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VISCOSE SPINNING PROCESS AND BATH

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This invention relates to an improved method for spinning high tenacity viscose (regenerated cellulose) products.

High tenacity viscose rayon has been produced by extruding viscose into an acid-salt bath and stretching the coagulated but only partially regenerated yarn thus produced (see U.S Patent No. 2,192,074), and also by extruding viscose into a strong acid plasticizing bath containing no added salt and stretching the plastic acid yarn (see, for example, U.S. Patents No. 1,683,199, No. 1,683,200, No. 1,820,811, No, 1,881,740, No. 2,133,715, etc.).

Various attempts have been made to reduce the acid concentrations of the latter high-acid spinning process. For example, it has been proposed to spin in a mixture of acetic and sulfuric acids (see U.S. Patent No. 1,949,919) and also to spin in a sulfuric acid bath saturated with sodium or ammonium bisulfates (see U.S. Patent No. 2,044,885).

Despite the very extensive amount of research carried out over the years, the rayon industry did not adopt the high-acid or so-called "Lilienfeld" process, because the high strength yarn produced has such a low elongation that it cannot be used as a tire yarn or in the other fields where high tenacity yarn having good fatigue is required.

Recently it was again attempted to revive the "Lilienfeld" process. According to one approach (see U.S. Patent No. 2,586,796) it is necessary to start out with cotton linters pulp containing no more than a small amount of very short cellulose chains, to avoid excessive chain degradation while producing the viscose, to xanthate to a definite degree (gamma value), and finally to correlate gamma value and percent sulfuric acid in the spin bath by an empirical formula. The spin baths of this patent contain 60–70% sulfuric acid, and the process therefore has many of the disadvantages of the old high acid process.

During the war there was a German attempt to improve the high acid spinning (Lilienfeld) process (see French Patent No. 901,431 and German Patent No. 838,936). However, the process developed is still a modified "Lilienfeld" process with many of its inherent disadvantages.

During the same period there was also an attempt made in Great Britain to revive the "Lilienfeld" spinning process (see, High-Tenacity Viscose Rayon, by L. Rose, Journal of the Society of Dyers and Colourists, Volume 61, pages 113–118, 1945), but, as far as is known, the development has been abandoned.

Thus, to date, despite extensive early and recent research, the industry has not been able to use the high-acid "Lilienfeld" spinning process to obtain a commercially acceptable product.

Unexpectedly it has been found that regenerated cellulose products having outstanding physical properties may be obtained by extruding viscose into a high-acid type bath containing a small amount of a dissolved aluminum salt. Although aluminum salts are not very soluble in the Lilienfeld-type baths, nevertheless, unexpected beneficial effects are produced by small additions thereof to the spin bath, well within the solubility limits thereof. Thus I have found unexpectedly that even very small amounts of an aluminum salt in a high-acid bath exert

an unusual effect on the spinning process. While I shall disclose sulfuric acid-aluminum sulfate baths in my specific examples, it is to be understood that the spin bath may contain any acids capable of plasticizing regenerated cellulose, for example, sulfamic acid, one of the acids disclosed in U.S. Patent No. 1,881,740, etc., together with an appropriate aluminum salt, alum, etc. One advantage of such use of an aluminum salt is that the acid content of the bath may be reduced from the 60–70% sulfuric acid generally required when only acid is used without losing the aforesaid beneficial effect of the aluminum ions present in the bath. The high acid-aluminum salt spin bath is preferably maintained at room temperature or lower, the freshly formed threads should be stretched while they are still acid, and they should be quenched quickly with cold water to avoid any possible degradation of the cellulose. I prefer to use "green," i.e., substantially unripened viscose and a spinning modifier in combination therewith.

