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PRODUCTION OF CELLULOSIC STRUCTURES

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This invention relates to the manufacture of articles of regenerated cellulose by the viscose process. More particularly, it relates to the composition of the coagulating and/or regenerating bath used in the preparation of such articles.

Although the invention is generally applicable to the preparation of films, caps, bands, ribbons, filaments, and other similar structures of regenerated cellulose when prepared by the viscose process, the invention will be discussed for convenience in connection with the spinning of viscose rayon yarn. When spun in accordance with the principles of this invention, it is found that these yarns possess improved physical properties that make them eminently suited for use not only in the manufacture of cords for the reinforcing of rubber articles such as tires, but also for use in other branches of the textile industry.

Viscose rayon yarns, and similar structures of regenerated cellulose produced by the viscose process, are customarily prepared by the extrusion of a viscose solution into an aqueous spinning bath containing from 7% to 13% sulfuric acid and from 18% to 25% sodium sulfate. In addition, the bath often contains up to 4% of an organic substance such as glucose, together with up to 1% of zinc sulfate. It has also been proposed to incorporate in the spinning bath such inorganic salts as ferric sulfate, magnesium sulfate, cadmium sulfate, manganese sulfate, aluminum sulfate, etc.; certain of these materials generally being added to the spinning bath to aid in the removal of those sulfur compounds such as H_2S that are formed during the spinning process. Because other more efficient means, such as aeration of the bath, can be used to remove these objectionable sulfur compounds, this group of inorganic salts is not commonly used in the spinning process.

Although it is possible to increase the dry tenacity of a rayon yarn by the use of an increased spinning tension, this increase in tenacity is generally accompanied by a decrease in the elongation and other properties of the yarn such as loop strength. When the original spinning tension is low, this decrease is not unduly great. However, for all spinning setups, there exists a spinning tension (known as the optimum spinning tension) beyond which any further increase in tenacity brought about by an increase in spinning tension is not commensurate with the accompanying decrease in yarn elongation, so that the resulting stronger yarn is not so desirable as the yarn spun at the lower optimum tension. This term, "optimum spinning tension,"

differs from the term, "maximum spinning tension," which indicates the breaking strength of the freshly spun yarn at the time it leaves the spinning bath and is ready to be collected. It is, of course, desirable that both the optimum and maximum spinning tensions be as high as possible.

The presence of from 0.5% to 1.0% of zinc sulfate in the spinning bath aids importantly in improving the physical properties of the yarn spun therein. The presence of these small amounts of zinc sulfate in the bath, among other things, increases the optimum spinning tension that can be employed, whereby it is possible to spin at a somewhat higher tension to produce a yarn of a greater strength and desirable elongation. Generally, 1% represents the highest concentration of zinc sulfate that can be practicably used. Although higher concentrations still further increase the optimum spinning tension that can be employed, these higher concentrations cause severe cratering of the spinneret openings with a resultant adverse effect on the spinning operation. It has been proposed to incorporate various additional substances including other inorganic salts and wetting agents in either the bath or spinning solution to correct for this cratering and thus make it possible to use a spinning bath containing high concentrations of zinc sulfate and obtain the advantages accruing therefrom. In this connection, U. S. Patent No. 2,114,915 to Davis suggests that the addition of small amounts of nickel sulfate to the spinning bath will permit satisfactory spinning of viscose yarn in a bath containing relatively large amounts of zinc sulfate (4% to 10%). In general, however, the art has not seen fit to resort to the use of such modifying agents and it has been general practice to spin viscose rayon yarn into baths which contain not more than 1% zinc sulfate. Because of the spinning difficulties (cratering) introduced by the use of high concentrations of zinc sulfate in the spinning bath, the art has been unable to take advantage of the improved physical properties which are made possible by the use of an increased concentration of zinc sulfate.

It is, therefore, an object of this invention to provide a process whereby regenerated cellulose structures, such as yarns of improved physical properties can be spun without at the same time introducing spinning difficulties such as cratering that will make the process impractical for use on a large scale.

It is also the object of this invention to provide such a process for the production of improved

yarn as will not involve the use of expensive bath modifying agents designed to eliminate cratering difficulty and will generally improve the spinning operation.

It is another object of this invention to provide an improved process for the high tension spinning of regenerated cellulose structures from viscose.

It is a further object of this invention to provide a viscose rayon yarn possessing improved physical properties including a high tenacity, a desirable elongation, and a greatly improved loop strength, which properties are desirable in yarns employed in the textile art and in the reinforcing of rubber articles such as tires.

Other objects of the invention will appear hereinafter.

The objects of this invention are accomplished, in general, by the extrusion of a viscose solution into a sulfuric acid spinning bath containing from 1% to 10% and preferably 5% of ferrous sulfate, and preferably also a small amount (from 0.1% to 1.0%) of zinc sulfate. The bath may also contain the usual amounts of sodium sulfate, glucose, ammonium sulfate, and/or inorganic salts of such metals as magnesium, manganese, lead, etc.

The invention is based on the discovery that the addition of ferrous sulfate to a viscose coagulating bath increases the optimum spinning tension that can be employed in the spinning of a high tenacity viscose rayon yarn of satisfactory elongation. Thus, it is possible to prepare yarns of higher tenacity without at the same time causing either the elongation or the loop strength of the yarn to fall to undesirably low levels. Cords, or plied structures prepared from yarns having such an improved tenacity together with a desirable elongation and loop strength, possess a greatly improved resistance to fatigue as well as an increased loop strength. These improved yarns are, therefore, eminently suited for use in the textile art and in the reinforcing of rubber articles such as tires.

(Loop strength in grams per denier is the force in grams necessary to break one or both of two interlocked loops of yarn divided by twice the denier of the yarn. The loop strength is measured in grams on the same type of machine used for measuring dry tenacity, the break occurring almost invariably at the point of contact of the two collapsed, interlocked loops. Resistance to fatigue is measured by the time expressed in hours which a ribbon of cords made up from a given number of ends of the same type of cord can withstand alternate elongation and relaxation before complete rupture. The elongation and relaxation of the cord are accomplished by mechanical means under conditions designed to make the test as reproducible as possible.)

The addition of the ferrous sulfate to the spinning bath in accordance with the present invention may be utilized to great advantage in any process involving the spinning of viscose in a sulfuric acid coagulating bath under high tension (at least 0.3 gram per denier). This includes known processes for the high tension spinning of high tenacity (over 2.5 grams per denier) tire cord yarn, the high tension spinning of staple, and the high tension spinning of crimped filaments and fibers.

The presence of ferrous sulfate in the spinning bath, similar to zinc sulfate, increases the optimum spinning tension that can be employed in the spinning of viscose rayon yarn. However,

ferrous sulfate does not cause cratering of the spinneret openings or otherwise impair the spinning performance as does a similar content of zinc sulfate. This, of course, is a matter of great importance in the commercial production of viscose rayon yarn.

The nature of this effect on cratering is illustrated in the following table, which indicates the relative effect of previously known baths and the bath of this invention on the cratering of spinneret holes in the spinning of high tenacity yarn of 275-denier, 120-filaments from a cotton linters viscose solution containing 7% cellulose and 6% caustic and ripened to a common salt index of 5.2.

Table I

Yarn	A-1	B-1	C-1	D-1
Bath composition:				
H ₂ SO ₄ per cent..	11.00	9.00	10.50	9.00
Na ₂ SO ₄ do.....	23.00	22.00	23.00	19.00
Glucose.....do.....	4.00	4.00	4.00	4.00
ZnSO ₄ do.....	0.85	0.85	3.00	7.00
FeSO ₄ do.....		4.50		
Cratering results:				
Duration of jet service.....hours..	72	92	68	24
Per cent holes having medium craters.....	14.60	11.80	22.50	36.90
Per cent holes having bad craters..	1.00		45.80	41.90

It has furthermore been found that by using both ferrous sulfate and zinc sulfate in the spinning bath better spinning results can be attained than by the use of either ferrous sulfate or zinc sulfate alone. As above stated, in view of its spinneret cratering effect, the zinc sulfate content of a sulfuric acid spinning bath is limited to about 1%. The solubility of ferrous sulfate in a sulfuric acid spinning bath containing the usual amount (15% to 23%) of sodium sulfate limits the content thereof in the bath to not more than 10%. The addition of ferrous sulfate to a sulfuric acid spinning bath containing a given quantity of zinc sulfate will increase both the optimum and maximum spinning tensions which may be employed without effecting any increase in the spinneret cratering of the bath.

The present invention, therefore, in its preferred procedure, contemplates the addition of from 1% to 10% and preferably about 5% of ferrous sulfate to a sulfuric acid spinning bath containing from 0.1% to 1.0% and preferably about 0.7% of zinc sulfate. The use of such a bath imparts a considerable increase in the maximum spinning tension which may be employed and an increased fatigue resistance of the resulting yarn obtainable without at the same time increasing to the slightest degree the formation of craters in the spinneret openings during the spinning operation. As will be shown later in the examples, the use of spinning baths containing 5% ferrous sulfate and no zinc sulfate permits the spinning of yarns possessing properties nearly comparable to those prepared with a bath containing no ferrous sulfate and approximately 1% zinc sulfate. On the other hand, the use of baths containing approximately 5% ferrous sulfate and 1% zinc sulfate enables the production of yarn with considerably better properties than yarns prepared in a bath containing only one of the above-said components. Moreover, yarns spun in a bath containing both of these components can be formed into cords of improved tenacity over cords prepared from yarns spun in baths containing various amounts of only one of these components.

As indicated in the following examples, which

serve to illustrate the invention, the invention finds its greatest use in the production of high tenacity yarns intended for use in the manufacture of cords for the reinforcing of rubber articles such as pneumatic tires and the like. These yarns are generally prepared by a spinning process wherein the yarn is passed through the spinning bath for a distance of 100 to 250 inches while being subjected at the same time to a high tension imposed by a plurality of roller guides or other suitable means. Yarns spun in accordance with this invention may be collected on a rotating bobbin as in the conventional bobbin process, in a rapidly rotating bucket as in the bucket process, or they may be advanced in a continuous manner under purifying sprays by means of yarn-advancing reels or yarn-conveying belts.

The following examples illustrate several embodiments of the invention. These examples, however, are to be considered only as illustrative of the principles of the invention and are not to be construed as limiting the extent of the invention.

EXAMPLE I

Cotton linters viscose containing 7% cellulose and 6% caustic and ripened to a salt index of 5.2 is extruded into a coagulating and regenerating bath containing 7.8% H_2SO_4 , 22% Na_2SO_4 , 0.7% zinc sulfate and 5% ferrous sulfate to form a yarn of 1100 denier, 480 filaments. The bath is maintained at a temperature of 52° C., the yarn being passed about a plurality of roller guides so arranged as to yield a bath travel of 208 inches and impart to the yarn a spinning tension of 0.96 gram per denier. The yarn is collected on a bobbin at a wind-up speed of 3600 inches per minute. The spinning operation is characterized by a measurable increase in the maximum spinning tension that can be employed over that which can be employed when spinning under identical conditions into a spinning bath similar to the present one save that it contains no ferrous sulfate. Furthermore, there is less cratering of the spinneret orifices than when using a bath containing a larger quantity of zinc sulfate which will permit the same maximum spinning tension to be used.

The spun yarn is washed free of acid and salt while on the bobbin and is then dried at constant length by passing about rotating drying drums, the dried yarn being finally twisted to four turns per inch. The wet and dry tenacities of the yarn are respectively 3.70 and 2.19 grams per denier and the wet and dry elongations are 18.9% and 9.8% respectively. The yarn possesses a loop strength of 2.76 grams per denier as compared to a loop strength of 2.63 grams per denier for a yarn spun under the same conditions, but in a prior art bath containing zinc sulfate, but no ferrous sulfate. Moreover, when these yarns are formed into cords of similar construction, the cord prepared from the yarn of this invention (spun in a bath containing 5% ferrous sulfate and less than 1% zinc sulfate) possesses a resistance to fatigue that is 150% better than that cord prepared from a yarn spun in the bath containing no ferrous sulfate.

EXAMPLE II

The viscose solution of Example I is extruded into coagulating and regenerating baths of the composition indicated in the table below to form yarns of 275-denier, 120-filament count. The baths are maintained at a temperature of 47.5° C. and spinning tensions of approximately 0.8 gram per denier are employed, the yarns being

collected on a spinning bobbin at a speed of 3600 inches per minute. The yarns are then formed into cords of given construction. The physical properties of these yarns and cords, shown in the table below, indicate the marked superiority of the bath containing both ferrous sulfate and zinc sulfate.

Table II

Yarn	A-2	B-2	C-2	D-2
Bath composition:				
H_2SO_4 per cent.	8.10	11.00	8.00	8.00
Na_2SO_4 do.	22.40	23.00	20.00	20.00
Glucose.....do.	4.30	4.00	4.00	4.00
ZnSO_4 do.	0.70	0.85	-----	0.80
FeSO_4 do.	4.40	-----	5.0	5.00
Yarn properties:				
Dry tenacity.....g. p. d.	3.21	3.13	3.05	3.08
Dry elongation.....per cent.	10.50	9.90	9.70	10.30
Loop strength.....g. p. d.	2.54	2.44	-----	-----
Cord properties:				
Cord tenacity.....g. p. d.	2.60	2.49	2.53	2.68
Fatigue resistance.....hours	12.75	8.80	5.80	13.50

EXAMPLE III

The viscose solution of Example I is spun under the conditions of Example II to yield yarns of 275-denier, 120-filament count into coagulating and regenerating baths of the compositions shown in the table below. The dried yarns are formed into cords of given construction. Although the properties of the yarns spun in these baths are almost identical, the following table indicates the substantial improvement in strength, particularly under conditions of high temperature and bone dryness, of cords prepared from yarns spun in the bath of this invention over yarns spun in the bath of the prior art. Moreover, there is a very marked improvement in cratering during the spinning operation in the case of the bath of this invention containing approximately 5% ferrous sulfate and 1% zinc sulfate.

Table III

Yarn	A-3	B-3
Bath composition:		
H_2SO_4 percent.	8.00	11.00
Na_2SO_4 do.	22.00	23.00
Glucose.....do.	4.00	4.00
ZnSO_4 do.	0.90	2.50
FeSO_4 do.	4.55	-----
Yarn properties:		
Dry tenacity.....g. p. d.	3.11	3.15
Dry elongation (at break).....percent.	20.10	20.30
Loop strength.....g. p. d.	2.59	2.54
Cord properties:		
Tenacity (70° C.—pounds 60% R. H.).....lbs.	13.99	13.99
Tenacity (120° C.).....do.	13.09	12.37
Tenacity (bone dry state).....do.	17.76	17.23

EXAMPLE IV

Cotton linters viscose containing 7% cellulose and 6% caustic and ripened to a salt index of 4.0 is extruded into a coagulating and regenerating bath containing 10.5% H_2SO_4 , 23% Na_2SO_4 , 0.85% zinc sulfate, and 5% ferrous sulfate to produce a high tenacity yarn of 150 denier, 40 filament. The bath is maintained at a temperature of 55° C., the yarn being passed about six roller guides so arranged as to yield a bath travel of 130 inches and impart to the yarn a spinning tension of 0.83 gram per denier. The yarn is collected on a bobbin at a windup speed of 3600 inches per minute. The tenacities and elongations of the yarn are approximately the same as those of a yarn spun under similar conditions in a similar bath containing no ferrous sulfate. However, the yarn possesses a loop strength of

2.70 grams per denier as against a loop strength of 2.40 grams per denier for a yarn spun in a similar bath containing no ferrous sulfate.

EXAMPLE V

The viscose solution of Example IV is spun under the conditions set forth therein into a bath containing 8.6% H_2SO_4 , 23% Na_2SO_4 , 0.85% zinc sulfate and 3% ferrous sulfate. The tenacities and elongations of the yarn are approximately the same as those of a yarn spun in a similar bath containing no ferrous sulfate. The loop strength of the yarn is 2.36 grams per denier as compared to 2.10 grams per denier for this reference yarn.

EXAMPLE VI

The viscose solution of Example I is spun under the conditions set forth therein into the four different spinning baths listed in Table IV below which designates the tenacities, elongations and loop strengths of the resulting yarns.

Table IV

Yarn	A-4	B-4	C-4	D-4
Bath composition:				
H_2SO_4 percent..	11.00	6.00	11.00	8.20
Na_2SO_4 do.....	23.00	23.00	23.00	23.00
ZnSO_4 do.....			0.85	0.85
FeSO_4 do.....		5.00		5.00
Yarn properties:				
Dry tenacity.....g. p. d..	2.84	3.02	3.08	3.20
Wet tenacity.....g. p. d..	1.55	1.98	1.90	2.21
Dry elongation.....percent..	12.00	7.00	8.00	11.00
Wet elongation.....do.....	11.00	11.00	17.00	18.00
Loop strength.....g. p. d..	2.09	2.32	2.30	2.60

EXAMPLE VII

A viscose solution containing 7% cellulose and 6% caustic and ripened to a salt index of 4.0 is extruded into a coagulating and regenerating bath comprising 11% H_2SO_4 , 23% Na_2SO_4 , and 1% ferrous sulfate to form a yarn of 150-denier, 40-filament count. The bath is maintained at a temperature of 55° C. and the yarn is subjected to a spinning tension of about 0.1 to 0.2 gram per denier. The bath travel is approximately 25 inches and the yarn is collected on a spinning bobbin at a spinning speed of 2,500 inches per minute. During the spinning operation, a black solid (presumably iron sulfide) forms at the alkaline interface of the filament with the bath. However, as the yarn becomes acid, this solid re-dissolves and the black color disappears, leaving a light brown gel yarn which washes free of the iron very readily. The freshly spun yarn is washed on the bobbin, twisted in a wet condition, and dried in a relaxed state, such as a skein. The finished yarn, which is suitable for use in the textile art, possesses a dry tenacity of 2.42 grams per denier and an elongation of 21%. This compares with a dry tenacity of 1.93 grams per denier and an elongation of 21% for a yarn spun under identical conditions in a similar bath from which ferrous sulfate has been omitted.

EXAMPLE VIII

The viscose solution of Example VII is spun under the conditions set forth therein into baths containing 11% sulfuric acid, 23% sodium sulfate, 4% glucose, and varying amounts of ferrous sulfate. The yarns are processed as in Example VII save that they are dried on the bobbin instead of in a relaxed state. As indicated in Table V below, the yarn properties, such as tenacities, elongations, and dyeing properties compare favorably with those spun into similar

baths containing 0.85% zinc sulfate in place of the ferrous sulfate. They show a distinct improvement over yarns spun in baths containing only sulfuric acid and sodium sulfate. It is interesting to note that in accordance with the process of this example, spinning baths containing 1% ferrous sulfate are as effective as baths containing 3% ferrous sulfate.

Table V

Yarn	A-5	B-5	C-5	D-5	E-5
Bath composition:					
H_2SO_4 per cent..	11.00	11.00	11.00	11.00	11.00
Na_2SO_4 do.....	23.00	23.00	23.00	23.00	23.00
Glucose.....do.....	4.00	4.00	4.00		
ZnSO_4 do.....				0.85	
FeSO_4 do.....	1.00	2.00	3.00		
Yarn properties:					
Dry tenacity.....g. p. d..	2.37	2.35	2.33	2.38	1.93
Wet tenacity.....g. p. d..	1.27	1.28	1.28	1.40	0.88
Dry elongation.....per cent..	18.00	17.50	18.50	21.00	21.00
Wet elongation.....do.....	36.00	34.00	34.00	40.00	26.00

EXAMPLE IX

A viscose solution containing 7% cellulose and 4% caustic and ripened to a salt index of 4.0 is spun into a series of baths containing 4% ferrous sulfate and varying amounts of sulfuric acid. The other spinning conditions are similar to those of Example VII save that the yarns are dried on the bobbin instead of being dried in a relaxed state. The physical properties of these yarns are indicated in Table VI below. They indicate that textile yarns of good physical properties can be obtained from viscose of low alkali content and baths containing sodium sulfate, glucose, ferrous sulfate and from 5.7% to 9.8% acid. The yarns compare favorably with yarns spun into baths containing zinc sulfate.

Table VI

Yarn	A-6	B-6	C-6	D-6
Bath composition:				
H_2SO_4 per cent..	5.70	7.70	9.80	11.00
Na_2SO_4 do.....	21.00	21.00	21.00	23.00
Glucose.....do.....	4.00	4.00	4.00	4.00
ZnSO_4 do.....				0.85
FeSO_4 do.....	4.00	4.00	4.00	
Yarn properties:				
Dry tenacity.....g. p. d..	2.32	2.29	2.30	2.26
Wet tenacity.....g. p. d..	1.22	1.13	1.16	1.13
Dry elongation.....per cent..	16.50	17.50	18.00	25.00
Wet elongation.....do.....	29.00	32.00	34.00	42.00

EXAMPLE X

The viscose solution of Example VII is spun under the conditions set forth therein into baths containing sodium sulfate, zinc sulfate, ferrous sulfate, and varying amounts of sulfuric acid. As indicated in Table VII below, these yarns possess excellent tenacities and elongations. Their other properties, such as softness, luster, and depth of dyeing, are satisfactory and make these yarns very suitable for use in the textile art.

Table VII

Yarn	A-7	B-7	C-7	D-7	E-7
Bath composition:					
H_2SO_4 per cent..	7.20	8.20	9.60	10.50	11.00
Na_2SO_4 do.....	23.00	23.00	23.00	23.00	23.00
ZnSO_4 do.....	0.85	0.85	0.85	0.85	0.85
FeSO_4 do.....	5.00	5.00	5.00	5.00	5.00
Yarn properties:					
Dry tenacity.....g. p. d..	2.22	2.26	2.23	2.13	2.06
Wet tenacity.....g. p. d..	1.67	1.24	1.18	1.22	1.20
Dry elongation.....per cent..	23.00	24.00	27.00	25.00	26.00
Wet elongation.....do.....	22.60	26.00	34.00	32.00	36.00

EXAMPLE XI

The viscose solution of Example VII is spun into a bath containing sodium sulfate, glucose and 10% ferrous sulfate, together with varying amounts of sulfuric acid. The spinning and yarn processing conditions are similar to those of Example VII save that the yarn is dried on the bobbin rather than in a relaxed state. The physical properties of the yarn so obtained are contained in Table VIII below. They indicate that yarns spun in such baths are more desirable than are yarns spun into baths containing no zinc sulfate or ferrous sulfate.

Table VIII

Yarn	A-8	B-8	C-8	D-8
Bath composition:				
H ₂ SO ₄ per cent..	8.00	10.40	11.00	11.00
Na ₂ SO ₄ do.....	15.00	15.00	23.00	23.00
Glucose.....do.....	4.00	4.00	4.00	-----
ZnSO ₄ do.....	-----	-----	0.85	-----
FeSO ₄ do.....	10.00	10.00	-----	-----
Yarn properties:				
Dry tenacity.....g. p. d..	2.40	2.50	2.18	1.93
Wet tenacity.....g. p. d..	1.21	1.32	1.13	0.88
Dry elongation.....per cent..	19.00	16.00	23.00	21.00
Wet elongation.....do.....	31.00	29.00	33.00	26.00

EXAMPLE XII

The viscose solution of Example VII is extruded into baths containing 15% sodium sulfate, 4% glucose, 10% ferrous sulfate, and varying amounts of sulfuric acid. The spinning and yarn processing conditions are similar to those of Example I and the yarns produced are of the high tenacity type suited for use in the reinforcing of rubber articles. The nature of the physical properties of these yarns is indicated in Table IX below. The tenacities and elongations of these yarns are comparable to those of yarns prepared in baths containing zinc sulfate. However, the loop strength of these yarns is not so high as that of yarns prepared by the use of both ferrous sulfate and zinc sulfate.

Table IX

Yarn	A-9	B-9	C-9	D-9
Bath composition:				
H ₂ SO ₄ per cent..	8.00	10.00	11.00	8.20
Na ₂ SO ₄ do.....	15.00	15.00	23.00	2.30
Glucose.....do.....	4.00	4.00	4.00	-----
ZnSO ₄ do.....	-----	-----	0.85	0.85
FeSO ₄ do.....	10.00	10.00	-----	5.00
Yarn properties:				
Dry tenacity.....g. p. d..	3.30	3.00	3.29	3.24
Wet tenacity.....g. p. d..	1.94	1.80	1.97	2.13
Dry elongation.....per cent..	9.00	7.50	10.00	11.00
Wet elongation.....do.....	11.00	13.50	12.50	18.00
Loop strength.....g. p. d..	2.10	2.10	2.30	2.60

The following two examples illustrate processes for spinning crimped filaments in baths comprising ferrous sulfate.

EXAMPLE XIII

A commercial viscose containing 7% cellulose (cotton linters) and 6% alkali is spun at a sodium chloride index of 5.1 into an aqueous regenerating bath containing 7.9% sulfuric acid, 20% sodium sulfate, 4% glucose, 0.7% zinc sulfate and 3% ferrous sulfate at a temperature of 52° C. The spinneret contained 60 holes and the viscose delivery was such as to form 150-denier yarn. The total bath travel in the coagulating and regenerating bath is approximately 160 inches. This travel is obtained by using a system of roller guides which are adapted to produce gradually increasing tension on the thread. The tension

on the thread at the point of its emergence from the bath is approximately 1.2 grams per denier. The thread is collected on a bobbin at 3500 inches per minute and immediately after collection is cut from the bobbin into lengths of about 2½ inches and permitted to fall into water 80° C. to 100° C. In the hot water, the fibers spontaneously crimp and retain this crimped form unchanged through the steps of washing, purifying and drying.

EXAMPLE XIV

Viscose filaments are spun as in Example I except that a 40-hole spinneret is used to produce a final filament denier of 3.75 or a total yarn denier of 150. The thread is not cut into staple but washed on the bobbin, dried under tension, twisted, and afterward relaxed in a bath of hot water in the form of loose skeins to produce a continuous filament crimped yarn.

The conditions necessary for producing this crimp in the yarn involve the steps of spinning into a bath, the composition of which is dependent on the composition of the viscose, the spinning being carried out under conditions of high tension and high stretch, followed by the development of the crimp while the yarn is completely relaxed in suitable swelling agents.

In the above two examples, the viscose used contained 7% cellulose and 6% caustic. A viscose solution of other composition can, of course, be used in the preparation of such a crimped yarn provided the necessary changes are made in the composition of the spinning bath. For a viscose containing 7% cellulose and 4% caustic, the spinning bath should preferably contain from 3% to 4% sulfuric acid.

Here again, the importance of using ferrous sulfate in this bath undoubtedly arises from the fact that the presence of this salt makes it possible to greatly increase the spinning tension employed so that a highly stretched gel yarn can be obtained, which yarn is readily adapted for use in preparing crimp.

As has been indicated, the ferrous sulfate may replace all or a portion of the zinc sulfate normally contained in the spinning bath used in the production of viscose rayon yarns. However, as indicated in certain of the examples, it is preferred that the bath should contain from 0.1% to 1.0% zinc sulfate in addition to the added ferrous sulfate. The chief advantage of the invention rests in the fact that this addition of ferrous sulfate to the bath serves to improve the physical properties of the yarn without at the same time adversely affecting the quality of the spinning operation by causing the formation of craters about the openings of the spinnerets.

This invention is not limited to use with certain definite viscose solutions. It may be used to good advantage with viscose solutions prepared from wood pulp, cotton linters, mixtures of these two or even other types of cellulose. Furthermore, the composition of the viscose solution may be varied over a wide range. For example, it may have a cellulose content of 3% to 12% and an alkali content of 4% to 8%. The solution should preferably be ripened to a salt index of from 3 to 7. However, the invention may also be used in connection with viscose solutions of other degrees of ripeness. In such a case, however, it may be necessary to alter the various spinning conditions somewhat so as to obtain yarns of satisfactory properties.

Spinning baths for use in connection with this invention will preferably contain from 5%

to 11% sulfuric acid; from 15% to 25% sodium sulfate; from 0% to 4% glucose; and from 0.1% to 1.0% zinc sulfate in addition to the ferrous sulfate. The ferrous sulfate may be contained in any concentration from 1% up to the saturation point. When the solution contains zinc sulfate, with or without the addition of glucose, the upper limits for the concentration of ferrous sulfate will be approximately 10%. If the bath contains no zinc sulfate or glucose, the concentration of ferrous sulfate may be slightly higher as, for example, 15%. In addition to these compounds, the spinning bath may contain such other salts as ammonium sulfate, magnesium sulfate, etc. Such added salts will not interfere with the beneficial action of the ferrous sulfate incorporated in the spinning bath in accordance with this invention.

Obviously, the concentrations of all of these substances in a given bath must be adjusted to each other and to the composition of the viscose solution employed. For a viscose solution containing 7% cellulose and 6% caustic, when from 5% to 8% ferrous sulfate is incorporated in the coagulating bath, the sodium sulfate concentration of the bath should be from 18% to 23%. In case glucose is not contained in the bath, the sodium sulfate should be near the upper limits. The desired sulfuric acid content is dependent upon concentrations of the other constituents as well as the cellulose and caustic content of the viscose. Again, using a viscose solution containing 7% cellulose and 6% caustic, it is necessary, as the concentration of glucose and sodium sulfate increases, to increase the bath acidity, while it should be decreased with the addition of ferrous sulfate. For use with a viscose solution containing 6% caustic, a bath containing 22% sodium sulfate, 0.7% zinc sulfate and 5.0% ferrous sulfate should contain approximately 7.2% sulfuric acid. If the caustic content of the viscose is reduced to 4%, the optimum bath acidity will be of lower concentration.

Spinning baths prepared in accordance with this invention may be maintained at any desired temperatures; preferably, at a temperature of 40° C. to 65° C. In the case of a greatly increased spinning speed, it may be desirable to increase this bath temperature to 90° C. or 100° C. or even higher.

Because this invention is most useful in connection with the spinning of high tenacity yarns for use in the reinforcing of rubber articles, such as tires, and because the invention permits the maximum spinning tension to be greatly increased, it is most useful when spinning with a high tension of the order of 0.8 gram per denier. Obviously, the spinning tension employed will depend on the exact type of yarn desired.

As indicated in the examples, the practice of the invention is not limited to the use of long bath travels. However, in the production of high tenacity yarns, it is suggested that the bath travel be maintained within the range of 80 to 350 inches. The optimum bath travel in any given case will, of course, be dependent upon the exact composition of the viscose solution and bath employed, the spinning speed, and the denier of the individual filaments, as well as the denier of the entire yarn bundle.

The examples disclose only single bath processes for the spinning of viscose rayon yarn. Naturally, if desired, the yarn spun in baths prepared in accordance with this invention may be passed through secondary water baths, or

dilute acid baths, of varied composition and temperature wherein the yarn may be subjected, if desired, to a further stretching operation as is well known in the art.

- 5 This invention is primarily concerned with the composition of the spinning bath employed in the preparation of viscose rayon yarns. The yarns, once spun, can be purified and dried in the known manner and with the usual purifying solutions.
- 10 If spun by the bobbin or bucket processes, the yarn can be purified in package form, or it can be wound to skeins and treated in that form. On the other hand, it can be purified in a continuous manner by the use of a conveyor belt or yarn advancing reels. Care must be taken, of course, to insure the complete removal of the iron salts from the yarn before it is subjected to the usual alkaline desulfuring solution; otherwise, undesirable, dark deposits of iron oxides will be formed within the yarn. These dark deposits are also frequently formed in the yarn during the preliminary wash treatment, particularly if the wash water employed is slightly alkaline. Even when the wash water is neutral (pH of 7), these undesirable deposits are occasionally found within the yarn cake, especially when the cake structure is such that certain isolated portions of the cake do not receive an adequate supply of wash water. It has been found that the formation of these dark spots can be prevented, however, if the wash water used is slightly acid (pH of about 4). Under such conditions, the formation of the undesirable oxides is prevented, while at the same time the acidity of the wash water is so low that any occluded spinning bath liquor is readily removed from the yarn. Yarn washed with such water can be safely subjected to the action of other purifying solutions, or it can even be subjected to immediate drying without harm. It has also been found that the presence of a reducing atmosphere (H₂S, etc.) about the yarn during the preliminary wash treatment aids somewhat in preventing the formation of these iron deposits within the yarn. By thus aiding the purification of yarns spun in a bath containing ferrous sulfate, these two steps (the use of a slightly acid wash water and the presence of a reducing atmosphere during the preliminary wash period) aid importantly in the production of satisfactory yarns in accordance with the principles of this invention.

This invention provides a process for the spinning of viscose rayon yarns of improved physical properties. Yarns produced in accordance with this process possess not only a high tenacity and a good elongation but a greatly increased loop strength. As has already been mentioned, this property of loop strength is a useful measurement in determining the durability of the yarn when subjected to repeated deformation or flexing treatments. Because yarns intended for use in the reinforcing of tires are subjected to such treatment, the measurement of loop strength is a very pertinent one.

This invention enables these improvements in yarn properties to be obtained without, at the same time, adversely affecting the continuity of the spinning operation. Furthermore, it provides a means whereby considerable improvement in the quality of the spinning operation can be effected without impairing the physical properties of the yarn so spun.

A further great advantage of this invention rests in the fact that a relatively inexpensive chemical is substituted for the higher-priced

chemical previously used in the spinning operation. The ferrous sulfate of this invention can be obtained at a fraction of the cost of zinc sulfate previously employed in the spinning of viscose rayon yarn.

Since it is obvious that many changes and modifications can be made in the details herein disclosed, without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to these details except as set forth in the appended claims.

I claim:

1. In the method of producing regenerated cellulose structures by the spinning, under high tension, of viscose in a sulfuric acid spinning bath the step which comprises incorporating in said bath from 1% to 10% ferrous sulfate together with from 0.1% to 1.0% zinc sulfate.

2. In the method of producing crimped re-

generated cellulose filaments by the spinning, under high tension, of viscose in a sulfuric acid spinning bath with the subsequent complete relaxation of said filaments in a swelling agent therefor, the step which comprises incorporating in said bath from 1% to 10% ferrous sulfate together with from 0.1% to 1.0% zinc sulfate.

3. A sulfuric acid spinning bath for the spinning, under high tension, of regenerated cellulose structures from viscose, said bath containing from 0.1% to 1.0% zinc sulfate together with 1% to 10% ferrous sulfate.

4. A sulfuric acid spinning bath for the spinning, under high tension, of regenerated cellulose structures from viscose, said bath containing from 5% to 11% sulfuric acid, 18% to 25% sodium sulfate, 0% to 4% glucose, 0.1% to 1.0% zinc sulfate and 1% to 10% ferrous sulfate.

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