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## FORMATION OF THREADS AND THE LIKE

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This invention relates to a process of producing modified regenerated cellulose products, particularly threads, from viscose containing casein.

In order to produce regenerated cellulose threads which have the dyeing characteristics, the hand, and the insulating properties of wool, casein has been added to the viscose and spun in the usual manner. However, in the method used heretofore there has been a very great loss in casein as much as 50% of the casein, and more. Furthermore, with the usual spinning baths such as those commonly used in the viscose rayon art, the yarn has been very harsh and at best a very poor substitute for natural wool fibers.

It is therefore an object of this invention to provide a process for forming products from viscose containing casein wherein there is no substantial loss of casein from the product.

Another object of this invention is to provide a suitable coagulating bath for viscose containing casein that will enable the production of soft, warm threads that are wool-like in characteristics.

Other objects will be apparent from the description that follows.

These objects are accomplished by coagulating a solution comprising viscose and casein in a bath containing a high concentration of ammonium sulfate, and processing the resulting products in the usual manner.

It is desired in general to use high grades of casein, such as lactic casein or acid casein, in the practice of this invention. Other types of casein may be also used. It is preferred to purify the casein solution further by supercentrifuging. Other purification methods can likewise be used so long as the casein to be added to the viscose is relatively pure. If low quality casein is added to the viscose, spinning difficulties will arise, and the filaments or fibers produced will have less strength.

The amount of casein which may be added to the viscose can be varied within wide limits, depending on the desired properties of the resulting yarn. For instance, as little as 15% or as much as 90% casein, based on the cellulose content of the spinning solution, may be used. By adding to the viscose about 28–40% based on the cellulose content, a product is obtained which dyes like natural wool fibers. Instead of dissolving the casein in an ammoniacal solution, caustic soda or other alkali may be used as the alkalizing agent. The dissolving of the casein in an ammoniacal or alkali solution will, of course, form an alkaline caseinate.

The casein solution is preferably continuously added to the viscose just prior to the spinning operation, such as after deaeration of the viscose and prior to delivery of the spinning solution to a metering pump. Alternatively, the casein may, if desired, be added either continuously or discontinuously at some stage earlier in the process. The latter procedure, however, is not preferred since it increases the tendency of the casein to ferment and increases the difficulty of deaeration due to the formation of foam.

The mixture of viscose and casein is then extruded into a coagulating bath containing a very high concentration of ammonium sulfate, preferably near its saturation point. Under certain circumstances the ammonium sulfate concentration may be as low as 350 grams per liter of bath, and still give very good results. The concentration of sulfuric acid in the coagulating bath may vary quite widely, for instance from 0 grams to 90 grams per liter of bath, though a concentration of 10–20 grams per liter is preferred. The temperature of the coagulating bath is preferably in the neighborhood of 40–50° C., although a temperature as low as 20° C and as high as 75° C. may be used in certain cases. A higher temperature bath is preferred as it permits a higher concentration of ammonium sulfate. The bath should preferably be free of heavy metal salts, such as of lead and iron. It is therefore desirable to purify the ammonium sulfate used, such as by means of sodium sulfide in an alkaline medium or potassium ferrocyanide in an acid medium.

The continuous filaments thus formed may be collected on or in any suitable device, for instance on a bobbin or in a rapidly revolving bucket, or a bundle of filaments merely allowed to pile up in a perforated can wherein they can be regenerated, washed, desulfured, and then drawn from the can along with a number of other filament bundles to form a large rope, and then cut into staple fibers and dried.

The regenerating baths may contain from 5–150 grams of sulfuric acid per liter and suitable quantities of sulfates such as ammonium sulfate, sodium sulfate, zinc sulfate or the like to moderate the action of the acid according to the requirements. A small amount of formaldehyde is also preferably added. If formaldehyde is not used in the regenerating bath, there is a slight loss of casein which amounts to about 5%. With the addition of 2 to 20 grams per liter of

formaldehyde the loss of casein is negligible. The regeneration may be accomplished either in the form of the package in which it is wound, or in a continuous operation by unwinding it from the collecting device and winding it up in another package, or after cutting a bundle of filaments into staple fiber lengths.

In order to more clearly understand the invention, the following example is given as an illustration:

*Example*

Lactic casein containing 2.7% ash as determined by calcination is dissolved to form a solution of the following composition:

| | | |
|---|---|---|
| Casein | kg | 3 |
| Distilled water | liters | 14.8 |
| Ammonia | cc | 350 |

This casein solution is supercentrifuged in an industrial centrifuge of the type sold by Sharples, at a speed of about 19,000 R. P. M. for a sufficient length of time to reduce the ash content of the casein to approximately 1.9%. The supercentrifuged product is filtered through fine cambric. A viscose solution is prepared in the usual manner to contain 7% cellulose and 6% caustic. After the viscose is filtered, deaerated, and ripened to a salt index of about 4 as determined by the process discussed on page 58, paragraph 2, of "Artificial Silk," by Reinthaler-Rowe, published in 1928, the supercentrifuged and filtered casein solution is introduced into the viscose just before the spinning pump by a suitable metering device to produce a viscose solution containing 35% casein, based on the cellulose content of the viscose solution.

The casein-viscose solution is extruded into an aqueous bath containing 440 to 460 grams of ammonium sulfate (previously purified to remove lead and iron salts) and 14 to 16 grams of sulfuric acid per liter of bath. The bath is maintained at a temperature of 50° C. A plurality of 4 denier filaments is produced using a spinneret having 800 holes about 0.004" in diameter and spinning at a speed of 40 meters per minute. The thread may be subjected to tension as usually during coagulation. Bundles of filaments are then collected in a can, where they are subjected to the action of an aqueous regenerating bath containing 300 to 350 grams of ammonium sulfate, 14 to 16 grams of sulfuric acid, and 20 c. c. of formaldehyde per liter of bath. It is preferred to keep the filaments after regeneration for about 15–20 hours in storage prior to washing and desulfuring. After freeing the yarn from acid with soft water, it is desulfured with a 2 gram per liter solution of sodium carbonate, or a 2 gram per liter soap solution. The fibers may be bleached, such as by means of hydrogen peroxide. The filaments and fibers are dried at a temperature below 65° C.

The filaments or fibers so produced have the hand and insulating properties commonly associated with wool and, when dyed with acid dyestuffs, very closely resemble wool in depth of color. The filaments or fibers are highly crenulated in cross section, and this rough surface facilitates the spinning operation of the cut staple. This regenerated cellulose fiber containing about 35% casein has good tenacity, being much better than that of most wool fibers and very much better than that of fibers produced from 100% casein.

Where concentrations "per liter" are referred to, it is understood that a liter of total bath is meant.

While the invention has been described with reference to filaments or threads, it is to be understood that it is also applicable to other articles from viscose and casein, such as films, caps, bands, and the like.

Since the invention is capable of considerable modification and variation from the details given above, any change which conforms to the spirit of the invention is intended to be included in the scope of the appended claims.

We claim:

1. The method of spinning thread which is wool-like in character from a mixture of viscose and casein which comprises adding to a viscose solution a solution of an alkaline caseinate in such an amount that the viscose solution contains at least 15% casein, based on the weight of the cellulose in the viscose, spinning a thread from said viscose solution, and coagulating the thread in a coagulating bath containing at least 350 grams of ammonium sulfate per liter of bath.

2. The method of spinning thread which is wool-like in character from a mixture of viscose and casein which comprises adding to a viscose solution a solution of an alkaline caseinate in such an amount that the viscose contains at least 15% casein, based on the weight of the cellulose in the viscose, spinning a thread from said viscose solution, and coagulating the thread in a coagulating bath containing at least 350 grams of ammonium sulfate and 0 to 90 grams of sulfuric acid per liter of bath.

3. The method of spinning thread which is wool-like in character from a mixture of viscose and casein which comprises adding to a viscose solution a solution of an alkaline casein in such an amount that the viscose contains between 15% and 90% casein, based on the weight of the cellulose in the viscose, spinning a thread from said viscose solution, and coagulating the thread in a coagulating bath containing at least 350 grams of ammonium sulfate per liter of bath.

4. The method of spinning thread which is wool-like in character from a mixture of viscose and casein which comprises adding to a viscose solution, immediately prior to the spinning thereof, a solution of an alkaline caseinate in such an amount that the viscose contains at least 15% casein, based on the weight of the cellulose in the viscose, spinning a thread from said viscose solution, and coagulating the thread in a coagulating bath containing at least 350 grams of ammonium sulfate per liter of bath.

5. The method of spinning thread which is wool-like in character from a mixture of viscose and casein which comprises adding to a viscose solution a solution of an alkaline caseinate in such an amount that the viscose contains at least 15% casein, based on the weight of the cellulose in the viscose, spinning thread from said viscose solution, and coagulating the thread in a coagulating bath substantially free of heavy metal salts and containing at least 350 grams of ammonium sulfate per liter of bath.

6. The method of spinning thread which is wool-like in character from a mixture of viscose and casein which comprises adding to a viscose solution a solution of an alkaline caseinate in such an amount that the viscose contains at least 15% casein, based on the weight of the cellulose in the viscose, spinning a thread from said viscose solution, and coagulating the thread in a coagulating bath containing at least 350 grams

of ammonium sulfate per liter of bath, and subjecting said coagulated thread to a regenerating bath containing formaldehyde.

7. The method of spinning thread which is wool-like in character from a mixture of viscose and casein which comprises adding to a viscose solution a solution of an alkaline caseinate in such an amount that the viscose contains at least 15% casein, based on the weight of the cellulose in the viscose, spinning a thread from said viscose solution, and coagulating the thread in a coagulating bath containing at least 350 grams of ammonium sulfate per liter of bath.

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