FIG. 1.

- SHRINKAGE IN WATER OF 90°C.
- DYNAMIC CREEP

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Fig. 2.

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PROCESS FOR IMPARTING CONTROLLED MECHANICAL CHARACTERISTICS TO THE HIGH TENACITY RAYON YARNS USED AS REINFORCING ELEMENTS IN ARTICLES OF RUBBER OR PLASTIC MATERIAL

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6 Claims

The present invention relates to high tenacity rayon yarns used in reinforcing textile material for articles made of rubber (natural and synthetic) or of plastic material. Such articles include e.g. pneumatic tires, V-belts and other transmission belts, conveyor belts, flexible tubes, moving staircases and so on.

The history of such reinforcing textile material begins with the adoption of natural fibers, e.g. cotton, subsequently replaced by rayon in particular by virtue of the continuity of the rayon filaments and of the possibility of readily graduating at will during manufacture the denier of the rayon filaments in accordance with the various requirements of ultimate use. The use of spun and stranded rayon filaments in articles having a composite structure, e.g. constituted by textiles and rubber, and the ever increasing severe performances which are required from them, have led to the necessity of improving the rayon tenacity.

Various types of rayon have been developed over the years. The so-called “high acidity rayon” obtained by coagulation of the viscose in an aqueous solution at 10–11% of sulphuric acid and with low stretching degrees, has in general a breaking load (tenacity) smaller than 4.3 g./den. Furthermore, there are the so-called, already known, “super rayons” or “high tenacity rayons,” which can be obtained by a slow coagulation of cellulose xanthogenate in a very dilute sulphuric acid bath, and these have relatively high stretching degrees and, correspondingly, breaking loads that are remarkably higher. These breaking loads vary from 5.2 g./den. in the case of Super I rayon to 6.5 g./den. in the case of Super IV rayon.

From the chemical and crystallographic point of view, the cellulose constituting the high acidity rayons has relatively large crystallites, a relatively limited chemical reactivity, and is known as “core cellulose”; it absorbs rather slowly the room humidity but swells considerably in water. On the contrary, in the super rayons, the cellulose mass is divided into a very large number of small crystallites having a relatively high chemical reactivity (“skin cellulose”); it absorbs the room humidity more rapidly than that of the high acidity rayon, but swells to a smaller degree.

Moreover, in the high acidity rayons the hydrogen links between the cellulose chains are rather scarce and irregular, contrary to what happens in the super-rayons where these hydrogen links are numerous and regular.

As indicated above, a very high degree of tenacity has been reached in the super rayons. However, the industrial use of rayons in general, and of the super rayons in particular, in the composite structures constituted by textiles and rubber has shown the two following substantial inconveniences:

1. The rayons in general, and in particular the super rayons, under the influence of dynamic stresses repeated at considerable frequency, are subjected to a sensible deformation which cannot be recovered when said stresses are released or discontinued. It has been moreover observed that said deformability tends to increase by increasing the original tenacity of the rayon material. This phenomenon, known by the expression “creep,” while not of great extent, may adversely affect the total exploitation of the tenacity of the super rayons.

2. The super rayons, in comparison to the normal rayons, have a lower dimensional stability during storage under the influence of the variations of temperature and humidity normally encountered.

The two above-indicated inconveniences are connected with one another in nearly all the composite structures constituted by rayon textiles and rubber and, according to the specific application, the one or the other predominates. So, for instance, in the field of pneumatic tires, the dynamic creep constitutes a factor of essential importance in view of the dynamic stresses of high degree and frequency to which said tires are subjected in service. However, in the same application the room instability also plays a critical role both in view of the tire heating during use, and of the climatic conditions in which the tire works.

The dimensional instability to humidity and temperature prevails also in other articles, as for instance tubes made of rubber and textile material, V-belts, flat belts or conveyor belts. The dynamic creep takes place also in these applications both in consequence of the pressure variation in the tubes, and of the vibrations and variations of load in the belts and in the conveyors.

The creep phenomenon is a feature of the cellulose material and can be considered as a mutual sliding of the molecular chains under the action of the applied stress; said sliding initiates the breaking down of the hydrogen links between the chains and their rebuilding in the new configurations taken by the chains themselves, so that when the stress is released, the chains are unable to resume their mutual initial positions.

