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PRODUCTION OF IMPROVED CELLULOSIC
CORDS AND YARNS

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This invention relates to the production of improved cellulosic cords and yarns, and particularly to a method of manufacturing cotton cords and yarns which possess remarkable resistance to the fatigue produced by continued oscillating stresses and which, therefore, are especially adapted for use in the construction of pneumatic tires, belting and the like.

In order for cords and yarns to be most suitable for use in tires, belting and other structures employing a mechanical fabric, they should possess both maximum tensile strength and maximum fatigue resistance, that is, resistance to fluctuations and repetitions of stress. Ordinary cotton cords have not been entirely satisfactory in either of these properties principally because of the fact that when such cords are employed in service, as in a tire for example, the heat developed by internal friction is sufficient to expel the moisture from the cords and consequently to cause a serious weakening in their tensile strength. Several methods for producing a cord which will maintain its tensile strength even when in a bone dry condition have already been proposed, but these expedients often do not improve the fatigue resistance of the cord and, therefore, do not provide cords entirely suitable for use in mechanical applications. For example, saturating cotton yarns and then twisting the yarns under tension while wet, is known to improve the bone dry tensile strength of the resultant cord, but the fatigue resistance of the cord is not appreciably affected. Prestretching a cord under a heavy load also improves its bone dry tensile strength but does not improve its fatigue resistance.

We have now discovered that cotton or cellulosic cords and yarns which exhibit greatly improved fatigue resistance as well as high tensile strength may be produced by treating yarn spun of cotton or other cellulosic filaments with an aqueous solution having a pH between 8 and 13 and containing certain chemical agents, to be hereinafter described; and then twisting the treated yarns while wet into plied yarns or cords.

The nature of the aqueous treating solution employed in our process may be varied widely but it is essential that the solution exhibit a pH within the range 8 to 13 and that it contain dissolved therein at least one electrolyte composed of a cation of a strong base and an inorganic anion. The expression "cation of a strong base" is used herein in its commonly accepted sense to designate a cation present in a base which in dilute solutions ionizes to an extent of 50% or more,

examples of such cations being the ions of the alkali metals such as lithium, sodium and potassium ions and the quaternary ammonium ions having the structure $(NR_4)^+$ wherein R is an organic radical such as tetramethyl ammonium ion, tetraethyl ammonium ion, trimethyl phenyl ammonium ion, dimethyl phenyl benzyl ammonium ion, trimethyl stearyl ammonium ion and the like. The aqueous treating solutions which may be employed, therefore, are solutions of electrolytes containing any of these cations and any inorganic anion, provided of course that in addition the solution has a pH between 8 and 13.

When the inorganic anion is the hydroxyl ion the treating solution may consist simply of a dilute aqueous solution of a strong base such as dilute aqueous solutions of sodium or potassium hydroxide or of a quaternary ammonium base since these solutions will possess the proper pH range. Moreover, when the anion is the anion of a weak acid (by which is meant an acid which ionizes in dilute solution to an extent less than about 20%) such as a phosphate, borate, carbonate, acetate or silicate ion or the like, the treating solution may consist simply of a dilute aqueous solution of a salt prepared by the reaction of a strong base and a weak acid such as solutions of sodium carbonate, sodium phosphate, potassium acetate, sodium silicate or the like, since such salts hydrolyze to give excess hydroxyl ions and therefore provide a solution having a pH within the range of 8 to 13. However, when the inorganic anion is the anion of a strong acid such as a nitrate, chloride or sulfate ion the treating solution will not consist simply of a dilute aqueous solution of a salt formed by the reaction of a strong base and a strong acid such as a solution of sodium chloride, sodium sulfate or the like since such solutions are neutral and have a pH of about 7, but instead the treating solution must contain a sufficient amount of added alkali to bring the pH within the range of 8 to 13.

In addition to electrolytes composed of a cation of a strong base and an inorganic anion, the treating solution may also contain small amounts of other electrolytes such as the water soluble salts of calcium, barium, strontium, zinc, mercury, manganese, cobalt, nickel, iron, copper, aluminum and ammonium and other water soluble inorganic salts which when in concentrated solutions have a tendency to swell, dissolve, plasticise or react with cellulose. In many instances the presence of these additional elec-

trolytes in the treating solution has been found further to increase the fatigue resistance and tensile strength of cords twisted from yarns which have been treated with such solutions.

