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PRODUCTION OF ACIDYL DERIVATIVES OF CELLULOSE AND OTHER ORGANIC SUBSTANCES

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This invention relates to the acidylation of cellulosic and other materials, and particularly to the production of cellulosic and other materials containing radicles of dibasic or other polycarboxylic acids.

As is well-known, the introduction of the radicle of acetic acid or other lower monobasic carboxylic acid into cellulosic materials can be effected comparatively simply by treating them with the anhydride of the acid in the presence of a suitable diluent, but when it is sought to apply this method to the introduction of the radicle of a di- or other polycarboxylic acid, for example, adipic acid or phthalic acid, it is found that if reaction takes place at all it does so only with difficulty and the products obtained are mono-esters of the polycarboxylic acids and contain free carboxy groups. In consequence they lack water-resistance and are frequently soluble in dilute alkali. Further, if it is found possible to introduce any substantial proportion of the radicle by carrying out the reaction at an elevated temperature, the result usually is that the cellulose molecule is considerably degraded and consequently the tenacity of yarns and other materials which have been treated is seriously reduced. Similar objections apply in the case when a dicarboxylic acid halide is employed. While, with this type of reagent, the introduction of the acid radicle is easier than when the anhydride is employed it is as a rule even more difficult to avoid serious damage to the tenacity and other mechanical properties of the materials treated.

It has now been discovered that the introduction of a di- or other polycarboxylic acid radicle into cellulosic or other materials may be satisfactorily effected with only a relatively small reduction in the mechanical properties of the materials by treating them, preferably at a temperature above 100° C. with an acidylation medium containing a mixed anhydride prepared from the polycarboxylic acid anhydride or acid and a lower monocarboxylic acid or anhydride respectively. Examples of lower monocarboxylic acids which may be employed are acetic, propionic, butyric, methoxy-acetic, ethoxy-acetic and chloracetic acids. Instead of the mono- or polycarboxylic acid the corresponding ester, e. g. the methyl or ethyl ester, may be used.

Polycarboxylic acids and anhydrides, which have been found to give very satisfactory results when acidylation is carried out according to the process of the present invention, are adipic, phthalic and tartaric acids and their anhydrides but other polycarboxylic acids and anhydrides may also be employed. As examples may be mentioned the malonic, succinic, pimelic, sebacic, azelaic, isophthalic, terephthalic, maleic, malic and citric acids and their anhydrides.

The process of the present invention is applicable to the treatment of cellulosic materials, for example cotton linters, for the production of cellulose derivatives which can be dissolved in organic solvents and converted into artificial filaments, foils, lacquers or other products and for this purpose acidylation may be carried out in the presence of a solvent for the cellulose derivative produced, for example, acetic acid, propionic acid, chloroform or methylene chloride. A particularly important aspect of the present invention, however, is its application to the acidylation of yarns and other formed articles, particularly articles having a basis of acetone-soluble cellulose acetate or other organic ester or ether of cellulose, for example, cellulose propionate or butyrate or ethyl, propyl or butyl cellulose. The most important articles of this nature are those produced by the shaping and setting of solutions of cellulose derivatives in organic solvents. Articles may, however, also be acidylated which are insoluble in organic solvents and have been produced. for example, by acidylating cotton or regenerated cellulose fibres or yarns in the presence of a non-solvent diluent and interrupting acidylation when only a low proportion of ester groups has been introduced, for example, 1 or 1½ groups per $C_6H_{10}O_5$ molecule. Further, yarns and other articles consisting of regenerated cellulose obtained, for example, by the viscose, cuprammonium or nitrocellulose process or by the saponification of cellulose ester articles may also be acidylated according to the process of the present invention.

The process is not limited to the treatment of cellulosic materials, but may be applied to the acidylation of other materials containing hydroxy groups as in the case of partially saponified polyvinyl esters. For example yarns made of a copolymer of vinyl chloride and vinyl acetate, which contains 85–95% of vinyl chloride and 15–5% of vinyl acetate and has a molecular weight of 10,000, 15,000 or 20,000 or more, may be partially saponified and then treated by the present process in order to increase their melting point and modify their solubility characteristics. The acidylation of materials containing free hydroxy groups is of course an esterification process. Materials containing —NH— groups, e. g. wool, casein and artificial fibre-forming polyamides may also be acidylated by the present process.

