mentioned above is below 500 and in the neighborhood of 100. Operating difficulties are encountered when spinning cuprammonium solutions having viscosities of over 500. The invention, however, is not restricted to this limit and the scope in no wise limited thereby except as set forth and claimed in the appended claims. It also has not been appreciated that the wet strength increases tremendously as the percent of alpha cellulose approaches 100.

Throughout this specification the terms "hydration", "hydrated cellulose" and "cellulose hydrate" are used to describe a physical condition of the cellulose as discussed on page 18 of Emil Heuser's "Textbook of Cellulose Chemistry", first English edition. That is, by "hydrated cellulose" I mean a swollen cel-

lulose or a cellulose capable of swelling. The term "alpha cellulose" is used to describe what the same textbook designates as pure cellulose and which it says occurs in untreated cotton to the extent of 90 percent, in spruce to about 60 percent, and in straw to about 35 percent.

Having secured a smooth uniform solution of cellulose with a high percent of alpha cellulose, preferably 97 percent or over for the cuprammonium process, and a relatively low degree of hydration by the principles above outlined, this solution must be spun and precipitated under such conditions that the degree of hydration will not be increased materially.

For example, with a cuprammonium cellulose solution this may be accomplished by a very thorough and rapid precipitation with an alkaline bath, before the filaments are treated with acid. The acid treatment must also be so carried out that hydration will not take place during the treatment and subsequent washing.

The thorough precipitation in the alkaline bath is aided by stretching the filaments near the orifice. This stretches the filaments at the time when the initial precipitation is taking place. It is very important that the filaments be stretched during their initial precipitation. If desired they may be further stretched later on. Stretching the filaments while the initial precipitation is taking place, by facilitating the thorough precipitation, reduces the chance of hydration during the operation of acidifying and washing, and increases the strength and softness of the finished product. It also gives to the finished silk a beautiful soft scintillating lustre as contrasted with the harsh metallic gloss obtained by subjecting the fibres to tension later in the process. This soft lustre is thought to be due to a certain orientation of the cellulose crystallites, which is obtained by this particular stretch treatment.

Likewise when a viscose solution is being spun the finished rayon is softer, stronger, has a soft lustre and dyes better if the filaments are stretched during the initial precipitation. This treatment accomplishes a more perfect precipitation and facilitates the removal, from the filaments, of the products of the chemical reaction involved in the precipitation. Whether or not the viscose filament is later further stretched or mechanically worked by passing it under guides, it is important that it be stretched at the time of initial precipitation as described above.

The coagulated cuprammonium thread consisting of several filaments, after being wound on the inside of a rotating pot, is removed from the pot and treated with acid to remove the copper and ammonia, and to complete the precipitation. Heretofore this operation has been carried out by winding the thread from the pot on to a rotating reel or drum slightly immersed in acid of about 8 percent strength, when sulfuric acid is used. I have found that there is less chance of hydration and a better rayon is produced if the threads are treated with much stronger acid, say about 20 percent, in such a way that when the acid leaves the thread its strength is largely spent, so that the last stages of the process of removing the copper from the thread are performed by very dilute acid, say about 2 or 3 percent strength, assuming that sulfuric acid is used. This not only results in a much lower consumption of acid but the finished rayon is softer and stronger and the copper is more perfectly removed, resulting in more even dyeing.

Illustrating my invention, I will now describe my preferred process for making rayon according to the principles above set forth.

A cuprammonium solution is prepared by the well-known process of covering copper wire with ammonia and blowing air through it until the solution thus formed contains approximately 4.5 percent copper and 11 percent ammonia. It is desirable to add a small percent of a sugar to the ammonia at the start. The presence of the sugar makes both the cuprammonium solution and the cuprammonium cellulose solution quite stable thereby greatly facilitating the whole operation. The temperature of the cuprammonium solution is maintained at 2° C. at the start and is gradually reduced to −5° C. at the finish of the operation.

Sufficient prepared cotton linters are weighed out to give 250 pounds of dry cotton. The linters from which the batch is weighed must have been most carefully prepared by kiering, bleaching, washing and drying so that they contain 99 percent or more alpha cellulose, have a low copper number and are of a fairly uniform viscosity. The preparation of linters is a well-known art and it is possible to obtain suitably prepared linters in the open market. The weighed batch of linters is placed in a mixer, previously cooled at 4° C. and chilled. 3150 pounds of the freshly prepared cuprammonium solution are run in, the cover of the mixer closed tightly, and the mass mixed for four hours at 4° C. Distilled water is then added slowly while the mixer is running till the percent of cellulose in the mass is reduced to 6. The mixing is continued till the viscosity of the solution is reduced to 100. After the water is added the temperature is allowed to rise to 12° C. at which point it is maintained until about a half hour before the batch is finished when it is allowed to rise to 20 degrees to assist in filtering. The design and operation of the mixer and selection of size of batch to fit the mixer used is of utmost importance in the exclusion of

air from the mass as it is being mixed. I prefer a vertical mixer with paddles arranged to cause the batch to circulate down in the center, and up at the periphery. The size of the mixer and paddles must be so chosen that before the water is added the exposed surface of the batch will not be disturbed sufficiently to work air into the mass. There must be as little space as possible above the solution after the water has been added, and the cover must be substantially airtight.

When the viscosity of the solution has been reduced to 100 it is dumped into a receiving tank. From the receiving tank it is run slowly into an evacuating tank where all traces of air are removed and some ammonia is removed.

The time, temperature and pressure are regulated in this evacuating operation so the finished solution will contain 6 percent cellulose, 5.5 percent ammonia and 2.5 percent copper. To accomplish this it is necessary to add a slight excess of water to the mixer to compensate for that lost in the evacuating tank.

