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

Certain cellulose yarns, for example, regenerated cellulose yarns, have the disadvantageous characteristic of deteriorating to a considerable extent when subjected to elevated temperatures. While certain materials, such as urea or biuret or phenyl biguanide, have been used successfully as heat aging inhibitors, more effective agents have been desired to reduce even further the extent of deterioration in the yarns.

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

It is another object of this invention to treat certain structures, for example, regenerated cellulose yarns having high dry tenacities, 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 cellulose or other yarns, as, for example, 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 cellulose yarns, for example, regenerated cellulose yarns which have been treated in such a manner as to increase their resistance by heat.

Other objects of the invention will appear hereinafter.

The objects of the invention may be accomplished, in general, by intimately associating the structures, for example, regenerated cellulose yarns, with a readily oxidizable metal. For purposes of this invention such a metal is one which at temperatures of about 150°C reacts with both air and water to form alkaline products. These products are in themselves heat-aging inhibitors. The metals preferred for use in the process of this invention are those which have only one positive valence and those whose hydroxides are no more water-soluble than strontium hydroxide.

It has been discovered that both moisture and oxygen hasten heat degradation and that when they are acting simultaneously a synergistic effect results. This invention, then, is based upon the removal of both water and oxygen by reaction with a metal. Advantageously, in the removal of degradative materials, as oxygen and water, by the process of this invention, increased useful life of the structure results. The desired application is conducted so that the resultant structure contains an optimum amount of the particular metal being used. Other factors being equal, the degree of increased resistance to deterioration by heat of the structures thus treated will be proportional to the amount of metal with which they are impregnated, up to a certain limit.

In accordance with the present invention, it has been discovered that cellulose and other structures, for example, regenerated cellulose threads such as viscose rayon threads, or cuprammonium rayon threads, may be stabilized against the deteriorative action of heat by impregnation of the threads with a metal such as aluminum or magnesium. Whereas an untreated regenerated cellulose thread subjected to heating at 150°C for a period of 4 hours in sealed tubes containing air and 12% moisture shows a loss of strength of over 50%, similar yarn when impregnated with about 0.2% of magnesium flake shows on heating for 4 hours at 150°C a loss of strength of only 14%. Likewise, structures constructed of certain cellulose derivatives may be stabilized by the process of this invention. For example, lowly-substituted ethers such as methyl or ethyl cellulose and esters of cellulose, such as the acetates or butyrates, may be stabilized against heat deterioration by impregnation of their respective structures with the metals of this invention. Further, yarns, threads, cords and the like of cotton, of nylons or polymeric esters may be similarly stabilized.

The examples given below are typical of the methods used to prepare structures stabilized against the deteriorative action of heat with a metal by the process of this invention. These examples, wherein parts are by weight, are illustrative only and are not to be construed as limitative.

**Example I**

A high tenacity regenerated cellulose yarn produced by the viscose process was passed through a slurry consisting of magnesium flake suspended in an 8% aqueous solution of polyvinyl alcohol (a 4% aqueous solution of this polymer at 20°C has a medium viscosity of 24 centipoises). The suspension was maintained by stirring. After the cord was run through the slurry, it was partially dried and then dipped into a bath containing an adhesive. The adhesive was a sorcinol-formaldehyde-rubber latex adhesive.
which was predominantly rubber latex. The yarn was then dried by hot air at a temperature of 150° C. The speed of yarn travel during these operations was about 5 yards per minute. The quantity of magnesium deposited on the yarn was about 0.3%. The heat aging was conducted in all cases in sealed tubes heated to a temperature of 150° C. and maintained at that temperature for 16 hours. These conditions were employed to simulate the conditions obtaining when the structures are covered with relatively impermeable coatings which prevent the free escape of degradation products.

The cords treated with magnesium and then dipped in the adhesive bath and dried lost only 14.8% of their original strength whereas dipped, untreated cords run as controls lost over 23% of their strength. As pointed out in pending application, Serial No. 717,612, now U. S. Patent No. 2,978,889, similar yarns protected with 0.25% 1-phenylbiguanide lost 16% of its original strength after 16 hours at 150° C. and yarn protected with 0.25% urea and similarly heat-aged lost 62% of its strength. Thus, it is shown that the presence of this invention is an effective means of stabilizing cellulose yarns against the deteriorative action of heat.

Example II

Several samples of cotton tire cord were heated at 150° C. for 17 hours in sealed tubes containing air and about 6% moisture. After this treatment the cords possessed, on the average, only 32% of their original strengths. A similar set of samples was impregnated with an amount of magnesium powder equal to 1% of the weight of the cotton. These impregnated samples were similarly aged. The impregnated cords were found to have, on average, 47% of their original strengths. Upon comparison of the above figures, the inhibiting effect of magnesium can readily be seen. Like cotton, structures those composed of polyamides, such as polyhexamethylene adipamide, polyhexamethylene sebacamide and the like, or polymeric esters, such as those prepared from terephthalic acid, are stabilized against degradation by heat by impregnation with magnesium as described above. Any of the metals of this invention may be used with structures composed of these non-cellulosic polymers to obtain greater heat stability.

