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# METHOD OF MAKING FIBERS OF REGENERATED CELLULOSE OF IMPROVED DYEING PROPERTIES

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This invention relates to the production of regenerated cellulose fibers and is more particularly concerned with the production of regenerated cellulose fibers of improved dyeing properties.

Heretofore, the dyeability of regenerated cellulose fibers has been such that only those dyestuffs possessed of an affinity for these fibers, such as direct dyes, sulfide dyes, and the like have been used. More recently, however, it has been desired to spin or weave regenerated cellulose fibers with fibers which are dyeable not only with direct dyes, but also with acid dyes, or acid mordant dyes, such as nylon, wool, and the like. There is thus an important need for regenerated cellulose fibers having an improved dyeability with respect to acid dyes and acid mordant dyes.

Studies have already been made as revealed by Japanese Patent No. 236,202 on a method of mixing high molecular compounds containing basic nitrogen with viscose mother solution for the purpose of improving the dyeability of the regenerated cellulose fibers. In this case, however, since the viscose mother solution is strongly basic, the high molecular compounds react with cellulose sodium xanthate, producing insoluble precipitates or coagulants during the operations of mixing and dissolving or they may, by such reaction, cause the spinning solution to solidify or undergo like undesired changes. Therefore, a process of this type wherein the high molecular compounds containing basic nitrogen are xanthogenized beforehand is employed to facilitate the dissolving operation (Japanese Patent No. 236,202) are required. However, even when high-molecular weight substances are mixed with the spinning solution by the application of such a process, ageing progresses in a very short time, and it is necessary to effect spinning in about one-half the time heretofore employed with regenerated cellulose fibers. For this reason, the stability of the viscose mother solution was very difficult to maintain under the conditions found in existing industrial installations for handling regenerated cellulose fibers.

It is an object of this invention to provide a process for producing regenerated cellulose fibers having excellent dyeing properties with respect to dyestuffs for which ordinary regenerated cellulose fibers have substantially no affinity, such as acid dyes and acid mordant dyes, the process making it possible to produce fibers by employing substantially the manufacturing methods already known in the production of regenerated cellulose fibers.

As a result of studies directed to a solution of the above-mentioned difficulties, we have discovered that the dyeability of regenerated cellulose fibers is markedly improved with respect to acid dyes, acid mordant dyes, and the like, and that no difficulty is encountered in the stability of the mother solution after mixing, and that regenerated cellulose fibers can be spun under well-known manufacturing conditions, when use is made of a spinning mother solution prepared by dispersing, in the viscose mother solution, dispersions or powders of water-insoluble starch derivatives containing the basic nitrogen introduced into the starch molecule by etherification with an epoxy compound containing basic nitrogen, ethyleneimine, its derivatives, or β-amino ethyl sulfuric acid.



No difficulties are encountered in the mixing and dispersing of such dispersions or powders in the viscose mother solution nor in the stability of the solution after mixing.

We have discovered that when the dispersions or powders of a water-insoluble derivative of a starch containing basic nitrogen are added to the initial or mother viscose solution prior to ageing or ripening in an amount sufficient to improve the dyeing properties of the fibers produced from the viscose solution in conventional manner, the dispersions or powders can be uniformly dispersed in the viscose solution without difficulty in the course of the usual manufacturing operations in the production of a viscose spinning solution. The ageing or ripening time of the initial or mother viscose solution to obtain the desired fluidity is essentially the same as that for conventional viscose solutions. Moreover, when such dispersions or powders of a water-insoluble derivative of a starch containing basic nitrogen are added to the initial or mother viscose solution, the solution is entirely stable, although the reason for such stability is not fully understood.

The fine particles of a water-insoluble derivative of a starch containing the basic nitrogen to be mixed and dispersed in the initial viscose solution should have a particle size which will not cause difficulty in the usual manufacturing operations applied to the initial solution and in the spinning process. Accordingly, it is preferable that the particle size be less than 30μ. In the method of the present invention, however, fine particles of a particle size ranging from fractions of microns to several microns are readily prepared and satisfactorily mixed and dispersed in the initial viscose solution. The particle size can be varied to meet the requirements of the mechanical properties and dyeability desired in the fibers in accordance with the fineness of the regenerated cellulose fibers manufactured.

The content of basic nitrogen in the starch derivative is suitably more than 0.2%, and the proportion of starch derivative particles mixed with the viscose mother solution is suitably from about 0.05% to 2% by weight of the cellulose present, calculated in terms of the content of the basic nitrogen contained in the derivative. When these proportions are observed, a marked enhancement in the dyeability of the fibers is observed with respect to acid dyes and acid mordant dyes, for which heretofore-produced regenerated cellulose fibers have had no affinity.

The regenerated cellulose fibers produced by spinning the mixed viscose mother solution prepared in accordance with this invention, can be scoured, bleached, and otherwise treated by the same conventional procedures employed in treating regenerated cellulose fibers produced from ordinary viscose mother solutions. The viscose mother solutions to which the above-described starch derivatives are added in accordance with this invention are those conventionally used in the viscose process for producing fibers of regenerated cellulose.

Compounds containing basic nitrogen suitable for use in accordance with the method of this invention include epoxy compounds containing basic nitrogen which may be formed by the reaction of epichlorohydrin with any alkyl or cycloalkyl secondary amine such as diethylamine, dibutylamine, didodecylamine, dihexylamine, methyl-ethylamine, cyclohexylamine, ethyl-butylamine, ethyleneimine, and the like, any of the derivatives of ethyleneimine having the ethyleneimine ring such as those formed by the reaction of ethyleneimine with melamine and phosphoric acid, and the like, and compounds such as β-amino-ethyl sulfuric acid.

The starch usable in the method of the present invention is any of the known starches such as potato starch,

Japanese arrowroot starch, sweet potato starch, wheat starch, rice starch, corn starch, tapioca starch, arrowroot starch (maranta starch), sago starch and like substances having the starch molecular structure. In addition, starch derivatives, such as acetyl starch, may be used.

The invention will be further understood from the following specific examples of practical application. However, it will be understood that these examples are not to be construed as limiting the scope of the present invention in any manner. In these examples, all parts are by weight, unless otherwise indicated.

*Example 1*

Ten grams of wheat starch (particle size: 2–3$\mu$) were thoroughly mixed with 2 g. of 1-dimethyl amino-2,3-epoxy propane and the mixture was reacted in a pressure-proof container at a temperature of 130° C. for a period of 3 hours. When the reaction was completed, the product was removed from the container and was thoroughly washed. There was thus recovered, in finely-divided powder form, a derivative of the wheat starch containing basic nitrogen. This powder was dispersed in water to form a 10% dispersion. The basic nitrogen-content of the powder was 1.8%. The dispersion was mixed and dispersed with constant agitation in a viscose mother or initial solution containing 8% cellulose and 6% caustic soda in an amount such that the quantity of nitrogen was 0.13% based on the cellulose. A viscose spinning solution was thus prepared.

This spinning solution was allowed to age or ripen. When its Hotten-Rot value was 9.5, which was achieved after 50 hours of ripening. Spinning was then carried in the manner employed with conventional viscose spinning solutions. The nitrogen content in the cellulose after spinning was 0.13%.

For purposes of comparison, regenerated cellulose fiber made as specified above by the method of the present invention and conventional viscose fiber, were both dyed with various colors, with the results shown in the following table. In this table, the quantity of dyeing is expressed as the quantity of color absorbed (mg.) per 1 g. of the fibers. The dyeing temperature was 80° C., and dyeing was conducted in accordance with conventional fiber dyeing procedures.

| Dye | Mixed spun fiber, mg./g. | Conventional fiber, mg./g. |
|---|---|---|
| Direct and acid Colors: | | |
| Nippon East Violet BB (2% based on the fiber) | 18.5 | 10.8 |
| Direct Blue 2B (2% based on the fiber) | 19.0 | 11.0 |
| Acid Brilliant Scarlet 3R (4% based on the fiber) | 38.0 | 0.2 |
| Brilliant Milling Green NS (4% based on the fiber) | 39.0 | 1.0 |
| Acid mordant color: | | |
| Sunchromine Brown RH (4% based on the fiber) | 39.0 | 0.5 |

Although improvement in the dyeing characteristics with respect to direct colors was observed, the satisfactory dyeing properties with respect to the acid colors and the acid mordant colors was fully established.

The existence of dyed fine grains may be ascertained upon inspection of the dyed fiber by means of an optical microscope.

*Example 2*

Ten grams of potato starch (particle size: 2–3$\mu$) were mixed with 3 g. of ethyleneimine and the mixture was allowed to react in a pressure-proof container at a temperature of 130° C. for a period of 3 hours. The fine powder of the derivative of potato starch containing basic nitrogen obtained after the completion of the reaction, was thoroughly washed to remove unreacted ethyleneimine. The fine powder was then completely dried at room temperature.



