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PROCESS FOR MAKING RAYON FILAMENTS

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The present invention relates to the manufacture of artificial filaments and provides a novel process. In particular the invention relates to the manufacture of artificial yarn admirably adapted for use as reinforcement in the manufacture of rubber goods such as automobile tires and especially adapted for use in heavy-duty truck tires and the like. The yarn produced by the process of the present invention exhibits fatigue resistance, as indicated by the bend test described hereinbelow, higher than any yarn heretofore manufactured of which we are aware.

It is therefore an object of the present invention to provide a process for the manufacture of artificial filaments of unusually high fatigue resistance.

It is a further object of the present invention to provide a novel process for the manufacture of thread or yarn from purified or refined chemical wood pulp.

It has been thought necessary in the manufacture of artificial filaments suitable for tire cord to use cotton linters as the source of cellulose. The process of the present invention produces artificial filaments of quality suitable for tire cord manufacture and in said process purified or refined chemical wood pulp, a cheaper raw material than linters, may be used as the source of cellulose. By the use of said process it is possible to produce a product which exhibits resistance to fatigue greater than that of any wood pulp product or any cotton linters product heretofore available. Thus the present invention not only offers the decided economical advantage of making it possible to use the less expensive wood pulp as a raw material, but it also makes available to the industry a product of improved quality.

In the customary manufacture of artificial filaments from refined chemical wood pulp or from cotton linters or blends of the two, the raw material is usually steeped in a caustic soda solution of mercerizing strength, normally about 18%, pressed to remove a certain amount of the caustic soda and shredded preparatory to the xanthation step. After shredding, the alkali cellulose is normally aged for a definite period of time in order to establish a desirable spinning viscosity in the spinning solution. The aged or unaged alkali cellulose is then xanthated by treatment with carbon disulphide. The xanthated cellulose is then dissolved in dilute caustic soda to form the spinning solution which is ordinarily known as viscose. Prior to spinning, the vscose is normally ripened and filtered to impart desired characteristics to the product and to insure successful spinning.

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The usual concentration of analytically determinable cellulose in the viscose or spinning solution is approximately 7.5%. The usual viscosity of the spinning solution is, as determined for instance by the time of fall of a ⅛" steel ball through 15 cm. in a viscosity tube of 1.4 cm. diameter (test made at 20° C.), about 30 seconds (46.5 poises). In commercial operation the cellulose concentration may be as low as 7% or as high as 8% or 8.5%, and in such instances the aging period of the alkali cellulose must be suitably adjusted to establish the usual spinning viscosity. In the use of any of the usual spinning methods it is not possible to secure successful spinning of viscose solutions having cellulose content below 6.5% because as the cellulose content is lowered the filaments produced become increasingly discontinuous, harsh, brittle and weak. This condition is emphasized if it is attempted to subject the filaments to substantial stretching between godets. Examples will be cited herein of attempts to spin viscose containing less than 6.5% cellulose in accordance with usual spinning methods. A concentration of above 8.5% is not normally used because of the tendency toward high viscosity and the necessity for unduly long aging periods.

We have discovered that by combining a number of changes over the usual spinning processes we are enabled to produce from refined wood pulp filaments having fatigue resistance as high as, if not higher than, that exhibited by the best artificial filaments heretofore produced, irrespective of the source of the cellulose used, while in the use of cellulose from any particular source our process provides marked improvement in the fatigue resistance of the resulting filaments. According to our invention such artificial filaments are produced from viscose of very low cellulose concentration, namely in the range from somewhat more than 3% to about 6.5%, which is adjusted to normal spinning viscosity and is spun under specific conditions to be set forth herein into a special setting bath and is subjected to considerable stretching between godets.

The range of cellulose concentrations within which the advantageous results of our invention may be secured in varying degree constitutes an entirely new range for thes pinning of viscoses into filaments of high fatigue resistance. A setting bath which is characterized by its content of not substantially less and preferably more than 2.5% of zinc sulphate is essential to successful

spinning within this range. Toward the upper end of our range the unusual characteristics of our yarn become rapidly less apparent, and when cellulose concentrations of the usual range of 7% to 8.5%, are employed no unusual results are achieved. Toward the lower end of our range, specifically that portion of the range in which the cellulose concentration is below 4%, the unusual characteristics of our yarn again become less apparent.

greater very little difference exists. The results on skeined and coned yarn have also been averaged.