It follows that in order to eliminate the permanent deformation which would occur in the structure, the manufacturer of pneumatic tires, V-belts or other industrial articles constituted of rubber and textiles, and provided with a rayon reinforcement, is compelled at the outset to increase the amount of textile material of the reinforcement with respect to the amount nominally required as calculated on the basis of the tensile strength of the textile material, without however being assured of the desired practical results. The situation becomes still worse in the case of high tenacity rayons (super rayon) which, as has already been said, are more liable to creep the higher is their tenacity, so that it is often observed in practice that in a reinforcement made of high tenacity rayon the amount of this material is increased up to 30%, or even more, in respect of the percentage nominally or theoretically required.

As regards the instability to temperature and humidity, this appears to be due to the stretching suffered by the rayon filaments during their spinning and the subsequent treatments, and to the liability of the hydrogen links which, under the action of heat and humidity, allow the chains to take again the condition of equilibrium they had before stretching. Therefore said instability is much more relevant in the case of super rayon than in the high acidity rayon.

According to the conventional prior technique, the rayon fabrics are rendered non-shrinking (namely, stable to humidity and heat) in a more or less relevant degree, by replacing the hydrogen cross links with less labile links of a different nature. For this purpose, the rayon fabrics are treated with dialdehydes or acetals (in general in aqueous solution) in the presence of an acid as catalyst. The dialdehydes generally used are glyoxal, methylglyoxal, glutaric aldehyde, succinic aldehyde, adipic aldehyde, glycic aldehyde and other aldehydes having up to 8 carbon atoms in the molecule. As regards the cata-
lyst, preference has up till now been given to sulphuric acid, although other acids, as for instance acetic or oxalic acid, may be used. The yarn, impregnated with the dialdehydic solution, is then subjected to a suitable heat treatment; for example, by being brought to a temperature of 120°–140° C. or more in order that the dialdehydic molecules may react with the cellulose chains and replace the original hydrogen links.

It is however known, and the prior art is quite in agreement on this fact, that the above-indicated treatment by means of the dialdehydes reduces to a considerable extent the tenacity of the rayon filaments and at the same time increases their brittleness (which can be evaluated by the so-called "knot resistance" test); consequently the treatment with dialdehydes is normally applied to the rayon fabrics, and not to the rayon yarns, in order not to affect the capacity of the latter of bending without breaking during weaving. The prior art is also in agreement on the fact that the stability with respect to heat and humidity in the fabrics treated with dialdehydes is always relative, since, to be entirely satisfactory, it would require such relatively high concentrations of dialdehydes as would be prejudicial for the tenacity and flexibility of the component filaments. It is easily understood that this condition is still worse in the case of super rayons, whose relatively high instability with regard to heat and humidity requires still greater concentrations of dialdehydes.

In conclusion, whilst a manufacturer of rayon fabrics or of domestic articles made with said fabrics can be satisfied with the progress achieved by means of the aforesaid treatment with dialdehydes, the manufacturer of industrial articles, as for instance pneumatic tires, V-belts and so on provided with reinforcements of rayon yarns, is still awaiting a process which may improve the mechanical characteristics of the rayons, or at least may improve some of them, and which may allow a control of the remaining characteristics in order to insure a satisfactory final issue, from the practical standpoint, in the individual industrial applications.

The characteristics of greater importance are:

- Tenacity (breaking load) expressed in g./den.;
- Elongation at break, expressed in percent of the original length of the yarn;
- Incremental breaking modulus (I.M.R.) intended as the incremental ratio between the load and the elongation in the breaking conditions;
- Shrinkage into water at 90° C., expressed in percent of the original length of the yarn, after 10 minutes dipping under a load of 0.01 g./den.

The general object of the present invention is that of providing a process for improving in a controlled way the mechanical characteristics of the high tenacity rayons in order to obtain yarns suitable to be used as reinforcements for individual applications in industrial articles having a composite structure, as for instance those constituted by rubber and textiles, or by plastic material and textiles.