As is well-known in the art, the "high-acid" or "Lilienfeld-type" viscose spin bath is an acid solution of sufficient strength to plasticize the cellulose precipitated therein so that it can be stretched strongly while still in the bath or shortly thereafter. These baths usually contain no added salt. The spin bath should contain not less than 50% sulfuric acid, preferably well over 55% (U.S. 1,683,199 and French 901,431). To obtain the full benefit of the Lilienfeld process, the spin bath should contain at least 60% sulfuric acid (U.S. 2,586,796 and German 838,936). Other acids, or a mixture of acids, may be used in the plasticizing bath. For example, a high-acid viscose spin bath may contain 25–40% hydrochloric acid, 60–90% nitric acid, 67.5–99% phosphoric acid, or 60–90% arsenic acid (U.S. 1,881,740). The spinning process has been modified in various ways so that the acid content of the high-acid type spin bath can be reduced. Thus, if the viscose contains no more than 5% sodium hydroxide the spin bath may contain 45–55% sulfuric acid (U.S. 1,683,200), if less than 25% carbon bisulfide is used in the xanthation step the spin bath may contain 40–50% sulfuric acid (U.S. 1,949,919), and if the alkali cellulose aging time is reduced substantially from the aging time normally used the spin bath may contain as low as 55% sulfuric acid (U.S. 1,820,811). These proposals were not generally adopted because, among other things, the required modifications of the viscose process led to difficulties.

The addition of sodium aluminate to viscose to be spun in a high acid type bath has been suggested (U.S. Patents No. 1,683,199, No. 1,683,200, and No. 1,820,811), but I know of no disclosure of the use of an aluminum salt in such spin baths, although the patents disclose the use of other salts. Patents mentioned earlier describe the use of acetic acid (see U.S. Patent No. 1,949,919), and sodium and ammonium bisulfates (U.S. Patent No. 2.044,885) in a 10–30% sulfuric acid bath. As has been pointed out, none of these modified high acid baths has gained acceptance.

It is therefore an object of the present invention to provide an improved method for producing viscose products, such as yarns, ribbons, films, etc.

Another object is to provide an improved method for spinning high tenacity viscose rayon.

A further object is to provide an improved method for producing regenerated cellulose products by extruding viscose into an acid-aluminum salt spin bath.

A still further object is to provide an improved method for spinning "green" viscose.

Another object is to provide an improved method for spinning viscose rayon in the presence of a dissolved and/or dispersed spinning modifier.

Still another object is to provide an improved high acid-type viscose spin bath.

Other objects of the invention will appear hereinafter.

The objects of this invention, in general, are accomplished by extruding viscose into a spin bath containing acid as described earlier to maintain the threads formed therein in a plastic condition so that they can be stretched strongly while still in the bath, or shortly thereafter and an aluminum salt. An improved product is obtained if the viscose is "green" or substantially unripened and has a high salt point, and if in the production of the viscose high quality cellulose is used, and care is taken to avoid excessive degradation of the cellulose chains. The aluminum salts have an acid reaction, and thus permit a reduction in the free acid content of a plasticizing type spin bath and, the aluminum ions exert a special, beneficial effect on the viscose during the regeneration thereof. It is desirable that the viscose used should have a gamma value, or degree of xanthation (number of hydroxyl groups substituted by —CSS— groups per 100 glucose, or $C_6H_{10}O_5$ units), of about 40 to 50, preferably of about 44 to 47.

"Green," i.e., substantially unripened viscose suitable for use in my improved spinning process is described, for example, in United States Patents No. 2,581,835 and No. 2,598,834.

Viscose produced by the methods described in United States Patent No. 2,586,796 and in German Patent No. 838,936 contains a minimum number of very short cellulose chains and has a gamma value of 40–50, and is also suitable for use in my process.

Viscose practically free of strongly degraded cellulose chains and especially suitable for use in my spinning process may be prepared, for example, as described in United States Patent No. 2,586,796 and German Patent No. 838,936, cited above, and in United States Patents No. 2,592,355 and No. 2,732,279.

Spinning modifiers suitable for use, singly or in combination, in my improved process must, obviously be sufficiently stable in the viscose and in the spin bath to exert their specific beneficial effect. The modifiers may be added to the viscose, to the spin bath, or to both, as convenience may dictate. It will be understood that a modifier added to the viscose will gradually accumulate in the spin bath and the spinning will then take place in the presence of the modifier.

Among the spinning modifiers suitable for use in my improved process are the aliphatic monoamines disclosed in United States Patent No. 2,535,044, the monoamines disclosed in United States Patent No. 2,535,045, the quaternary compounds disclosed in United States Patent No. 2,536,014, the N-substituted dithiocarbamates disclosed in United States Patent No. 2,696,423, the diaryl thioureas disclosed in United States Patent No. 2,777,775, the polyethylene polyamines disclosed in United States Patent No. 2,784,107, the dithiocarbamates disclosed in British Patent No. 739,072, the mercaptothiazoles disclosed in British Patent No. 755,469, and quinoline as disclosed in British Patent No. 765,905. The polyalkylene glycols, their ethers and esters, as disclosed in United States Patent No. 2,397,338, in British Patent No. 557,218, and in copending application Serial No. 458,018, filed September 23, 1954, are also suitable spinning modifiers.

The spinning modifiers used here are not to be confused with the spinning assistants used in minute amounts (0.001%) in high zinc baths to prevent spinnerette incrustation. While 0.01% or a much smaller amount of a spinning assistant produces satisfactory results, it is generally necessary to use 0.10% or more, preferably at least 0.15%, of the spinning modifier to improve the yarn properties.

The following examples illustrate various methods of applying the principles of the invention.

Example 1

Viscose prepared according to Example 1 of United States Patent No. 1,683,200 was extruded into a spin bath at 22° C. containing about 55% H_2SO_4 and about 0.5% $Al_2(SO_4)_3$. The plastic product was stretched in the acid condition about 200%, quickly quenched with cold water, and then further washed, finished, and dried as usual.

The product had high tensile strength and good physical properties.

Among others, the viscoses disclosed in the other examples of United States Patent No. 1,683,200, as well as those disclosed in United States Patents No. 1,683,199, No. 1,820,811, and No. 1,881,740, may be spun in the above bath.

Example 2

Viscose prepared according to Example 1*a* of United States Patent No. 2,044,885 was extruded into a spin bath at 20° C. containing about 55% H_2SO_4 and about 1% $Al_2(SO_4)_3$. The plastic product was stretched about 200% while still in the acid condition, was quickly quenched with cold water, further washed, finished, and dried as usual.

The product had good strength and physical properties. The properties are improved if the viscose used contains 0.2% of triethylamine, or one of the other spinning modifiers disclosed in United States Patent No. 2,535,044.

Example 3

Viscose prepared according to Example 5 of United States Patent No. 2,598,834 was extruded into a spin bath at about 15° C. containing about 55% H_2SO_4 and about 0.5% $Al_2(SO_4)_3$. The plastic product was processed as set forth in the previous examples.

The properties are improved if the spin bath contains 0.15% of dibutylamine, or one of the other spinning modifiers disclosed in United States Patent No. 2,535,045.

Example 4

Viscose prepared according to Example 2 of United States Patent No. 2,586,796, having the analytical properties therein disclosed, and containing 0.2% tetramethylammonium chloride, was extruded into a spin bath at 12° C. containing about 53% H_2SO_4 and about 0.5% $Al_2(SO_4)_3$, stretched about 210% while still acid, quickly quenched with cold water, further washed, finished, and dried in conventional manner.

The high tenacity regenerated cellulose had good physical properties.

One of the other spinning modifiers disclosed in United States Patent No. 2,536,014 may be used in the viscose in place of tetramethylammonium chloride.

Example 5

Viscose prepared as described in German Patent No. 838,936 was extruded into a spin bath at 15° C. containing about 55% H_2SO_4 and 0.75% $Al_2(SO_4)_3$, stretched about 200% and after-treated in conventional manner as set forth above to produce regenerated cellulose of high strength.

The yarn properties are improved when the viscose contains 0.25% benzyltrimethylammonium hydroxide, or one of the other modifiers disclosed in United States Patent No. 2,536,014.

It is possible to increase the elongation of the finished product by allowing the yarn to relax while still acid, as disclosed in United States Patents No. 2,078,339 and No. 2,586,796, and in French Patent No. 901,431.

The spin baths disclosed herein are the aqueous baths used by the industry for reasons of economy. However, the beneficial results of my invention are obtained with high acid type spin baths containing a non-aqueous, water-soluble solvent such as the water-soluble alcohols, i.e., methanol, the glycols, etc., or an aqueous solution thereof.

As is well-known, basic aluminum residues are tena-

ciously retained by cellulose which has been treated with an aluminum salt. The presence of even small amounts of such aluminum residues may cause dyeing difficulties, but their hydrophobic properties may offer an actual advantage if the regenerated cellulose yarn, or fabric made therefrom, is not to be dyed. Unevenly distributed aluminum residues, or spots, may be deliberately left in the yarn so that novel color effects will be produced when fabrics knitted or woven from such yarn are dyed. Treatment with hot dilute acid solution before the yarn is first dried will remove aluminum residues.

My improved spinning process may be used in connection with any of the conventional methods (spool, pot, continuous, etc.) of producing viscose rayon. It is especially useful in connection with the continuous method and apparatus described in co-pending application, Serial No. 389,421, filed October 30, 1953, now U.S. Patent No. 2,898,627.

It is intended to make by reference the disclosures of the patents cited throughout this specification a part of the invention.

The process may obviously be modified without departing from the scope of the invention as set forth in the appended claims.

What is claimed is:

1. In a process for producing regenerated cellulose by extruding viscose into a high acid spin bath, the improvement which comprises extruding said viscose into a spin bath comprising an acid solution of strength sufficient to plasticize regenerated cellulose precipitated therein, and an aluminum compound dissolved therein.

2. In a process for producing regenerated cellulose by extruding viscose into a high acid spin bath, the improvement which comprises extruding said viscose into a spin bath comprising at least 50% by weight of sulfuric acid, and an aluminum compound dissolved therein.

3. In a process for producing regenerated cellulose by extruding viscose into a high acid spin bath, the improvement which comprises extruding said viscose into a spin bath comprising at least 50% by weight of sulfuric acid, and at least about 0.5% of an aluminum compound dissolved therein.

4. A process in accordance with claim **1** in which the spinning takes place in the presence of a small amount of spinning modifier.

5. A process for producing regenerated cellulose products comprising extruding viscose prepared from cellulose containing less than 25% by weight of molecular chains with a degree of polymerization below 500, and less than 4% by weight of molecular chains with a degree of polymerization below 250, said viscose being prepared from alkali cellulose having a mean degree of polymerization after ripening of at least 450, into a spin bath comprising an acid solution of strength sufficient to plasticize regenerated cellulose precipitated therein, and an aluminum compound dissolved therein.

6. A process in accordance with claim **5** in which the spin bath contains at least about 0.5% of an aluminum compound dissolved therein.

7. A process in accordance with claim **5** in which the spinning takes place in the presence of a small amount of a spinning modifier.

8. A process in accordance with claim **5** in which the spinning takes place in the presence of a small amount of a spinning modifier, and at least about 0.5% of an aluminum compound dissolved in the spin bath.

9. In a process for producing regenerated cellulose products in which a viscose prepared from cellulose containing less than 25% by weight of molecular chains with a degree of polymerization below 500, and less than 4% by weight of molecular chains with a degree of polymerization below 250, via alkali cellulose having a mean degree of polymerization after ripening of at least 450, is extruded into a plasticizing spin bath, the improvement which comprises extruding such viscose, containing a spinning modifier, into a spin bath comprising at least about 50% by weight of sulfuric acid, and an aluminum compound dissolved therein.

10. A process in accordance with claim **9** in which the viscose has a gamma value between 40 and 50.

11. A process in accordance with claim **5** in which the viscose has a gamma value between 40 and 50.

12. A process in accordance with claim **9** in which the viscose has a gamma value between 44 and 47.

13. A viscose spin bath capable of plasticizing cellulose regenerated therein comprising at least 50% by weight of sulfuric acid, a small amount of an aluminum compound and a small amount of a spinning modifier, said compound and modifier being ionized in said bath.

References Cited by the Examiner

UNITED STATES PATENTS

1,949,919	3/34	Parker	18—54
2,276,315	3/42	Kirk	8—94.29
2,364,273	12/44	Cox	18—54
2,403,437	7/46	Kohorn	18—54
2,535,045	12/50	Cox	18—54
1,699,983	1/55	Drisch et al.	18—54
2,805,119	9/57	Studer	18—54
2,852,333	9/58	Cox et al.	

OTHER REFERENCES

Mellor: Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. 5, published in 1924 by Longmans, Green & Co., page 336 is relied upon.

Rayon Journal, vol. 2, page 24, column 2, February 1927.

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