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PROCESS FOR WET-SPINNING CELLULOSE TRIACETATE

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This invention relates to solutions of cellulose esters and especially to solutions of complete or substantially complete esters of cellulose, and to the manufacture of shaped products from such solutions.

The ordinary cellulose acetate of commerce is not a completely acetylated cellulose, but has been subjected to a "ripening" or hydrolysis whereby its acetyl content (reckoned as acetic acid) has been reduced to a value usually between about 53% and 56% as compared with a theoretical value of 62.5% for cellulose triacetate. The valuable properties of shaped products such as yarns and films made from this partly hydrolysed cellulose acetate are of course very well known. For certain purposes, however, cellulose acetate having an acetyl content above about 60% (corresponding to a degree of substitution above about 2.8) would be preferred owing to its higher melting point, more hydrophobic nature and better dielectric properties; such cellulose acetates (which are commonly referred to, and will in the present specification be referred to, as cellulose triacetate) are unfortunately insoluble in acetone, and while other solvents are available, they are in general less satisfactory as spinning solvents for cellulose triacetate than is acetone as a spinning solvent for cellulose acetate of acetyl content about 53% to 56%. In consequence, the production of filaments, yarns, films and other similar shaped articles from cellulose triacetate is attended with difficulty.

This difficulty has to some extent been overcome by employing, instead of a single solvent, a mixture of about 90 to 95 parts of methylene chloride with 10 to 5 parts of methanol or ethanol. Solutions of cellulose triacetate in these solvent mixtures can be wet-spun, for example into a coagulating bath of alcohol, but interruptions due to instability of spinning are liable to occur, especially when the cellulose triacetate has a fairly high viscosity.

We have now found that cellulose triesters of lower fatty acids containing up to 4 carbon atoms in the molecule, in particular cellulose triacetate, can be dissolved in solvent mixtures of methylene chloride or ethylene dichloride and a lower fatty acid containing up to 4 carbon atoms in the molecule. We have also found that the solutions so obtained are very suitable for the production of shaped articles by extrusion or casting methods, preferably with the aid of a liquid coagulating medium, and more especially for the production of filaments by wet

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spinning methods. Advantageously, the lower fatty acid in the solvent mixture is the same as that combined in the cellulose ester or, in the case of mixed esters, as one of the combined acids. Thus, cellulose triacetate may be dissolved in a mixture of methylene chloride or ethylene dichloride and acetic acid, and the solution employed for the production of filaments by wet-spinning methods or of films, foils and the like by wet extrusion or casting methods. Similarly, cellulose tripropionate may be dissolved in a mixture of methylene chloride or ethylene dichloride and propionic acid, and cellulose acetate propionate in a mixture of methylene chloride or ethylene dichloride and acetic or propionic acid. The main advantages of the invention are to be found in the production of filaments by wet spinning solutions of cellulose triacetate, especially of acetyl content above 61%.

The proportion of the fatty acid in the solvent mixture should be considerably higher than the proportion of the alcohol in the previously known solvent mixtures referred to above, and is preferably between about 25% and 50%, and especially between 30% and 45%, by volume. For instance cellulose triacetate may be dissolved in a mixture of about 2 parts by volume of methylene chloride and 1 part by volume of acetic acid.

In the production of filaments, films, foils and like shaped articles from the new solutions by wet methods, we prefer to use a coagulating liquid of which the main or sole constituent is an aliphatic alcohol containing at most 4 carbon atoms in the molecule. For example aqueous ethyl alcohol or denatured ethyl alcohol containing up to 10% of water, e. g. methylated spirit, may be used. Other coagulating liquids may however be used, for instance aqueous acetic acid, acetone or a liquid homologue thereof, a liquid ether, e. g. di-isopropyl ether, or a liquid hydrocarbon, e. g. benzene or cyclohexane. The bath may be at a temperature approximately equal to or above room temperature; for instance solutions of cellulose triacetate in mixtures of methylene chloride and acetic acid may be extruded into a bath of aqueous acetic acid at a temperature sufficient to vaporise the methylene chloride. In general, however, it is preferred to use a coagulating bath capable of dissolving both components of the solvent mixture and at a temperature below the boiling point of the methylene chloride or ethylene dichloride; for example a solution of cellulose triacetate in methylene chloride or ethylene dichloride and

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acetic acid may be extruded into aqueous ethyl alcohol of concentration 90% to 95% at room temperature.

The invention is illustrated by the following examples:

Example 1

A cellulose triacetate of acetyl value 62.3% and viscosity 14.7 (determined and expressed as described below) was dissolved in a mixture of 2 volumes of methylene chloride and 1 volume of acetic acid to give a solution of concentration 16.6%; the solution was filtered, de-aerated by standing at room temperature, and then spun into filaments through orifices of diameter 0.08 mm. at room temperature into a bath of 93% aqueous ethyl alcohol. On leaving the bath the filaments were passed successively round two rollers by means of which they were stretched by about 25%, and they were then wound up and given a low degree of twist while still wet from the coagulating bath. A yarn was obtained having a filament denier of 9.0, white in colour and of a dull lustre, and having a dry tenacity of 1.52 g. p. d. with an extension of 6% and a melting point of 292° C. The spinning operation was considerably more satisfactory than when a 90:10 methylene chloride:alcohol solution was used, and no breaks or interruptions occurred.

Example 2

A cellulose triacetate of acetyl value 62.2% and viscosity 25.0 was dissolved in the same methylene chloride:acetic acid mixture to give a solution of concentration 14%. The solution was spun, and the filaments obtained were stretched and wound up as described in Example 1, giving a similar product having slightly lower tenacity and a melting point of 295° C. In spite of the high viscosity of the cellulose triacetate, spinning proceeded in a very satisfactory manner, and again better than when a methylene chloride:alcohol solution was used. Moreover, the filaments had a better appearance than filaments spun from a methylene chloride:alcohol solution of the same cellulose triacetate.

Similar results are obtainable if ethylene dichloride is substituted for the methylene chloride in these examples.

The viscosity of the cellulose triacetate was measured in a 6% solution in 90:10 methylene chloride:alcohol and is expressed in terms of the time in seconds taken by a steel ball of diameter $\frac{3}{8}$ in. to fall freely through 3 ins. of the solution at a temperature of 25° C.

Microscopic examination of the filaments produced using methylene chloride:acetic acid and methylene chloride:alcohol spinning solutions respectively showed that the former had a much more nearly circular and much less variable cross-section than the latter, thus further demonstrating the superiority of the solvent mixture containing acetic acid.

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

1. Process for the production of shaped articles

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from cellulose triacetate, which comprises extruding a solution of cellulose triacetate in a solvent mixture comprising 75-50% by volume of a chlorinated hydrocarbon selected from the group which consists of methylene chloride and ethylene chloride and 25-50% by volume of acetic acid into a coagulating bath which comprises as the main constituent an aliphatic alcohol containing at most 4 carbon atoms in the molecule.

2. Process for the production of shaped articles from cellulose triacetate, which comprises extruding a solution of cellulose triacetate in a solvent mixture comprising 70-55% by volume of a chlorinated hydrocarbon selected from the group which consists of methylene chloride and ethylene chloride and 30-45% by volume of acetic acid into a coagulating bath which comprises as the main constituent an aliphatic alcohol containing at most 4 carbon atoms in the molecule.

3. Process for the production of shaped articles from cellulose triacetate, which comprises extruding a solution of cellulose triacetate in a solvent mixture comprising 75-50% by volume of a chlorinated hydrocarbon selected from the group which consists of methylene chloride and ethylene chloride and 25-50% by volume of acetic acid into aqueous ethyl alcohol containing up to 10% of water.

4. Process for the production of shaped articles from cellulose triacetate, which comprises extruding a solution of cellulose triacetate in a solvent mixture comprising 70-55% by volume of a chlorinated hydrocarbon selected from the group which consists of methylene chloride and ethylene chloride and 30-45% by volume of acetic acid into aqueous ethyl alcohol containing up to 10% of water.

5. Process according to claim 4, wherein the viscosity of the cellulose triacetate in terms of the time taken for a $\frac{3}{8}$ " diameter steel ball to fall through 3" of a 6% solution of the triacetate in 90:10 (by volume) methylene chloride/ethyl alcohol at 20° C. is at least 10 seconds.

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