

UNITED STATES PATENT OFFICE

2,091,968

CELLULOSE ESTERS AND PRODUCTS
THEREOF

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No Drawing. Application January 4, 1935, Serial
No. 326. Renewed April 16, 1937. In Great
Britain January 13, 1934

16 Claims. (Cl. 8—20)

This invention relates to the treatment of cellulose acetate and other organic esters of cellulose and particularly to a process for reducing the acetyl 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 known that in general where mineral alkalies are employed to saponify materials of the type referred to above, the saponification 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 alkali metal salts of alkaline reaction which are themselves saponifying agents without the presence of the salt 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.

Alkaline salts particularly suitable for use in the process of the invention are found among the alkali metal salts of very weak acids, for example carbonic acid and hydrosulphurous acid. The acid may be organic or inorganic. It is of great advantage to saponify filaments, threads and like materials non-superficially, i. e. so that there is no sharp and substantial change in the degree of saponification from the surface of the material to a point at some depth below the surface. With this end in view it is in general of advantage to employ the salt in as small a concentration as is consistent with obtaining the desired speed of saponification. The proportion in which a particular salt should be employed depends largely upon the nature of the salt, for example the strength of the acid from which it is formed. With salts such as the sulphides and carbonates of sodium and potassium, for example, very small quantities, for instance 1-2 or 3% or even less, enable non-superficial saponi-

fication to be effected very rapidly. Other salts, for example the borates and phenates of sodium and potassium, require somewhat higher concentrations, for instance 4-5 or 6%, to bring about a similar acceleration of the saponifying process and the results are somewhat less satisfactory. The alkali metal salt is preferably introduced into the saponifying bath itself, although other suitable methods of application are not excluded.

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 acylation. 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 the alkaline salt. 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. Amines containing more than one amino group, and particularly aliphatic diamines of relatively low molecular weight, for example ethylene diamine, 60

symmetrical dimethyl ethylene diamine, mono-methyl ethylene diamine and propylene diamine may also be used. Preferably at least one of the amino groups of such amines should be 5 unsubstituted or monosubstituted. Amines containing more than two amino groups may also be employed, 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 10 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. The use of bases of the heterocyclic series, for example piperidine is not excluded.

15 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 the alkaline salt in solution. Generally speaking concentrations of 20 non-metallic base of about 10-30%, for instance 15-25% will be found suitable. Although it may be of advantage in some cases to work at atmospheric temperature, or even at a lower temperature, somewhat higher temperatures are in general 25 to be preferred, 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 30 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 35 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 40 minutes, or even longer where a relatively slow acting base is employed. The material should not be allowed to remain in the bath after saponification is complete.

Saponification may be effected in the presence 45 of other substances capable of accelerating the reaction in addition to the alkaline salt. The use of certain metals in accelerating saponification by methylamine and like acting bases is described in the co-pending U. S. applications S. 50 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 55 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 60 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.

65 Due regard should, of course, be had to the possibility of reaction between the alkaline salt and the metal.

The saponifying medium may also contain 70 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.

75 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. 5 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. 10 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 15 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 20 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 25 saponification. In general it is necessary to 30 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 35 winch dyeing machine.

The materials prior to saponification may be subjected to a treatment adapted to facilitate penetration of the saponifying agent. This may 40 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 original acidyl content of the ester by 8%, 10% or even less, but is 45 preferably somewhat higher, for example sufficient to remove 20-25 or 30% of the acidyl content. 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 55 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 60 properties referred to above, a high tenacity, good 65

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 especially 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.

10 The following examples illustrate the invention:

Example 1

15 Cellulose acetate yarn is led continuously in warp formation from a creel through a saponifying bath containing a 15-30% aqueous solution of mono-methylamine in which is dissolved a small quantity of sodium carbonate. The bath is maintained at 50-60° C. The speed of travel of the materials is arranged so that the desired 20 degree of saponification is obtained by the time the materials leave the bath. The saponified materials are led continuously from the saponifying bath through a washing bath wherein any constituents carried over from the saponifying 25 bath are removed and are dried by passage over steam, heated rolls and collected by suitable means.

Example 2

30 The process is carried out as described in Example 1, except that instead of sodium carbonate, sodium sulphide is employed and the materials are collected wet in a centrifugal spinning box. As in the preceding example the materials are 35 freed from contamination with constituents of the saponifying bath before being dried.