In order to obtain the best results according to the present invention, particularly as regards the avoidance of any substantial loss of tenacity, it is important that the ratio of acidylation medium to the cellulosic or other materials should be high, for example 50, 100 or even 150:1, and that the concentration of organic acid radicles in the medium should be low. For example, the concentration of adipyl, phthalyl or other polycarboxylic acid radicle in the medium is preferably only about .5 to 3 or 5%. The concentration of monocarboxylic acid radicle is preferably below 1%, for example .5 or .75%.

The acidylation medium is preferably prepared by heating a mixture of the anhydride and acid, e. g. for 15–30 minutes, distilling off any free monocarboxylic acid and dissolving the residue in a large excess of diluent, e. g. 20, 50 or more times its volume. Free acid may alternatively be removed by passing ketene through the mixture or by adding to it an organic base, e. g. pyridine or lime or other suitable inorganic base, for example, barium or strontium oxide. These inorganic bases react with lower aliphatic acids such as acetic acid without affecting anhydrides or polycarboxylic acids.

When the acidylation medium is prepared from adipic acid and acetic anhydride the process may, for example, be carried out by heating fused adipic acid with excess acetic anhydride at 100–110° C., preferably using about 40% of adipic acid based on the weight of anhydride, diluting the mixture with xylene to form a 2–5% solution, adding about 2% of quick lime and then refluxing a cellulose acetate fabric in the medium for 1–2 hours.

The acidylation temperature and the duration of acidylation will depend to some extent upon the nature of the acid radicles present in the acidylation medium and the degree of acidylation which it is desired to effect, but, in general, temperatures of 140–180 or 200° C. and acidylation times of about 1–5 or 6 hours are satisfactory. For example, yarns having a basis of acetone-soluble cellulose acetate can be acidylated in 1–2 hours at a temperature of about 165–175° C., using a medium prepared from a mixture of acetic anhydride and adipic, phthalic or tartaric acid, to obtain a product which has a much improved ironing point and melting point, in insoluble or substantially insoluble in acetone and still has a good breaking strength.

Lower temperatures, e. g. 100° or 50° C., may be employed, but in such cases it is generally necessary to continue the treatment for a longer time, e. g. 10 or 15 hours, and it is also desirable to use a fairly high concentration of acid and anhydride, e. g. 3 or 5% of each on the weight of the acidylation medium.

Acidylation may be facilitated, particularly at lower temperatures, by the use of catalysts, especially ferric, zinc or stannic chloride in a concentration of e. g. .5, 1 or 2% of the weight of the materials.

In order to facilitate control of the reaction temperature it is convenient to employ a solvent or diluent of such a character that it forms a medium which boils at the temperature at which it is desired to carry out the reaction. One of the best diluents for high temperature acidylation is a kerosene fraction having a boiling point of about 170° C., particularly for the esterification of ordinary cellulose acetate yarn. Xylene may also be employed and, if necessary, its boiling point may be raised somewhat by mixing it with paraffin wax in, for example, about equal proportions by weight. Mixtures of xylene and anthracene or xylene and naphthalene may also be employed, as may mixtures or xylene and ortho-dichlorbenzene, particularly containing about 60–70% of xylene.

The following examples illustrate the process of the present invention:

Example 1

A warp-knitted fabric made of acetone-soluble cellulose acetate yarn is heated for about 1½ hours at boiling point in an acidylation medium prepared by heating 4 parts of adipic acid with 10 parts of acetic anhydride, driving off free acetic acid and dissolving the residue in about 1000 parts of a mixture containing 15% of orthodichlorbenzene and 85% of xylene. The volume ratio of acidylation medium to yarn is about 150:1. After completion of the reaction the fabric is washed in boiling carbon tetrachloride, air dried, and then washed in boiling water for 1 hour and finally dried.

Example 2

A woven fabric made of acetone-soluble cellulose acetate yarn is acidylated in a manner similar to that described in Example 1 except that the acidylation medium is prepared from sebacic acid instead of adipic acid, the diluent employed is xylene alone and the reaction continued for about three hours at boiling point.

Example 3

An acidylation medium is prepared as described in Example 1 by heating 7.5 parts of phthalic acid with 10 parts of acetic anhydride, driving off free acetic acid and dissolving the residue in about 1000 parts of kerosene. A fabric made of acetone-soluble cellulose acetate yarn is then heated in the medium at a temperature of about 170° C. for one hour, the volume ratio being about 50:1. It is then removed, thoroughly washed and dried.

Example 4

A cellulose acetate fabric is esterified as described in Example 3 except that the medium is prepared from tartaric acid instead of phthalic acid.

Example 5

A fabric made of acetone-soluble cellulose acetate yarn is esterified in a medium prepared by heating about 5 parts of acetic acid with 10 parts of phthalic anhydride, driving off the residual acetic acid and dissolving the residue in about 1000 parts of kerosene. The reaction temperature is about 170° C. and heating is continued for about 1 hour. The fabric is then removed, thoroughly washed and dried.

The fabrics treated in all the above examples are first scoured and dry-cleaned in order to remove any lubricant. In each case a product is obtained which is water-resistant, has a considerably increased ironing temperature and melting point and is insoluble in most solvents, for example boiling acetone.

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

1. Process for the treatment of filaments, yarns, threads or fabrics made therefrom, which comprises heating such formed articles having a basis of an organic derivative of cellulose containing free hydroxyl groups, at a temperature between 100 and 180° C., in a liquid acidylation

medium which is a non-solvent for said organic derivative of cellulose and containing the mixed anhydride of an organic poly-carboxylic acid and a lower aliphatic mono-carboxylic acid, the volume ratio of the acidylation medium to the articles being treated being at least 50:1.

2. Process for the treatment of filaments, yarns, threads or fabrics made therefrom, which comprises heating such formed articles having a basis of cellulose acetate containing free hydroxy groups, at a temperature between 100 and 180° C., in a liquid acidylation medium which is a non-solvent for said cellulose acetate containing the mixed anhydride of an organic poly-carboxylic acid and a lower aliphatic mono-carboxylic acid, the volume ratio of acidylation medium to the articles being treated being at least 50:1.

3. Process for the treatment of filaments, yarns, threads or fabrics made therefrom, which comprises heating such formed articles having a basis of acetone-soluble cellulose acetate, at a temperature between 100 and 180° C., in a liquid acidylation medium which is a non-solvent for said cellulose acetate containing the mixed anhydride of a lower aliphatic mono-carboxylic acid and tartaric acid, the volume ratio of acidylation medium to the articles being treated being at least 50:1.

4. Process for the treatment of filaments, yarns, threads or fabrics made therefrom, which comprises heating such formed articles having a basis of acetone-soluble cellulose acetate, at a temperature between 140 and 180° C. in a liquid acidylation medium which is a non-solvent for said cellulose acetate containing the mixed anhydride of a lower aliphatic mono-carboxylic acid and tartaric acid and a hydrocarbon boiling at at least 140° C., the volume ratio of acidylation medium to the articles being treated being at least 50:1 and the concentration of tartaric and mono-carboxylic acid radicles in the medium being below 3% and 1%, respectively.

5. Process for the treatment of filaments, yarns, threads or fabrics made therefrom, which comprises heating such formed articles having a basis of acetone-soluble cellulose acetate, at a temperature between 100 and 180° C., in a liquid acidylation medium which is a non-solvent for said cellulose acetate containing the mixed anhydride of a lower aliphatic mono-carboxylic acid and adipic acid, the volume ratio of acidylation medium to the articles being treated being at least 50:1.

6. Process for the treatment of filaments, yarns, threads or fabrics made therefrom, which comprises heating such formed articles having a basis of acetone-soluble cellulose acetate, at a temperature between 100 and 180° C., in a liquid acidylation medium which is a non-solvent for said cellulose acetate containing the mixed anhydride of a lower aliphatic mono-carboxylic acid and phthalic acid, the volume ratio of acidylation medium to the articles being treated being at least 50:1.

7. Process for the treatment of filaments, yarns, threads or fabrics made therefrom, which comprises heating such formed articles having a basis of acetone-soluble cellulose acetate, at a temperature between 140 and 180° C. in a liquid acidylation medium which is a non-solvent for said cellulose acetate containing the mixed anhydride of a lower aliphatic mono-carboxylic acid and adipic acid and a hydrocarbon boiling at at least 140° C., the volume ratio of acidylation medium to the articles being treated being at least 50:1 and the concentration of adipic and monocarboxylic acid radicles in the medium being below 3% and 1%, respectively.

8. Process for the treatment of filaments, yarns, threads or fabrics made therefrom, which comprises heating such formed articles having a basis of acetone-soluble cellulose acetate, at a temperature between 140 and 180° C., in a liquid acidylation medium which is a non-solvent for said cellulose acetate containing the mixed anhydride of a lower aliphatic mono-carboxylic acid and phthalic acid and a hydrocarbon boiling at at least 140° C., the volume ratio of the acidylation medium to the articles being treated being at least 50:1 and the concentration of phthalic and monocarboxylic acid radicles in the medium being below 3% and 1%, respectively.

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