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STABILIZED CELLULOSE YARNS AND METHOD OF PREPARING SAME

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This invention relates to regenerated cellulose yarns, threads, cords and the like, and more particularly to the treatment of regenerated cellulose yarns, threads, cords, and the like with a material for increasing the resistance of such structures to deterioration by heat.

Heretofore, regenerated cellulose yarns possessed the disadvantageous characteristic of deteriorating very considerably when subjected to elevated temperatures.

It is an object of the present invention to treat regenerated cellulose yarns in such a manner as to increase their resistance to deterioration by heat.

It is another object of this invention to treat regenerated cellulose yarns, particularly regenerated cellulose yarns having a high dry tenacity, in such a manner that the resultant yarns will have an increased resistance to deterioration by heat.

It is a further object of this invention to prepare articles containing regenerated cellulose yarns which articles are suitable for use at elevated temperatures.

The still more specific object of this invention is the production of rubber goods reinforced with regenerated cellulose yarns which have been treated in such a manner as to increase their resistance to deterioration by heat.

These and other objects of the invention are accomplished, in general, by intimately associating regenerated cellulose yarns with urea. This may be accomplished by immersing the yarns in a solution of urea and drying the same. Under certain circumstances, it may be desired to subject the yarn so treated to a mild heating or baking procedure at a suitable temperature for a suitable period of time. Other factors being equal, the degree of increase in resistance to deterioration by heat of the regenerated cellulose yarn thus treated will be proportional to the amount of urea with which it is impregnated, up to a certain limit.

In accordance with the present invention, it has been discovered that regenerated cellulose yarn, such as viscose rayon yarn or cuprammonium rayon yarn, may be stabilized against the deteriorative action of heat by impregnation of the yarn with urea. Whereas an untreated regenerated cellulose yarn, subjected to heating for a period of 24 hours at a temperature of 170° C., shows a loss of strength of about 50 per cent, the same yarn, when impregnated with various amounts of urea, shows, on heating, losses decreasing in proportion to the amount of urea con-

tained therein. This effect is demonstrated by the data in the following table:

Urea content	Loss of strength after heating 24 hrs. at 170° C.
Per cent	Per cent
None	50
3.0	41
6.2	34
7.6	22
10.4	10

That this effect is by no means peculiar to the temperature of 170° C. is demonstrated by its stabilizing action at 125° C., as indicated by the following data:

Urea content	Loss of strength after heating 336 hrs. at 125° C.
Per cent	Per cent
None	33
10.4	1+3

Gain in strength.

The stabilizing action of urea is likewise demonstrated by comparison of the rate of strength loss of the untreated regenerated cellulose yarn with that of same yarn impregnated with about 10 per cent urea. The comparative data are given in the following table:

Hours heating at 170° C.	Strength in grams at room temperature	
	Untreated yarn	Treated yarn
0	907	850
1	(880)	883
2	(861)	927
3	(850)	924
3½	847	902
4	(825)	891
7	(754)	864
8	738	(847)
16	597	(798)
24	473	757

() Graphically interpolated values.

In respect to the above data, it is seen that the stabilizing action of the urea is manifested in two ways; first, by causing a slight increase in the strength of yarn up to a maximum of about 930 grams after about 2½ hrs. of heating, and second, by causing a much slower rate of loss thereafter than for the untreated yarn. The difference in strength before heating, between the

untreated and the treated yarn as shown in the above table is the result of the impregnation.

