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PRODUCTION OF TEXTILE AND OTHER ARTICLES

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This invention relates to improvements in the production of textile and other articles, for example articles having a basis of organic esters of cellulose.

It has been discovered that the properties of textiles, foils, films and other shaped articles made of an organic derivative of cellulose, particularly acetone-soluble cellulose acetates, may be improved in a number of respects by introducing into them both the radicle of an aliphatic polycarboxylic acid, and also the radicle of a higher monocarboxylic aliphatic acid containing at least six carbon atoms, for example caproic, caprylic, lauric or palmitic acid. Preferably the monocarboxylic acid radicle is the radicle of lauric acid or a higher homologue thereof and the polycarboxylic acid radicle is the radicle of a dicarboxylic acid, such as adipic, tartaric or phthalic acid. Examples of other polycarboxylic acid radicles which may however be employed are the radicles of succinic, citric, tricarballic, α - β - γ -butane tricarboxylic and α - β - γ - δ -butane tetracarboxylic acids. In this manner articles may be obtained which are substantially waterproof and have a melting point higher than that of the untreated articles or even than that of articles into which the radicle of a polycarboxylic acid only has been introduced. Improvement takes place also in safe ironing temperature and crease resistance of fabrics containing yarns of an organic derivative of cellulose, while their breaking strength and rubbing properties are better than those of fabrics esterified with a polycarboxylic acid alone. It is surprising that the introduction of so small a proportion of higher aliphatic monocarboxylic acid radicle, which in general need only be of the order of .5-1%, should have such a pronounced effect on the properties of the articles.

The process is also applicable to the treatment of articles made of other cellulosic materials, for example cotton, linen and regenerated cellulose materials obtained by the viscose or cuprammonium processes or by the saponification of materials made of organic esters of cellulose. Articles containing synthetic hydroxy-containing compounds may be treated, examples of such compounds being partially saponified polymerised vinyl acetate and partially saponified copolymers of vinyl acetate with vinyl chloride. Other articles which may be treated are articles made of wool, silk and synthetic nitrogen-containing compounds, e. g. polyamides obtainable from diamines and dibasic acids or from aminoacids.

Articles to which the process may be applied include yarns, for example in the form of hanks or in fabric form, and foils, films and similar articles. As examples of types of yarns may be mentioned ordinary acetone-soluble cellulose acetate yarns, stretched or stretched and shrunk cellulose acetate yarns and regenerated cellulose yarns obtained by the saponification of such yarns, especially yarns of high tenacity, for example 4 or 5 grams per denier, obtained by stretching cellulose acetate yarns in steam or hot water and then saponifying them.

The introduction of the acid radicles is preferably effected by heating the articles in a non-solvent medium containing a liquid organic non-solvent and a low concentration of the mixed anhydrides of a lower fatty acid and a polycarboxylic acid and of a lower fatty acid and a higher aliphatic monocarboxylic acid. The mixed anhydrides may be prepared by heating a medium containing a non-solvent for the articles to be treated and a low concentration of a mixture of a lower fatty acid and the anhydrides of the other acids or a mixture of these acids and a lower fatty acid anhydride. Preferably the introduction of the articles into the medium is effected after formation of the mixed anhydrides and removal of any fatty acid formed or present in excess, since the presence of such acid during acidylation, except in a very small amount, tends to affect the articles deleteriously, especially articles made of an organic ester of cellulose. The articles may, however, be introduced into the medium before formation of the mixed anhydrides.

The introduction of the polycarboxylic acid radicle and of the higher monocarboxylic acid radicle need not be effected simultaneously. For example, the articles may first be heated with a mixture of a lower carboxylic acid anhydride and a polycarboxylic acid and subsequently with a mixture of the anhydride and a higher monocarboxylic acid.

When yarns, foils or other articles are acidylated the acidylation is preferably carried out in the presence of a high boiling liquid which is a non-solvent for the materials. Moreover, when the articles have a basis of an organic ester of cellulose the conditions should be such that any lower monocarboxylic acid present or formed during the reaction is distilled over, since, as indicated above, the presence of such an acid in the esterification medium may have a deleterious effect on the properties of the product. A reaction temperature of between 100 and 150° C. is

usually satisfactory. Xylene, which boils at about 140° C., has been found to give particularly good results as a non-solvent diluent, though other diluents, e. g. toluene, mesitylene or kerosene, may also be used. The time of reaction is generally a few hours, for example 2, 4 or 6 hours at a temperature of 130 or 140° C.

The concentration of organic acid radicles in the acidylation medium should be low, for example of the order of .5-1 up to about 3 or 5% of each. Lower monocarboxylic acid radicles in the form of the acid are, as already stated, preferably absent from the medium or present only in a very low concentration.

