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STABILIZING CELLULOSE YARNS

John S. Reese, IV, Wilmington, Del., assignor to
E. I. du Pont de Nemours and Company, Wil-
mington, Del., a corporation of Delaware

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

Heretofore, certain cellulosic yarns, for example, regenerated cellulose yarns, have had the disadvantageous characteristic of deteriorating to a considerable extent when subjected to elevated temperatures.

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

It is another object of this invention to treat certain cellulosic yarns, for example, 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 cellulosic yarns, particularly regenerated cellulose yarns, which articles are suitable for use at elevated temperatures.

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

Other objects of the invention will appear hereinafter.

The objects of the invention may be accomplished, in general, by intimately associating cellulosic yarns, for example, regenerated cellulose yarns, with biuret, and drying the same. Other factors being equal, the degree of increased resistance to deterioration by heat of the cellulosic yarns thus treated will be proportional to the amount of biuret with which they are impregnated, up to a certain limit.

In accordance with the present invention, it has been discovered that cellulosic threads, for example, regenerated cellulose thread such as viscose rayon thread, or cuprammonium rayon thread, may be stabilized against the deteriorative action of heat by impregnation of the thread with biuret. Whereas an untreated regenerated cellulose thread, subjected to heating for a period of 24 hours at a temperature of 170° C., shows a loss of strength of about 50%, the same yarn, when impregnated with various amounts of biuret, shows, on heating, losses decreasing approximately in direct proportion to the amount of biuret thereon up to the point where at a 12 to 13 per cent biuret content, no loss is suffered.

This effect is demonstrated by the data in the following table:

Biuret content	Loss on heating (24 hrs. at 170° C.)
Percent	Percent
None	50
3.7	48
4.9	26
5.4	35
6.1	28
7.4	26
8.5	19
9.1	15

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:

Biuret content	Loss of strength after heating 336 hrs. at 125° C.
Percent	Percent
None	33
9.1	3

The method of impregnation consists simply in the immersion of the yarn in an aqueous solution of biuret of the desired concentration at whatever temperature is required to maintain the biuret in solution, for a suitable period of time. The immersion is accomplished either by passing a single thread of the yarn continuously through a bath of the solution with a suitable length of yarn immersed at any instant and at a suitable rate of travel. Or, the immersion may be accomplished by simply dipping an entire skein in the solution and allowing it to remain there for a suitable period of time. 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 stabilizing activity from a given amount of biuret.

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 excessive liquor on removal by wringing out in a centrifuge or by other suitable means. In both methods, the concentration of the biuret solution is determined by the extent to which it is desired to impregnate the yarn. A bath of the solution contain-

ing a given number of parts of biuret per hundred parts by weight of solvent will produce an impregnation of approximately an equal number of parts, or perhaps slightly greater of biuret per hundred parts by weight of yarn. It is apparent that one may stabilize the yarn to the desired degree by varying the amount of biuret applied to the yarn; or the extent of the impregnation.

That the regenerated cellulose, or similar cellulosic thread impregnated with biuret 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 the viscosity of 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 table shows that, as a result of heating for 24 hours at 170° C., regenerated cellulose yarn impregnated with biuret has by no means been degraded so far as the untreated yarn:

Viscosity of cuprammonium solution containing 2.5% cellulose obtained from yarns heated 24 hrs. at 170° C., centipoises	
Regenerated cellulose thread impregnated with biuret.....	8.0
Untreated yarn.....	5.0

Cotton yarn containing biuret is likewise stabilized against the deteriorative action of heat. Although the effect is not so pronounced as in the case of regenerated cellulose thread, it is nevertheless real. The treatment of the cotton yarn is similar to that for rayon, except that a wetting agent such as one of the sulfated alcohol type may be used in suitable quantities to assist the impregnation. Whereas an untreated cotton yarn when heated for 24 hours at 170° C. loses 50-55% of its initial strength, cotton yarn, when treated with a 5% aqueous solution of biuret, loses with the same heating, 42-47% of its initial strength.

The examples given below are typical of the methods used to prepare cellulosic threads stabilized with biuret against the deteriorative action of heat.