A particular aim of the invention is that of conveniently reducing the dynamic creep of the rayon filaments and/or of increasing their dimensional stability in respect of the environmental factors according to the requirements of the above-indicated individual applications, without however compromising the tenacity which is considered to be satisfactory for such applications.

The process according to the present invention includes the method of impregnating the rayon fibers with an aqueous solution of a dialdehyde such as referred to above (glyoxal), and of heat treating the fibers so obtained, provided however that the rayon is of the high tenacity type as defined in the present application, and is further characterized in that: (a), the yarn is caused to pass continuously through said solution until it reaches an absorption degree of dialdehyde selected at a value between 4% and 16% by weight of the total dry weight of the yarn; (b), the speeds of the yarn at its entrance and at its exit from the solution are adjusted in such a way that the outgoing yarn may have a controlled residual shrinkage selected at a value between 2% and 9%; and (c), the yarn under tension is heat treated at the same speed it has upon leaving the solution.

As regards the expression "controlled residual shrinkage"—hereinafter simply indicated by the letters RRC—it must be taken into account that all the high tenacity rayon yarns presently available in the trade show a certain shrinkage when they are dipped into water for a stated time. The shrinkage percentage suffered by a yarn dipped into water at 90° C. for 10 minutes under a load of 0.01 g./den., is hereinafter indicated at "total shrinkage." It is evident that if a load greater than the conventional 0.01 g./den. is applied to the yarn, and if this is dipped into water at 90° C. for 10 minutes, the shrinkage of the yarn is smaller than the "total shrinkage." Similarly, by repeating the test under a load of 0.01 g./den., but for a time shorter than 10 minutes, or by employing a temperature lower than the conventional 90° C., or else by combining a load greater than 0.01 g./den. and a temperature lower than 90° C., the shrinkage of the yarn never reaches the value of the total shrinkage. In all these cases the difference between the total shrinkage and the real shrinkage suffered by the yarn represents the "controlled residual shrinkage" (RRC).

In order to give a numeric example, it may be supposed that a commercial yarn of super rayon has a total shrinkage of 12% (water at 90° C., load 0.01 g./den., time 10 minutes). By suitably controlling the three factors (temperature, load and time), the yarn is allowed to shrink for instance 7% only, namely a shrinkage of 7% is applied to it. Consequently the RRC amounts to 12−7−5%=2%, by maintaining unvaried the value of said shrinkage, namely the length of the yarn, the yarn is dried in an oven at 120°–140° C., and then it is subjected to the conventional test of the shrinkage into water, the shrinkage which it suffers is hardly equal to the above indicated calculated value of 5%, and this is the reason why, in the present specification and in the appended claims, the expression "residual shrinkage" is always accompanied by the word "controlled."

In connection with the term "yarn," it is understood that this term may refer to a single filament, or it may be taken as referring to corded super rayon yarns. Moreover, the term "dialdehyde" is here used to indicate both the dialdehydes as such, and compositions able to generate said dialdehydes in situ during the heating of the yarn in the oven, in compliance with the per se well known teachings of the prior art. The dialdehyde in question can therefore be selected from amongst dialdehydes, acetics and like compositions already broadly known in the techniques of rayon stabilization. In general however, at least in the present condition of the market, it is preferred to use glyoxal for reasons of economy.

As acid catalyst to be used in the aqueous bath containing the dialdehyde, it is preferred to use weak acids having a low hydrolyzing power, as for instance acetic, oxalic, glyoxylic and boric acids. Sulphuric and other similar strong acids having a high hydrolyzing power in respect of cellulose are less suitable for use in the present process.

The percentage of the acid to be employed is adjusted in such a way that the pH of the resulting dialdehyde solution may range between 1 and about 2.5. The preferable pH is 2; and by employing acetic acid and glyoxal, this pH is reached with 0.257 parts by weight of acid per part of anhydrous glyoxal present in the solution, g./den.

Moreover, it has proved advantageous to maintain in the acid solution a small percentage (e.g., about 1% by weight) of sodium sulphate, which seems to have a favorable action on the flexibility of the treated yarn. Yarns treated with glyoxal in absence of sodium sulphate are in fact much more brittle.
In order to indicate still more fully the nature of the present invention, the following examples of typical procedure are set forth in conjunction with a description of suitable apparatus and certain pertinent performance curves as shown in the accompanying drawings, it being understood that the description is being continued by way of illustration only and not as limiting the scope of the invention. In the examples, all parts are by weight unless specifically indicated otherwise.

