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SAPONIFICATION OF CELLULOSE ESTERS

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This invention relates to the treatment of cellulose acetate and other organic esters of cellulose and particularly to a process for reducing the acidyl content of such esters. The invention is specially applicable to the saponification of filaments, threads, yarns, ribbons and the like made of or containing such esters.

It is well known that caustic soda and other strong mineral bases can be employed to saponify materials of the type referred to above, but that saponification, when effected by such agents, tends to be superficial, so that while the surface of the material is intensively saponified, a core of substantially unsaponified ester remains. Moreover, saponification by such agents when applied to filaments, threads, ribbons and like materials may seriously affect the serimetric properties of the materials. It has been discovered that materials comprising organic esters of cellulose can be saponified by means of non-metallic bases, for example methylamine, ethylene diamine and other aliphatic amines, particularly those of low molecular weight, in such a way that the saponification is relatively deep-seated and may even extend throughout the material, while the serimetric properties of the material may actually be improved by the process. I have now found that saponification by means of such non-metallic bases may be considerably accelerated by the presence during saponification of small quantities of caustic soda or like acting mineral bases without the presence of the caustic soda leading to superficial saponification. The process in fact provides a rapid method of obtaining threads and like materials of good tenacity, extensibility and elasticity which are saponified to a considerable depth below the surface or even throughout the whole cross section.

The mineral alkali is preferably contained in the saponifying bath itself, although other suitable methods of application are not excluded. The quantity of mineral alkali employed should be relatively small. The quantities may be very low, for instance 0.05 to 0.1%, or from 0.2 or 0.5% to 0.8, or above 1%, for instance 1.5 or 2%. Preferably the concentration should be relatively low, for instance below 1%. Equivalent concentrations of other strong mineral alkalis may be employed, for instance caustic potash. The material should not be allowed to remain in the bath after saponification is complete.

The organic ester of cellulose treated may be of normal or low viscosity, for example in the case of cellulose acetate the viscosity may be of the order of 30 to 50, 100, 200 or even higher, these figures being obtained by comparison of a 6% solution of the ester in acetone at 25° C. with glycerine at the same temperature taken as a standard of 100. Such esters of high viscosity may readily be made by methods in which degradation of the cellulose molecule is substantially avoided during acidylation, for example the methods of U. S. Patent No. 1,708,787. On the other hand, the viscosity of the cellulose acetate employed may be of the order of 10–20 or even lower, or between 20 and 30, measured on the scale referred to above.

The invention is of particular importance in connection with the saponification of filaments, threads, ribbons, fabrics and like materials having a basis of cellulose acetate and will be described with special reference to the treatment of such materials.

The materials treated may be made by any suitable dry or wet spinning method. Where high tenacity is required in the final products it is of particular advantage to produce the filaments and the like by wet spinning methods in the course of which they are stretched to a considerable extent, or to soften and stretch the materials after their production whether by a wet or a dry spinning process. By applying the process of the invention to materials which have been stretched considerably, for example to 200% of their original length or even more, materials of particularly valuable serimetric properties are obtainable.

Particularly good results are obtained by the use of saponifying baths containing methylamine and caustic soda. Other strong aliphatic organic bases, for example ethylamine, propylamine, amylamine and triethylamine, may also be employed. Again, somewhat weaker bases of the same series, for example trimethylamine and allylamine, may be used. Further, considerably stronger bases of the same series may be employed, even very strong bases such as tetramethyl ammonium hydroxide, provided care be taken to avoid damaging the materials. Again, amines containing more than one amino group, and particularly aliphatic diamines of relatively low molecular weight, for example ethylene diamine, symmetrical dimethyl ethylene diamine, monoethyl ethylene diamine, and propylene diamine may also be used. Preferably at least one of the amino groups of such amines should be unsubstituted or monosubstituted. Amines containing more than two amino groups may also be em-

ployed, for example 1.2.3-triamino propane. The effect of one or more hydroxy groups in the amine appears to be to favour the penetration of the materials by the saponifying agent, and with this object in view substances of the type of $\alpha\gamma$-diamino-β-hydroxy propane may be used with advantage. Again, bases of the heterocyclic series, for example piperidine may be used.

