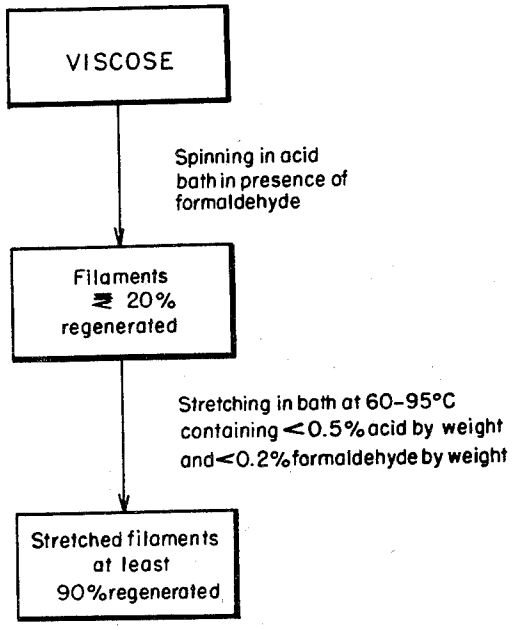
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METHOD FOR MAKING HIGH TENACITY REGENERATED CELLULOSE STAPLE FIBER

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METHOD FOR MAKING HIGH TENACITY REGENERATED CELLULOSE STAPLE FIBER

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This application relates to the manufacture of high tenacity rayon filaments and in particular to the manufacture of high tenacity rayon staple fiber.

In recent years there has appeared on the market a new type of rayon fiber characterized by a high degree of crystallinity, a high tenacity, a more or less circular, non-crenulated cross section and the absence of any appreciable skin-core structure. In general such fibers are made by extruding a substantially unripened viscose, the cellulose of which has a high degree of polymerization, into an aqueous bath relatively low in regenerative power and stretching the filaments while they remain substantially unregenerated.

Various specific techniques have been suggested for carrying out this general process. In particular it has been suggested that formaldehyde be incorporated in the spinning bath to retard regeneration of the filaments and that the filaments be stretched in a subsequent hot bath containing, say, 1–4% acid. This process, when operated under optimum conditions, and particularly when used for the manufacture of continuous filaments can give excellent results. However, it is open to several drawbacks.

Thus, for example, in the manufacture of staple fiber it is necessary that the filaments be substantially entirely regenerated before they are cut. Cutting necessarily involves relaxation and if the filaments, having been stretched, are allowed to relax before they are regenerated, the effect of the stretch is largely lost. The hot acid stretch bath used in prior processes, while it is regenerative for filaments spun in high zinc baths, is not very regenerative for filaments spun in the presence of formaldehyde. The cellulose xanthate methylol ester formed as the result of such spinning must be hydrolysed in regeneration and its hydrolysis is suppressed by the presence of H^+ ions.

Because acid stretch baths are inefficient for regeneration it is necessary either to greatly extend the travel of the filaments through the bath or to add a subsequent separate regeneration step. Neither of these alternatives is very attractive, particularly when staple fiber is being made, since it is ordinarily desirable to cut the staple as soon as possible and conduct the washing, desulfurization and like after treatments on the cut fiber.

In addition, the hot dilute acid bath, which always contains some formaldehyde carried over by the filaments, favors the formation of various undesirable byproducts, notably trithiane, which tend to discolor the threads and are difficult to remove from the bath liquor.

Finally the temperature required in the bath, which is normally just below boiling, demands a considerable heat expenditure and gives rise to fume problems through vaporization of formaldehyde.

In accordance with the invention, these and other problems are overcome by maintaining the stretch bath acid concentration below about 0.5% and normally between about 0 and about 0.4%. By maintaining the acid concentration at this level, regeneration is accelerated, permitting the filaments to be relaxed as soon as they are removed from the bath. Moreover, the formation of trithiane is suppressed and the temperature of the bath is substantially reduced.

The invention therefore envisions, in a method for making high tenacity rayon filaments, wherein viscose is extruded into an aqueous acid coagulating bath in the presence of small quantities of formaldehyde to form filaments, the filaments are removed from said coagulating bath while still not more than about 20% regenerated, and are then stretched in a regenerating bath, the improvement which comprises maintaining the acid concentration of said regenerating bath at less than about 0.5% by weight.

THE VISCOSE

The viscose used in the present process is preferably made from pulp whose cellulose has a high degree of polymerization, (DP), say over 600. Of course, cellulose having lower DP, say 300–600, can be used, at a sacrifice of tenacity in the product. The viscose can be manufactured in conventional manner, but preferably the alkali cellulose is not aged, and the viscose is preferably spun without substantial ageing. It may contain, for example, from 2 to 7% cellulose, and from 2 to 9% NaOH. It may have a salt (NaCl) figure of 12 to 23, a gamma number of not less than 60, normally 75 to 90, or even higher, and a viscosity (ball fall) of 30 to 400 seconds, which will be determined by the cellulose content and DP of the viscose.

SPINNING BATH

The viscose is preferably spun into a spinning bath having relatively low regenerative power. Normally it will contain from say 3 to 9% H_2SO_4. The sodium sulfate concentration is normally allowed to reach the equilibrium value determined by the acid concentration of the bath and the soda concentration of the viscose. Usually it will be from say 4 to 18%. Sinc sulfate is preferably omitted or, if present, is maintained below about 0.2%.

The bath will also contain a small quantity, say between about 0.5 and about 2.0%, preferably between about 0.5 and about 1.0%, of formaldehyde, to retard regeneration. If desired, formaldehyde may be added to the viscose. However, if this is done it is recommended that the techniques described in the copending application of Klein et al., Serial No. 192,322, filed May 4, 1962, and assigned to the assignee of the present application, be employed, i.e. that the formaldehyde be in substantially monomeric form prior to injection and that it be injected just prior to spinning.

The temperature of the spin bath will normally range from say 20° C. to 35° C.

The spinning speed will normally be determined by the viscosity of the viscose. It can range from say 20 m./m. to 50 m./m. The extrusion ratio is preferably around 0.5, say from about 0.2 to 0.7. The residence time of the filaments in the spinning bath will be determined by the spinning speed, extrusion ratio and stretch to be applied. In most instances it will be between about 1 and about 4 seconds.

STRETCH CONDITIONS

As noted above, the viscose is preferably spun at a gamma value of about 75 to about 85. As the coagulated filaments are removed from the spinning bath, their gamma value is still above about 65, or not less than 80% of its value prior to spinning. Thus the filaments are not more than say 20% regenerated, are plastic and are capable of being stretched to a large degree. In accordance with the invention, the filaments are now passed through an aqueous stretch bath containing not more than about 0.5% H_2SO_4 and, while in said bath, are stretched by an amount which may range from say 150% to say 350%.

As noted, the acid concentration of the bath is main-

tained at below 0.5%. There is really no lower limit to the concentration, except that the pH must be 7 or less in order to prevent reformation of the sodium cellulose xanthate. Conveniently, fresh water is constantly added to the bath and a small amount of bath is continually removed. The small amount of acid carried over by the thread is relied upon to maintain the bath on the acid side. Under normal circumstances the acid concentration will be less than about 0.2%, say 0 to 0.1%.

The foregoing figures are, of course, given in terms of sulfuric acid. It is possible to operate with other acids, and in this case the values defined above may be converted to the equivalents in terms of hydrogen ions formed.

It is also important to maintain the formaldehyde content of the bath below that which would retard regeneration, bearing in mind that some formaldehyde is carried into the bath with the filaments. In general the formaldehyde concentration should be kept below about 0.2%, usually below about 0.1%. Under the spinning conditions described, these limits are normally automatically reached when the acid concentration in the stretch bath is maintained constant by continually withdrawing a small quantity of the bath and replacing it with fresh water.

As noted, the temperature of the stretch bath may be maintained considerably below that normally required. For example, a temperature of 60 to 80° C. is in general adequate, though higher temperatures up to say 95° C. may be used.

The filaments are maintained in the stretch bath until they are at least 90% regenerated, i.e. until their gamma values have decreased to say 7 to 8.

After removal from the bath, the filaments may be cut up into staple, if desired, or processed as continuous filaments in accordance with conventional practice.

The invention will be further described with reference to the following specific examples which are given for purposes of illustration only and are not to be taken as in any way limiting the scope of the appended claims.

Example I

A viscose containing 5.0% cellulose, 6.5% NaOH, and having 52% carbon disulfide based on cellulose ($\gamma=79$) was spun at a salt figure of 19.0 and a ball fall viscosity of 130 seconds into an aqueous spinning bath containing 6.15 H_2SO_4, 12% Na_2SO_4 and 0.8% HCHO. The bath temperature was about 27° C. After a total residence time in the spinning bath of about 1 second the filaments, still less than 20% regenerated, were removed from the spinning bath and stretched 260% in a secondary bath. The secondary bath had a temperature of 80° C. It contained about 0.1% H_2SO_4 and had a pH of somewhat less than 2. It contained about 0.1% HCHO.

After removal from the stretch bath, the filaments were cut up to form staple fiber, washed in the usual manner and dried. The final product (1.55 denier) had a dry tenacity of 5.27 g./den., a dry elongation of 6.9%, a wet tenacity of 4.20 g./den. and a wet elongation of 7.1%.

Example II

A viscose containing 3.0% cellulose, 4% NaOH, and having 52% CS_2 on cellulose was spun at a salt figure of 20 into a bath containing 6.8% H_2SO_4, 6% Na_2SO_4 and 0.5% HCHO at 27° C. It was removed while having a gamma number of 85 and stretched 300% in the secondary bath maintained free from CH_2O and H_2SO_4, cut into staple, washed, and dried. The final product (1.20 denier) had a dry tenacity of 5.05 g./den., a dry elongation of 4.9%, a wet tenacity of 3.52 g./den. and a wet elongation of 5.9%.

The fiber obtained in Examples I and II was white and showed no tendency toward yellowing or other discoloration. Small quantities of trithiane could be detected in the effluent from the bath. However, these were much less than normal and because of the low acid content of the bath, it was economical to throw the effluent away, thus avoiding the problem of separating the impurity.

What is claimed is:

1. In a method for making high tenacity rayon filaments wherein viscose is extruded into an aqueous acid coagulating bath in the presence of small quantities of formaldehyde to form filaments, the filaments are removed from said coagulating bath while still not more than 20% regenerated and are then stretched in an aqueous stretch bath having a temperature between 60° C. and about 95° C., the improvement which comprises maintaining the acid concentration of said stretch bath at less than 0.5%, and the formaldehyde concentration at less than 0.2%, by weight and maintaining the filaments in said secondary bath until they are at least 90% regenerated.

2. The method claimed in claim 1 wherein the stretch bath contains less than 0.1% by weight formaldehyde.

3. The method claimed in claim 1 wherein the stretch bath has a temperature of between about 60° C. and about 80° C.

4. In a method for making high tenacity regenerated cellulose staple fiber wherein viscose is extruded into an aqueous acid coagulating bath in the presence of small quantities of formaldehyde to form filaments, the filaments are removed from the coagulating bath while not more than 20% regenerated, are then stretched in an aqueous stretch bath having a temperature between about 60° C. and about 95° C. and are subsequently cut up to make staple, the improvement which comprises maintaining the acid concentration of the stretch bath at less than 0.5%, and the formaldehyde concentration at less than 0.2%, by weight and maintaining the filaments in said stretch bath until they are at least 90% regenerated.

5. The method claimed in claim 4 wherein the stretch bath contains less than 0.1% by weight formaldehyde.

6. The method claimed in claim 4 wherein the stretch bath is at a temperature between about 60° C. and about 80° C.

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