In the accompanying drawings,

FIGURE 1 is a diagram representing the curves of shrinkage of water at 90°C and of dynamic creep of a super rayon yarn as a function of the percentage of glyoxal (ordinates) absorbed by the yarn and of the RRC (abscissae) as the yarn leaves the glyoxal bath;

FIGURE 2 is a similar diagram representing the curves of the incremental breaking modulus (MIR) and of the tenacity of the same super rayon yarn of FIGURE 1; and

FIGURE 3 is a schematic representation of suitable apparatus for carrying out the process in accordance with the invention in the various forms which will be described in detail herebelow.

It is not in passing that the curves of the dynamic creep (FIGURE 1), of the MIR and of the tenacity (FIGURE 2) represent percentage values in respect of the untreated yarn (100%).

For carrying out the process in accordance with the present invention, it is substantially necessary to provide a tank 10 (or other suitable container) containing an acid bath 11 of glyoxal, and a curing oven 12 (FIG. 3).

The yarn 14 to be treated is supplied to the bath 11 by means of a pair of rollers 15, having a controlled speed, and is removed from the bath by means of a pair of rollers 16, also having a controlled speed. The portion of yarn comprised between the pairs of rollers 15, 16 is always stretched, and for this purpose the peripheral speeds of said rollers are suitably adjusted. The speeds of the yarn, at its entrance to and exit from the oven 12, are controlled by means of pairs of rollers 17, 18, respectively, between which the yarn may be stretched in a continuous way. However, in one form embodying a more precise regulation, the peripheral speeds of the rollers 16, 17, 18 are identical to each other so that the yarn, which continuously moves forward, does not suffer any variation in its length between its exit from the glyoxal bath 11 and its exit from the oven 12. Both in the tank 10 and in the oven 12 the yarn may be reeled, rolled, or other means which serve to extend the travel of the yarn in the respective devices in a way already known per se.

The temperature of the acid bath 11 is maintained at a value ranging between about 120°C and 140°C, which is the preferred range. However, lower or higher temperatures can be employed, taking into account that lower temperatures require longer curving times, and vice versa.

Whichever form the practice of the present process may take, it is first of all necessary to know the characteristics (tenacity, MIR, elongation at breaking, total shrinkage into water at 90°C) of the original yarn, in order to choose subsequently the two values, namely the absorption of glyoxal and the RRC, which correspond to the desired final result, as will be seen hereinafter. Assuming, e.g., that the original yarn has a total shrinkage of 11%, and that the chosen RRC amounts to 3%, a shrinkage of 8% is to be applied to the yarn upstream of the pair of rollers 16 where the yarn leaves the glyoxal bath 11. This can be carried out in different ways.

According to a first form of the invention, the glyoxal bath 11 is brought to a suitably high temperature, preferably between 60°C and 90°C; the peripheral speed of the rollers 16 is adjusted in order that the time of immersion be sufficient to impart the desired shrinkage of 8% and the peripheral speed of the rollers 15 is adjusted in order that the exit speed shall be the desired 8% lower than the entrance speed. Downstream of the rollers 16 the yarn has therefore an RRC corresponding to 3%, and passes through the curing oven 12 in stretched condition at the same speed it had at its exit from the bath 11, since the peripheral speed of the rollers 17 and 18 is equal to that of the rollers 16. In the oven 12 the glyoxal absorbed by the yarn reacts with the cellulosic chains, and substitutes the hydrogen links in the desired manner. Then the yarn leaving the oven 12 can be enfilled and dried in the conventional way.

It is, however, advantageous to carry out these operations under conditions of "constant length," namely by maintaining constant the shrinkage imparted to the yarn in the bath 11.

