TREATMENT OF CELLULOSIC FIBERS

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This invention relates to an improved method of treating naturally occurring cellulosic fibers to improve their tensile strength and more particularly to such a method which is an improvement over the method disclosed in U. S. patent to H. M. Buckwalter No. 2,297,536.

The Buckwalter patent covers the treatment of native cellulosic fibers with non-volatile, non-waxy, water-soluble, cotton-wax-peptizing agents which contain a tricyclic hydroaromatic condensed nucleus, particularly with aqueous solutions of alkali salts of rosin acids, to improve the tensile strength thereof.

The naturally occurring waxes in the native cellulosic fibers to which the present invention is applied, such as grey cotton, flax, hemp, jute, and the like, which contain at least 75% of the original naturally occurring waxes, and generally substantially all of said waxes, impart lower tensile strengths to cords made therefrom than such cords would have if these waxes were not present. In the laboratory these waxes have been removed by alcoholic extraction and the resulting de-waxed cords have thereby been caused to experience an appreciable gain in tensile strength. These waxes are defined as that group of non-cellulosic water-insoluble components of native cellulosic fibers which are characterized by extreme solubility in hot ethyl alcohol. It is now assumed that when a grey cotton cord is subjected to tension, the cotton waxes behave as lubricants allowing the fibers to slip over each other more readily. This lubricating action is thought to account for the relatively low tensile strength of cord made of untreated grey cotton containing the original naturally occurring waxes. The lubricating action of such waxes is also thought to explain the increase in tensile strength brought about when such cord is extracted with hot alcohol to remove these cotton waxes.

Alcohol extraction of the naturally occurring waxes from grey cotton or similar naturally occurring cellulosic fibers is not commercially practical. However, the aforementioned Buckwalter patent is based upon the discovery of a commercially practical method of greatly increasing the tensile strength of grey cotton cord and cord made from other naturally occurring cellulosic fibers. This method involves treating the grey cotton cord or the like with a water solution of a material typified by sodium rosinate, whereby an appreciable gain in tensile strength results. Experiments have shown that the cotton cords need not be immersed for long periods of time, immersion times as short as five seconds being sufficient to effect the tensile improvement. This fact suggests the possibility that in this type of treatment the cotton waxes or similar naturally occurring waxes are not removed but are merely pepitized. However, experimental studies have indicated that it is not enough for a material to be a pepitzing agent but it must also be a de-plasticizing agent with respect to the waxes if it is to effect the desired improvement in tensile strength. Most common pepitzing agents are plasticizing agents for the waxes and therefore are valueless as tensile improvers. However, the alkali salts of rosin acids, e. g., sodium rosinate, are both de-plasticizing and pepitzing agents for the cotton waxes or like waxes. It appears therefore that the success of the process disclosed in the Buckwalter patent is due to the fact that the naturally occurring waxes act as lubricants in cords made from the naturally occurring cellulosic fibers and that water solutions of alkali salts of rosin acids serve to both pepitize and de-plasticize these waxes, thus destroying their lubrication action with a resulting increase in tensile strength.

In the commercial practice of the invention described in the Buckwalter patent, a plurality of the grey cotton cords or the like, disposed in parallel relationship, are passed through a tank of aqueous solution of sodium rosinate or the like maintained at constant level. The concentration of sodium rosinate or other alkali salt of a rosin acid typically is in the range of 7.0 to 8.5% by weight. Passage of the cords through such a solution serves to impregnate them thoroughly with the sodium rosinate. Wetting and complete saturation of the cords with the solution take place almost instantaneously. From the treating tank the cords pass through a squeegee rolls which are so located that the liquor is drained back into the tank to be re-used. Upon leaving the squeegee rolls the cords pass through a counter-flow wash tank in which they are thoroughly washed with water which serves to remove surplus treating solution. Fresh water is continuously introduced at the rear of the washing tank and continuously overflows at the front. The motion of the cords is from the front to the rear of the washing tank. The thus-treated cords typically are then "solutonized" with an aqueous mixture comprising rubber in the form of latex, with or without a dissolved resinous-formaldehyde resin, after which the solutioned cords are assembled with unvulcanized rubber into reinforced rubber articles, e. g., a pneumatic tire, and the rubber articles are then vulcanized in the conventional manner.