As indicated above saponification is preferably effected by subjecting the materials to an aqueous bath containing methylamine or a like acting base and small quantities of a strong mineral alkali in solution. Generally speaking it is advantageous to employ the non-metallic base in a concentration of 10–30% and particularly 15–25%. The bath may be at ordinary atmospheric temperature, or even at a lower temperature. It may, however, be maintained at a somewhat higher temperature, for example from 25 or 30° C. to 40, 50 or even 60° C. or higher, depending on the boiling point of the solution. With a view to preventing excessive evaporation of the base it is of advantage, particularly when working at relatively high temperatures, to cover the surface of the saponifying bath with a layer of an oil, wax or like substance which is immiscible with the bath. The time during which the materials are in contact with the bath will naturally vary according to the amount of saponification to be effected, the nature of the bath and the temperature of treatment. Thus the time of treatment may vary from less than one minute, for instance 15–30 or 45 seconds to two or three minutes, or even longer where a relatively slow acting base is employed.

Saponification may be effected in the presence of other substances capable of accelerating the reaction in addition to the mineral alkali. The use of certain metals in accelerating saponification by methylamine and like acting bases is described in U. S. applications S. Nos. 756,284 and 756,285 filed December 6, 1934. Such metals may be introduced in suitable form to the saponifying bath or may be applied to the materials prior to the saponification, or may even be introduced into the spinning solutions from which the materials are made. By way of example, copper oxide may be introduced into the saponifying bath in quantity sufficient to produce a concentration of 0.01–0.5%. When such metals are employed in the saponifying bath it will in general be necessary to remove them from the materials after saponification. In the case of copper removal may readily be effected by treating the materials with a dilute acid, for example 20% acetic acid or 2% sulphuric acid.

The saponifying medium may also contain swelling agents, solvents or latent solvents for the cellulose ester, for example cyclohexanol, methyl cyclohexanol, glycerol, ethylene glycol and its monomethyl and dimethyl ethers, diacetone alcohol, benzyl alcohol, acetone, dioxane or methylene ethylene ether.

When the materials are treated in the form of filaments, threads, yarns and the like, it is of advantage to effect saponification "in warp formation", i. e. by drawing a large number of ends through the bath in substantially parallel relationship one to another and in the same plane. Thus, yarn may be drawn from a creel by means of rollers or like devices extending across the entire assembly of ends or so-called "warp" and immersed or partially immersed in a bath containing the saponifying agent, through a reed into the bath, and after passing through the bath the materials may be drawn by a second roller, pair of rolls or the like, situated outside the bath, through a reed and out of the bath, whence they are forwarded to suitable collecting means or to means for effecting any subsequent treatment to be applied. Preferably the materials are washed and dried before being wound.

The saponifying agent may be applied by other means. Thus, for example, the materials in hank form may be suspended from rods which are caused to traverse the length of the bath, and at the same time to rotate so as to expose each portion of the yarn to the same depth in the bath for the same period. Again, the materials may be treated in the form of bobbins, cheeses or other packages. Any suitable means may in fact be adopted in applying the saponifying agent to the materials. Materials in yarn or like form may be treated continuously with their production and/or with a stretching step. Again, in the case of such materials, stretching may be effected during saponification or, provided saponification has not been carried too far, after saponification. In general it is necessary to soften the materials to enable them to be stretched to the desired extent, and in choosing a suitable softening agent due regard should be had to the extent to which the materials have been saponified.

As indicated above, the materials may be saponified in fabric form. This may conveniently be effected by passing the fabric continuously through a bath containing the saponifying agent, for example in an apparatus of the type of the winch dyeing machine.

The materials prior to saponification may be subjected to a treatment adapted to facilitate penetration of the saponifying agent. This may comprise the application of water to the materials, or they may be treated with aqueous wetting agents, for example soaps.

The degree of saponification effected may be sufficient to reduce the acidyl content of the ester by 8%, 10% or even less, but is preferably somewhat higher, for example sufficient to reduce the acidyl content by 20–25 or 30%. Considerably higher degrees of saponification may be effected, for instance so as to remove 35 or 40 to 50 or 55% of the acidyl content or more, even up to complete saponification, according to the particular purpose in view. The saponification may be sufficient to render cellulose acetate insoluble in substantially anhydrous acetone but soluble in acetone containing a considerable percentage, for example 25–30% of water. Or saponification may render the material insoluble in such mixtures as well as in anhydrous acetone. The saponification may raise the safe ironing point considerably. The material may gain an affinity for cotton dyes and may or may not retain its affinity for cellulose ester dyes. Materials saponified according to the invention may have, in addition to the valuable properties referred to above, a high tenacity, good extensibility and elasticity. Materials of particular value in the manufacture of high twist yarns may be made by the process of the invention. Thus, high twist yarns partially saponified according to the invention have been found specially useful as weft in the manufacture of crêpe fabrics. Again, by the process of the invention it is possible to obtain completely saponified materials of excellent tensile properties.