The evacuated solution is filtered and run into a spin tank from which it is forced to the spinning machine.

For the spinning operation I prefer a machine of the bucket type in which the thread, after it leaves the alkaline coagulating bath, passes up over a rotating takeup drum and then down through a guide into a rotating pot, where by means well-known to those skilled in the art the thread is caused to build up a cake of even thickness, against the sides of the pot. This apparatus is shown diagrammatically in "Fig. 3". The takeup drum "E" has a peripheral speed of 2000 inches per minute and the pot "H" rotates at 5000 revolutions per minute. The thread is prevented from slipping on the takeup drum by passing it under a snub guide "F" which causes it to wrap around the drum with a large arc of contact. The pot is provided with a cover "I" which fits the pot with an air-tight seam and is provided at its center with a hole two inches in diameter. If the seam between the cover and the pot is not airtight, a current of air is set up which spoils the build of the cake.

The solution is extruded from a multiple hole spinneret "C" into a bath composed of 25 parts by weight of caustic soda, 2 parts of glucose and 75 parts of water, and maintained at 10° C. It has been thought heretofore that the alkaline bath should contain around 35 percent caustic soda and must be maintained at a temperature of from 15° C. to 50° C. I have found that if the bath is maintained at a temperature below 13° C. a lower concentration of caustic can be used and a much better coagulation is obtained. The more perfect coagulation produced by the intense dehydrating action of the caustic at the low temperature reduces the tendency to hydration in the acidifying operation at the reel. When thus coagulated the filament retains practically all the copper which was in the solution and is very tough and elastic. This makes it possible to spin much finer filaments and greatly reduces the loss due to injury of the filaments during the spinning and reeling operations.

The spinneret is submerged 4 inches below the surface of the bath. A spinneret is chosen with an orifice diameter such as will give about 40 percent stretch to the filament as it is being spun. After the desired amount of thread has been spun the pot is removed from the machine and allowed to stand for fifteen minutes to complete the coagulation before the thread is acidified.

The pot is then placed in a substantially horizontal position near the top of the reel. This is shown diagrammatically in "Fig. 4". The thread is passed over and/or through a guide "J" set in the center of the top opening of the pot, carried down and under a small diameter guide "K" immersed about 6 inches in 20 percent sulfuric acid, brought up and over another guide located above the acid bath then carried down and through a traverse guide which causes the thread to build up in an even layer on a rotating horizontally located cylinder "N" whose lower surface is immersed in 2½ percent sulfuric acid. The acid baths are maintained at 20° C. and the thread is reeled, at the rate of 80 yards per minute. The time the thread is immersed in the 20 percent acid bath can be regulated so the acid carried over will keep the lower bath at a constant percent strength. Fresh acid is added to the upper bath to maintain it at 20 percent strength. The guide "K" is provided with means by which it can be raised above the 20 percent acid bath for threading and is not immersed until the thread is started on the reel. The guide "K" being of small diameter subjects the filament to a mechanical working which aids the reaction, assisting diffusion.

After the desired amount of thread is reeled, the cylinder "N" is allowed to idle in the lower bath for about one minute to complete the acidification of the thread last wound. The cylinder is then removed and the acid and salts washed from the thread by rotating it slowly under a water spray until the thread is neutral. It is then passed under a spray of softened water at 60° C. containing a small percent each of borax and a neutral soap, allowed to drain, and dried.

While the above outline covers my preferred process, it is not intended that it shall be understood that I am restricted to the procedure outlined. Other means for accomplishing the same results will be obvious to

those skilled in the art. For example, the solution may be made by mixing copper hydroxide, cotton, and ammonia. The viscosity may be reduced by a mechanical working of the mass in a closed mixer, in an atmosphere of nitrogen. While I prefer a cuprammonium solution containing 6 percent cellulose, 5.5 percent ammonia, and 2.5 percent copper, cuprammonium cellulose solutions of other proportions can be used. For example it is desirable when spinning fine denier to use a 5 percent cellulose solution. The reeling can be performed on a perforated cylinder, which permits washing with a suction washing machine in which the water is drawn through the silk. I wish it also to be understood that while I prefer to use a cuprammonium cellulose solution for producing rayon according to the principles outlined above, which shall have, among other desirable characteristics, a high tensile strength when wet, I do not wish to restrict myself to that type of solution.

For example the same results can be obtained, though to a somewhat lesser degree, by a proper application of the principles outlined to a viscose solution. In the appended claims the term or expression "cellulose solution" is intended to cover spinning solutions such as cuprammonium cellulose, viscose and the like.

Without further analysis, the foregoing will so fully reveal the gist of this invention that others can, by applying current knowledge, readily adapt it for various applications without omitting certain features that, from the standpoint of the prior art, fairly constitute essential characteristics of the generic and specific aspects of this invention, and therefore such adaptations should and are intended to be comprehended within the meaning and range of equivalency of the following claims.

I claim:

1. A process of producing threads, which comprises treating cellulose containing not less than 98% of alpha cellulose with a cuprammonium solution, subjecting the mass to a mechanical working in a closed mixer while excluding oxygen in an amount sufficient to excessively degrade the cellulose until a smooth spinnable solution is produced and the viscosity based on a 6% cellulose solution is reduced to less than 500, and then spinning said solution.

2. A method of producing threads which comprises treating cellulose containing not less than 98% of alpha cellulose with a cuprammonium solution, subjecting the mass to mechanical working in a closed mixer while excluding oxygen in an amount sufficient to excessively degrade the cellulose until a smooth spinnable solution is produced and the viscosity based on a 6% cellulose solution is reduced to about 100, and then spinning said solution.

Signed at Little Falls, in the county of Passaic and State of New Jersey, this 1st day of February, 1926.

WILLIAM HENRY BRADSHAW.