The preferred method of impregnation consists simply in the immersion of the yarn in an aqueous solution of urea of the desired concentration at room temperature for a period of time not less than five seconds. The immersion is accomplished either by passing a single thread of the yarn continuously through a bath of the solution under such conditions that an immersion of at least five seconds prevails or by simply dipping an entire skein in the solution and allowing it to remain there preferably for at least several minutes. If the impregnation is by passage of the single strand or yarn through a bath, it is important that this be done without the application of undue tension to the yarn or with as little tension as practicable in order to attain the greatest activity from a given amount of urea. If, on the other hand, the impregnation is by dipping a skein of the yarn in the bath all at once, the skein is freed of excess liquor on removal by wringing out in a centrifuge or by other suitable means. The concentration of the urea solution is determined by the extent to which it is desired to impregnate the yarn. For an impregnation of 11 per cent of the weight of yarn, a 10 per cent solution is taken; for 6 per cent, a 5 per cent solution; for 3 per cent, a 2.5 per cent solution; etc. It is apparent that one may stabilize the rayon to the desired degree by varying the amount of urea applied to the yarn or the extent of the impregnation.

Whereas the method of treatment as above described is complete in itself, an additional process may be found desirable. This is especially true for the stabilization of rayon at temperatures above the melting point of urea where its decomposition is likely to occur. The products of decomposition, if prevented from escaping, may prove very deleterious to the rayon and thus counteract the stabilizing activity of the urea. It has been discovered, however, that a baking of the yarn after impregnation may be employed to advantage if volatile products are allowed to escape. A desirable effect may be produced under a variety of conditions, but a satisfactory baking, for example, is for a period of 2-3 hrs. at 170° C. These conditions of baking, though preferred, are also illustrative of what may be obtained by a proper conjunction of time with temperature.

That regenerated cellulose yarn impregnated with urea is not only stabilized against deterioration by heat in respect to its physical properties, such as strength, but also in respect to chemical degradation of the cellulose, is demonstrated by viscosity in its cuprammonium solution. It is a recognized fact that the viscosity of a cuprammonium solution of cellulose is an index of its state of degradation. The following data show that as a result of heating for 24 hours at 170° C., rayon yarn impregnated with urea has by no means been degraded so far as the untreated yarn.

Viscosities of cuprammonium solution containing 2.5% cellulose obtained from yarn heated 24 hrs. at 170° C. centipoises.

Urea impregnated rayon yarn-----	11.7
Untreated rayon yarn-----	5.0

The examples given below are typical of the methods used to produce regenerated cellulose rayon yarn stabilized with urea against deterioration by heat.

Example I

A given length of a viscose rayon yarn prepared in the manner described in the copending application of H. H. Parker, Serial No. 676,463, Patent No. 2,133,714, said yarn consisting of 275 denier, 120 filaments, and 7 turns per inch of twist, is immersed in a bath consisting of 3 parts by weight of urea dissolved in 100 parts of water by the continuous passage of a single strand of the yarn through the same. This is accomplished by running the yarn over a simple system of freely rotating pulleys so as to give a length of yarn of about 60 cm. immersed at any instant and being wound up on a mechanically driven reel. The reel is rotated at such a speed that the rate of travel of the yarn through the bath is about 12 cm. per second and the period of immersion is therefore about five seconds. After passage through the bath, the yarn is allowed to remain on the reel until air dry.

The yarn treated in this fashion will have increased in weight by the impregnation with urea to the extent of 3 per cent. When measured at 50 per cent relative humidity and 25° C., the yarn possesses an initial strength of about 900 grams, whereas after the above treatment, it will have a strength of about 840 grams. After exposure to a temperature of 170° C., for 24 hours, the strength will have decreased to 533 grams, a loss of about 41 per cent of its original strength.

Example II

A given length of the same viscose rayon yarn as in Example I above is treated in precisely the same manner except that the bath consists of a solution of 6 parts by weight of urea in 100 parts of water. The yarn so treated will have been impregnated with urea to the extent of 6.5 per cent. Its strength will have decreased from 900 grams to 858 grams, which, after heating for 24 hours at 170° C., will have decreased again to 652 grams, a loss of about 28 per cent of the original strength.