Example III

Several samples of nylon tire cord were heated at 150° C. for 16 hours in sealed tubes containing air and 3.4% moisture. After this treatment, the cords possessed on the average only 40% of their original strength. A similar set of samples was impregnated with an amount of magnesium powder equal to 1% of the weight of the nylon. These samples were similarly aged. The impregnated samples were found to have lost appreciably less than 25% of their original strength.

Example IV

Skeins of yarn taken from one spool of bobbin-spun, high tenacity, regenerated cellulose yarn used commercially in preparing tires were treated in the following manner: Six of the skeins were dipped in a finish comprising about 1.5% of the composition Z described below, about 0.5% polyvinyl alcohol and 98% water. The composition Z consisted of about 25 parts of sulfated peanut oil, 25 parts of a sulfated fatty acid ester such as the sulfated glyceride of oleic acid or other higher fatty acids, 17 parts of mineral oil, 17 parts of peanut oil and 17 parts of a fatty acid ester. These six skeins were not heat aged. Strengths, that is dry tenacities, were measured on these directly to obtain a representative figure for comparison to heat-aged yarns. Four skeins, referred to as lot A in the table below, were similarly dipped and then aged. An additional six skeins were treated by running the yarn through a bath containing in addition to the above finish 0.5% of aluminum flake. These aluminum containing skeins were dried at 60° C. and allowed to condition in the standard testing laboratory atmosphere. Two of the aluminum containing skeins were not heat aged (lot B) and 4 of the aluminum containing skeins were heat aged (lot C).

A similar set of magnesium containing skeins were prepared in a comparable manner using magnesium flake instead of the aluminum powder. The non-aged, magnesium containing yarn is designated below as lot D, the heat aged as lot E. All heat aging was conducted for four hours in sealed tubes containing air and 12% moisture maintained during that time at a temperature of 150° C. The results are recorded in the following table:

<table>
<thead>
<tr>
<th>Yarn</th>
<th>Percent Strength Losses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lot A: Finihol, heat aged controls</td>
<td>42.3</td>
</tr>
<tr>
<td>Lot B: Aluminum impregnated, unaged</td>
<td>0.0</td>
</tr>
<tr>
<td>Lot C: Aluminum impregnated, heat-aged</td>
<td>41.3</td>
</tr>
<tr>
<td>Lot D: Magnesium impregnated, unaged</td>
<td>33.8</td>
</tr>
<tr>
<td>Lot E: Magnesium impregnated, heat-aged</td>
<td>33.8</td>
</tr>
</tbody>
</table>

By comparison of the above figures it can be seen that in these experiments the magnesium containing yarns have the lowest strength losses on heat-aging. Further improvement in the use of magnesium for increasing the resistance of cellulose yarns to deterioration of heat may be obtained by using magnesium flake of very small mesh. The magnesium flake used in the above experiment was 100 mesh whereas the aluminum used was in the form of a fine powder. It is difficult to obtain a proper dispersion of the magnesium in the finish when such large particles are used. Further, it can be seen that a loss in strength of 3.7% occurs merely in impregnating with magnesium whereas no loss occurs in impregnating with aluminum. It is believed that the 3.7% loss is due to abrasion of the yarn caused by the large particles of magnesium. For example, better results may be obtained by the use of magnesium in fine flake form. Further, the finer the particle size the more intimate is the contact of the inhibitors with air and moisture. Thus, for best results it is preferred to use the metals in finely divided form. Of course, the metals incorporated will be substantially unoxidized. The magnesium, after heat-aging, looks like an ash, the magnesium particles having reacted with moisture and air to form magnesium oxide or magnesium hydroxide or magnesium carbonates. Such alkaline materials act further as inhibitors for heat aging, since they neutralize any acidic compounds present.