The following example is given to illustrate the process of the present invention:

Example

An esterification medium is prepared by boiling a mixture containing about 3% of stearic acid, 4% of adipic acid and 1% of acetic anhydride dissolved in xylene for about one hour and allowing the vapours formed to distil over. One part by weight of acetone-soluble cellulose acetate yarn in fabric form is then boiled in 100 parts by weight of this esterification medium, the vapours formed being withdrawn and condensed so that accumulation of acetic acid in the medium is prevented. Esterification is continued until the materials have increased in weight by between 12 and 20%, preferably about 15%.

Instead of adipic acid, phthalic or tartaric acid may be employed and palmitic acid may be employed instead of stearic acid. Further, another lower fatty acid anhydride, for example propionic or butyric anhydride may be employed though the best results are usually obtained with acetic anhydride.

Having described our invention, what we desire to secure by Letters Patent is:

1. Process for the treatment of textiles, foils, films and the like, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of a polycarboxylic acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms.
2. Process for the treatment of textiles, foils, films and the like, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of a dicarboxylic acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms.
3. Process for the treatment of textiles, foils, films and the like having a basis of cellulosic material, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of a polycarboxylic acid and of a fatty acid containing less than 6 carbon atoms, and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms.
4. Process for the treatment of textiles, foils, films and the like having a basis of cellulosic material, which comprises acidylating them with retention of their structure by heating them in a

non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of a dicarboxylic acid and of a fatty acid containing less than 6 carbon atoms, and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms.

5. Process for the treatment of textiles, foils, films and the like having a basis of an organic derivative of cellulose, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent having a boiling point above 100° C., a mixed di-anhydride of a polycarboxylic acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms.

6. Process for the treatment of textiles, foils, films and the like having a basis of an organic derivative of cellulose, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent having a boiling point about 100° C., a mixed di-anhydride of a dicarboxylic acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms.

7. Process for the treatment of textiles, foils, films and the like having a basis of cellulose acetate, which comprises acidylating them with retention of their structure by heating them at a temperature of 140-160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of a polycarboxylic acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms.

8. Process for the treatment of textiles, foils, films and the like having a basis of cellulose acetate, which comprises acidylating them with retention of their structure by heating them at a temperature of 140-160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of a dicarboxylic acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms.

9. Process for the treatment of textiles, foils, films and the like having a basis of cellulosic material, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of adipic acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of a fatty acid containing at least 12 carbon atoms and of a fatty acid containing less than 6 carbon atoms.

10. Process for the treatment of textiles, foils, films and the like having a basis of cellulosic material, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of phthalic acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of

a fatty acid containing at least 12 carbon atoms and of a fatty acid containing less than 6 carbon atoms.

11. Process for the treatment of textiles, foils, films and the like having a basis of cellulosic material, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of tartaric acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of a fatty acid containing at least 12 carbon atoms and of a fatty acid containing less than 6 carbon atoms.

12. Process for the treatment of textiles, foils, films and the like having a basis of an organic derivative of cellulose, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent having a boiling point above 100° C., a mixed di-anhydride of adipic acid and of acetic acid and a mixed anhydride of a fatty acid containing at least 12 carbon atoms and of acetic acid.

13. Process for the treatment of textiles, foils, films and the like having a basis of an organic derivative of cellulose, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent having a boiling point above 100° C., a mixed di-anhydride of phthalic acid and of acetic acid and a mixed anhydride of a fatty acid containing at least 12 carbon atoms and of acetic acid.

14. Process for the treatment of textiles, foils, films and the like having a basis of an organic derivative of cellulose, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent having a boiling point above 100° C., a mixed di-anhydride of tartaric acid and of acetic acid and a mixed anhydride of a fatty acid containing at least 12 carbon atoms and of acetic acid.

15. Process for the treatment of textiles, foils, films and the like having a basis of cellulosic material, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of a polycarboxylic acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms, each of the acid radicles being present in a concentration of less than 5% of the total weight of the acidylation medium.

16. Process for the treatment of textiles, foils, films and the like having a basis of an acetone-soluble cellulose acetate, which comprises acidylating them with retention of their structure by heating them at a temperature between 140–160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of acetic acid and of adipic acid and a mixed anhydride of acetic acid and of a fatty acid containing at least 12 carbon atoms, each of the organic acid radicles being present in a concentration of less than 5% of the total weight of the acidylation medium and acidylation being effected under such conditions that any acetic acid present or formed is distilled over and thus removed from the medium.

17. Process for the treatment of textiles, foils,

films and the like having a basis of an acetone-soluble cellulose acetate, which comprises acidylating them with retention of their structure by heating them at a temperature between 140–160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of acetic acid and of phthalic acid and a mixed anhydride of acetic acid and of a fatty acid containing at least 12 carbon atoms, each of the organic acid radicles being present in a concentration of less than 5% of the total weight of the acidylation medium and acidylation being effected under such conditions that any acetic acid present or formed is distilled over and thus removed from the medium.