Example III

A given length of the same viscose rayon yarn as in Example I, above, is treated in precisely the same manner except that the bath consists of a solution of 10 parts by weight of urea in 100 parts of water. The yarn so treated will have been impregnated with urea to the extent of 10.4 per cent. Its strength will have decreased from 900 grams to 833 grams, which, after heating for 24 hours at 170° C., will have decreased again to 811 grams, a loss of about 10 per cent of its original strength. This yarn so treated and heated for two weeks at 125° C., will have recovered in strength from 833 grams to about 930 grams, or to slightly more than its original strength.

Example IV

A skein of the same viscose rayon yarn as used in the previous examples, 200 m. in length, is immersed in a bath consisting of a solution of 6 parts by weight of urea in 100 parts of water for 2½ hours. On removal from the bath, the skein is wrung out immediately in a small centrifuge and hung up till air dry. The skein is beaten out gently during the drying to straighten out the kinks and free the strands one from another. The yarn so treated will have been impregnated with about 6.2 per cent urea. Its strength will have decreased from about 900 grams to 820 grams, a loss of about 9 per cent.

On heating for 24 hours at 170° C., the strength of yarn will have decreased again from 820 grams to 590 grams, a loss of about 34 per cent of its original strength.

Example V

A given length of the same viscose rayon yarn as in Example I above is treated in precisely the same manner except that the bath consists of a solution of 10 parts by weight of urea in 100 parts of water. The yarn so treated will have a urea content of about 10-11 per cent. On becoming air dry, it is heated in an oven at 170° C. for a period of three hours. On reconditioning, the yarn will be found to contain about 7-8 per cent urea and to possess a strength of 924 grams, showing therefore, slight increase over the initial strength of 900 grams. After exposure to a temperature of 170° C. for 24 hours, the strength will have decreased to 625 grams, a loss of about 30 per cent from the strength of the original untreated yarn.

Example VI

A given length of the same viscose rayon yarn as in Example I, above, is treated in precisely the same manner except that the bath consists of a solution of 10 parts by weight of urea in 100 parts of water. The yarn so treated will contain about 10-11 per cent urea and will have a strength of 803 grams. After air drying, heating in an oven at 155° C. for a period of 4½ hours, and reconditioning, the yarn will contain about 7 per cent urea and will possess a strength of 872 grams, showing an increase of 69 grams over its strength before heating. After exposure to a temperature of 170° C. for a period of 24 hours, the strength will have decreased to 665 grams, a loss of about 26 per cent of its original strength.

Although it will generally be desired to treat a yarn with an aqueous solution of urea of a concentration slightly less in per cent than the per cent urea content desired for the yarn, it is also possible to immerse the yarn in solutions of much higher concentrations, followed by a washing to remove the excess urea, leaving behind the desired amount. This washing may be accomplished either before or after the treated yarn has become air dry. The use of the solutions of higher concentrations results in proportionately greater losses of initial tenacity, but the removal of excess urea by washing restores the strength of yarn to that value normal for the remaining urea content. Likewise, the stabilization of the yarn against deterioration by heat is proportional to the remaining amount of urea, in the same degree as though the yarn had been directly treated with solutions of the appropriate concentrations. This manner of treatment is illustrated by the following examples:

Example VII

A length of the same viscose rayon yarn as in Example I, previously cited, is treated in precisely the same manner except that a solution of 15 parts by weight of urea in 100 parts of water is used and that the yarn immediately after passage through this solution is run through a bath of water. The length of yarn immersed at any instant in the bath of water is 33 cm. The yarn so treated instead of possessing the usual 15-16 per cent content of urea and a strength of about 750 grams, contains 7.6 per cent urea and has a strength of 839 grams. After exposure to a temperature of 170° C. for a period of 24 hours, the

strength will have decreased to 698 grams, a loss of about 22 per cent of its original strength.

Example VIII

A length of the same viscose rayon yarn as in Example VII is treated in precisely the same manner except that a solution of 25 parts by weight of urea in 100 parts of water is used and that the washing process is repeated after the skein becomes air dry. The yarn so treated, instead of possessing a urea content of perhaps 25 per cent and a strength of 688 grams, contains about 10 percent urea and has a strength of 827 grams. After exposure to a temperature of 170° C. for a period of 24 hours, the strength will have decreased to 710 grams, a loss of about 21 per cent of its original strength.

In addition to the finished yarn, it is also possible to treat it while still wet from the spinning operation or in the gel state. This gel yarn may be treated in the same manner as the finished yarn and the stabilizing action of urea is similarly effective, as illustrated in the following example:

Example IX

A length of viscose rayon yarn in the gel state is treated in precisely the same manner as in Example I, above, except that a solution of 7 parts by weight of urea in 100 parts of water is used. As a result of this treatment, the yarn possesses a urea content of about 7 per cent and when dry its strength will be about 797 grams, rather than about 900 grams, the strength of the untreated yarn when dried. After exposure to a temperature of 170° C. for a period of 24 hours, its strength will have decreased again to 649 grams, a loss of about 28 per cent of its original strength when dried.

Although aqueous solutions may prove the more convenient, other solvents may be used to treat the yarn with urea. For instance, solutions of urea in ethyl alcohol may be used and the yarn so treated and containing urea possesses likewise the increased resistance to deterioration by heat, shown by yarn similarly treated from aqueous solutions. The use of other solvents is illustrated by the following example:

Example X

A length of the same viscose rayon yarn as in Example I, above, is treated in precisely the same manner except that a solution of 2 parts by weight of urea in 100 parts of ethyl alcohol is used. The yarn so treated possesses a urea content of about 2 per cent and a strength of 847 grams. After exposure to a temperature of 170° C. for a period of 24 hours, its strength will have decreased to 500 grams, a total loss of about 44 per cent.

The treatment of viscose rayon yarn with urea according to the methods described above may precede their treatment with a resin-latex adhesive preparation of the type described by Charch and Maney in their patent application, Serial No. 12,739, filed March 23, 1935, Patent No. 2,128,635, or any other adhesive treatment. Such adhesives are frequently applied to textiles of regenerated cellulose used for reinforcement of articles made of rubber, such as rayon tire cords, in order to effect a stronger binding between the textile and the rubber, as described in said application.

The tenacity values of the thread or yarn as above expressed in grams refers to the breaking

strength of the thread as determined by a Scott testing machine regulated under identical conditions with the same rate of loading.

The methods of treatment of yarn described above whereby through the intimate association of urea with the cellulose, the resistance to deterioration by heat of the yarn is increased, may be varied over a wide range. The yarn may be impregnated with urea from its solution in any solvent for urea which is itself not deleterious to the yarn either at room or elevated temperatures. In the case where a heating or baking of the yarn after treatment with a solution of urea is preferred, there are no limits to the temperature or period of heating except such as would destroy the ultimate usefulness of the yarn. Generally, however, a minimum temperature of about 135° C. is to be preferred. A great number of combinations of temperatures and periods of heating may be chosen, realizing that with higher temperatures, shorter periods may be used to achieve the same effects and vice versa. The optimum results, however, are obtained in the range of 140° to 170° C. and for from six to two hours. Temperatures much in excess of 170° C. are to be avoided because of their destructive effects upon the yarn even for short periods.

Regenerated cellulose yarn, so treated as to associate urea intimately with the cellulose, may be used for all purposes to which such a yarn might otherwise be put and which subject it eventually to elevated temperatures such as would more rapidly destroy the usefulness of the untreated than the treated yarn. The yarn treated according to this invention may be twisted into cords or other materials for use as reinforcement for rubber articles, including motor vehicle tires and steam hoses. Such treated yarn will withstand, far better than the untreated yarn, deterioration during the manufacture of the rubber products involving such operations as vulcanization at an elevated temperature, or in uses where the products are subjected to elevated temperatures. Also, yarn so treated may in one or another form be woven into fabrics for uses at elevated temperature, such as the covering of laundry mangles or as zinc oxide fume bags.