In the above-described commercial operation of the Buckwalter process it has been found that periodic blowing or blistering occurred during the curing of articles of rubber reinforced with cords which had been treated by the Buckwalter procedure. This blowing or blistering is extremely serious and causes an unduly high number of rejects, thereby greatly increasing the cost of production. Exhaustive investigation indicated that this blowing or blistering was attributable to the maintenance of the flow of wash water at too high a rate with the result that the concentration of sodium rosinate in the wash water fell to such a low level as to permit hydrolysis of sodium rosinate to occur to a substantial degree in accordance with the following equation:

\[(\text{CaHsCOO})_n + \text{HO} \rightarrow \text{CaHsCOOH} + \text{Na}^+ + \text{OH}^-\]

The sodium rosinate thereby formed transferred to the cords and in some manner caused blowing of the rubber articles during Vulcanization.

Efforts were made to overcome this difficulty by controlling the flow of wash water through the washing tank as to keep the concentration of sodium rosinate in the wash water above a certain minimum level, typically above 1.0% by weight. However, even after the direct relation between hydrolysis of sodium rosinate in the washing operation and the occurrence of blowing during vulcanization was established and efforts were made to control it by maintaining the concentration of sodium rosinate in the wash water above the minimum level by reducing the flow of wash water through the washing tank, there still occurred what might be termed "epidemics" of blowing or blistering during vulcanization and efforts to find the cause of this were fruitless for a long
time. Our invention is based upon our discovery of the cause of such “epidemics” of blowing during cure and our discovery of a simple and commercially feasible method of completely preventing the same.

The accompanying drawing portrays diagrammatically one arrangement of apparatus for practicing the method of our invention.

After great difficulty and much experimentation, we have traced the occurrence of blowing during vulcanization of rubber articles reinforced with cotton or like cords treated by the above-described Buckwalter process to the following facts: (1) the cotton cords selectively absorb a substantial amount of alkali as they pass through the wash water and this absorption results in depletion of the wash water in alkali and lowering of the pH; and (2) the pH of the wash water as it enters the washing tank is at a rather low level, typically about 7. We have found that occasionally, due to operating variables, these two factors become accentuated to such a degree as to produce the hydrolysis reaction described above to occur despite maintenance of the concentration of the alkali salt of the resin acid in the wash water above a minimum value. As previously indicated, the occurrence of this hydrolysis reaction in some or yet unknown manner causes blistering of the tires or other rubber articles during vulcanization.

We have further found that these difficulties can be overcome in a simple, economical and commercially feasible manner by simply maintaining the hydrogen ion concentration of the wash water at a value not greater than the value for Ca+ given by the following Equation 2:

\[ C_{H^+} = \frac{K_w}{C} \]

where \( C_{H^+} \) is hydrogen ion concentration, \( K_w \) is the ionization constant of water (in dilute solutions)

\[ K_w = C_{H^+} \times C_{OH^-} \]

and at ordinary temperature the ionic product can be assumed to be \( 10^{-14} \) and is assigned a value of \( 10^{-14} \). Ka is the ionization constant of the resin acid and C is the concentration of the alkali salt of the resin acid in the wash water. We prefer to maintain the hydrogen ion concentration of the wash water substantially below the value calculated for Ca+, in order to provide an adequate margin of safety. Typically, we maintain the wash water at a pH value equal at least 0.5 above the pH value corresponding to the calculated value for Ca+.

In the typical practice of our invention, we simply dissolve, in an any suitable way, an alkali, especially an alkali metal hydroxide, in the incoming wash water before it comes into contact with the impregnated grey cotton or like fibers, introducing such an amount of alkali as to keep the hydrogen ion concentration from exceeding the value for Ca+ as determined by the above Equation 2. We typically prepare a water-soluble solution of the alkali to be added and meter this solution, which usually is of relatively low strength, say 1% by weight, in accurately controlled proportions into admixture with the incoming wash water in such manner that a completely homogeneous solution is obtained before the wash water enters the washing tank.

