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## PROTECTION OF CELLULOSE FIBER AGAINST HEAT AGING

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This invention relates to the protection of cellulose fibers against deterioration by heat aging.

Deterioration of cellulose fiber upon subjection to elevated temperatures for prolonged periods of time is a very serious problem in the art. This problem is encountered particularly in the case of rubber articles which are reinforced with cellulose fiber, almost invariably stranded and in the form of cords or fabric, which may be a woven fabric having warp and woof threads or a so-called "weftless fabric" or "web fabric" composed of parallel cords joined together by a dry deposit of rubber latex, as described for example in the patent to Hopkinson No. 1,424,020. Such cellulose fiber reinforced rubber articles include pneumatic tires, steam hose, power transmisison belts, conveyor belts, etc. These articles are subjected to elevated temperature in normal use, either because they are subjected to external heating, or because they generate heat within themselves by reason of repeated rapid flexing, as in the case of pneumatic tires. The deterioration of the reinforcing cellulose fiber under the action of heat is particularly evidenced by progressive reduction in tensile strength of the fiber, leading to eventual breakage. This deteriorating action of prolonged heating on cellulose fibers is a principal cause of failure of such articles as pneumatic tires and steam hose.

The principal object of the present invention is to provide an improved method of protecting cellulose fiber, especially when stranded and in the form of a fabric, against deterioration by heat aging. Another object is to provide articles of manufacture embodying cellulose fibers protected against heat deterioration, such articles of manufacture including cellulose fibers themselves, whether unstranded, stranded, or in the form of a fabric, and vulcanized rubber articles reinforced with such cellulose fibers, such as pneumatic tire casings reinforced therewith. Other objects will more fully hereinafter appear.

According to the present invention, cellulose fiber is protected against deterioration by heat aging by treatment with guanidine salts of certain weak acids, namely, acids having an ionization constant of $1.75\times10^{-5}$ or less. I have found that guanidine salts of the class defined are effective chemicals in imparting to cellulose fibers the ability to withstand deterioration by the action of heat over extended periods of time. Such salts include guanidine carbonate, acetate, stearate, borate, etc., guanidine carbonate being especially preferred because it is remarkably effective.

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In carrying out my invention, the guanidine salt of the class defined may be applied to the cellulose fiber in any suitable manner, conveniently by immersing the fiber to be treated in a solution or dispersion of the treating agent for a time sufficient for the fiber to become substantially impregnated with the solution or dispersion. The cellulose fiber employed is usually ordinary grey cotton fiber, although the process of the invention may also be employed advantageously with the various regenerated cellulose fibers such as viscose rayon, etc. The invention is applicable to native cellulose fibers in general, such as flax, hemp, etc., as well as to scoured, bleached and mercerized cotton, etc.

For convenience, I usually employ the guanidine salt of a weak acid of the class defined in the form of an aqueous solution, typically at a concentration of 10% by weight, although marked improvement in heat age resistance is also obtainable with surprisingly dilute solutions, e. g., solutions containing 0.25% of the guanidine salt. If desired, more concentrated solutions may be employed, e. g., a 15.0% solution. In place of immersing the fibers in the treating liquid, I may incorporate the guanidine salt in the fiber in any other suitable manner, such as by spraying or brushing the treating liquid on the fiber.

The treatment with guanidine salts of acids having an ionization constant of $1.75\times10^{-5}$ or less, may be carried out at room temperature, or at elevated temperatures, for example, up to the boiling point of the treating solution. The time of contact between the cellulose fiber and the guanidine salt of the class defined should be sufficient to permit substantial penetration of the fiber. Usually treatment times of from 30 seconds to 10 minutes at the boiling point are adequate for this purpose, although longer treatment times are without adverse effect and may be employed if desired.

In order to obtain the benefits of the treatment of this invention it is necessary that the guanidine salt, as previously defined, remain in the cellulose fiber and be actually present as such in the fiber at the time the fiber is subjected to the high temperature service conditions which would ordinarily cause deterioration. I have found that a guanidine salt of a weak acid having an ionization constant of $1.75\times10^{-5}$ or less, present in the cellulose fiber in amount from 0.25 to 10.0% on the weight of the fiber, is effective to produce substantial improvement in the heat age resistance of the fiber.

The following example will illustrate the practice of my invention in more detail.

*Example*

Grey cotton tire cord was immersed in a boiling (100° C.) 10% by weight aqueous solution of guanidine carbonate for 2 minutes. The cord was then removed from the solution, and the excess solution was allowed to drain off the cord. The cord was then dried at 110° C. The cord was thereafter aged in the air at a temperature of 165° C. for 72 hours. This type of aging is known as "open heat aging." This temperature of 165° C. is in excess of the temperature (125° C.) at which grey cotton cord ordinarily suffers serious progressive irreversible loss of tensile strength due to chemical deterioration of the cotton by the action of heat. After such aging the tensile strength of the treated cotton cord was determined at 70° F. and 60% relative humidity, and the results were compared to control samples of the grey cotton cord as follows:

| | Tensile Strength | Percent of Original Strength Retained | Relative Strength |
|---|---|---|---|
| Control; Untreated, Unaged | 16.6 | 100 | |
| Control; Untreated, Aged | 6.4 | 39 | 100 |
| Guanidine Carbonate Treated, Aged | 11.7 | 70 | 183 |

The foregoing data show that while the untreated cord retained only 39% of its original strength after the aging test, the guanidine carbonate treated cord retained 70% of its original strength. The guanidine carbonate treated cord was more than 1.8 times as strong as the untreated cord after subjecting to the heat deterioration conditions.

The foregoing example was again repeated, using, in place of guanidine carbonate, guanidine salts of certain other weak acids, namely, guanidine acetate, guanidine stearate, and guanidine borate. These salts, and other guanidine salts of acids having an ionization constant of $1.75\times10^{-5}$ or less, were effective heat-age protective agents. This behavior was in marked contrast to the behavior of guanidine salts of acids having an ionization constant greater than $1.75\times10^{-5}$, such as guanidine sulfate, nitrate, hydrochloride, thiocyanate, etc., which were found to be ineffective for protecting cellulose fiber against progressive deterioration at elevated temperatures.

I have found that it is advantageous to combine the guanidine salt treatment of the present invention with the treatment of grey cotton fiber with sodium rosinate-silicate and the like to increase the tensile strength of the fiber, as described in my U. S. Patent 2,297,536, issued September 29, 1942. In this form of the invention, the two treatments can be carried out simultaneously by adding the guanidine salt to the sodium rosinate-silicate solution, or the treatments may be carried out successively in any desired order. If desired, the treated cord may be stretched, or stretched and shrunk, to effect still further increase in tensile strength. The sodium rosinate-silicate treatment protects the grey cotton fiber against the temporary, reversible loss of tensile strength which normally occurs substantially instantaneously upon heating grey cotton to elevated temperature, e. g., 120° C., while the guanidine compound treatment protects against the progressive, irreversible loss of strength which occurs after extended exposure to temperatures of 125° C. or higher. The progressive, irreversible loss of strength is due to actual



pyrolysis; that is, chemical deterioration induced by heat.

From the foregoing it is evident that the invention provides a method of treating cellulose fibers in general, whether in the form of fiber, yarn, cord or fabric, whereby the resistance of the fiber to the deteriorating effect of prolonged exposure to elevated temperatures is substantially enhanced. Thus, the improved cellulose fibers of this invention, containing a guanidine salt of an acid having an ionization constant of $1.75\times10^{-5}$ or less, are capable of improved serviceability, especially when employed for such purposes as reinforcing tires, steam hose, and similar rubber-fabric composite articles, which normally have a limited service life because of the deteriorating action of heat on the fiber reinforcement therein.

The treated fibers of this invention can be encased in rubber which may be subsequently vulcanized without any adverse effects due to the presence of the guanidine compound. The guanidine salts employed do not decompose or liberate gases at vulcanizing temperatures and because they remain in the fiber and retain their chemical identity, they are available for protecting the fiber on subsequent exposure of the vulcanized article to high temperature conditions over extended periods of service.

As indicated previously, the guanidine salt must actually remain as such in the cellulose fiber and must be present, preferably in amount of from 0.25% to 10.0% on the weight of the fiber, while the fiber is exposed to elevated temperature service conditions in order to obtain the beneficial effects of the treatment. Therefore, it is undesirable to extract the treated cords with solvents in a manner which would substantially remove the guanidine salt, or to contact the cord with any chemical reagent which would react with substantial quantities of the guanidine salt so as to change its chemical identity and make it ineffective for its purpose.

While I have exemplified my invention with particular reference to a preferred treatment of cotton cord intended to be used for reinforcing rubber articles, it will be understood that the guanidine salt containing fibers of this invention are susceptible of many other uses wherein resistance to heat is a desirable characteristic. However, the impregnated fibers containing the guanidine salts defined are especially adapted to production of vulcanized rubber-fabric composite articles, because the guanidine salts employed have no deleterious effect on the vulcanization and resist vulcanizing temperatures, and thereby result in improved vulcanizing rubber-fabric articles having materially increased high temperature service life.

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

1. The method of improving the resistance of cellulose fibers to the deteriorating effect of heat aging which comprises incorporating guanidine carbonate as such in the fiber, in amount of from 0.25% to 10.0% on the weight of the fiber.

2. The method of improving the resistance of cellulose fibers to the deteriorating effect of heat aging which comprises impregnating the fibers with an aqueous solution containing from 0.25% to 15.0% by weight of guanidine carbonate as such.

3. A cellulose fiber characterized by improved resistance to the deteriorating effect of heat aging containing guanidine carbonate as such in

amount of from 0.25% to 10.0% on the weight of the fiber.

4. A grey cotton fiber characterized by improved resistance to the deteriorating effect of heat aging containing guanidine carbonate as such in amount of from 0.25% to 10.0% on the weight of the fiber.

5. A regenerated cellulose fiber characterized by improved resistance to the deteriorating effect of heat aging containing guanidine carbonate as such in amount of from 0.25% to 10.0% on the weight of the fiber.

6. A vulcanized rubber article reinforced with cellulose cords containing guanidine carbonate as such in amount of from 0.25% to 10.0% on the weight of the fiber.

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