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MANUFACTURE OF RAYON

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This invention relates to the manufacture of rayon, and more particularly to the manufacture of rayon having a wool-like character. The invention is applicable to any type of regenerated cellulose rayon, but for the sake of convenience will be described in its specific application to yarns produced by the viscose process.

In the textile industry it is frequently desirable to mix rayon yarns with natural wool yarns in the production of fabrics, but this practice has been limited, because of the lack of affinity of rayon yarns for the acid wool dyes employed in the dyeing of natural wool, the result being undesirable differences in coloration of the fabric.

It has been sought to overcome this obstacle by the addition of substances to the viscose spinning solution capable of giving to the rayon a wool-like character and at the same time effect an affinity for acid wool dyes. For this purpose it has been proposed to mix proteinous materials such as casein, albumins and the like with the spinning solution to be spun. However, while the rayon yarns produced in this manner have exhibited the desired affinity for acid wool dyes, they have been so defective from the standpoint of tensile strength that they have been of little practical value. The reason for this low tensile strength may be ascribed to the failure to obtain a homogeneous mixture of proteinous material with the cellulosic solution, the result being that the spun threads have not been of homogeneous structure.

In order to produce an improved spinning solution comprising a homogeneous mixture of viscose and proteinous material, it has been proposed to effect a high dispersion of the protein in the viscose solution by means of suitable apparatus. However, a degree of dispersion sufficient to impart homogeneity to the spinning solution was found to be of little advantage, since it was very unstable and subsequently separated into its components.

It has also been proposed to mix with the viscose spinning solution a water-soluble protein such as glue, gelatine or the like, in order to thus obtain a homogeneous mixture. In this case, however, the water-soluble protein coagulated too slowly in the precipitating bath and therefore was not retained sufficiently in the finished thread. For this reason the yarn spun therefrom lacked the desired wool-like character.

It is an object of the present invention to produce a homogeneous spinning solution from a mixture of a protein with a cellulosic solution.

Another object of the invention is the manufacture of an improved rayon yarn spun from a cellulosic solution containing a protein.

A further object of the invention is a method of manufacturing an improved rayon yarn having a wool-like character.

It has been determined that a homogeneous spinning solution can be produced from a cellulose-protein mixture, for example a viscose-casein mixture, if the casein is subjected to a measured chemical decomposition prior to its addition to the viscose solution. The decomposition of the casein need only be carried out to such an extent that it will mix readily with the viscose and will coagulate rapidly enough in the acid precipitating bath so that it will be carried forward with the spun yarn and become a part thereof. The extent to which decomposition should be carried out in order to produce a homogeneous mixture of casein and viscose may be easily determined by a microscopic study of a portion of the mixture, which should appear homogeneous throughout, and the addition of a dilute acid should instantly cause substantially complete coagulation.

Other proteins that are suitable for use in conjunction with the present process are soy bean proteins and zein.

The decomposition of the proteinous material may be effected by hydrolysis with steam under pressure, or by the use of acids, alkalies, or enzymes. For example, if casein is employed as the proteinous material the casein may be subjected to an alkaline hydrolysis, carried out to such an extent that the reaction product may be homogeneously mixed directly with the viscose solution to be spun.

During the normal manufacture of rayon, the freshly spun yarn is subjected, after leaving the spinning bath, to various after-treating operations for the purpose of washing out impurities, neutralizing acids, desulphurizing, bleaching, etc., wherein alkaline treating agents are employed. Threads spun from solutions of proteins, or from cellulosic solutions containing proteins, are attacked by alkaline solutions, the protein content frequently dissolving out and destroying the wool-like character of the thread. In order to prevent the protein from reacting with the alkaline solution, the thread is usually treated with aldehydes, particularly formaldehyde solutions, to harden the protein content and render the threads resistant to the alkaline after-treatment. It has now been found that this hardening treatment of the yarn can be

eliminated and the protein content rendered insoluble, if the aldehydes or compounds splitting off aldehydes are mixed with the protein solution, preferably prior to its incorporation in the cellulosic spinning solution. The quantity of aldehyde necessary may be determined by any suitable method, for example by the Sorensen titration method, but the amount employed must be such that the free amino groups of the protein are neutralized.

By the direct addition of aldehyde to the protein solution an insoluble methylene compound is precipitated in the yarn upon extrusion of the spinning solution into an acid precipitating bath, so that hardening of the yarn after it has been spun is no longer required.

The amount of protein to be added to the cellulosic spinning solution is dependent upon the effect desired. For example, for ordinary purposes in manufacturing a viscose yarn having an affinity for acid wool dyes, wherein the proteinous material consists of milk casein, from 20% to 25% of casein calculated on the cellulose content of the viscose solution should be employed. Spinning may be effected in any precipitating bath suitable for spinning viscose rayon. The addition of tanning agents to the precipitating bath or special treating baths may be desirable to prevent stickiness of the spun yarn.