Example I

A given length of a viscose rayon yarn, consisting of 275 denier, 120 filaments, and 7 turns of twist per inch, produced by the method described in the copending application of H. H. Parker, Serial No. 676,463, filed June 19, 1933, Patent No. 2,133,714, is immersed in a bath consisting of 8 parts by weight of biuret and 100 parts of water, maintained at a temperature of 50-60° C., 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 rate of traverse 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 biuret to the extent of 8 to 9 per cent. Whereas the yarn initially possessed a strength of about 900 grams, after the above treatment its strength is

864 grams. After exposure to a temperature of 170° C. for 24 hours, the strength will have decreased to 735 grams, a loss of about 18 per cent of its original strength. An untreated yarn exposed to the same heat treatment will have a loss in strength of about 50%.

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 5 parts by weight of biuret in 100 parts of water at room temperature. The yarn so treated will not have suffered in strength, the initial strength of 900 grams being substantially the same as the strength after treatment. After exposure to a temperature of 170° C. for 24 hours, the strength will have decreased to 665 grams, a loss of 26 per cent.

Example III

A skein of the same viscose rayon yarn as used in Example I above and of a given length is immersed in a bath consisting of a solution of 8 parts by weight of biuret in 100 parts of water maintained at 50-60° C. for one hour. On removal from the bath the skein is wrung out immediately in a centrifuge and, before becoming air dry, the skein is rewound to straighten out the kinks and free the strands one from another. The yarn so treated will have virtually retained its initial strength. This yarn will contain 8-9 per cent biuret and on exposure to a temperature of 170° C. for 24 hours, it will have decreased in strength to 701 grams, a loss of 22 per cent.

Example IV

A given length of 23 count singles Sak cotton yarn is treated in precisely the same fashion as the rayon yarn in Example I above, except that the bath consists of a solution of 5 parts by weight of biuret in 100 parts of water and to which is added 0.03 of a part of sodium pentadecyl-8 sulfonate. The yarn so treated will contain 6-7 per cent biuret and will possess a strength of 450 grams which strength is not lower than that often possessed by the untreated yarn. After exposure to a temperature of 170° C. for 24 hours, its strength will have decreased to 260 grams, a loss of 42 per cent.

Although it will generally be desired to treat cellulosic threads according to the methods above described, solvents other than water may also be used. Furthermore, it is possible to impregnate a thread such as viscose rayon yarn while still in the gel state. In the case of cotton, the use of a wetting agent to facilitate the impregnation, while it may be used, is not necessary since similar results may be obtained without its use by a previous boiling-out of the cotton in a dilute solution of sodium carbonate. Also, any type of wetting agent which readily allows the yarn to be wetted by the solution may be used. Like rayon, the cotton yarn may also be treated by the immersion of a whole skein in the bath, all at once.

Although the use of a purified biuret is implied throughout the above description, it is also possible to use the unpurified or crude material, such as is formed by the heating of urea at temperatures well above its melting point. Whereas the data and examples heretofore cited were obtained with a biuret mixture with a melting point of 190-191° C., (M. P. of pure biuret=193° C.) preparations with melting points of 175° C. or less when applied to the viscose rayon yarn in the same manner as before will give equally satis-

factory results. This is illustrated by the following data:

M. P. of biuret	Biuret on yarn	Loss of strength on heating 24 hrs. at 170° C.
	Percent	Percent
175° C.	7	25
175° C.	8	26
170° C. (approx.)	7	27
170° C.	6.5	24

In effect, this means that the product obtained by the heating of urea to a temperature of 145–155° C. for periods of 8 to 10 hours and probably composed largely of urea, biuret, and cyanuric acid, as well as similar mixtures obtained by various degrees of purification may be used as well as the pure biuret itself. However, where the yarn so treated according to this invention is to be put to a use where the further decomposition products of the urea present are prevented from free escape, the use of substantially pure biuret is to be preferred.

The treatment of cellulosic threads with biuret 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.

The methods of treatment of cellulosic threads described above, whereby through the intimate association of biuret with 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 biuret from any solvent for biuret which is itself not deleterious to the particular yarn in question, and at whatever temperature is required to maintain the solution.

The tenacity values of the yarn as above expressed in grams refer to the breaking strength of the yarn as determined by a Scott testing machine regulated under identical conditions with the same rate of loading.

The increased resistance to deterioration by heat imparted to the cellulosic yarn by the treatment makes the yarn particularly useful where it is to be subjected to elevated temperatures. Viscose rayon yarn, or similar cellulosic yarns so treated to associate biuret intimately with the yarn, 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 hose. 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 elevated temperatures or in use 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 temperatures 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 elec-

trically 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.

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, or cotton yarn was heated in a sealed tube for 24 hours at 170° C., it had no strength left at all. When cotton yarn was impregnated with biuret to the extent of 5 per cent, it lost only about 45 per cent of its initial strength under the same conditions of heating. When regenerated cellulose yarn was impregnated with biuret to the extent of 8 per cent and subjected to the same test, it lost less than 40 per cent of its initial strength.

Whereas present cellulosic yarn, such as viscose rayon yarn is ordinarily deteriorated on exposure to heat, the present invention makes possible the treatment of this yarn so that it possesses a marked stability under the same conditions. The use of biuret has the further advantage that impregnation of a cellulosic yarn will cause very little loss of the initial strength of the yarn. The use of biuret is furthermore advantageous in that it has a high decomposition point (193° C.). The use of biuret is also advantageous in that it will not activate any of the widely used rubber accelerators when used for reinforcement of rubber articles.

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 cellulose yarns against deterioration by heat which comprises impregnating said yarns with biuret to the extent of at least 3.7% by weight of said yarns.

2. The process of stabilizing regenerated cellulose yarns against deterioration by heat which comprises impregnating said yarns with biuret to the extent of at least 3.7% by weight of said yarns.

3. The process of stabilizing cellulose yarns against deterioration by heat which comprises treating said yarns with a solution of biuret in such a manner as to impregnate said yarns with biuret to the extent of at least 3.7% by weight of said yarns, and drying the biuret-impregnated yarns.

4. The process of stabilizing cellulose yarns against deterioration by heat which comprises immersing said yarns in a solution of biuret for a period of at least 5 seconds in such a manner as to impregnate said yarns with biuret to the extent of at least 3.7% by weight of said yarns, and drying the biuret-impregnated yarns.

5. The process of stabilizing cellulose yarns against deterioration by heat which comprises passing said yarns through a solution of biuret with a minimum amount of tension in such a manner as to impregnate said yarns with biuret to the extent of at least 3.7% by weight of said yarns, and drying the biuret-impregnated yarns.

6. A cellulose yarn containing, as an agent for stabilizing said yarn against deterioration by heat, biuret impregnated therein to the extent of at least 3.7% by weight of said yarn.

7. A regenerated cellulose yarn containing, as

an agent for stabilizing said yarn against deterioration by heat, biuret impregnated therein to the extent of at least 3.7% by weight of said yarn.

8. The process of stabilizing viscose rayon yarns against deterioration by heat which comprises impregnating said yarns in the gel state with biuret to the extent of at least 3.7% by weight of said yarns.

9. The process of stabilizing cotton yarns against deterioration by heat which comprises treating said yarns with a solution of biuret and a wetting agent in such a manner as to impregnate said yarns with biuret to the extent of at least 3.7% by weight of said yarns, and drying the biuret-impregnated yarns.

10. The process of stabilizing cellulose yarns against deterioration by heat which comprises impregnating said yarns with biuret to an extent

sufficient to stabilize said yarns against deterioration by heat.

11. The process of stabilizing regenerated cellulose yarns against deterioration by heat which comprises impregnating said yarns with biuret to an extent sufficient to stabilize said yarns against deterioration by heat.

12. A cellulose yarn containing, as an agent for stabilizing said yarn against deterioration by heat, biuret impregnated therein to an extent sufficient to stabilize said yarn against deterioration by heat.

13. A regenerated cellulose yarn containing, as an agent for stabilizing said yarn against deterioration by heat, biuret impregnated therein to an extent sufficient to stabilize said yarn against deterioration by heat.

JOHN S. REESE, IV.