The concentration of the electrolytes in the treating solution may vary over a wide range but in general dilute aqueous solutions are to be preferred. Thus if the only solute present in the treating solution is an electrolyte composed of a cation of a strong base and an inorganic anion, the concentration of this electrolyte should preferably be less than 5% by weight of the solvent, and still more preferably concentrations of $\frac{1}{4}$ to 3% by weight should be employed. Similarly, if the solution contains several dissolved electrolytes, the total concentration of solute should preferably be less than 5% by weight of the solvent. It is understood, of course, that concentrations of solutions which do not give the proper pH such as concentrated solutions of sodium hydroxide are not contemplated in this invention.

The preferred treating solutions are dilute aqueous solutions of strong bases, dilute aqueous solutions of salts formed by the reaction of a strong base and a weak acid and dilute aqueous solutions containing such a base or salt and an additional electrolyte, provided such solutions containing such a base or salt and an additional electrolyte, provided such solutions have a pH within the range of 8 to 13, and more preferably within the range of 9 to 11. Dilute aqueous solutions of alkali metal hydroxides, carbonates, phosphates, silicates and the like, give particularly good results.

The treatment of the cotton or cellulosic fibers with the above solutions may be accomplished in any desired manner and at any convenient time in the processing operations. However, since it is essential that the fibers be twisted after the treatment with the solution and while they are still wet it is generally desirable to treat the single cotton yarns produced in the spinning operation immediately before these yarns are run to the yarn twister or to treat twisted yarns or plied yarns with the solution immediately before they are twisted into plied yarns or cords or cables. The treatment is conveniently effected by immersing the yarns in the treating solution contained in a trough such as is provided in the common wet-twisting apparatus, but other wetting means such as spraying the yarns with the treating solution are also possible. The treating solution need not be at any specified temperature during the treatment nor is it necessary that the yarns remain in contact with the solution for any specified time, simply wetting the yarns with the solution at room temperature being sufficient.

After the yarns are treated with the solution and while they are still wet they are twisted into plied yarns or cords. This may be accomplished in the usual manner, any desired degree of twist being employed. As a matter of fact, treatment with the solutions before twisting permits of wider variation in the degree of twist which may be applied to the yarns and cords since it has been found that this expedient helps to prevent the development of an unbalanced condition in the finished cords.

In connection with the practice of this invention it is often desirable to make use of other processing expedients which in themselves do not produce a fatigue resistant cord but which, when employed together with the process described hereinabove of treating the yarns with the described aqueous solutions and then wet-twisting

the yarns into plied yarns or cords, either increase the fatigue resistance or tensile strength of the resultant cord or yarn or serve some other useful purpose. Thus it may be desirable to include wetting agents such as sodium lauryl sulfate, sodium isobutyl naphthalene sulfonate or any of the commercially available wetting agents known by the trade-names "Tergitol," "Alphasol," "Triton," "Naccanol," "Nekal," "Penetrant," etc., in the aqueous treating solutions described hereinabove since the presence of these agents facilitates the wetting of the cotton fibers by the aqueous solutions. Substances which prevent mildewing of the cotton fibers such as formaldehyde, phenol, sulfanilamide, resorcinol and the commercial mildewicides such as "Dowicide," "Hydrocide," "Germicide 1622," etc., may also conveniently be included in the treating solution. Moreover, the aqueous treating solutions may be applied to the yarns or plies before or during twisting in combination with aqueous dispersions of substances which leave a coating on the yarns or plies such as natural or synthetic latex, and other aqueous dispersions of natural or synthetic resins and the like. The impregnated cords so formed possess excellent fatigue resistance in addition to the other desirable properties of an impregnated cord.

It is also desirable in most cases to stretch the cords produced by the process of this invention before they are used in the construction of mechanical fabrics such as tire cord fabric or the like. This stretching or tensioning process may be applied either during twisting of the cords or after twisting and may be carried out in the manner well known to the art. Great improvements in tensile strength and heat resistance as well as fatigue resistance are often brought about by this tensioning especially if extreme tension is applied to the cord after the wet twisting process hereinabove described.