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

1. Process for reducing the acidyl content of an organic ester of cellulose, which comprises 40 saponifying the ester by means of a nitrogenous organic base in the presence of an alkali metal salt of an alkaline reaction which is itself a saponifying agent for the cellulose ester.

45 2. Process for reducing the acidyl content of an organic ester of cellulose, which comprises saponifying the ester by means of mono-methylamine in the presence of an alkali metal salt of an alkaline reaction which is itself a saponifying 50 agent for the cellulose ester.

55 3. Process for the saponification of filaments, threads, ribbons and like materials having a basis of organic ester of cellulose, which comprises treating the materials with a nitrogenous non-aromatic organic base in the presence of an alkali metal salt of an alkaline reaction which is itself a saponifying 60 agent for the cellulose ester.

60 4. Process for the treatment of filaments, threads, ribbons and like materials having a basis of organic ester of cellulose, which comprises subjecting the materials to substantially complete saponification by means of a nitrogenous non-aromatic organic base in the presence of an alkali metal salt of an alkaline reaction which is itself a saponifying 65 agent for the cellulose ester.

65 5. Process for the saponification of filaments, threads, ribbons and like materials having a basis of organic ester of cellulose, which comprises treating the materials with a lower aliphatic amine in the presence of an alkali metal salt of an alkaline reaction which is itself a saponifying 70 agent for the cellulose ester.

6. Process for the saponification of filaments, threads, ribbons and like materials having a basis of organic ester of cellulose, which comprises 5 treating the materials with ethylene diamine in the presence of an alkali metal salt of an alkaline reaction which is itself a saponifying agent for the cellulose ester.

7. Process for the saponification of filaments, threads, ribbons and like materials having a basis of cellulose acetate, which comprises treating the 10 materials with mono-methylamine in the presence of an alkali metal salt of an alkaline reaction which is itself a saponifying agent for cellulose acetate.

8. Process for reducing the acidyl content of an 15 organic ester of cellulose, which comprises saponifying the ester by means of a nitrogenous non-aromatic organic base in the presence of an alkali metal carbonate.

9. Process for reducing the acidyl content of an 20 organic ester of cellulose, which comprises saponifying the ester by means of a nitrogenous non-aromatic organic base in the presence of an alkali metal sulphide.

10. Process for the saponification of filaments, 25 threads, ribbons and like materials having a basis of cellulose acetate, which comprises treating the materials with a 15-30% aqueous solution of mono-methylamine containing an alkali metal carbonate.

30 11. Process for the saponification of filaments, threads, ribbons and like materials having a basis of cellulose acetate, which comprises treating the materials with a 15-30% aqueous solution of mono-methylamine containing an alkali metal sulphide.

35 12. Process for reducing the acidyl content of an organic ester of cellulose, which comprises saponifying the ester by means of a nitrogenous non-aromatic organic base in the presence of an 40 alkali metal salt of alkaline reaction which is itself a saponifying agent for the ester.

45 13. Process for reducing the acidyl content of an organic ester of cellulose, which comprises saponifying the ester by means of a nitrogenous non-aromatic organic base in the presence of a 55 small quantity of copper and an alkali metal salt of an alkaline reaction which is itself a saponifying agent for the cellulose ester.

50 14. Process for the treatment of filaments, threads, ribbons and like materials having a basis of cellulose acetate, which comprises saponifying the materials to remove from 20 to 30% of the original acetyl content by means of a nitrogenous non-aromatic organic base in the presence of an 55 alkali metal salt of an alkaline reaction which is itself a saponifying agent for cellulose acetate.

60 15. Process for the saponification of filaments, threads, ribbons and like materials having a basis of organic ester of cellulose, which comprises 65 treating the materials with a nitrogenous organic base containing pentavalent nitrogen in the presence of an alkali metal salt of alkaline reaction which is itself a saponifying agent for the ester.

65 16. Process for the saponification of filaments, threads, ribbons and like material having a basis of cellulose acetate, which comprises treating the materials with tetramethyl ammonium hydroxide in the presence of an alkali metal salt of alkaline 70 reaction which is itself a saponifying agent for the cellulose acetate.

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