**Example**

Following is a working example of a typical method of operating in accordance with our invention. Sodium rosinate is used in aqueous solution in accordance with the following formulation to treat grey cotton cords. The treating solution has the following formulation:

- **“Dresinate XX” (Sodium rosinate—made by Hercules Powder Company).................................................................................................................. 600 lbs.**
- **Caustic.................................................................................................................. 3 lbs.**
- **Water sufficient to make 1,000 gallons of solution.**
- **Kerosene............................................................................................................. 5 gals.**

The caustic soda is added to 400 gallons of water. The mixture is agitated and heated to the boiling point. Then the “Dresinate XX” is added with the solution temperature held at about 205°F. for at least 15 minutes after which water is added in amount such as to bring the volume of the solution to 1,000 gallons. The solution is maintained at a temperature of 165°F. ± 5°F. while the cords are being passed through it. The kerosene is added not over 5 minutes before the solution is to be used. The kerosene serves as an antifoam to minimize foaming which would otherwise normally occur to an excessive extent in the handling of the sodium rosinate solution.

Since abietic acid, which is the principal acid in rosin, is a very weak acid, the value for Ka for it being 3.14 × 10⁻⁹, and since it is highly insoluble in water, it precipitates as it is formed and causes the equilibrium indicated by the above Equation 1 to be shifted to the right. The pH at which the equilibrium occurs is calculated by the use of the above expression for the hydrogen ion concentration where \( K_w \) has a value of 10⁻¹⁴, as stated above, Ka has a value of 3.14 × 10⁻⁹, and C is the concentration of sodium rosinate in the wash water. Since, in ordinary commercial operation, the concentration of sodium rosinate in the wash water is approximately 1%, the value of C can be assumed to be 0.031 moles of sodium rosinate per liter. Substituting in the above Equation 2 and performing the calculation of the hydrogen ion concentration at the point at which equilibrium would occur is found to be 10⁻⁸. This value was found to correspond closely to the value obtained in practice on the wash water in which the products of hydrolysis began to appear at pH values of 9 and under.

Applying our invention, sodium hydroxide or other suitable alkali is dissolved in the wash water in an amount such as to always maintain the hydrogen ion concentration at not over 10⁻⁸. Actually, for safety, we prefer to add alkali in such amount as to maintain the hydrogen ion concentration substantially below 10⁻⁻⁸, typically at not over 10⁻⁹ (which corresponds to a pH of at least 9.5), and still more preferably at a value not greater than 10⁻⁻⁹ (i.e., at a pH of 10 or over). Assuming that the pH of the available wash water is 7, the amount of sodium hydroxide necessary to raise its pH to 10 is calculated to be 1.6 grams per 100 gallons of wash water. This neglects the above-mentioned absorption effects of the cotton cord, but in actual practice it has been found that the addition of the above amount of sodium hydroxide will give a pH (in the wash water) in the range of 9.5 to 9.6 which is considered to be a quite safe operating range since the danger point is 9. The specified amount of alkali (1.6 grams of sodium hydroxide per 100 gallons of incoming wash water) is conveniently added in the form of a 1% solution by means of a metering pump to the fresh, typically demineralized, water before it enters the wash tank so as to form a completely uniform washing liquid free from stratification or localized spots of high or low concentration.

In the drawing, a web 2 partially impregnated grey cotton cords enters treating tank 2 which contains an aqueous solution of sodium rosinate or other alkali salt of a resin acid. This solution is replenished via inlet 3. Web 1 is guided through the aqueous solution by rolls 4 and is thoroughly impregnated with the treating solution in tank 2. The web 1 then passes upwardly through a pair of rubber-covered squeeze rolls 5 which squeeze out excess solution which runs back into tank 2. The web 1 then passes around guide rolls 6, thence into wash tank 7 through which the web is guided by rolls 8 and thence through a pair of rubber-covered squeeze rolls 9 which squeeze out excess aqueous material. The web then goes to latex solutioning means or any other subsequent treating means (not shown).

Fresh wash water is continuously introduced into wash tank 7 via inlet 10 and continuously overflows via outlet
11. after traversing tank 7 counter-currently to the cords. In accordance with our invention a dilute (say 1%) solution of sodium hydroxide or other suitable alkali in water is placed in supply tank 12 and is fed continuously at an accurately controlled rate by means of pipe 13, metering pump 14, and pipe 15 into admixture with the incoming wash water, e.g., demineralized water, entering the system via pipe 16.

Normally we operate in such a way that the concentration of sodium rosinate or other alkali salt of a rosin acid in the water in the wash tank ranges from 1.0 to 2.0%. It is believed that we are not limited to operation with any particular level of sodium rosinate or the like in the wash water since the above expression takes into account variations in this concentration. Similarly although our invention is usually applied with an alkali metal salt of ordinary rosin, we are not limited thereby since if other rosin acids are used as the basis of the salt used to improve the tensile strength of the grey cotton cord or the like, the appropriate ionization constant for such acid will simply be substituted in the above expression.

Similarly, we are not limited to the use of sodium hydroxide or other alkali metals as the means of maintaining pH H of the wash water in the washing tank. We can use any other alkali metal hydroxide although potassium hydroxide is the only one of these that is cheap enough to be considered. Instead of an alkali metal hydroxide, we can use any other water-soluble alkaline material capable of maintaining the desired pH in the wash water provided such alkaline material is not objectionable in the finished cord. Examples of such other alkaline materials include ammonium hydroxide and water-soluble organic amines, e. g., alkamolamines such as triethanolamine and diethanolamine, alkyl amines and quaternary ammonium hydroxides, e. g., trimethylbenzyl ammonium hydroxide, etc.

The invention is of special utility in connection with the production of tire cord from which rubberized fabric plies are made, which in turn become part of the pneumatic tire carcass. By reason of the improved tensile strength of the unrubberized tire cord, it is possible to make a standard quality tire with less tire cord, or in the alternative to make a superior tire with the usual quantity of tire cord. The chemically treated grey cotton cords may, with or without intermediate drying, be immersed in a rubber latex composition for the making of weftless cord fabric for tire carcasses. The latex composition, when dry, ultimately acts to bind the cords in parallel relation.

The invention may be applied to treating finished tire cords made of grey cotton, or to grey cotton fibers in any form as for example, yarn, plied yarn, cabled yarns, twisted products from plied yarns, fabrics woven from yarns or cords, unspun cotton, etc. It will be understood that the reference herein to cord is intended to include treatment of a single cord or a plurality of cords disposed in parallel relationship to form a sheet or web.

While rubberizing of the treated cotton has been referred to above as illustrative of further processing, it will be apparent that various uses of the grey cotton will not require rubberizing and the production of rubberized fabrics including the treated cotton is within the scope of the invention.

The rosin acid, the alkali salt of which is used in the initial treating solution, is usually ordinary rosin (which is mainly abietic acid—either wood or gum rosins can be used), but it can be any of the rosin acids found in ordinary rosin such as pure or substantially pure abietic acid, d-pimaraic acid, or napinic acid, or it can be a modified rosin, i. e., rosin which has been chemically modified to change the rosin nucleus, e. g., heat treated rosin, isomerized rosin, polymerized rosin, hydrogenated rosin, disproportionated rosin, etc. The rosin acid can be pure or substantially pure dehydroabietic acid, tetrahydroabietic acid, or dihydroabietic acid.

The term "rosin acid" is used herein in a generic sense to include the isomeric abietic acid, sapinic acid, and d-pimaraic acid which occur in varying amounts in wood and gum rosins of different geographical origins, also the heat treated, isomerized, polymerized, hydrogenated, disproportionated and dehydrogenated derivatives of such acids, and also the content of such acids and derivatives in tall oils, disproportionated tall oils and refined tall oils.

The material which is combined with the rosin acid, replacing the hydrogen of the carboxylic acid group thereof, is usually an alkali metal, especially sodium or potassium. However, it can be the ammonium group or it can be the group resulting from neutralization of the rosin acid with an organic amine such as an alkanolamine, an alkylamine, or a quaternary ammonium hydroxide.

From the foregoing description many advantages of our invention will be apparent to those skilled in the art. The principal advantage is that the invention provides a simple, easily applied, economical, commercially feasible, and highly effective method of preventing the occurrence of blowing or blistering during vulcanization of rubber articles reinforced with grey cotton or like fibers which have been treated by the above-mentioned Buckwalter process as commercially practiced. Another advantage is that use of our invention requires but little added expense in the way of chemicals, equipment and control. Another advantage is that our invention makes it unnecessary to maintain any minimum value for the concentration of sodium rosinate or the like in the wash water, as is referred to above, although in actual practice we usually operate with a concentration of sodium rosinate or the like in the wash water of from 1.0 to 2.0%.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. In a process of improving the tensile strength of naturally occurring cellulosic fibers containing at least 75% of the original naturally occurring waxes by impregnating said fibers with an aqueous solution of an alkali salt of a rosin acid, removing excess solution from the impregnated fibers and then washing the impregnated fibers with water flowing countercurrently to the impregnated fibers, the improvement which comprises maintaining the hydrogen ion concentration of the wash water at a value substantially below the value for Ca+ given by the equation

$$\log C_{a+} = \log \frac{K_w \times K_a}{C}$$

where $C_{a+}$ is hydrogen ion concentration, $K_w$ is the ionization constant of water and is taken as equal to $10^{-14}$, $K_a$ is the ionization constant of sodium rosinate, and C is the concentration of said salt in the wash water, by dissolving alkali in the wash water prior to contact thereof with said impregnated fibers, said alkali being selected from the group consisting of alkali metal hydroxides, ammonium hydroxide, and water-soluble organic amines.

2. In a process of improving the tensile strength of naturally occurring cellulosic fibers containing at least 75% of the original naturally occurring waxes by impregnating said fibers with an aqueous solution of sodium rosinate, removing excess solution from the impregnated fibers and then washing the impregnated fibers with water flowing countercurrently to the impregnated fibers, the improvement which comprises maintaining the hydrogen ion concentration of the wash water at a value substantially below the value for Ca+ given by equation

$$\log C_{a+} = \log \frac{K_w \times K_a}{C}$$

where $C_{a+}$ is hydrogen ion concentration, $K_w$ is the ionization constant of water and is taken as equal to $10^{-14}$, $K_a$ is the ionization constant of abietic acid and is taken as equal to $3.14 \times 10^{-4}$, and C is the concentration of sodium rosinate in the wash water, by dissolving sodium...
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hydroxide in said wash water prior to contact thereof with said impregnated fibers.

3. In a process of improving the tensile strength of naturally occurring cellulosic fibers containing at least 75% of the original naturally occurring waxes by impregnating said fibers with an aqueous solution of sodium rosinate removing excess solution from the impregnated fibers and then washing the impregnated fibers with water flowing countercurrently to the impregnated fibers under such conditions that the concentration of sodium rosinate in said wash water is approximately 1%, the improvement which comprises maintaining the hydrogen ion concentration of said wash water at a value substantially below 10⁻⁹ by dissolving sodium hydroxide in said wash water prior to contact thereof with said impregnated fibers.

4. A process as set forth in claim 3 wherein the amount of said sodium hydroxide is such as to maintain the hydrogen ion concentration of said wash water at a value not greater than 10⁻⁵⁻⁶.

5. In a process of improving the tensile strength of grey cotton containing at least 75% of the original naturally occurring waxes by impregnating said grey cotton with an aqueous solution of an allai metal salt of a rosin acid, remaining solution from the impregnated grey cotton and then washing the impregnated fibers with water flowing countercurrently to the impregnated grey cotton, the improvement which comprises maintaining the hydrogen ion concentration of the wash water at a value substantially below the value for Ca⁺ given by the equation

\[ C_{a^+} = \sqrt{\frac{K_wK_a}{C}} \]

where Ca⁺ is hydrogen ion concentration, Kw is the ionization constant of water and is taken as equal to 10⁻¹⁴, Ka is the ionization constant of said rosin acid, and C is the concentration of said salt in the wash water, by dissolving alkali metal hydroxide in said wash water prior to contact with said impregnated fibers.

6. A process as set forth in claim 5 wherein the hydrogen ion concentration of said wash water is maintained at a level corresponding to a pH value at least 0.5 greater than the pH value corresponding to the value for Ca⁺ given by said equation.

7. In a process of improving the tensile strength of grey cotton containing at least 75% of the original naturally occurring waxes by impregnating said grey cotton with an aqueous solution of sodium rosinate, removing excess solution from the impregnated fibers and then washing the impregnated fibers with water flowing countercurrently with respect thereto under such conditions that the concentration of sodium rosinate in the wash water is approximately 1%, the improvement which comprises maintaining the hydrogen ion concentration of said wash water at a value substantially below 10⁻⁹ by dissolving sodium hydroxide in said wash water prior to contact thereof with said fibers.

8. A process as set forth in claim 7 wherein the amount of said sodium hydroxide is such as to maintain the hydrogen ion concentration of said wash water at a value not greater than 10⁻⁵⁻⁶.

9. A process as set forth in claim 1 wherein the hydrogen ion concentration of said wash water is maintained at a level corresponding to a pH value at least 0.5 greater than the pH value corresponding to the value for Ca⁺ given by said equation.

10. In a process of making vulcanized rubber articles reinforced with cords made from naturally occurring cellulosic fibers containing at least 75% of the original naturally occurring waxes by impregnating said cords with an aqueous solution of an alkali salt of a rosin acid, removing excess solution from the impregnated cords by squeezing and thereafter washing the impregnated cords with water flowing countercurrently to the impregnated cords, assembling the resulting cords with unvulcanized rubber to form rubber articles reinforced with said cords, and vulcanizing the resulting rubber articles, the improvement which comprises eliminating blowing or blistering during the vulcanization of said articles by maintaining the hydrogen ion concentration of said wash water at a value substantially below the value for Ca⁺ given by the equation

\[ C_{a^+} = \sqrt{\frac{K_wK_a}{C}} \]

where Ca⁺ is hydrogen ion concentration, Kw is the ionization constant of water and is taken as equal to 10⁻¹⁴, Ka is the ionization constant of said rosin acid, and C is the concentration of said salt in the wash water, by dissolving alkali in the wash water prior to contact thereof with said impregnated cords, said alkali being selected from the group consisting of alkali metal hydroxides, ammonium hydroxide, and water-soluble organic amines.

11. In a process of making vulcanized rubber articles reinforced with grey cotton cords containing at least 75% of the original naturally occurring waxes by impregnating said cords with an aqueous solution of sodium rosinate, removing excess solution from the impregnated cords by squeezing and thereafter washing the impregnated cords with water flowing countercurrently to the impregnated cords, assembling the resulting cords with unvulcanized rubber to form rubber articles reinforced with said cords, and vulcanizing the resulting rubber articles, the improvement which comprises eliminating blowing or blistering during the vulcanization of said articles by maintaining the hydrogen ion concentration of said wash water at a level corresponding to a pH value at least 0.5 greater than the pH value corresponding to the value for Ca⁺ given by the equation

\[ C_{a^+} = \sqrt{\frac{K_wK_a}{C}} \]

where Ca⁺ is hydrogen ion concentration, Kw is the ionization constant of water and is taken as equal to 10⁻¹⁴, Ka is the ionization constant of said rosin acid, and C is the concentration of said sodium rosinate in the wash water, by dissolving sodium hydroxide in said wash water prior to contact thereof with said impregnated cords.

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