According to a further form of the invention, the glyoxal bath 11 can be maintained at room temperature. However, as said temperature is too low to provide any considerable shrinkage in a reasonable time, said shrinkage can be obtained by means of a bath 19 of hot water at 90°C, contained in a tank 20 disposed upstream of the tank 10. The tank 20 is also provided with rollers 21 and 22, like the tank 10 containing the glyoxal solution. In this case the speed adjustment involves the rollers 21 concerned with the water bath and to the rollers 16 concerned with the glyoxal bath; therefore, with a shrinkage of 8%, the peripheral speed of the rollers 16 is the desired 8% smaller than that of the rollers 21 so that in its travel through the two baths, the yarn may suffer the shrinkage of 8%, with an RRC of 3% at its exit from the glyoxal bath 11. If the whole shrinkage of 8% is to be imparted to the yarn in the water bath 19, then the rollers 22 and 15 must rotate at a peripheral speed equal to that of the rollers 21; alternatively, the rollers 22 and 15 can be made to rotate at an intermediate speed between those of the rollers 21 and 16, so that only a partial shrinkage is imparted to the yarn in the water bath 19 and the total shrinkage is reached by means of the glyoxal bath 11, which in this case is advantageously maintained at a relatively high temperature, for instance about 80°-90°C.

As regards the percentage of dialdehyde which must be absorbed by the yarn 14, the simplest control consists in maintaining in the bath 11 the same concentration (between 4% and 16%) that is desired for the yarn, and in causing the latter to absorb in the bath a percentage equal to 100% of the dry weight of the dialdehyde solution. The mode of application is then skewed out of the yarn by means of the rollers 16, whose pressure on the yarn may be conveniently adjusted with known means, not illustrated. When the process is carried out with the aid of the supplementary bath 19 of hot water, the rollers 22 may also be adjustable squeezing rollers, so that the bath of dialdehyde 11 is not unduly diluted with water dragged over by the yarn, and consequently the yarn may absorb the aldehydic solution more quickly.

EXAMPLE 1

A commercial super rayon yarn, denier 1650, having a breaking load (bone dry) of 5.62 g./den., is chosen. This yarn has an elongation at break of 8.8%, a dynamic creep of 0.51% and a total shrinkage of 11% in hot water at 90°C.

The total shrinkage is indicated by point A on the axis of abscissae in FIGS. 1 and 2. It is apparent from the two scales ("shrinkage" and "RRC") along the axis of the abscissae, that by imparting to said yarn a shrinkage for instance of 8%, the RRC amounts to 3%.

The total shrinkage is determined for conditions already mentioned in the present specification. The dynamic creep is evaluated under the following conditions:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>120°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-tension of the specimen</td>
<td>75 g.</td>
</tr>
<tr>
<td>Static load</td>
<td>0.100 kg.</td>
</tr>
<tr>
<td>Imposed dynamic deformation</td>
<td>1 percent</td>
</tr>
<tr>
<td>Frequency</td>
<td>20 c/sec.</td>
</tr>
<tr>
<td>Time</td>
<td>6 hours</td>
</tr>
</tbody>
</table>
The treatment is carried out in the apparatus represented in FIG. 3, including the water bath 19 at 90° C. The peripheral speed of the rollers 22 at the exit of the yarn from the water bath 19 is 6% lower than that of the rollers 21 at the bath entrance, and this corresponds to a shrinkage of 6% and therefore to an RRC of 5%. The rollers 15, 16, 17 and 18 rotate at the same peripheral speed as the rollers 22, so that the yarn leaving the dissoldey bath 11 has still an RRC of 5% with respect to the original yarn and does not suffer any further variation of its length in the passage through the oven 12.

The bath 11 is constituted by an aqueous solution containing 1.03% by weight of acetic acid, 1% of sodium sulphate, 4% of glyoxal, and has a pH of 2.0. The temperature of the bath 11 is room temperature (20° C.). The oven 12 is maintained at 130° C. and the time during which the yarn is cured in the oven is 30 seconds.

Under these conditions, the yarn suffers a shrinkage of 6% in the bath of hot water, absorbs 4% by weight of glyoxal in the bath 11, and is cured at 130° C. for 30 seconds in the oven.