In one representative embodiment of this invention a 22(s)/5/3 cotton cord was prepared in the normal manner except that the plied yarns were treated with an aqueous solution having a pH of about 9 and containing 1% by weight of sodium carbonate, $\frac{1}{2}$ % by weight of a commercial wetting agent and $\frac{1}{2}$ % by weight of a mildewicide immediately before they were twisted into the cord. Another cord of the same construction was twisted in the normal manner as a control. A comparison of the properties of the two cords revealed the following:

Table I

	Treated cord	Control
Tensile strength (conditioned).....	17.6	17.8
Tensile strength (bone dry).....	17.8	14.6
Elongation 10 lbs.....	8.5	9.4
Fatigue life (hours).....	20.6	4.5

It is to be noted that the bone dry tensile strength of the cord prepared by the method of this invention was equal to its conditioned tensile strength and that the fatigue life of the treated cord was well over 400% of that of the control. The fatigue life was measured by determining the length of time required for a vibrating vertically suspended cord subjected to an elevated temperature to break. The remarkable fatigue resistance of the treated cord could not have been obtained by simply wet twisting the cord from a solution of the wetting agent alone, but in order to obtain this fatigue resistance it

was necessary that the solution contain the sodium carbonate and possess the proper pH.

The following table shows the results obtained with various other cords which were treated with sodium hydroxide solutions and then wet twisted together with the results obtained with a control.

Table II

Solution	pH	Per cent elong. at 10#	Pounds tensile strength	Fatigue life in hrs. at 300° F.
Dry twisted control.....		8.22	16.32	5.4
Distilled water.....	7	8.44	18.46	5.4
NaOH solution.....	11.2	8.82	18.36	7.0
Do.....	12.5	9.00	17.86	7.5
Do.....	12.8	9.36	18.50	8.7
Do.....	13.4	9.28	17.88	4.6
Do.....	14.3	9.67	16.55	1.4

The above results show that wet twisting cords from solutions of sodium hydroxide having a pH less than 13 greatly improves the fatigue resistance, tensile strength and elongation of the cords over that of the control and that when a solution having a pH over 13 is used the fatigue resistance very rapidly decreases. Moreover, it is seen that simple wet twisting from water alone does not improve the fatigue resistance of the cord over that of the dry twisted control.

The remarkable increase in the fatigue resistance of cords wet twisted from solutions containing still other electrolytes composed of a cation of a strong base and an inorganic anion is shown by the following table. In all the solutions used the pH was between 8 and 13 and the relative fatigue resistance was determined by taking the fatigue life of a cord dry twisted as being 100%.

Table III

Treating solution	Relative fatigue resistance
	Per cent
Trisodium phosphate, 1%.....	230
Sodium carbonate, 1%.....	215
Sodium carbonate, 1%.....	233
Sodium carbonate, 3%.....	270
Sodium silicate, 1%.....	200
Boric acid, sodium hydroxide and potassium chloride (pH=10.1).....	202
Dimethyl phenyl benzyl ammonium hydroxide, 2½%.....	237
Trimethyl phenyl ammonium hydroxide, 2½%.....	274
6% solids consisting of sodium hydroxide, resorcinol-formaldehyde resin and latex.....	190

The above table illustrates the use of various salts of strong bases and weak acids, quaternary ammonium bases, and a strong base in combination with a substance which forms a coating on the cord (latex), all of which remarkably increase the fatigue life of the cords.

The advantages resulting from the practice of this invention in the production of yarns and cords which have improved resistance to the fatigue produced by oscillating stresses and which additionally have excellent bone dry tensile strength and heat resistance are apparent from the above description. As a result of this invention we are able to produce yarn, twine, cord or other fabric composed of cotton or cellulosic fibers which will stand up well in service when subjected to repeated stresses and high temperatures. It is evident that articles such as tires, belts and other articles embodying a mechanical fabric which have been produced in the manner herein described will have a longer life of usefulness than has previously been obtained by any known process of manufacturing cotton fibers into fabric for such use.