Similar alkaline products are formed when aluminum is used. However, aluminum does not appear to be changed as extensively as magnesium. This is to be expected since magnesium is the more reactive metal. Any common metal which becomes oxidized with comparative ease at elevated temperatures, for example, about 150° C. and which reacts with water or steam may be
employed providing it or its reaction products will not react with the physical structure to
deteriorate it. Thus, metals other than mag-
nesium and aluminum may be employed, such as
strontium or calcium. It is preferred to use
those metals whose hydroxides are not more
water-soluble than strontium hydroxide. The
reactiveness of alkali metals and bariun and the
alkalinity of their hydroxides limits their use-
fulness in this invention. Certain other metals,
such as zinc, cadmium, lead and tin, can form
peroxides which tend to degrade certain struc-
tures, as, for example, those of cellulose.
Accordingly, it is preferred to use those metals
which do not have a variable valence and which
do not form peroxides. Of those metals which
have only one valence, it is preferred to use
magnesium or aluminum, this preference being based
upon their chemical reactivity, upon their avail-
ability and upon the inerexness of the metals, their
oxides and salts toward cellulose.
One method of application consists of simply
immersing the structure in a proper medium con-
taining the metal suspended therein in proper
concentration. The medium may also contain a
finish. The application of finish is not necessary
to obtain the inhibition effect, as shown above in Example I, but is preferred because
inter-filament lubrication is obtained which facil-
itates the obtaining of proper twisting and the
desired mobility of the filaments in the final
structures. In commercial operation the metal
may be applied either immediately previous to or
in conjunction with the application of a rubber
adhesive in the preparation of useful rubber arti-
cles. Thus, it is not necessary to employ an
extra size or finish. The rubber adhesive being
used in the particular commercial operation may
act as a vehicle for the metal flake such as the
magnesium flake. The treatment of the cellu-
losic threads with a resin latex adhesive may be
in the manner of Church and Maney, U. S.
2,126,635 and the types of adhesives disclosed
therin or any other adhesive treatment may
be employed in this invention. While the process of this invention is applicable to uncoated
structures, it is used chiefly in the preparation of
coated structures. The coatings may be pre-
pared from any of the commercially available
polymers. It is preferred to use a coating hav-
ing a low permeability to air and moisture.
For the most part, such coatings reduce the amount of
air and moisture diffusing into the yarn to an
amount less than that which may be taken up by
the inhibitors. As pointed out above, the pro-
cess of this invention is particularly useful in
the preparation of rubber articles, employing either
natural or synthetic rubbers. Other polymers
which may be used, among a large number, are
vinyl polymers as polyvinyl chloride, polyvinyl
acetate, polyvinyl butyral, polyethylenel inter-
polymers of vinyl chloride-vinyl acetate, vinyl
chloride-vinyl cyanide, hydrolyzed ethylene vinyl
acetate interpolymers, vinylidene chloride interpol-
ymers, rubber hydrochloride, chlorinated
rubber, etc.
In immersion processes, the structure, such as
a yarn, in a form of a single strand or a fabric,
may be passed continuously through the bath so
that a suitable length of the structure is im-
mersed at any instance and so that it runs at a
suitable rate or the immersion may be accom-
plished by simply dipping an entire structure, for
example, a skein, in the solution and allowing it
to remain there for a suitable period of time. If
the impregnation is by passage of a single strand
of 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 is prac-
ticable in order to attain the penetration of and
hence the greatest stabilizing activity from a
given amount of metal. 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 30 inches 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 traverse of the yarn through the bath is about
105 yards per minute and the period of immer-
sion is, therefore, about 0.5 seconds. Other yarn
speeds ranging from 10 to 300 yards per minute
may also be used. After passage through the
bath, the yarn is allowed to remain on the reel
until dry. Drying may also be accomplished
using ovens, contact driers or air drying means.
The temperatures for drying may vary from
about 70° C. to about 110° C.
If the impregnation is by dipping the struc-
ture, such as a skein or yarn, in a bath all at
once, the structure may be freed of excessive liquor
by wringing out in a centrifuge or by other
suitable means. When bath medicaments are used,
they may be unheated or heated as desired.
Methods other than immersion processes may be
employed. For example, the metal may be
melted in an arc or a flame and then blown as
a fine spray onto the structure in any of the well
known methods of applying metals to textiles.
In any of the methods, it is preferred to apply
the metal to the finished structure to avoid losses
which occur in twisting operations. For ex-
ample, it has been shown that such losses of metal oc-
cur when the metal is applied to yarn which is
then twisted. The loss of metal which occurs
depends, among other factors, upon the degree
of subdivision or the metal used and upon the
nature of the finish, size or adhesive employed.
Further, in any of the methods, the concentration
of the metal in the bath or in the spray is de-
termined by the extent to which it is desired to
impregnate the yarn or cord. It is apparent that
one may stabilize the yarn to the desired degree
by varying the amount of metal applied to the
yarn or the extent of the impregnation. Effective
results are obtained using concentrations of
magnesium from about 0.3% to about 2.0% by
weight of the yarn or cord. For reasons of
practicability and economy, the preferred con-
centration is from about 0.5 to about 1.5%. Simi-
lar concentrations of aluminum flake or other
metals may be used.
Although it will generally be desired to treat
the structures according to the immersion
method described above, other bath ingredients
may be used than those mentioned. Instead of
water as a vehicle, organic liquids or mixtures of
these with or without water may be employed.
For example, cyclohexane, benzene, and similar
liquids may be employed in the immersion baths
providing these liquids permit the formation of
the desired dispersion of metal. Likewise, it is
possible to use the adhesive as a dispersing
medium. Other liquids may be added to the ad-
hesive to give the desired fluidity. The adhesive,
which is used to obtain more stable impregna-
tions, is not essential and may be dispensed with,
as, for example, in the spraying methods of im-
regnation. In these methods or other methods
it is possible to spray the adhesive on along with,
Finishes other than composition Z mentioned above may be employed and sizing agents other than polyvinyl alcohol may be used. In general, any of the numerous, well-known cellulose finishes and sizes may be employed in the baths to obtain better adhesion of the metal to the structural material, such as cellulose, providing, of course, the compositions are not reactive toward the agents of this invention. Dispersing agents may also be incorporated in the baths to obtain stable dispersions of the metal. The particular dispersing agents may be chosen from the multitudes of well-known dispersants taking into consideration the nature of the size, finish or adhesive in admixture with which the metal is to be applied. While finishes, sizes and peptizing agents are not essential to the process of this invention, they may be used frequently to obtain better uniformity of impregnation and greater adhesion. Generally, it is preferred to use a bath containing about 1.25 to about 1.75% of a finish, about 0.4 to about 0.8% of a size such as polyvinyl alcohol and about 0.4 to about 0.8% of magnesium flake. A bath of this composition when used in the process of this invention will lead to the impregnation of the structure to an extent which effectively protects it for a considerable length of time at high temperatures without loading it excessively.

Furthermore, the process of this invention may be applied to the impregnation of thread such as viscose rayon yarn while it is still in the gel state.

The increased resistance to deterioration by heat imparted by the processes of this invention to the structures of this invention, such as cellulose yarn or cord, makes the yarn particularly useful where it is to be subjected to elevated temperatures. Viscose rayon yarn or similar cellulose yarns so treated to associate the metal intimately with the yarn, may be used for all purposes to which such a yarn might otherwise be put and which subject it 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 cord 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 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 form or another be woven into fabrics for uses at elevated temperatures, as for example, coverings for laundry mangles and as zinc oxide fume bags.

Among other uses for treated structures of this invention are 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; strainers for hot oil and other nonaqueous materials; belt driers such as on blue-print machines; and conveyor belts for hot materials. In general, this invention may be applied to the manufacture of coated fabrics or similar articles which are exposed to elevated temperatures.

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. This is true also for structures composed of cellulose derivatives, of polyamides or polymeric esters. The use of metal such as aluminum and magnesium has the further advantage in that impregnation of organic textile structures will cause very little loss of the initial strength of the structures. The use of these metals is furthermore advantageous in that the protective chemical reactions which induce them do not occur extensively at low or room temperatures. That is, the metals are retained for use at the high temperatures at which they are needed, no loss of metal or protective action occurring because of consumption of the protecting agent at lower temperatures. Even if the metal is converted to some compound at low temperatures, its oxide or a salt, such as its carbonate, no loss is sustained since these alkaline products are effective heat age inhibitors. The metal, heat-aging inhibitors of this invention are further advantageous in that they are relatively inexpensive materials and very readily obtainable.

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

I claim:

1. A heat stabilized article comprising a yarn produced from regenerated cellulose impregnated with about 0.2% to about 2.0% of fine particles of a metal selected from the group consisting of aluminum and magnesium, said impregnated yarn being coated with a rubber.

2. A heat stabilized article comprising a yarn produced from regenerated cellulose impregnated with about 0.2% to about 2.0% of fine particles of magnesium, said impregnated yarn being coated with a synthetic rubber.

3. A heat stabilized article comprising a yarn produced from regenerated cellulose impregnated with about 0.2% to about 2.0% of fine particles of magnesium, said impregnated yarn being coated with a natural rubber.

WILLIAM EARL ROSEVEARE.

References Cited in the file of this patent

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Price</th>
<th>Date</th>
</tr>
</thead>
<tbody>
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<td>1,184,015</td>
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<td>September 31, 1938</td>
<td>May 23, 1916</td>
</tr>
<tr>
<td>1,235,262</td>
<td>Taylor</td>
<td>September 31, 1938</td>
<td>Sept. 29, 1931</td>
</tr>
<tr>
<td>2,034,908</td>
<td>Taylor</td>
<td>September 31, 1938</td>
<td>Mar. 17, 1936</td>
</tr>
<tr>
<td>2,227,843</td>
<td>Quenelle</td>
<td>September 31, 1938</td>
<td>Jan. 7, 1941</td>
</tr>
</tbody>
</table>

FOREIGN PATENTS

<table>
<thead>
<tr>
<th>Number</th>
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<th>Date</th>
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</thead>
<tbody>
<tr>
<td>432,019</td>
<td>Great Britain</td>
<td>July 15, 1928</td>
</tr>
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</table>