After the treatment, the characteristics of the yarn are as follows:

- Breaking load (bone dry) = 4.68 g./den.
- Elongation at break = 8.5 percent
- Dynamic creep = 0.46
- Shrinkage into water at 90° C. = 3.63

EXEMPLARY 2

The process is carried out as in Example 1, the only difference this time being that the yarn is impregnated with 16% of glyoxal (bath 11 containing 16% of glyoxal).

The characteristics of the resulting yarn after the treatment are as follows:

- Breaking load (bone dry) = 4.03 g./den.
- Elongation at break = 5.2 percent
- Dynamic creep = 0.12
- Shrinkage into water at 90° C. = 2.7

EXEMPLARY 3

The process is carried out as in Example 1, but this time imparting to the yarn a shrinkage of 9% (RRC=2%).

The characteristics of the resulting yarn after the treatment are as follows:

- Breaking load (bone dry) = 4.5 g./den.
- Elongation at break = 10.4 percent
- Dynamic creep = 0.57
- Shrinkage into water at 90° C. = 0.00

EXEMPLARY 4

The process is carried out as in Example 1, but the yarn is impregnated with 16% of glyoxal and given a shrinkage of 9% (RRC=2%).

The following yarn characteristics are obtained:

- Breaking load (bone dry) = 3.8 g./den.
- Elongation at break = 5.6 percent
- Dynamic creep = 0.20
- Shrinkage into water at 90° C. = 0.00

EXEMPLARY 5

The process is carried out as in Example 1, but the yarn is impregnated with 16% of glyoxal and given a shrinkage of 3% (RRC=8%).

The following yarn characteristics are obtained:

- Breaking load (bone dry) = 4.21 g./den.
- Elongation at break = 4.7 percent
- Dynamic creep = 0.11
- Shrinkage into water at 90° C. = 4.7

EXAMPLE 6

In the apparatus shown in FIG. 3 the water bath 19 is eliminated. The yarn is supplied directly to the glyoxal bath 11 at a controlled speed by means of the inlet rollers 15, whereas the outlet rollers 16 rotate at a peripheral speed 6% lower than the entrance speed. The glyoxal bath contains 4% glyoxal and is maintained at a temperature of 90° C., so that the yarn is subjected therein to a shrinkage of 6% (RRC=5%). The other conditions are the same as indicated in Example 1.

The yarn so treated has the same characteristics as those obtained in Example 1.

EXAMPLE 7

By way of comparison Example 6 is repeated, but with the difference that the yarn is treated "without tension," namely under conditions of the maximum possible shrinkage both in the glyoxal bath and in the oven 12.

The following yarn characteristics are obtained:

- Breaking load (bone dry) = 4.22 g./den.
- Elongation at break = 0.1 percent
- Dynamic creep = 0.58
- Shrinkage into water at 90° C. = 0.6

EXAMPLE 8

Example 7 is repeated, but this time an acid solution containing 16% of glyoxal is employed.

The following yarn characteristics are obtained:

- Breaking load (bone dry) = 3.52 g./den.
- Elongation at break = 3.6 percent
- Dynamic creep = 0.61
- Shrinkage into water at 90° C. = 0.00

From the comparison between Examples 6 and 8 on the one hand and Examples 1 and 5 on the other, the effect of the "controlled shrinkage" on the characteristics of the treated yarn can be clearly seen. In the case of Examples 7 and 8, a considerable reduction of the breaking load and of the elongation at break, and an undesired increase of the dynamic creep, instead of its reduction, are noticed.

From a comparison between Example 6 and the preceding examples it will be noticed that the shrinkage of the yarn (namely the RRC) can be imparted before or during the impregnation of the yarn with the glyoxal solution, without any difference in the final result. Likewise, no difference is noted in the results obtained by imparting a partial shrinkage during immersion in the hot water bath 19 and a partial shrinkage during immersion in the glyoxal bath 11.

Super rayon "pot" yarns have, as is known, a substantially null total shrinkage, so that their production cycle comprises a "slashing" step during which the yarn is subjected to a longitudinal stretching in order to impart to it better features of tenacity. Of course, the resulting yarn has practically the same inconveniences already discussed in the present specification. Therefore said yarns can be treated as described in detail in accordance with the present invention. However, on the other hand, the present process can be included in the production cycle, in substitution for the "slashing" step, in order to obtain an already improved yarn having controlled characteristics. According to this embodiment the "slashing" apparatus is replaced by the apparatus shown in FIG. 3, in which the bath 19 of hot water has the function of a stretching bath, whilst the controlled shrinkage (and therefore also the RRC) is imparted to the yarn in the glyoxal bath maintained at 90° C. So, for instance, when it is wished to impart to the yarn a stated RRC, for instance 3%, the yarn is stretched in the bath 19 at a temperature ranging from 60° to 90° C. In an amount corresponding at least to 3% of the total shrinkage and then, in the bath 11, a shrinkage equal to the difference between said total shrinkage and the desired RRC is imparted to the yarn.
To give a more detailed description, it is assumed that the yarn is stretched in the bath 19 to for instance an extent of 8%; if this yarn were shrunk in the same bath or in the further glyoxal bath, it would have to amount to 3.5% instead of 6.5%. As the desired RRC is 3%, a shrinkage of 6.5-3=3.5% will be imparted to the yarn in the glyoxal bath 11.

In practice, assuming the peripheral speed of the inlet rollers 21 as equal to 100, the speed of the rollers 21 and 15 will amount to 108 (stretching of 8%); on the other hand, the speed of the rollers 16 must be 3.5% lower than that of the rollers 15, and consequently it will amount to about 104.2.

The diagrams of FIGS. 1 and 2 allow the determination of the RRC (namely of the shrinkage) and the concentration of glyoxal necessary to impart to an original yarn the desired final characteristics. So, for instance, with an original yarn as employed in Examples 1-5, having a MIR=0.500, it is possible to obtain for instance the following yarn characteristics:

<table>
<thead>
<tr>
<th>Breaking load</th>
<th>g./den.</th>
<th>4.23</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIR</td>
<td></td>
<td>0.625</td>
</tr>
<tr>
<td>Dynamic creep</td>
<td>percent</td>
<td>0.38</td>
</tr>
<tr>
<td>Shrinkage into water</td>
<td></td>
<td>1.6</td>
</tr>
</tbody>
</table>

when it is treated in a glyoxal bath at 10% concentration of glyoxal, and an RRC of 3% (shrinkage of 8%) is imparted to it correspondingly to the point of position B, which is determined by the respective percentage variations of the respective characteristics. In fact, the breaking load of 4.23 g./den. corresponds to 76% of the initial value (5.62 g./den.)—Example 1—the creep of 0.38% corresponds to 75% of the initial creep (0.51%), and so on.

It is therefore to be understood that the present process allows one to vary in a controlled way the mechanical characteristics of the original yarn in order to render it suitable for a specific composite structure made of textile material and rubber.

It is to be observed from FIG. 1 that below 4% of glyoxal, the curves indicating the shrinkage into water have a low slope and those indicating the dynamic creep have a steep slope; percentages of glyoxal lower than 4% are therefore to be avoided. On the other hand, RRC values higher than 9% involve a considerable shrinkage into water, whereas values smaller than about 2.5-3% involve a remarkable reduction of the breaking load and an increase of the creep.

By means of the process according to the present invention, relatively more advantageous results are obtained with glyoxal concentrations comprised between 6% and 12% and with RRC values comprised between 3% and 8%; this preferred field is indicated by the rectangle F in FIGS. 1 and 2. However, it is possible to employ glyoxal concentrations up to about 16% and to increase the RRC to 9%, as is indicated by the rectangle G in FIGS. 1 and 2, in particular when the consequent greater reduction of the breaking load is not a matter of concern in respect of the quality of the article constituted by textile material and rubber of which the yarn constitutes the reinforcement, or, in other words, in the case in which the original yarn is constituted by a super rayon having a higher breaking load (6.2-6.5 g./den.).

So, for instance, in the case of carcasses for pneumatic tires in which a high breaking load is at least as important as a low creep and a satisfactory stability to humidity, it is undoubtedly advantageous to employ super rayon having high tenacity (6.2-6.5 g./den.) and to carry out the treatment under the condition shown in the rectangle F; in this way it is possible to obtain a textile reinforcement having a breaking load that is at least 25% above the breaking load of the yarn into water is reduced by at least 50%, and with the possibility of reducing the dynamic creep by 40-50%. For instance, by applying the treatment described in Example 1 to a super rayon of 6.5 g./den., with an RRC of 8% and by using a solution having 12% of glyoxal, it is possible to obtain a yarn having a breaking load of 5.23 g./den., with a shrinkage into water reduced to about 54%, a dynamic creep reduced to about 52%, and an incremental breaking modulus (MIR) increased to about 55%.

On the contrary, in the case of V-belts, it is convenient to carry out the treatment of the yarns with solutions at 14–16% glyoxal content, with an RRC of 3–6%. In this way the dynamic creep is reduced by even 70% and the incremental breaking modulus increases to 170% with respect to the original modulus; the reduced breaking load, which amounts to about 70% of the original breaking load, does not cause particular difficulties, since it is not yet in the so-called field of "over sizing" of the reinforcements (up to 30% and more) which up to this time was considered normal, but with the advantage of representing a "safe" breaking load, on account of the reduced creep and of the high thermal stability of the yarn obtained with the described process.

It is to be understood that the above considerations refer only to the super rayon yarns which all have characteristic diagrams similar to those illustrated in FIGS. 1 and 2, which can be experimentally drawn from data obtained by means of the common testing methods; they cannot be applied on the contrary to the high acidity rayons on account of the substantial differences between the latter and the super rayons already mentioned in the introductory paragraphs of the present specification.

While specific examples of preferred embodiments embodying the present invention have been described above, it will be apparent that many changes and modifications may be made in the details thereof without departing from the spirit of the invention. It will therefore be understood that the examples cited and the particular method of procedure set forth above are intended to be illustrative only, and are not intended to limit the scope of the invention.

What is claimed is:

1. A process for imparting in a controlled way improved mechanical characteristics to high tenacity rayon yarns intended for use as reinforcements in composite articles of rubber or plastic material by impregnating the yarn with an aqueous solution of dialdehyde and thereafter heat-treating the yarn so treated, the improvement comprising the steps of passing the yarn continuously through said solution to bring about absorption of said dialdehyde by said yarn to an extent of between about 4% and 16% by weight based on the dry weight of the yarn; adjusting the speeds of the yarn at the entrance to and at the exit from said solution in such a way that the yarn leaving the solution has a controlled residual shrinkage of between 2% and 9%; and heat-treating the yarn under tension while moving at the same speed as it leaves said solution.

2. A process as defined in claim 1, wherein the aqueous solution of dialdehyde is maintained at a temperature ranging between about 80° and 90° C.

3. A process as defined in claim 1, wherein, before entering the aqueous solution of dialdehyde, the yarn is passed through a hot water bath maintained at a temperature ranging from about 60° to 90° C, while a predetermined ratio is maintained between the speed of the yarn at its entrance to and its exit from the bath and the speed of the yarn at its exit from the aqueous solution of dialdehyde, so that the yarn leaving the latter bath has said controlled residual shrinkage.

4. A process as defined in claim 1, wherein, before entering the aqueous solution of dialdehyde, the yarn is stretched in a hot water bath at a temperature ranging from about 60° to 90° C, while a value corresponding to a value of total shrinkage not lower than the value of the controlled shrinkage selected in the range between 2% and 9%, and in which a shrinkage equal to the difference between said value of total shrinkage and the value of...
the controlled residual shrinkage is imparted to the yarn while passing through the aqueous solution of dialdehyde.

5. A process as defined in claim 1, wherein the aqueous solution of dialdehyde contains also a small amount of a weak acid.

6. A process as defined in claim 1, wherein the aqueous solution of dialdehyde contains also a small amount of a weak acid and a small amount of sodium sulphate.

References Cited

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NORMAN G. TORCHIN, Primary Examiner.
J. P. BRAMMER, Assistant Examiner.
3.9 UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,449,059 Dated June 10, 1969

Inventor(s) Pietro TONO

It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

In the heading, change "14,359/62" to -- 17,336/62 --.

Column 5, line 17, change "moduls" to -- modulus --.

Column 9, line 69, change "condition" to -- conditions --.

SIGNED AT
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NOV 3 1980

(SEAL)
Attest:
Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents