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PROCESS OF MANUFACTURING REGENERATED CELLULOSE FIBER

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The present invention relates to a process for the manufacture of regenerated cellulose articles such as fibers, films, and tubes by the viscose process. More particularly, it relates to a process for preparing a high quality grade of rayon staple.

This application is a continuation-in-part of Serial No. 75,062, filed December 7, 1960, and now abandoned.

It is well known that the physical properties of regenerated cellulose fibers, such as tensile strength, water swelling, abrasion resistance, etc., are controlled predominantly by the degree of orientation and lateral order of the cellulose chains. Regular viscose rayon staple fiber has a moderate degree of crystallinity, but poor orientation resulting from the nature of the spinning process. Relatively few crystallites are produced during regeneration of the cellulose xanthate and these grow rapidly without very much orientation.

Early high tenacity rayon employed zinc to retard xanthate regeneration and high stretch to orientate the crystallites before completing the regeneration of the cellulose. This resulted in slightly smaller, but a greater number of, crystallites which were more highly orientated along the fiber axis. More recently, high tenacity rayons, and more specifically those intended for pneumatic tires, have employed viscoses in which the cellulose has a higher degree of xanthate substitution and which contain retarders often referred to as "viscose modifiers" or "spinning modifiers," generally selected from the classes consisting of polyoxyethylene glycol derivatives or simple aliphatic amines, which delay the regeneration of xanthate groups still further. Tire rayons spun from this type of viscose are very highly oriented and have still smaller crystallites. Compared to regular textile rayon, such tire yarns have many more interlinks between crystallites per unit volume. With small crystallites of the order of 450 A. long, a molecule of average D.P. (degree of polymerization), e.g., 350, which has a length of about 1800 A. has a much greater chance of running between two or more crystallites in tire yarn than in a textile rayon in which the crystallite may be 600 A. long and the average molecule has a D.P. of about 200 and a length of 1,000 A. Hence, such tire yarns are tougher and resist abrasion and stretch-compression mechanical action to a very high degree. Nonetheless, it is the case that such tire yarns and fabrics made from them are, when wet, easily stretched (normal rayon textile staple fiber and high tenacity rayon tire yarn both have an elongation at rupture in the wet state of about 25%, while cotton has an elongation at rupture in the wet state of about 12%) or shrunk, depending on the amount of tension applied to the yarn or fabric while it is dried and attempts to produce a superior rayon staple by employing modern tire yarn viscoses and spinning processes have not met with much success.

It is, therefore, an object of the present invention to produce artificial fiber of enhanced properties, i.e., of physical properties more closely approaching those of natural cellulose fiber.

It is a further object to produce a viscose rayon fiber which more closely resembles cotton, particularly in its ability to resist shrinkage or stretching when wet, or, in other words, which has a high wet modulus. Of course, "high wet modulus" is a relative term as here employed, since it is not desirable to produce completely inflexible yarns which impart to garments made therefrom no more elasticity than results from the weave employed.

There are processes described in the patent literature for producing yarns possessing the desirable degree of elongation discussed in the above paragraph. However, such yarns are generally produced by spinning processes including the steps of coagulating of cellulose xanthate, applying very high stretch to the cellulose xanthate thread, and regenerating the stretched thread, and they have, invariably, been too brittle. Another object of the present invention is, therefore, the production of high wet modulus rayon fibers which are not brittle, but which have abrasion resistance in the class of high tenacity tire rayon.

After successive launderings and ironings, cellulose fabrics, both natural and artificial, show gradual reduction in degree of polymerization of the cellulose molecules until finally wet tenacity is affected and the garment is mechanically damaged during laundering. Still another object of the present invention is to produce yarns having high wet tenacity similar to cotton.

"Secondary swelling" is defined as the ratio of centrifuged wet weight of yarn to oven dry yarn weight and yet another object of this invention is to produce yarns which more closely resemble cotton in secondary swelling.

According to a broad aspect of this invention there is provided a process of manufacturing regenerated cellulose fiber suitable for use as a substitute for natural fibers including cotton fibers in textiles to be laundered comprising spinning viscose into a spinbath having a temperature in the range of about 0° C. to 40° C., the viscose having a gamma value in the range of about 45 to 65 and a cellulose to sodium hydroxide ratio in the range of about 1.05/1 to 1.70/1 parts by weight and the spinbath having sodium sulfate and sulfuric acid concentrations in grams per liter in accordance with the equations

Na_2SO_4=240–130 (weight of cellulose/weight of sodium hydroxide)

H_2SO_4=150–60 (weight of cellulose/weight of sodium hydroxide)

the fiber resulting from the spinning having a wet initial modulus at 5% strain of from about 10 to 20 grams per denier, a wet breaking tenacity of from about 1.57 to 2.8 grams per denier, and a secondary swelling of from about 1.70 to 1.90. In other words, it has now been found that rayon yarns having lower tenacities, in dry and wet states, but having at the same time lower elongations at rupture, are produced by reducing the temperature of the acid spinbath into which the viscose is extruded from about 65° to about 40° C. to 0° C. and, preferably to 25° C. This is surprising, since those familiar with this art would not expect to obtain yarn at all when the temperature of the spinbath used, in for instance, tire yarn spinning is dropped from 65° to 25° C., the rates of the relevant chemical reactions being almost halved for each 10° C. decrease. Moreover, the spinning speeds have been varied between 30 and 70 meters per minute with surprisingly little influence on the resulting desirable physical properties of the yarn.

Further, it has been found that the spinbath temperature lowering step of the process of the present invention produces its desirable effects more pronouncedly if the viscose to be spun is young or underripe, i.e., has a gamma value in the range of 45 to 65 and, preferably, in the range of 50 to 60, and has a reduced alkalinity. A suitable ratio of cellulose to sodium hydroxide in the viscose falls in the range of 1.05/1 to 1.70/1 parts by weight and a preferred ratio of cellulose to sodium hydroxide in the viscose falls in the range of 1.15/1 to 1.30/1 parts by weight.

In the spinbath employed in accordance with the invention, the sodium sulfate concentration should be kept at the lowest possible value commensurate with caustic concentrations in the viscose. Higher concentrations of sodium sulfate demand higher acid concentrations and it has been found, empirically, that the preferred concentrations of sodium sulfate and sulfuric acid are related to the weight ratios of cellulose to sodium hydroxide and are in grams per liter, given by the following formulae:

Na_2SO_4=240–130 (cellulose/sodium hydroxide)
H_2SO_4=150–60 (cellulose/sodium hydroxide)

Again, in the spinbath, while it is not essential, it is preferable to include zinc sulfate for regeneration retardation and to permit the use of higher godet stretches in the hot dilute acid bath. Godet stretches of 80% or somewhat less and, preferably, 125% for spinning viscosities in the range of about 40 to 300 poises and, preferably, 90 to 150 poises are also in accordance with the practice of the process of the present invention. For optimum results from about 2 to 75 grams per liter of zinc sulfate are employed in the spinbath and, where modifiers such as polyoxyethylene glycol derivates and aliphatic amines or mixtures of both have been added to the viscose to impart stretching ease in amounts ranging from 1% to 4% by weight, 50 grams per liter of zinc sulfate is preferred.

According to another aspect of this invention there is provided regenerated cellulose fiber suitable for use as a substitute for natural fibers including cotton fibers in textiles to be laundered having a wet initial modulus at 5% strain of from about 10 to 30 grams per denier, a wet breaking tenacity of from about 1.57 to 2.8 grams per denier, and a secondary swelling of from about 1.70 to 1.90, said fiber being made by a process comprising spinning viscose into a spinbath having a temperature in the range of about 0° C. to 40° C., the viscose having a gamma value in the range of about 45 to 65 and a cellulose to sodium hydroxide ratio of about 1.05/1 to 1.70/1 parts by weight and the spinbath having sodium sulfate and sulfuric acid concentrations in grams per liter in accordance with the equations.

Na_2SO_4=130 (weight of cellulose/weight of sodium hydroxide)
H_2SO_4=150–60 (weight of cellulose/weight of sodium hydroxide)

For a further understanding of the present invention, reference should be had to the following examples:

EXAMPLE 1

Natchez Tyrecell wood pulp was steeped in 18% caustic soda solution at 22° C. for 45 minutes, pressed to 3.1 times the original bone dry weight, and then shredded for 60 minutes at 26° C. After aging the alkali cellulose for 24 hours at 26° C., it was xanthated with 39% carbon disulfide by weight based on the cellulose content of the alkali cellulose. Xanthation was carried out for 75 minutes at 28° C. The crumbs were then dissolved to form a 7% cellulose, 6% caustic viscose. At the end of the mixing cycle, 2% based on cellulose content in viscose of comercially available phenol ethoxylated with 15 moles of ethylene oxide (a product sold by Atlas Power Co. as G 1707) and 1% of commercially available beef tallow amines ethoxylated with 20 moles of ethylene oxide (a product sold by Atlas Powder Co. as G3780) were added to the viscose. The viscose was kept cool during filtration and deaeration in order to preserve the degree of xanthate substitution.

At spinning time, the viscose had a xanthate substitution of 0.58 group per glucose unit, generally referred to as 58 gamma (degree of xanthate substitution×100), and a total sulfur content of 2.1%. Ripening or maturity, as determined by the NaCl salt test, was 10–11. The viscose was extruded through 0.0020" diameter holes into a spinning bath containing 80 gm./liter H_2SO_4, 50 gm./liter $ZnSO_4$, 80 gm./liter Na_2SO_4, and having a specific gravity measured at 20° C. of 1.165. Bath temperature was 25° C. The thread was immersed 28 inches in the bath, then was stretched 125% between two godets while immersed 30 inches in a bath containing 10 gm./liter H_2SO_4, 10 gm./liter $ZnSO_4$, and 15 gm./liter Na_2SO_4 at 92° C. The yarn was then immersed in 60 gm./liter H_2SO_4 at 60° C. with 2.1% relaxation to reduce the zinc content of the yarn, then washed with hot water and collected in skein form at 50 meters per minute and dried in this form tension-free.

The properties of the rayon made by the process described herein are given in column 3 of Table I below, in comparison with the properties of regular textile yarn, high tenactity tire yarn, and cotton.

Table I

	Conventional Textile Rayon Staple	Tire Cord Rayon	Yarn from Example	Cotton
Denier	1.5	1.5	1.5	1.7
Conditioned tenacity, gm./denier	2.1	4.8	4.2	2.9
Wet tenacity, gm./denier	1.2	3.7	2.8	3.0
Conditioned elongation, percent	18	20	8.5	8.5
Wet elongation, percent	24	28	10.5	12.5
Wet initial modulus at 5% strain, gm./denier	4	4	22	10
Secondary swelling	1.90	1.85	1.70	1.38
Degree of polymerization	180	400	375	~2,000

EXAMPLE 2

Viscoses were prepared in similar fashion to that of Example 1, except that aging was carried out for 24 hours at 23° C., different viscose compositions were employed as shown in the Table II below, and the spinbath was closer to the composition normally used for tire yarn spinning. The object of this example was to show the importance of spinbath temperature and caustic content in viscose in changing the character of the yarn from high tenacity tire yarn to the high wet modulus yarn of the present invention having lower tenacities than tire yarn.

Table II

Viscose: 6% cellulose; 39% CS_2; 3% G1707 on cellulose; 70–90 poises viscosity.
Spinbath: 80 gm./liter H_2SO_4; 80 gm./liter $ZnSO_4$; specific gravity=1.235.
Spinning: Yarn collected at 40 meters/min.; 28 inches immersion; 100% stretch.

Acid Temp.	Percent NaOH in Viscose	Tenacity, gm./denier		Elongation, Percent		Wet Modulus at 5% Strain	Secondary Swelling
		Air Dry	Wet	Air Dry	Wet		
25°	5.5	3.21	1.83	9.0	10.6	12.6	1.86
	4.5	2.38	1.79	6.7	9.8	15.8	1.84
35°	5.5	4.03	2.36	11.9	15.4	11.2	1.77
	4.5	2.35	1.57	6.9	9.5	13.2	1.90
45°	5.5	4.63	2.96	16.9	24.2	6.8	1.67
	4.5	2.61	2.34	8.7	10.1	11.2	1.91
65°	5.5	4.70	3.22	25.4	29.8	3.4	1.67
	4.5	2.66	2.20	12.0	12.7	7.0	1.97

Wet modulus at 5% strain is said to be closely related to the degree of progressive shrinkage in fabrics resulting from repeated launderings. Cotton has a value of about 10, so that values of at least 10 are desirable. At 45° and 65° C., and with the higher caustic content in viscose, yarn properties were equal to those of good quality tire yarn. At lower temperatures, yarn elongations decreased markedly, and wet moduli increased. Higher caustic contents in viscose tended to give higher tenacities, higher elongations, lower moduli and lower secondary swelling values.

We claim:

1. A process of manufacturing regenerated cellulose fiber suitable for use as a substitute for natural fibers in-

cluding cotton fibers in textiles to be laundered comprising spinning viscose into a spinbath having a temperature in the range of about 0° C. to 40° C., the viscose having a gamma value in the range of about 45 to 65 and a cellulose to sodium hydroxide ratio in the range of about 1.05/1 to 1.70/1 parts by weight and the spinbath having sodium sulfate and sulfuric acid concentrations in grams per liter in accordance with the equations

Na_2SO_4=240–130 (weight of cellulose/weight of sodium hydroxide)

H_2SO_4=150–60 (weight of cellulose/weight of sodium hydroxide)

the fiber resulting from the spinning having a wet initial modulus at 5% strain of from about 10 to 20 grams per denier, a wet breaking tenacity of from about 1.57 to 2.8 grams per denier, and a secondary swelling of from about 1.70 to 1.90.

2. A process of manufacturing regenerated cellulose fiber suitable for use as a substitute for natural fibers including cotton fibers in textiles to be laundered comprising a first step of spinning viscose into a spinbath having a temperature in the range of 0° C. to 40° C., the viscose having a gamma value in the range of about 45 to 65 and a cellulose to sodium hydroxide ratio in the range of about 1.05/1 to 1.70/1 parts by weight and the spinbath

having sodium sulfate and sulfuric acid concentrations in grams per liter in accordance with the equations

Na_2SO_4=240–130 (weight of cellulose/weight of sodium hydroxide)

H_2SO_4=150–60 (weight of cellulose/weight of sodium hydroxide)

and a second step of stretching the spun material from about 80% to 125% in a hot dilute acid solution, the fiber resulting from the spinning having a wet initial modulus at 5% strain of from about 10 to 20 grams per denier, a wet breaking tenacity of from about 1.57 to 2.8 grams per denier, and a secondary swelling of from about 1.70 to 1.90.

3. The process of claim 1 when zinc sulfate is absent from the spinbath and its temperature is not lower than about 0° C. and not higher than about 20° C.

4. The process of claim 2 when zinc sulfate is absent from the spinbath and its temperature is not lower than about 0° C. and not higher than about 20° C.

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