We have also shown at the bottom of Table I characteristic average bend tests upon yarn spun in accordance with our process and under conditions identical with those in the upper portion of the table, except that the viscoses were prepared from a raw material comprising 100% cotton linters.

Table I

Test No.	1	2	3	4	5	6	7	8	9
Cellulose, per cent	4.0	4.5	4.9	5.1	6	6.5	7.0	7.5	8.3
NaOH, per cent	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Aging Temp., °C	20	20	20	20	20	20	20	20	20
Aging Time, Hrs	3	11	19	19	35	43	51	59	67
Viscosity	[1] N	N	N	N	N	N	N	N	N
Stretch per cent between godets	77	77	77	77	77	77	77	77	77
Tension in grams between godets	434	514	320	424	413	398	389	413	436
Ripening Temp., °C	19	19	19	19	19	19	19	19	19
Ripening Time, Hrs	48	48	48	48	48	48	48	48	48
Ripening Index [2]	10–12	10–12	10–12	10–12	10–12	10–12	10–12	10–12	10–12
Strength—dry, g./d	3.26	3.49	3.12	3.42	3.39	3.41	3.41	3.43	3.55
Strength—wet, g./d	2.22	2.22	2.24	2.44	2.21	2.12	2.15	2.15	2.19
Extensibility—dry, per cent	17.6	20.8	19.3	20.4	21.0	20.3	20.0	20.0	17.2
Tensile factor	127.4	161.0	134.9	170.3	157.4	146.6	146.6	147.5	133.9
Bend—skeins	604	850	819	795	735	466	425	440	336
Bend—cones	1,284	2,000	1,399	1,300	1,058	467	420	353	201
Average	944	1,425	1,109	1,047	897	467	422	396	268
NOTE.—All above yarns prepared from wood pulp.									
Average bend test when 100% Cotton Linters used as raw material	-------	1,583	-------	-------	1,058	-------	-------	498	------

[1] Normal (averaging 30 seconds, i. e., 46 poises).
[2] Balaczynski Maturimeter, 12.5% NH_4Cl.

In Table I there is set forth a series of nine tests in which wood pulp viscoses of normal viscosity were spun into a setting bath characterized as above through spinnerets having openings of our preferred diameter and subjected to a high degree of stretch, in this instance, 77%. These nine tests differ from each other only in the percentage of cellulose contained in the viscose and in the aging period of the alkali cellulose. Thus Table I shows the effect of variations in cellulose concentration of viscose spun under our preferred conditions which will be more fully discussed hereinbelow. It will be observed that tests were made with viscoses ranging in cellulose concentration from 8.3% down to 4%. In this Table I as in all of the other tables and examples in this specification the fatigue resistance is measured by using the Schopper bending tester D. P. 5, in which the yarn, conditioned at 48% relative humidity and 78° F., is clamped between two jaws and a weight of 0.375 gram per denier applied directly by lowering a cam supporting the bottom jaw, the yarn being then bent forwards and backwards through 180°, 120 times (cycles) per minute until it breaks. The number of cycles automatically registered is the bend test. Since the logarithm of the bend test is inversely proportional to the load applied to the thread it is understood that comparison has to be made within the same denier range with the same number of filaments and with the same load per denier. The denier range of the yarns whose tests are shown in these tables is between 1150 and 1250, with 480 filaments, and the load per denier is 0.375 gram.

Bend tests are given for yarn in skeins and yarn wound on cones. It will be observed in Table I that in the lower ranges of cellulose concentration the yarn wound on cones exhibits much higher fatigue resistance than that in skeins, whereas in cellulose concentrations of 6% and

From a consideration of Table I it will be observed that optimum fatigue resistance is secured in a yarn spun from a viscose solution of normal spinning viscosity containing 4.5% analytically determinable cellulose. It also will be observed that the fatigue resistance of yarn spun under the same conditions from viscoses having cellulose concentrations within the range of 7% to 8.3% is very much lower than that of yarn spun from viscoses having cellulose concentrations within our new range. It furthermore will be observed that as the cellulose concentration is lowered progressively to 4.5% there is a sharply increasing rate of improvement in fatigue resistance of the yarn and that further lowering of cellulose concentration is accompanied by a decrease in fatigue resistance. However, the fatigue resistance of yarn spun from viscose having cellulose concentration of 4%, for example, although lower than that of the 4.5% yarn is still very much higher than that of any yarn within the range of 7% to 8.3%.

The following group of specific examples of the process and product of our invention is taken from Table I:

Example 1.—A viscose solution of normal spinning viscosity of approximately 45 poises is prepared by the usual steps of steeping, shredding, xanthating and dissolving a chemical wood pulp (for example, that sulfite wood pulp sold under the trade name "Tenacell" by Riordon Sales Corporation Ltd., of Montreal, Canada). This viscose solution is so prepared that it contains 4.5% analytically determinable cellulose and 6.5% NaOH, and in order that normal spinning viscosity may be obtained the alkali cellulose is aged for 11 hours at a temperature of 20° C. The viscosity thus established is about 46.5 poises which, as discussed above, is the normal viscosity for spinning rayon from a 7.5% cellulose viscose in accordance with usual practice. In this specifi-

cation and in the appending claims the words "normal viscosity" mean a viscosity of approximately this value. The viscose is ripened for 48 hours at a ripening temperature of 19° C., during which time suitable filtering takes place, and is spun under the following conditions: a spinneret having holes of .0025" diameter is employed and the viscose emerges from the spinneret into a setting bath containing from 8% to 9% sulphuric acid and 4% zinc sulphate, the specific gravity at 20° C. of said setting bath being 1.30. The yarn emerging from the spinning bath is then stretched between godets at elevated temperature in a manner well known in the art. Preferably a high degree of stretch is imparted, and we have found it desirable to stretch the yarn about 77% with a temperature in the intermediate bath of about 87° C. We have also found desirable a 20" immersion in the setting bath and a 17" immersion in the hot water or intermediate bath at a spinning speed at the top godet of 50 m. per minute. The yarn produced in accordance with this specific example exhibits a dry strength of 3.49 grams per denier with an extensibility of 20.8%, a wet strength of 2.22 grams per denier and a tensile factor of 161.0. The tensile factor is a useful empirical value, the product of g./d. dry times g./d. wet times extensibility (dry) in percent. The bend test carried out on the Schopper bending tester aforementioned shows 850 bends required to break the skeined yarn and 2000 bends required to break the coned yarn, and the average of these results is 1425 bends.

The yarn produced in accordance with this specific example spins without difficulty. Furthermore, there is no evidence of milkiness or milky streaks in yarn if bleached as for textiles. It will be appreciated from the characteristics discussed herein and tabulated in Table I under test No. 2 that this yarn shows wet and dry strengths and other characteristics of commercially acceptable standard for tire yarn, and that in addition the bend test demonstrates a resistance to fatigue more than four times that of yarn spun under the same conditions from a viscose containing 7.5% cellulose. (See test No. 8 in Table I.)

Example 2.—A viscose solution is prepared and spun under conditions identical with those in Example 1 except that the cellulose concentration is 4% and the alkali cellulose is aged for only three hours to establish in the viscose of this concentration a normal spinning viscosity. The yarn produced in accordance with this example exhibits characteristics of strength comparable to those of the yarn in Example 1 and exhibits an average bend test of 944, derived from a bend test in skeins of 604 and a bend test in cones of 1284. No difficulty was experienced in achieving continuous spinning under the conditions specified for this specific example.

Example 3.—A viscose solution is prepared and spun under the conditions set forth in Example 1 except that the cellulose concentration of the viscose is 4.9% and the aging time for the alkali cellulose necessary to establish in the viscose of this concentration a normal spinning viscosity is 19 hours. The yarn produced in accordance with this example exhibits strength characteristics fully comparable to those of the preceding examples and exhibits an average bend test of 1109, derived from a bend test of 819 in skeins and 1399 in cones.

Example 4.—A viscose solution is prepared and spun under the conditions set forth in Example 1 except that the cellulose concentration of the viscose is 5.1% and the aging time for the alkali cellulose necessary to establish in the viscose of this concentration a normal spinning viscosity is 19 hours. The yarn produced in accordance with this example exhibits strength characteristics fully comparable to those of the preceding examples and exhibits an average bend test of 1047, derived from a bend test of 795 in skeins and 1300 in cones.

Example 5.—A viscose solution is prepared and spun under the conditions set forth in Example 1 except that the cellulose concentration of the viscose is 6% and the aging time for the alkali cellulose necessary to establish in the viscose of this concentration a normal spinning viscosity is 35 hours. The immersion in the setting bath is 30" in this example and for higher cellulose concentrations in accordance with our finding of slightly improved results with the longer path for concentrations of 6% and higher. The yarn produced in accordance with this example exhibits strength characteristics fully comparable to those of the preceding examples and exhibits an average bend test of 897, derived from a bend test of 735 in skeins and 1058 in cones.

Example 6.—A viscose solution is prepared and spun under the conditions set forth in Example 1 except that the cellulose concentration of the viscose is 6.5% and the aging time for the alkali cellulose necessary to establish in the viscose of this concentration a normal spinning viscosity is 43 hours. The immersion is 30" as in Example 5. The yarn produced in accordance with this example exhibits strength characteristics fully comparable to those of the preceding examples and exhibits an average bend test of 467, derived from a bend test of 466 in skeins and 467 in cones.

Example 7.—A viscose solution is prepared and spun as set forth in any of Examples 1 through 6 except that cotton linters is used as the source of cellulose instead of wood pulp. The yarn produced in each instance exhibits slightly higher tensile properties than wood pulp yarn and also slightly higher bend test as can be seen in Tables I and III.

In the preceding examples we have specified the use of a setting bath which we have found to be a practical optimum in so far as the production of yarn of high fatigue resistance is concerned. We have also specified the use of spinnerets having holes of .0025" diameter and the stretching of the yarn about 77% at elevated temperature. Each of these latter factors has also been found by us to be optimum conditions for the production of yarn having the characteristic high bend test of the present invention when they are used in conjunction with the special setting bath and the low cellulose content viscose. In Table II we have set forth four tests in which the difference between a setting bath containing 4% zinc sulphate and a normal setting bath containing 1% zinc sulphate is illustrated. We have also illustrated herein the effect of stretching yarns spun into the special setting bath and into a normal setting bath. We have also shown in Table II the effect of spinneret holes of a diameter of .0025" as compared to spinneret holes of .0032". In the four tests included in Table II we have also shown the effect of differing periods of viscose ripening. In all four of the tests in Table II the viscose has a cellulose concentration of 4.2% and contains 6.5% NaOH.

Table II

Setting Bath	Normal Setting Bath		Special Setting Bath	
S. Grav. at 20° C.	1.300		1.300	
Sulphuric Acid	10%		8%	
Zinc Sulphate	1%		4%	
	No Stretch	Stretch 77%	No Stretch	Stretch 77%
Ripeness of Viscose: 56 hours or more at 19° C.	No spinning possible.	No spinning possible.	Good spinning; G./denier-dry, 2.39; G./denier-wet, 1.32; Per Cent Extensibility, 39.5; Tensile Fact., 124.5; Bend Test, 532.	Good spinning; G./denier-dry, 3.65; G./denier-wet, 2.22; Per Cent Extensibility, 21.8; Tensile Fact., 176.6; Bend Test, 1324.
56 to 40 hours at 19° C.	Fair spinning. Yarn very harsh; Tensile Fact., 15.7.	No continuous spinning, breaks every few minutes. Yarn very harsh; Tensile Fact., 10.1.	Good spinning; G./denier-dry, 2.28; G./denier-wet, 1.26; Per Cent Extensibility, 39.2; Tensile Fact., 112.6; Bend Test, 429.	Good spinning; G./denier-dry, 3.36; G./denier-wet, 2.09; Per Cent Extensibility, 20.3; Tensile Fact., 142.5; Bend Test, 1699.
40 hours and less at 19° C.	Yarn very harsh; Tensile Fact., 8.8.	Practically no spinning. Yarn very harsh; Tensile Fact., 9.7.	Would not spin continuously, but better with .0025" spinneret than with .0032", G./denier-dry, 2.11; G./denier-wet, 1.01; Per Cent Extensibility, 39.5; Tensile Fact., 84.2; Bend Test, 282.	Good spinning. Poor spinning with .0032" spinneret at 32 hrs. but good with .0025". G./denier-dry, 3.50; G./denier-wet, 2.23; Per Cent Extensibility, 29.4, Tensile Fact., 151.4; Bend Test 943.

From a study of Table II it will be apparent that viscose having a cellulose concentration of 4.2% cannot be spun with any success in a normal setting bath containing 1% zinc sulphate. When the viscose was ripened 56 hours or more at 19° C. no spinning was possible with or without stretching.

With shorter ripening periods between 40 and 56 hours fair spinning could be achieved without stretching, but the yarn produced was very harsh and had an unusually low tensile factor. When it is attempted to stretch this yarn no continuous spinning can be achieved. What little yarn is produced is exceedingly harsh and its tensile factor again unusably low.

With even shorter ripening periods of 40 hours and less a yarn may be spun without stretching, but it again is very harsh and exhibits again an unusably low tensile factor. When it is attempted to stretch this yarn spinning becomes very difficult and such yarn as is produced is very harsh and again exhibits an unusably low tensile factor.

Thus over a very broad range of variations in ripening time it remains a virtual impossibility to produce yarn by spinning a 4% cellulose, 6.5% NaOH viscose into a normal setting bath. None of the yarn produced in the attempt is of a quality remotely approaching that required for tire yarn.

Table II also shows the results achieved in two tests wherein the only difference over the preceding tests is that the setting bath contained 4% zinc sulphate instead of the 1% zinc sulphate in the normal setting bath. In these tests with 4% zinc sulphate the 4% cellulose, 6.5% NaOH viscose, aged 56 hours or more at 19° C. was spun without difficulty of any nature, both with and without stretching. The unstretched yarn shows very good strength characteristics and a high tensile factor of 124.5. Its extensibility of 39.5% of course renders it unusable in the manufacture of tire yarn, but this yarn is an interesting, semi-high-tenacity yarn of rather unusual type which should have commercial possibilities. With stretching of 77% between godets the extensibility is brought down to 21.8% and both the dry and wet strength of the yarn is markedly increased. The tensile factor of 176.6 is excellent, and using the Schopper Bending Tester as specified hereinabove a bend test of 1324 is exhibited.

With shorter ripening periods of from 56 hours down to 40 hours at 19° C. no difficulty in spinning was noted, with or without stretching. The strength characteristics of the yarn are approximately the same as those of yarn spun in our special setting bath with 56 hours or more of ripening. While the tensile factor is somewhat lower in each case it will be observed that in the case of the stretched yarn a bend test of 1699 was secured. This particular test has led us to the conclusion that a ripening time of somewhat more than 40 hours is optimum for the production, in accordance with our invention, of yarn having an unusually high resistance to fatigue.

With ripening periods of 40 hours and less some spinning difficulty was observed. For example, without stretching and with spinneret holes of .0032" diameter we could not achieve continuous spinning and while we also could not achieve continuous spinning with spinneret holes of .0025" diameter, and without stretching the results with the smaller spinneret holes were markedly better. Here again the yarn produced without stretching has a high extensibility of 39.5% and is not useful as a tire yarn. With stretching we found good spinning with spinneret holes of .0025" (this was particularly noticeable in connection with a viscose ripened for 32 hours) whereas with spinneret holes of .0032" diameter poor spinning occurred. The yarn thus produced with stretching and .0025" spinneret holes shows a high degree of strength and a high tensile factor and an extensibility of 19.4%. The bend test on this particular yarn was 943, which while considerably less than that achieved with yarn ripened for somewhat longer periods, is still far in excess of the bend test achieved in yarn spun from viscose containing about 7% or more of cellulose (see Table I).

In each of the specific examples set forth above we have made use of the special setting bath found by us to be a practical optimum. In Table II we have examined the effect of using in connection with a 4% cellulose, 6.5% NaOH viscose a normal setting bath and our optimum special setting bath. We have pointed out that our optimum setting bath contains 4% zinc sulphate and 8% sulphuric acid. We do not wish to be limited to this specific setting bath inasmuch as we have found that yarns of extremely high fatigue resistance may be produced in accordance with our process wherein the setting bath contains as little as about 2.5% zinc sulphate. In Table III we show the results of tests in which several yarns were spun in accordance with our process

and in which the amount of zinc sulphate in the setting bath varied from 1% to 10%.

Table III

Viscose (all tests): Cellulose / NaOH	4.2% (derived from Tenacell or cotton linters as indicated) 6.5%					
Spinning bath: Sulphuric acid / Zinc sulphate	10% 1%		8% 2.5%	8% 4%		8% 10%
Source of cellulose	Linters	Tenacell	Tenacell	Linters	Tenacell	Tenacell
Tensile factors: Ripening time, hours—						
40	No spinning.	No spinning.	70	169	151	139
48	do	do	116	182	142	160
56	do	do	108	186	176	138
Bend Test average: Ripening time, hours—						
40	No spinning.	No spinning.	1,151	1,296	943	1,179
48	do	do	960	1,400	1,699	1,727
56	do	do	1,294	1,257	1,324	1,471

A study of Table III will reveal that spinning of a 4.2% cellulose, 6.5% NaOH viscose was impossible when a setting bath containing 1% zinc sulphate was used. When the setting bath contained 2.5% zinc sulphate spinning was successful and the yarn produced exhibited excellent bend test as shown in the table. With this 2.5% zinc sulphate setting bath we found occasional instances of spinning difficulty, and occasional batches of yarn were considerably weaker than others. From this we conclude that our setting bath should not contain substantially less than about 2.5% zinc sulphate. This conclusion is supported by the fact that when the setting bath contained 4% zinc sulphate no spinning difficulties were encountered and the yarn uniformly exhibited excellent strength characteristics and the very high bend tests shown in Table III.

A comparison of the results of using a setting bath containing 4% zinc sulphate and the results of using a setting bath containing 10% zinc sulphate as set forth in Table III serves to illustrate that while some advantage is achieved by raising the zinc sulphate concentration to 10% the improvement in the yarn is not proportionate to the expense of such increase. It is apparent that zinc sulphate concentrations of 10% or more may be used if so desired. It is also apparent that there is considerably more advantage in increasing the zinc sulphate concentration from about 2.5% to 4% than there is in increasing the concentration substantially above 4%. It is for this reason that we have concluded that a 4% zinc sulphate concentration constitutes a practical optimum. Nevertheless, for the purposes of achieving the novel results of our invention the special setting bath needs only to be characterized as containing not substantially less than about 2.5% of zinc sulphate.

Table III also shows a comparison of the results of using cotton linters and wood pulp as the source of cellulose. It will be observed that with the spinning bath containing 1% zinc sulphate no spinning was possible with either a linters or wood pulp viscose. When a spinning bath containing 4% zinc sulphate is used excellent spinning is achieved with either form of viscose.

For all our experiments with viscoses containing 6.5% caustic soda we have used 105 to 110 grams per litre acid. We have to emphasize the fact that the range 100 to 115 grams per litre acid is the best range for very low cellulose concentrations, for instance 4.5%. We may also note that this range is the limiting range for soft yarn when 6.5% caustic soda is used in the viscose.

As the cellulose concentration is increased the tolerance towards variation in acidity also increases, and the general tendency is for slightly better bend test with lower acidity. However, below 90 grams per litre and even with 7.5% cellulose there are spinning troubles which would prevent commercial use. In all our discussions on acidity we refer to tests on the acid entering the spinning machine. Figures in the spinning trough would be 5 to 10 grams per liter lower.

Regarding stretching, we have standardized all our experiments on 77% stretch between godets, having in mind low extensibility in the resulting yarn and yet perfect spinning. We have employed lower stretch down to 50% and have produced satisfactory high-tenacity yarn with the same relation of bend tests for different percentages of cellulose, but the extensibility of the yarn is too high for easy slashing to tire yarn level. Similarly we have employed higher stretch up to 85% but have not found this to be justified by results.

With regard to spinning speeds, all our experiments have been made with 50 meters per minute, but our invention is not limited to this speed. The relative improvement in bend test due to low cellulose for higher spinning speed is just as great as with 50 meters per minute, if not greater.

In all of the above examples and tests the viscose solution has contained varying concentrations of cellulose but the concentration of sodium hydroxide has remained constant at 6.5%. It is not critical that the percentage of NaOH be limited to 6.5%. Higher concentrations of NaOH may be used and the results of such use are about those to be expected as a result of experience in varying NaOH concentration in viscoses of the usual cellulose content of about 7.5%. Table IV sets forth the results of a series of tests in which the effect of changing the concentration of NaOH is examined. Table IV is also important to the present disclosure in that it makes a very thorough comparison between the yarn spun from a viscose containing 6% cellulose in accordance with our invention and a yarn spun from 7.5% cellulose viscose under the same conditions. This is of particular importance in that in many manufacturing plants it is possible with existing equipment to lower the cellulose concentration of the viscose to 6% while it may not be possible without the installation of larger viscose tanks and the like to lower the concentration below 6%. Thus our invention

gives to the art a yarn of tire cord quality which may be manufactured from wood pulp with existing equipment.

It should be expected that yarn having very high degree of polymerization possesses certain advantages with regard to mechanical properties.

Table IV

Viscous Composition: Cellulose, percent	6			6			7.5			7.5		
NaOH, percent	6.5			8.5			6.5			8.5		
Steeping	Normal			Normal			Normal			Normal		
Shredding	Normal			Normal			Normal			Normal		
Aging Temp., °C	20			19			20			19		
Aging Time, Hours	35			35			59			59		
Xanthation	Normal			Normal			Normal			Normal		
Ripening Temp., °C	19			19			19			19		
Ripening Time, Hours	40	48	56	40	48	56	40	48	56	40	48	56
Ripening Index (maturimeter 12.5% NH_4Cl)	12.7	11.6	11.6	17.7	14.9	14.6	11.4	------	10.1	13.8	13.7	13.5
Tension in grams between godets	439	493	443	525	525	593	431	418	444	494	482	471
g./d. strength-dry	3.28	3.39	3.41	3.23	3.50	3.61	3.40	3.46	3.52	3.47	3.72	3.72
g./d. strength-wet	2.14	2.22	2.23	2.27	2.30	2.35	2.13	2.13	2.18	2.27	2.23	2.27
Per cent Extensibility-dry	20.6	21.3	21.4	19.9	20.4	21.7	20.4	20.5	20.7	20.9	20.8	21.4
Tensile Factor	145	160	162	146	165	184	148	152	159	164	173	180
Bend Test, average	927	916	780	1,304	1,057	980	452	460	471	719	478	472
Setting Bath:												
H_2SO_4 g./l	110			151.7			110			151.7		
$ZnSO_4$ g./l	52.6			52.8			52.6			52.8		
D_{20}	1.298			1.317			1.298			1.317		

Stretch between godets	percent	77.5
Temp. of the intermediate bath	°C.	87
Immersion	inches	30
Immersion in hot water	do	17
Spinneret holes	do	.0025
Spinning speed at top godet	meters per minute	50
Circulation of the bath per spindle	liters per minute	1.5
Circulation of the intermediate bath	do	1.8

From a study of Table IV it will be apparent that there is an enormous increase in fatigue resistance in the yarn prepared in accordance with our invention from a viscose containing 6% cellulose compared to that of yarn prepared from 7.5% cellulose viscose. It is also apparent that the yarn made in accordance with our invention from 6% cellulose, 8.5% NaOH viscose is somewhat superior to that made from 6.5% cellulose, 6.5% NaOH viscose. The degree of superiority is very obviously smaller than the superiority of either of the 6% cellulose viscose yarns over the 7.5% cellulose viscose yarns. It is thus graphically illustrated that the cellulose concentration is more important than the ratio of cellulose to caustic.

From a consideration of the various tables set forth above it will be apparent that there is a tendency towards higher wet strength in the yarns spun from viscoses of low cellulose content.

We believe that it should be pointed out here that since with lower cellulose concentrations the alkali cellulose is aged a very much shorter time, the regenerated cellulose in the yarn will have a correspondingly higher degree of polymerization. In this connection we have been able to relate the degree of polymerization to the concentration of cellulose in viscose by the equation: D. P.=268.5+48(7—C). In this equation C equals cellulose concentration in percentage. Therefore a yarn made with 7.5% cellulose viscose would have a D. P. averaging 244 while a yarn made with 4% cellulose viscose would have a D. P. averaging 412. It may be mentioned that our figures for D. P. are based on Staudinger's formula and are lower than those based on more recently developed formulas.

However, the advantage of our novel process and the yarn produced thereby is not confined to any advantage resulting from the higher degree of polymerization. This is demonstrated by tests which we have made in which we have aged the alkali cellulose for the same period of time as would have been involved had we been preparing a 7.5% viscose. We then prepared viscoses of cellulose concentration varying between 6.5% and 4%, which viscoses, of course, had viscosities considerably below the normal spinning viscosity. We spun such low cellulose viscoses under the conditions necessary in the carrying out of our invention and the product was high tenacity yarn showing an improvement in bend test of intermediate degree.

It is known that tire yarn has to be slashed or strained in order to decrease the extensibility to the level of 10% required by the tire manufacturers. We had found that the relative improvement of bend test on slashed yarn when lowering the cellulose is as great as if not greater than that on the unslashed yarn.

From the above disclosure it will be apparent that we have provided a process and a product fulfilling the objects of our invention. The essential features of our process are the spinning of a viscose containing from 6.5% to about 3% cellulose and a desirable quantity, say 6.5% or 3.5%, of NaOH into a spinning bath containing about 2.5% or more zinc sulphate. Preferably the spinneret holes have a diameter not substantially greater than .0025". This particular feature is of value throughout our range of cellulose concentrations and is of most importance where the viscose has been ripened for a relatively short period of, say, 32 hours. The yarn is stretched in

spinning to a high degree, as for example about 77.5%, at elevated temperatures. The bend test results on yarns made in accordance with our invention are far in excess of those on any yarns with which we are familiar, whether from wood pulp, linters, or blends. In this connection we have tested substantially all of the yarns commercially available and actually in use in the manufacture of tire cords. Such commercial yarns are made from viscose containing a large proportion, and in many instances containing 100%, of cotton linters cellulose. We have never found a commercial yarn exhibiting a bend test above 600 when such bend test is made under the conditions specified herein or corrected for denier, slashing, and the like.

In the above disclosure frequent reference has been made to the value of our process in the manufacture of tire yarn. It is obvious that the benefits of high fatigue resistance which we secure are of value in textile yarn. An additional advantage of our process is that by lowering the cellulose content the very common defect of milkiness and milky streaks in the yarn is progressively reduced and eliminated. This, of course, refers to comparisons upon viscoses of the same ripeness. This latter benefit is of great importance in textile yarn.

The advantages of our process are clearly of value in the manufacture of staple fibre as well as special types of artificial straw, horse-hair, films, and the like.

Our process, which makes it possible to spin solutions of very low cellulose concentration, has a further value which should not be overlooked. It is much easier to obtain solutions of low cellulose content than solutions of a cellulose content around 7.5%. This applies not only to viscose solutions but to spinning solutions in which cellulose or its esters and ethers is dissolved in alkaline solutions or in other solvents such as ammonium quaternary compounds, zinc chloride solutions, cuprammonium, cupri-ethylenediamine and the like and also applies to the direct or one-stage viscose processes. Indeed, with many solvents it is practically possible to obtain solutions of cellulose only in a concentration around 4%, well outside the range in which spinning heretofore has been commercially practicable.

In certain claims the words "bend test value" are used. These words define the average number of bends required to break the yarn on the Schopper bending tester D. P. 5 under the conditions specified above and in the denier range specified.

The improvement in bend test, due to low cellulose concentrations, is relatively similar for textile yarns of lower denier, for example 100, 150, 300, 400 and 600 deniers, but of course the absolute value of the bend test at the same load per denier increases as the denier decreases.

From the above disclosure it will be apparent that modifications and variations may be resorted to by those skilled in the art and it is intended that the scope of this invention shall be limited only by the appended claims.

We claim:

1. In a method of producing rayon filaments of the class which when spun as yarn of 1150 to 1250 denier comprising 480 filaments have a bend test value above 1000 the step of projecting a ripened viscose solution having a normal viscosity on the order of 46 poises and having a cellulose concentration of about 4.5% into a spinning bath containing about 4% zinc sulfate and about 8% sulfuric acid.

2. In a method of producing rayon filaments of the class which when spun as yarn of 1150 to 1250 denier comprising 480 filaments have a bend test value above 1000 the steps of projecting a ripened viscose solution having a normal viscosity on the order of 46 posies and having a cellulose concentration of about 4.5% into a spinning bath containing about 4% zinc sulfate and about 8% sulfuric acid and stretching at elevated temperature the filaments leaving said spinning bath to the extent of at least 50% of their original length.

3. In a method of producing rayon filaments of the class which when spun as yarn of 1150 to 1250 denier comprising 480 filaments have a bend test value above 1000 the steps of projecting a ripened viscose solution having a cellulose concentration of about 4.5% into a spinning bath containing about 4% zinc sulfate and about 8% sulfuric acid and stretching at elevated temperature the filaments leaving said setting bath to the extent of about 77% of their original length.

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