The basic nitrogen content of this powder was 1.5% and the powder was mixed and dispersed with constant agitation in a viscose mother or initial solution containing 8% cellulose and 6% caustic soda in an amount such that the quantity of the powder was 0.1% based on the cellulose calculated in terms of the nitrogen content, i.e. a mixture containing 0.1% nitrogen based on the cellulose. The resultant spinning solution was then allowed to age. When its Hotten-Rot value reached 9.5 after 50 hours of ripening the spinning solution was spun by conventional viscose spinning means. Just before spinning, the viscose solution was observed through an optical microscope to ascertain the extent of dispersion and the particle sizes. No abnormal conditions were found to exist by such observation. After spinning, the fiber was treated by the conventional scouring and bleaching processes. When the fibers were dyed, the results were entirely satisfactory both with acid colors and with acid mordant colors, as well as with direct colors. The colors were almost completely absorbed and the results were substantially the same as those shown in Example 1.

*Example 3*

Ten grams of Japanese arrowroot starch (particle size: 1$\mu$) were mixed with 5 g. of 1-dimethylamino-2,3-epoxypropane of 5 g. in 50 g. of dioxane and the entire mixture was maintained at a temperature of 90° C. for a period of 5 hours during which time reaction occurred. The reaction product was filtered and thoroughly washed. The product, which was in powder form, was a derivative of the starch treated and contained the basic nitrogen. The basic nitrogen content of the fine powder was 1.0%.

This product powder was mixed and dispersed with constant agitation in a viscose mother solution consisting 8% cellulose and 6% caustic soda to provide a proportion of powder to cellulose of 0.12% calculated as the quantity of basic nitrogen.

The resultant spining solution was then allowed to age or ripen. When the Hotten-Rot value of the solution reached 9.5 after 55 hours of ageing, spinning was effected by the usual viscose spinning process. The fibers thus obtained were treated in accordance with conventional scouring, bleaching and dyeing processes. Very satisfactory dyeing results, similar to those shown in Example 1, were obtained. Namely, the fiber exhibited not only fully adequate dyeing properties with direct dyes but also with acid dyes and acid mordant dyes.

*Example 4*

Ten grams of potato starch were added to an aqueous solution containing 5 g. of $\beta$-amino-ethyl sulfuric acid and 2 g. of caustic soda. The entire mixture was treated at a temperature of 130° C. for a period of 2 hours. The resultant fine powder (particle size: 2–3$\mu$) contained basic nitrogen in the amount of 1.0%.

This fine powder was mixed and dispersed with constant agitation in a viscose mother solution containing 8% cellulose and 6% caustic soda so that the proportion of fine powder to the cellulose was 0.1% calculated on the basis of the quantity of nitrogen. The resultant spinning solution was allowed to age or ripen and when its Hotten-Rot value reached 9.5, after 50 hours of ageing, spinning was effected in conventionad manner as in the preceding examples.

The nitrogen content contained in the fibers after spinning was 1.0%. After spinning, the fibers were subjected to the usual scouring, bleaching and dyeing processes. The results of dyeing were entirely satisfactory even when acid dyes were used. The dyes applied were almost completely absorbed in the manner shown in Example 1.

In accordance with the present invention, the water-insoluble starch derivatives containing basic nitrogen can be produced with any desired particle size by selecting a starch for introduction of basic nitrogen which has the

desired particle size, obtained by suitable pulverization, if necessary, so as to conform with the denier of the fiber to be manufactured, as well as the color-fastness and physical properties required in the fiber.

It will be understood that, unless otherwise indicated, and as previously mentioned, conventional operations and conventional apparatus are employed in carrying out the process of this invention including conventional mixing and emulsifying units as well as conventional apparatus used in the viscose rayon process. The conditions and the relative relationships set forth in the examples are those preferred in carrying out the process of the invention but it will be understood that other conditions and relationships may be used within the scope of the invention. The viscose rayon process is a well-known process and is described, for example, in the chapter on Viscose Rayon in Industrial Chemistry by Emil R. Reigel (Reinhold Publishing Corp.). Examples of starches and starch derivatives suitably for use in the invention have been given above but it will be understood that any of the known starches and starch derivatives such as those described in "Starch—Its Sources, Production and Uses," by Charles A. Brautlecht (Reinhold Publishing Corp.), can be used.

It will also be understood that various changes and modifications in addition to those indicated above may be made in the embodiments herein described without departing from the scope of the invention as defined in the appended claims. It is intended, therefore, that all matter contained in the foregoing description shall be interpreted as illustrative only and not as limitative of the invention.

I claim:

1. A process of producing fibers of regenerated cellulose of improved properties which comprises adding to a viscose mother solution water insoluble starch derivatives in finely-divided form, mixing and dispersing said derivatives in said solution and spinning said fibers from the resultant spinning solution, said derivatives containing at least about 0.2% basic nitrogen and being the products resulting from reaction of starch with a member of the group consisting of epoxy compounds containing basic nitrogen, ethylene-imine, the reaction product of ethylene-imine with melamine, the reaction product of ethylene-imine with phosphoric acid, and β-amino ethyl sulfuric acid.

2. A viscose spinning solution effective to provide fibers of regenerated cellulose consisting essentially of a viscose mother solution water containing insoluble starch derivatives in finely-divided form dispersed therein, said derivatives containing at least above 0.2% basic nitrogen and being the products resulting from reaction of starch with a member of the group consisting of epoxy compounds containing basic nitrogen, ethylene-imine, the reaction product of ethylene-imine with melamine, the reaction product of ethylene-imine with phosphoric acid, and β-amina ethyl sulfuric acid.

3. A process of producing fibers of regenerated cellulose of improved properties which comprises adding to a viscose mother solution water-insoluble starch derivatives in finely-divided form, mixing and dispersing said derivatives in said solution and spinning said fibers from the resultant spinning solution, said derivatives containing at least about 0.2% basic nitrogen and being the products resulting from reaction of starch with a member of the group consisting of epoxy compounds containing basic nitrogen, ethylene-imine, the reaction product of ethylene-imine with melamine, the reaction product of ethylene-imine with phosphoric acid and β-amino ethyl sulfuric acid, the amount of said derivatves in said viscose mother solution being at least about 0.05% by weight of the cellulose present, calculated in terms of the content of the basic nitrogen contained in said derivatives.



4. A viscose spinning solution effective to provide fibers of regenerated cellulose consisting essentially of a viscose mother solution containing water-insoluble starch derivatives in finely-divided form dispersed therein, said derivatives containing at least about 0.2% basic nitrogen and being the products resulting from reaction of starch with a member of the group consisting of epoxy compounds containing basic nitrogen, ethylene-imine, the reaction product of ethylene-imine with melamine, the reaction product of ethylene-imine with phosphoric acid, and β-amino ethyl sulfuric acid, the amount of said derivatives in said viscose mother solution being at least about 0.05% by weight of the cellulose present, calculated in terms of the content of the basic nitrogen contained in said derivatives.

5. A process of producing fibers of regenerated cellulose of improved properties which comprises adding to a viscose mother solution water-insoluble starch derivatives in finely-divided form, mixing and dispersing said derivatives in said solution and spinning said fibers from the resultant spinning solution, said derivatives containing at least about 0.2% basic nitrogen and being the products resulting from reaction of starch with a member of the group consisting of epoxy compounds containing basic nitrogen, ethylene-imine, the reaction product of ethylene-imine with melamine, the reaction product of ethylene-imine with phosphoric acid, and β-amino ethyl sulfuric acid, the amount of said derivatives in said viscose mother solution being about 0.05% to 2% by weight of the cellulose present, calculated in terms of the content of the basic nitrogen contained in said derivatives, the derivatives being in particle form having a particle size of at most about 30μ.

6. A viscose spinning solution effective to provide fibers of regenerated cellulose consisting essentially of a viscose mother solution containing water-insoluble starch derivatives in finely-divided form dispersed therein, said derivatives containing at least about 0.2% basic nitrogen and being the products resulting from reaction of starch with a member of the group consisting of epoxy compounds containing basic nitrogen, ethylene-imine, the reaction product of ethylene-imine with melamine, the reaction product of ethylene-imine with phosphoric acid, and β-amino ethyl sulfuric acid, the amount of said derivatives in said viscose mother solution being about 0.05% to 2% by weight of the cellulose present, calculated in terms of the content of the basic nitrogen contained in said derivations, the derivatives being in particle form having a particle size of at most about 30μ.


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# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 50, in the table, first column, line 2 thereof, for "East" read -- Fast --; column 4, line 38, for "spining" read -- spinning --; line 62, for "conventionad" read -- conventional --; column 5, line 51, for "above" read -- about --; line 57, for "-amina" read -- -amino --; column 6, line 5, for "derivatves" read -- derivatives --; line 56, for "derivations" read -- derivatives --.

Signed and sealed this 13th day of August 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents