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ART OF CUPROAMMONIUM RAYON MANUFACTURE

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This invention relates to the art of manufacturing cuproammonium rayon.

Heretofore, for the most part, cuproammonium yarn has been spun from a solution made with cotton linters, ordinarily by mixing copper hydroxide, ammonia and the linters. This process has a number of disadvantages but I will here mention only the cost of raw materials and the difficulty and expense of preparing the "goo."

It has also been proposed to make the cellulose solution or "goo" from wood pulp but heretofore without commercial success. It was necessary to highly fluff the wood pulp. This is objectionable because a relatively small quantity of wood pulp when fluffed occupies a very large volume and will not go into solution effectively. Furthermore, the control of viscosity of the "goo," which is very important in the spinning of rayon, was a very difficult matter when using wood pulp. This necessitated the production of wood pulp of relatively low viscosity which usually resulted in permanent degradation of the cellulose and poor spinning properties.

I have found that I can use wood pulp for making the "goo" without the need of fluffing it and the pulp can be of high viscosity and, if desired, be in ordinary sheet form. I further can very quickly dissolve the wood pulp and, when needed, can control the viscosity of the spinning solution in a very simple, inexpensive and effective manner affording a process which gives accuracy and ease of control and, therefore, uniformity of product over long periods of operation.

In the previous attempts to use wood pulp, the wood pulp manufacturers, as stated, have been under the necessity of supplying wood pulp of very low viscosity obtained by the use of oxidizing agents permanently degrading the cellulose. This has, in turn, necessitated in some instances control of the cellulosic solution by the addition of coagulants to raise the viscosity which is objectionable, not only because of the cost involved but because the control was not very accurate. I overcome these difficulties and need employ no coagulants. In this respect my process reduces viscosity to the desired point. I can use pulps of the highest viscosity. I find that I can very effectively prepare solutions heavy in cellulose concentration and of high viscosity, such for example as are used in the so-called "stretch spinning" of rayon, or solutions of high cellulose concentration but of low viscosity, or solutions which have a relatively low concentration of cellulose and of low viscosity, such as are suitable for direct spinning. By direct spinning, I mean solutions which can be spun through spinnerets, the holes of which are approximately the size of the filaments to be spun.

Solutions prepared in accordance with my invention are stable and in contradistinction to all other processes of which I am aware, the cellulose is completely dissolved so that there is no need for the filtering out of undissolved fibers or of undissolved chemicals. In my process filtering, if resorted to, is a relatively minor matter and employed primarily for the purpose of removing any foreign matter present.

In the preferred practice of my invention I take the sheets of wood pulp and, without pretreatment, and irrespective of its viscosity, dissolve them either in the sheet form or by tearing them up into pieces, say about four to six inches square.

Using the smaller squares for illustration, the following is typical of the preferred procedure and proportions. I take 486 grams of wood pulp in squares and immerse them in 1804 cc. of a solution containing 212 grams of NaOH, the squares preferably being immersed singly to be sure that they are thoroughly wet. The wetted squares which have absorbed the 1804 cc. are now placed in a press and 731 cc. of the solution squeezed out. The squeezed material is now placed in an agitator such as a stirrer or shredder and is thereby "riced," after which is added 5 pounds of cracked ice and 2 pounds of water preferably in that order. The riced material is churned until it makes a smooth slurry.

To the slurry is added 690 cc. of 26° Bé. ammonia and one pound of cracked ice, the churning being continued.

After this I add 3 liters of tetrammonium copper sulphate containing 250 grams of $CuSO_4:5H_2O$ and 68 grams of NH_3, per liter, and 5 pounds of cracked ice, churning being continued. The temperature lowers to about 0° C.

The amount of caustic soda left behind in the squares after the pressing operation is in the ratio of 2 mols of caustic soda to 1 mol of the copper sulphate. The mols of NH_3 are in excess of the theoretical 4 mols for purposes of stability. The slurry is immediately affected by the tetrammonium copper sulphate, the latter removing combined caustic soda and forming in situ what I term the double salt of copper sulphate ammonia and caustic soda which is an extremely active solvent of cellulose. The tetrammonium copper sulphate quickly penetrates the pulp and this is expedited by the continued churning.

Thus the dissolving action is very rapid and in about 20 minutes time the cellulose is completely in solution. No copper hydroxide is formed except as the salt of copper sulphate ammonia and caustic soda combines with the cellulose in the dissolving.

I then dilute with 4 pounds of water and 25 cc. of a solution of ammonium persulphate of 40 grams per liter strength. The ammonium persulphate is the viscosity adjuster and the amount thereof may be varied as required to give the desired viscosity to the "goo" for spinning. With a solution containing about 3.8% to 4% of cellulose the amount of persulphate mentioned just above gives a viscosity suitable for direct spinning.

I may use another so-called oxidizing agent such as sodium hypochlorite. Such oxidizing mediums when used in the low percentages which I employ apparently have no oxidizing effect to speak of and presumably dissolve gum present in the cellulose. If they acted as true oxidizers, the cellulose would be degraded which is not the case as I employ it.

For a "goo" containing about 3.8% of cellulose (or 38 grams per liter), the presence of about 30 grams of NH_3 per liter in the solution, makes the solution stable at most temperatures. In cold weather the amount of NH_3 might even be as low as around 25 grams per liter. In warmer weather the amount of NH_3 might be increased.

The solution is preferably spun in an ordinary caustic soda solution of about 40–45 grams NaOH per liter.

There is no degradation of cellulose in my process. The initial subjection of the wood pulp to the caustic soda chemically alters the structure of the cellulose by what is in effect a mercerizing action and the cellulose in its chemically altered form is put into solution and, as spun, retains this chemically altered form. The spinning merely converts from the liquid to the solid phase producing the jell-like filaments of which rayon yarn is composed. After the filaments leave the precipitating bath it is, of course, to be understood that they are subjected to the usual acid end water washes and drying.

As above indicated there is no copper hydroxide, as such, in the solvent solution, the only copper hydroxide present being in combination with the cellulose. This is of importance for even the presence of a small amount of copper hydroxide in the solution attacking the cellulose would materially interfere with the dissolving action and would impair the spinning properties of the ultimate "goo."

As contrasted with the preparation of "goo" from copper hydroxide ammonia and cellulose—which is the ordinary way of preparing cuproammonium "goo"—, my process requires but a few minutes instead of the several hours to secure dissolving of the cellulose and very little power is required to operate the churner as contrasted with the kneading mill required to knead the doughy mass which results when the cellulose is subjected to the copper hydroxide and ammonia.

It will also be noted that the ammonia content by contrast is low. When making a spinning solution from copper hydroxide ammonia and cellulose over double the amount of ammonia needed to keep the cellulose in solution is usually required to put the cellulose in solution, after which it has been customary to evacuate about one-half the ammonia by a vacuum pump. In other words I am able to make my solution with much less ammonia than has heretofore been required and without the need of evacuating ammonia as heretofore. The lower the ammonia content, the better the spinning properties and the less chemical required in the setting bath to secure a better end product. Obviously the reduction in the amount of ammonia and the elimination of the vacuum pump greatly reduce costs.

Once the cellulosic solution has been prepared it is stable at ordinary temperatures for long periods of time and can therefore be stored.

Other copper salts forming a compound with ammonia may be employed such, for example, as copper chloride, copper nitrate and copper carbonate. Therefore, I do not strictly limit myself to copper sulphate. In using the other salts mentioned the procedure is just the same and as before, the caustic soda should be used in the ratio of two molecules of caustic soda to one molecule of the salt with the same relative proportion of ammonia, as hereinbefore given.

My invention makes it possible to commercially produce cuproammonium yarn from standard wood pulp in competition with viscose. I can and desirably do eliminate much of the treatment in the pulp mill heretofore required for wood intended for cuproammonium processes.

Insofar as viscosity control is concerned, my method works as well on cotton linters, and degradation of such linters avoided.

What I claim is:

1. The process of making a cellulosic spinning solution which comprises subjecting wood pulp to a caustic soda solution in the following proportions, for 486 grams of wood pulp using 1804 cc. of a solution containing 212 grams of NaOH, squeezing the wood pulp until it contains approximately 1170 cc. of liquid agitating the squeezed wood pulp, adding approximately 5 pounds of cracked ice and 2 pounds of water, agitating to a smooth slurry, adding approximately 690 cc. of 26° Be. ammonia and one pound of cracked ice while agitating, adding 3 liters of tetrammonium copper sulphate solution in the following proportions, 250 grams of $CuSo_45H_2O$ and 68 grams of NH_3 per liter, and 5 pounds of ice, while agitating.

2. The process of preparing a cellulosic solution for spinning rayon which comprises subjecting wood pulp to a caustic soda solution of mercerizing strength, removing a substantial portion of said solution, adding ammonia to the treated wood pulp, and then adding tetrammonium copper sulphate, the copper sulphate and caustic soda in the pulp after removal of said caustic soda solution being in the ratio of 2 mols of caustic soda to 1 mol of copper sulphate and ammonia being employed in an amount roughly approximating 30 grams per liter for a concentration of cellulose in the solution approximating 3.8 grams per liter.

3. The process of preparing a cellulosic solution for spinning rayon which comprises subjecting wood pulp to a caustic soda solution of mercerizing strength, removing a substantial portion of said solution, adding ammonia to the treated wood pulp, and then adding tetrammonium copper sulphate, the copper sulphate and caustic soda in the pulp after removal of said caustic soda solution being in the ratio of 2 mols of caustic soda to 1 mol of copper sulphate and ammonia being employed in an amount roughly approximating 30 grams per liter for a concentration of cellulose in the solution approximating 3.8 grams per liter, the solution

being prepared in the cold and being characterized by the absence of excess caustic soda and any appreciable amount of precipitated copper hydroxide.

4. The process of preparing a cellulosic solution for spinning rayon which comprises treating wood pulp with a caustic soda solution of mercerizing strength, removing a substantial portion of said solution, and thereafter subjecting the treated pulp to an ammoniacal solution of a tetrammonium copper salt, the ratio of caustic soda in the pulp to the copper salt, after said removal of caustic soda solution, being 2 mols of the soda to 1 mol of the salt, and the amount of ammonia present being at least 25 grams per liter of ammonia for a solution containing 3.8 grams per liter of cellulose.

5. The process of preparing a cellulosic solution for spinning rayon which comprises treating wood pulp with a caustic soda solution of mercerizing strength, removing a substantial portion of said solution, and thereafter subjecting the treated pulp to an ammoniacal solution of tetrammonium copper sulphate, the ratio of caustic soda in the pulp to the copper sulphate, after said removal of caustic soda solution, being 2 mols of the soda to 1 mol of the sulphate, and the amount of ammonia present being at least 25 grams per liter of ammonia for a solution containing 3.8 grams per liter of cellulose.

6. The process of preparing a cellulosic solution for spinning rayon which comprises treating wood pulp with a caustic soda solution of mercerizing strength, removing a substantial portion of said solution, churning the treated pulp in the presence of cold water to produce a slurry, and thereafter subjecting the treated pulp to an ammoniacal solution of a tetrammonium copper salt, the ratio of caustic soda in the pulp to the copper salt, after said removal of caustic soda solution, being 2 mols of the soda to 1 mol of the salt, and the amount of ammonia present being at least 25 grams per liter of ammonia for a solution containing 3.8 grams per liter of cellulose.

7. The process of preparing a cellulosic solution for spinning rayon which comprises treating wood pulp with a caustic soda solution of mercerizing strength, removing a substantial portion of said solution, and thereafter subjecting the treated pulp to an ammoniacal solution of a tetrammonium copper salt, the ratio of caustic soda in the pulp to the copper salt, after said removal of caustic soda solution, being 2 mols of the soda to 1 mol of the salt, and the amount of ammonia being at least 25 grams per liter of ammonia for a solution containing 3.8 grams per liter of cellulose; and the preparing being done in the cold.

8. The process of preparing a cellulosic solution for spinning rayon which comprises treating woodpulp with a caustic soda solution of mercerizing strength, removing a substantial portion of said solution, and thereafter subjecting the treated pulp to an ammoniacal solution of a tetrammonium copper salt, the ratio of caustic soda in the pulp to the copper salt, after said removal of caustic soda solution, being 2 mols of the soda to 1 mol of the salt, and the amount of ammonia being at least 25 grams per liter of ammonia for a solution containing 3.8 grams per liter of cellulose; and the preparing being done in the cold produced by employing some of the water in the system in the form of ice.

9. The process of preparing a cellulosic solution for spinning rayon which comprises treating wood pulp with a caustic soda solution of mercerizing strength, removing a substantial portion of said solution, adding ammonia to the treated wood pulp, and thereafter subjecting the treated pulp to a solution of a tetrammonium copper salt, the ratio of caustic soda in the pulp to the copper salt, after said removal of caustic soda solution, being 2 mols of the soda to 1 mol of the salt, the amount of ammonia employed being at least 25 grams per liter for a solution containing 3.8 grams per liter of cellulose.

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