Should discoloration of the proteinous material occur during its partial decomposition a reducing agent may be employed. For example, if an alkaline agent is used the reducing agent may be a sulfite, hyposulfite, or the like; whereas, if decomposition is effected in an acid medium, stannous chloride or titanous chloride may be employed. Activated carbon may likewise be employed to prevent discoloration of the solution.

The method by which a homogeneous spinning solution is obtained has already been described, and yarn spun from such a solution is of homogeneous composition. However, I have found that the spun yarn may be greatly improved and its tensile strength increased considerably if the yarn, after spinning, is passed through a second bath containing salts and a small amount of acid, and is subjected therein to a stretch in the neighborhood of 65%.

The following examples will serve to illustrate methods for conducting the present invention.

Example I

180 grams of casein are dissolved in 800 grams of water and 7.2 grams NaOH. To this solution 20 grams NaOH and 5 grams of Na_2SO_3 are added and the mixture heated at 95°C . until a drop of the solution can be homogeneously mixed with several drops of normal viscose solution. The entire reaction should require about 25 minutes and the homogeneity of the solution may be easily determined under the microscope. The alkaline protein solution is thereupon cooled and filtered.

The protein solution is now treated with formaldehyde, the amount required in order to saturate the free amino groups of the protein, as determined, for example, by the Sorensen titration method, being in the ratio of 26 grams of commercial formalin to each kilogram of protein solution.

500 grams of the protein-formalin solution are now mixed with 5 kilograms of normal viscose, containing about 8% cellulose. The mixture is then spun in a precipitating bath which contains 5% MgSO_4 , 15% Na_2SO_4 and 8% H_2SO_4 , and the

so-formed thread is washed acid-free, dried and then desulfurized with Na_2S .

A determination of the nitrogen content of the spun thread indicates that the thread contains 86% of the protein which was added to the viscose solution.

The finished yarn, when viewed under the microscope, exhibits a homogeneous structure throughout, and when dyed with Neolanviolet R (Ciba), dyes in the same dye bath ratio and with substantially the same intensity as natural wool.

Example II

5 kilograms of normal viscose are mixed with an alkaline protein solution obtained by the decomposition of 80 grams of soy bean protein with an excess of NaOH, in the same manner as described in Example I. The spinning solution so-formed is spun in a precipitating bath consisting of 70% H_2O , 10% Na_2SO_4 , 10% MgSO_4 , 8% H_2SO_4 and 2% of the condensation product of cresyl sulfonic acid and formaldehyde at a temperature of 42°C .

The thread is then conducted through a second bath consisting of 10% Na_2SO_4 , 1% H_2SO_4 and 89% water at a temperature of 85°C . and is stretched therein to the extent of about 65%. Thereupon the thread is cut into staple fibers of the desired length, and subsequently washed, desulfurized, dried and finished.

The finished thread, when mixed with natural wool and the whole dyed with acid anthracene red 3 B, exhibits practically no color differences.

Example III

100 grams of casein are boiled with 1 liter of 15% sulfuric acid and 10 c. c. of a solution of titanous chloride in HCl, for two hours in a reflux condenser and the resulting solution decolorized with a little activated carbon. The solution is diluted with an equal volume of water and then neutralized with 30% lye until it reacts light red to methyl red, a thick precipitate resulting. This precipitate is filtered off, washed and dissolved in 400 grams of 2% NaOH. After the addition of 15 grams of commercial formalin the solution is mixed with 5 liters of a normal viscose and further treated as indicated in Example II. The spinning solution is homogeneous throughout.

Having now described the invention, it is to be understood that the method is not to be construed as limited to the particular materials or procedures specified in the foregoing specification, as it is to be limited only by the scope of the appended claims.

What is claimed is:

1. A method of manufacturing viscose threads of wool-like character which comprises dispersing casein in an alkaline solution and heating the dispersion to hydrolyze the casein to an extent sufficient to be homogeneously mixed with a viscose solution, saturating the free amino groups of the casein with formaldehyde, mixing the casein-formaldehyde solution with a viscose solution, spinning the mixture through an acid precipitating bath to form threads therefrom and completing the regeneration of the threads in a second bath maintained at a temperature of about 85°C . while stretching the same, whereby substantially the entire casein content is retained in the thread and may be dyed with acid wool dyes.

2. A method of producing a homogeneous vis-

cose-protein spinning solution comprising partially hydrolyzing a protein of the class consisting of casein, soy-bean protein and zein, said hydrolysis being sufficient to cause the protein to mix homogeneously with a viscose solution determinable under the microscope and sufficient to cause the solution to coagulate immediately with a dilute acid, and mixing the partially hydrolyzed protein with a viscose solution.

3. A method of producing a homogeneous viscose-protein spinning solution comprising par-

5 tially hydrolyzing a protein of the class consisting of casein, soy-bean protein and zein, said hydrolysis being sufficient to cause the protein to mix homogeneously with a viscose solution determinable under the microscope and sufficient to cause the solution to coagulate immediately with a dilute acid, adding an aldehyde to the partially hydrolyzed protein to harden the same and finally mixing the protein-aldehyde solution
10 with a viscose solution.

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