Although we have herein described representative embodiments of our invention it is not intended that the invention be limited solely thereto for many variations and modifications which will occur to those skilled in the art may be effected without departing from the spirit and scope of the invention as defined in the appended claims.

We claim:

1. The process for producing highly fatigue resistant cotton cords and yarns which comprises treating cotton yarns with a dilute aqueous solution of an electrolyte composed of a cation of a strong base and an inorganic anion, said solution having a pH of 8 to 13, and twisting the treated yarns while wet.
2. The process for producing highly fatigue resistant cotton cords which comprises treating cotton yarns with a dilute aqueous solution of an electrolyte composed of a cation of a strong base and an inorganic anion, said solution having a pH of 9 to 11, and twisting the treated yarns while wet.
3. The process for producing a highly fatigue resistant cotton cord which comprises treating cotton yarns with a dilute aqueous solution of a strong base, said solution having a pH of 8 to 13, and twisting a plurality of the treated yarns while wet to form a cord.
4. The process for producing a highly fatigue resistant cotton cord which comprises treating cotton yarns with a dilute aqueous solution of an alkali metal hydroxide, said solution having a pH of 9 to 11, and twisting a plurality of the treated yarns while wet to form a cord.
5. The process for producing a highly fatigue resistant cotton cord which comprises treating cotton yarns with a dilute aqueous solution of a salt of a strong base and a weak acid, said solution having a pH of 8 to 13, and twisting a plurality of the treated yarns while wet to form a cord.
6. The process for producing a highly fatigue resistant cotton cord which comprises treating cotton yarns with a dilute aqueous solution of a salt formed by the reaction of an alkali metal hydroxide and a weak acid, said solution having a pH of 8 to 13, and twisting a plurality of the treated yarns while wet to form a cord.
7. The process for producing a highly fatigue resistant cotton cord which comprises treating cotton yarns with a dilute aqueous sodium carbonate solution having a pH of 8 to 13, and twisting a plurality of the treated yarns while wet to form a cord.
8. The process for producing a highly fatigue resistant cotton cord which comprises treating cotton yarns with a dilute aqueous sodium phosphate solution having a pH of 8 to 13, and twisting a plurality of the treated yarns while wet to form a cord.
9. The process for producing a highly fatigue resistant cotton cord which comprises treating cotton yarns with a dilute aqueous solution containing an electrolyte composed of a cation of a strong base and an inorganic anion and a water soluble inorganic salt which, in concentrated solutions, swells or dissolves cellulose, said solution having a pH of 8 to 13, and twisting the treated yarns while wet.
10. The process for producing a highly fatigue resistant impregnated cotton cord which comprises treating cotton yarns with a dilute aqueous solution having a pH of 8 to 13 and containing an electrolyte composed of a cation of a strong base and an inorganic anion and with an aqueous

dispersion of a substance which deposits a coating on said yarns, and twisting the treated yarns while wet.

11. The process for producing a highly fatigue resistant impregnated cotton cord which comprises treating cotton yarns with a dilute aqueous solution having a pH of 8 to 13 and containing an electrolyte composed of a cation of a strong base and an inorganic anion and with latex, and twisting yarns while wet.

12. The process for producing a highly fatigue resistant cotton cord which comprises treating cotton yarns with a dilute aqueous solution of an electrolyte composed of a cation of a strong base and an inorganic anion, said solution having a pH of 8 to 13, twisting a plurality of the treated cords while wet to form a cord, and stretching the twisted cord under tension.

13. A highly fatigue resistant cotton cord or

yarn, said cord or yarn being produced by the process of claim 1.

14. A highly fatigue resistant cotton cord, said cord being produced by the method of claim 2.

15. A highly fatigue resistant cotton cord, said cord being produced by the method of claim 3.

16. A highly fatigue resistant cotton cord, said cord being produced by the method of claim 4.

17. A highly fatigue resistant cotton cord, said cord being produced by the method of claim 9.

18. A highly fatigue resistant cotton cord, said cord being produced by the method of claim 10.

19. A highly fatigue resistant cotton cord, said cord being produced by the method of claim 11.

20. A highly fatigue resistant cotton cord, said cord being produced by the method of claim 12.

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