Among other uses for this treated yarn are covers and protectors for sun exposed objects such as awnings and beach umbrellas; automobile top materials; masks and protectors around steel furnaces and the like; fabric tubes for discharge ends of chutes for hot materials as in cement mills; bags for heating pads and electrically heated clothing; strainers for hot oil and other hot non-aqueous materials; belt driers such as on blueprint machines; and conveyor belts for hot materials.

Whereas viscose rayon yarn is ordinarily deteriorated on exposure to heat, the present invention makes possible a yarn possessing marked stability under the same conditions. Thus, a yarn which on exposure to a heating of 24 hours at 170° C. is so deteriorated as to have lost 50 per cent of its original strength, may be so treated according to this invention as to lose little or none of its strength, on the same exposure to heat. Furthermore, under conditions of use where the decomposition products resulting from this treatment are prevented from free escape as would perhaps be the case in a tire, and be therefore deleterious to the cellulose, one of the

modifications of the invention allows this effect to be largely mitigated.

In order to approximate more nearly the heat deteriorating conditions existing inside a rubber tire operating at high speed on the road, certain heat tests have been made in sealed tubes. When untreated regenerated cellulose yarn of the type described in Example I was heated for 24 hours at 170° C. in a sealed tube, it charred black and a heavy condensate of a tarry substance and moisture formed in the tube. After heating the yarn had no strength, having suffered a loss of 100% of its initial strength. When the same yarn was treated to contain 10% urea and heated for the same length of time and at the same temperature in a sealed tube, it lost only about 40% of its initial strength.

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

I claim:

1. The process of stabilizing unmodified regenerated cellulose yarns against deterioration by heat which comprises impregnating said yarns with urea to the extent of at least 3% by weight of said yarns.

2. The process of stabilizing unmodified regenerated cellulose yarns against deterioration by heat which comprises treating said yarns with a solution of urea in such a manner as to impregnate said yarns with urea to the extent of at least 3% by weight of said yarns, and drying the urea-impregnated yarns.

3. The process of stabilizing unmodified regenerated cellulose yarns against deterioration by heat which comprises immersing said yarns in a solution of urea for a period of at least 5 seconds in such a manner as to impregnate said yarns with urea to the extent of at least 3% by weight of said yarns, and drying the urea-impregnated yarns.

4. The process of stabilizing unmodified regenerated cellulose yarns against deterioration by heat which comprises treating said yarns with a solution of urea in such a manner as to impregnate said yarns with urea to the extent of at least 3% by weight of said yarns, and baking the urea-impregnated yarns at a temperature above the melting point of urea and under such conditions that volatile products are allowed to escape from said yarns.

5. The process of stabilizing unmodified regenerated cellulose yarns against deterioration by heat which comprises passing said yarns through a solution of urea with a minimum amount of tension in such a manner as to impregnate said yarns with urea to the extent of at least 3% by weight of said yarns, and drying the urea-impregnated yarns.

6. An unmodified regenerated cellulose yarn containing, as an agent for stabilizing said yarn against deterioration by heat, urea impregnated therein to the extent of at least 3% by weight of said yarn.

7. The process of stabilizing unmodified regenerated cellulose yarns against deterioration by heat which comprises treating said yarns with a solution of urea in such a manner as to impregnate said yarns with urea to the extent of at least 3% by weight of said yarns, and baking the urea-impregnated yarns for a period from 6 to 2 hours at a temperature in the range of

140° C. to 170° C. and under such conditions that volatile products are allowed to escape from said yarns.

8. The process of stabilizing unmodified regenerated cellulose yarns against deterioration by heat which comprises treating said yarns with a solution of urea in such a manner as to impreg-

nate said yarns with urea to the extent of at least 3% by weight of said yarns, air drying the urea-impregnated yarns, and baking the same at a temperature above the melting point of urea and under such conditions that volatile products are allowed to escape from said yarns.

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