18. Process for the treatment of textiles, foils, films and the like having a basis of an acetone-soluble cellulose acetate, which comprises acidylating them with retention of their structure by heating them at a temperature between 140–160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of acetic acid and of tartaric acid and a mixed anhydride of acetic acid and of a fatty acid containing at least 12 carbon atoms, each of the organic acid radicles being present in a concentration of less than 5% of the total weight of the acidylation medium and acidylation being effected under such conditions that any acetic acid present or formed is distilled over and thus removed from the medium.

19. Process for the treatment of textiles, foils, films and the like having a basis of cellulosic material, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of a polycarboxylic acid and of a fatty acid containing less than 6 carbon atoms, and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms, the volume ratio of acidylation medium to articles being at least 50:1.

20. Process for the treatment of textiles, foils, films and the like having a basis of an organic derivative of cellulose, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of a polycarboxylic acid and a fatty acid containing less than 6 carbon atoms and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms, the volume ratio of acidylation medium to articles being at least 50:1.

21. Process for the treatment of textiles, foils, films and the like having a basis of cellulosic material, which comprises acidylating them with retention of their structure by heating them in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of a polycarboxylic acid and of a fatty acid containing less than 6 carbon atoms and a mixed anhydride of an aliphatic monocarboxylic acid containing at least 6 carbon atoms and of a fatty acid containing less than 6 carbon atoms, each of the acid radicles being present in a concentration of less than 5% of the total weight of the acidylation medium, and the volume ratio of acidylation medium to articles being at least 50:1.

22. Process for the treatment of textiles, foils, films and the like having a basis of an organic derivative of cellulose, which comprises acidylat-

ing them with retention of their structure by heating them at a temperature between 140-160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of acetic acid and of adipic acid and a mixed anhydride of acetic acid and of a fatty acid containing at least 12 carbon atoms, each of the organic acid radicles being present in a concentration of less than 5% of the total weight of the acidylation medium and acidylation being effected under such conditions that any acetic acid present or formed is distilled over and thus removed from the medium and being continued until the articles have increased in weight by between 12-20%.

23. Process for the treatment of textiles, foils, films and the like having a basis of an organic derivative of cellulose, which comprises acidylating them with retention of their structure by heating them at a temperature between 140-160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of acetic acid and of phthalic acid and a mixed anhydride of acetic acid and of a fatty acid containing at least 12 carbon atoms, each of the organic acid radicles being present in a concentration of less than 5% of the total weight of the acidylation medium and acidylation being effected under such conditions that any acetic acid present or formed is distilled over and thus removed from the medium and being continued until the articles have increased in weight by between 12-20%.

24. Process for the treatment of textiles, foils, films and the like having a basis of an organic derivative of cellulose, which comprises acidylating them with retention of their structure by heating them at a temperature between 140-160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, a mixed di-anhydride of acetic acid and of tartaric acid and a mixed anhydride of acetic acid and of a fatty acid containing at least 12 carbon atoms, each of the organic acid radicles being present in a concentration of less than 5% of the total weight of the acidylation medium and acidylation being effected under such conditions that any acetic acid present or formed is distilled over and thus removed from the medium and being continued until the articles have increased in weight by between 12-20%.

25. Process for the treatment of textiles, foils, films and the like having a basis of an acetone-soluble cellulose acetate, which comprises esteri-

fyng them with retention of their structure by heating them at a temperature between 140 and 160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, the radicles of acetic acid, of adipic acid and of a fatty acid containing at least 12 carbon atoms, at least one of said radicles being present in the form of an anhydride, each of the organic acid radicles being present in a concentration of less than 5% of the total weight of the esterification medium and esterification being effected under such conditions that any acetic acid present or formed is distilled over and thus removed from the medium and being continued until the articles have increased in weight by between 12 to 20%.

26. Process for the treatment of textiles, foils, films and the like having a basis of an acetone-soluble cellulose acetate, which comprises esterifying them with retention of their structure by heating them at a temperature between 140 and 160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, the radicles of acetic acid, of phthalic acid and of a fatty acid containing at least 12 carbon atoms, at least one of said radicles being present in the form of an anhydride, each of the organic acid radicles being present in a concentration of less than 5% of the total weight of the esterification medium and esterification being effected under such conditions that any acetic acid present or formed is distilled over and thus removed from the medium and being continued until the articles have increased in weight by between 12 to 20%.

27. Process for the treatment of textiles, foils, films and the like having a basis of an acetone-soluble cellulose acetate, which comprises esterifying them with retention of their structure by heating them at a temperature between 140 and 160° C. in a non-solvent liquid medium comprising a liquid organic non-solvent, the radicles of acetic acid, of tartaric acid and of a fatty acid containing at least 12 carbon atoms, at least one of said radicles being present in the form of an anhydride, each of the organic acid radicles being present in a concentration of less than 5% of the total weight of the esterification medium and esterification being effected under such conditions that any acetic acid present or formed is distilled over and thus removed from the medium and being continued until the articles have increased in weight by between 12 to 20%.

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