The following examples illustrate the invention:—

Example 1

Cellulose acetate yarn is led continuously in warp formation from a creel through a saponifying bath containing a 15–20% aqueous solution of mono-methylamine which contains a small quantity, say less than 1% of caustic soda or the equivalent of another strong mineral alkali.

The temperature of the bath is maintained at 25–45° C. and the rate of travel is adjusted so that the desired degree of saponification is obtained.

Example 2

The process is carried out as described in Example 1 except that the saponifying bath is maintained at a temperature of 50–60° C.

Example 3

The process is carried out as described in Example 1 or 2, except that the saponifying bath contains in addition 0.05–0.5% of copper.

What I claim and desire to secure by Letters Patent is:—

1. Process for reducing the acidyl content of an organic ester of cellulose comprising saponifying the ester by means of a water-soluble nitrogenous organic base in which each carbon atom that is directly attached to a nitrogen atom is directly attached to three other atoms apart from said nitrogen atom in the presence of relatively small quantities of a strong mineral alkali.

2. The process of treating filaments, threads, ribbons and like materials comprising organic esters of cellulose comprising saponifying the materials by means of a water-soluble nitrogenous organic base in which each carbon atom that is directly attached to a nitrogen atom is directly attached to three other atoms apart from said nitrogen atom in the presence of relatively small quantities of a strong mineral alkali.

3. Process for reducing the acetyl content of cellulose acetate comprising saponifying the cellulose acetate by means of an aqueous solution of mono-methylamine containing relatively small quantities of a strong mineral alkali.

4. Process for the saponification of filaments, threads and like materials comprising cellulose acetate which comprises passing the materials continuously in warp formation through an aqueous bath containing from 15–30% of monomethylamine and a quantity of caustic soda less than 1% at 25–45° C.

5. The process of treating filaments, threads, ribbons and like materials having a basis of organic esters of cellulose comprising saponifying the materials by means of a lower aliphatic amine in the presence of relatively small quantities of a strong mineral alkali.

6. The process of treating filaments, threads, ribbons and like materials having a basis of organic esters of cellulose comprising saponifying the materials by means of mono-methylamine in the presence of relatively small quantities of a strong mineral alkali.

7. The process of saponifying filaments, threads, ribbons and like materials having a basis of organic esters of cellulose comprising treating the materials with a bath containing a water-soluble nitrogenous organic base in which each carbon atom that is directly attached to a nitrogen atom is directly attached to three other atoms apart from said nitrogen atom and small quantities of a strong mineral alkali and of copper in solution.

8. The process of treating filaments, threads, ribbons and like materials having a basis of cellulose acetate comprising saponifying the materials by means of a 15–30% aqueous solution of mono-methylamine containing strong mineral alkali in a concentration equivalent to 0.1–1% of caustic soda.

9. The process of treating filaments, threads, ribbons and like materials having a basis of cellulose acetate comprising saponifying the materials by means of a 15–30% aqueous solution of mono-mehtylamine containing in solution 0.05–0.5% copper and strong mineral alkali in a concentration equivalent to 0.1–1% of caustic soda.

10. The process of saponifying filaments, threads, ribbons and like materials having a basis of cellulose acetate comprising treating the materials at 50–60° C. with a 15–30% aqueous solution of mono-methylamine containing strong mineral alkali in a concentration equivalent to 0.1–1% of caustic soda.

11. Process for the treatment of filaments, threads, ribbons and like materials having a basis of organic esters of cellulose, which comprises subjecting the materials to substantially complete saponification by treating the materials with a water-soluble nitrogenous organic base in which each carbon atom that is directly attached to a nitrogen atom is directly attached to three other atoms apart from said nitrogen atom in the presence of relatively small quantities of a strong mineral alkali.

12. Process for the treatment of filaments, threads, ribbons and like materials having a basis of cellulose acetate, which comprises saponifying the materials to such an extent that the acetyl content of the materials is reduced by 20–30% by treating the materials with a water-soluble nitrogenous organic base in which each carbon atom that is directly attached to a nitrogen atom is directly attached to three other atoms apart from said nitrogen atom in the presence of relatively small quantities of a strong mineral alkali.

13. The process of saponifying filaments, threads, ribbons and like materials having a basis of organic esters of cellulose, which comprises treating the materials with a medium containing a water-soluble nitrogenous organic base containing pentavalent nitrogen and in which each carbon atom that is directly attached to a nitrogen atom is directly attached to three other atoms apart from said nitrogen atom, and a strong mineral alkali.

14. The process of saponifying filaments, threads, ribbons and like materials having a basis of cellulose acetate, which comprises treating the materials with a medium containing tetramethyl ammonium hydroxide, and a strong mineral alkali.

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