Patented Aug. 4, 1936 2,049,430

UNITED STATES PATENT OFFICE

2,049,430

PROCESSES FOR THE DE-ESTERIFICATION OF FILAMENTS, YARNS, FABRICS, AND THE LIKE OF CELLULOSE ESTERS

Henry Dreyfus, London, England

No Drawing. Application February 8, 1933, Serial No. 655,778. In Great Britain February 19, 1932

8 Claims. (Cl. 8—20)

This invention relates to improvements in de-esterification, and is more particularly concerned with processes for the saponification of cellulose esters and especially the organic esters of cellulose in filament, yarn, fabric or other form.

It is well known that the saponification of cellulose acetate yarns, fabrics or other materials was first proposed with the object of conferring upon the materials an affinity for cotton dyes, and was usually effected by means of caustic soda, caustic potash, or alkaline salts of soda or potash in an aqueous medium. With the advent of the dispersed insoluble dyestuffs dyeing difficulties were largely removed with the result that the saponification process did not become of commercial importance.

In recent years interest in saponification methods has been revived, not with the object of conferring upon the cellulose acetate different dyeing properties, but with the object of increasing its safe ironing point, and with this object in view special measures have been taken to achieve a very uniform saponification. Processes in which caustic soda or caustic potash or strongly alkaline salts are applied to the material in aqueous media generally result in a substantial decrease in the tensile strength of the materials. While this is not of great moment when the materials are treated in fabric form, though even here considerable damage may result from such saponification treatments, it is of great importance when the materials are treated in the form of yarns and have subsequently to be woven, knitted or otherwise made up into fabrics.

The present invention is concerned with an improved process for the saponification of cellulose esters, and particularly cellulose esters in the form of yarns, filaments, ribbons, fabrics and the like, in which the deleterious effect of the caustic soda or like agent applied in an aqueous medium is decreased considerably or is eliminated.

According to the present invention the saponification is effected by means of caustic soda, caustic potash or an alkaline salt or reagent, for example sodium silicate or trisodium phosphate, present in solution in a quantity less than and preferably considerably less than that necessary to effect the desired degree of saponification, and in presence of an auxiliary agent which is alkaline in character though less alkaline than the saponifying agent proper or which is capable of reacting with sodium or potassium acetate or other salt formed by the saponification of the cellulose ester to re-form the saponifying reagent. Preferably such an auxiliary agent is substantially insoluble or has only relatively low solubility in the medium in which it is applied. Examples of suitable reagents for this purpose are lime, calcium carbonate, baryta, barium carbonate, strontia or the like or corresponding hydroxides or even basic salts. Such a reagent may be present in the medium as a saturated solution or in a finely divided state or in the form of a milk or fine suspension. By this means it is possible to effect the saponification of the cellulose ester in presence of an amount of caustic soda or other saponifying agent which is considerably less than that theoretically necessary to effect the amount of saponification desired, so that deleterious action of the chemically equivalent quantity of caustic soda or like agent upon the cellulose acetate, or upon the reconstituted cellulose, is diminished or avoided.

The medium in which the combined saponifying reagents characteristic of the invention are applied may be wholly aqueous or may be mixed aqueous alcoholic or even wholly alcoholic, or any other suitable medium capable of dissolving the caustic soda or like reagent and of carrying the lime or similar body may be used.

The saponification may be, and preferably is, conducted at about normal atmospheric temperature or below or at temperatures not greatly exceeding normal atmospheric temperatures. However, higher temperatures, for example up to 70° C. or more, may be used.

The saponifying medium may be applied to the goods by any suitable process, for example by bath or padding treatments, which are preferred, or by spraying methods or simple printing methods, and may be applied either uniformly over the goods or where local effects are desired applied with the aid of stencils or with the aid of suitable printing rollers. Padding, spraying and like methods where a limited quantity of the saponifying medium is applied are preferably followed by a batching process and/or by a process in which the saponifying agent is caused to react quickly, as for example by passage over heated drums. In general I prefer the slower bath methods or methods in which batching at ordinary temperatures is employed.

In addition to the saponifying reagents themselves, the medium may contain any other desired substances, as for example buffer salts, for instance sodium chloride, sodium acetate or soaps, or substances, such as glycerine or poly-

hydric alcohols, adapted to render more uniform the action of the saponifying agent.

In treating filaments and yarns it is preferable to apply the saponifying agent to the filaments or yarns in warp formation and reference in this connection is made to U. S. applications S. Nos. 283,999 and 284,000 both filed 8th June, 1928.

The degree of saponification effected in accordance with the present invention may vary with the object which it is desired to achieve. Relatively low saponification, such as a saponification resulting in a loss of weight of 2 to 5 or 10 or 15% on the weight of the cellulose acetate, may be applied with the object of conferring upon the material an affinity for cotton dyes or with the object of increasing the safe ironing point. For this latter purpose a loss in weight of 10 to 20 or 30% or more is desirable. The invention also envisages a process in which the ester groups are completely or substantially completely eliminated from the cellulose ester so as to produce a product which is wholly or almost wholly reconstituted cellulose and therefore resembles the artificial silks and other products made from viscose.

The process of the invention may be applied to the treatment of cellulose acetates or other saponifiable esters of cellulose, for instance cellulose formate, propionate or butyrate, of all kinds. Esters of low, medium or high viscosity may be present in the treated yarns, fabrics or other materials, for instance cellulose acetates having a viscosity of 5–10, 20–30 or 50–100 or 200 or more as measured by comparing the viscosity of a 6% solution in acetone against a standard of glycerine taken as 100. The yarns or other materials treated may consist wholly of the cellulose ester or may contain other materials not deleteriously affected, as for instance natural or artificial cellulosic materials.

Furthermore the materials may be subjected to a stretching operation before, during or after the saponifying treatment with a view to obtaining products of increased tenacity. This stretching of the yarns or other products may be carried out by any suitable process, as for example those specifically described in U. S. Patent No. 1,709,470 and U. S. application S. No. 378,684 filed 16th July, 1929, or the intermittent stretching of U. S. application S. No. 573,424 filed 6th November, 1931. As described in U. S. application S. No. 602,844 filed 2nd April, 1932, considerable economy and other advantages accrue from carrying out the stretching operation with the yarns, threads or the like in warp formation. Such a warp may be carried continuously through the stretching and saponifying operations. The stretching is facilitated by means of solvents, latent solvents or swelling agents for the cellulose acetate or other cellulose esters, for example aqueous solutions of thiocyanates, such as those of the alkali metals, ammonium or alkaline earth metals, or aqueous solutions of zinc chloride; acetic acid, formic acid, lactic acid, diacetone alcohol, acetone, the ethers and esters and ether-esters of olefine and polyolefine glycols, for instance glycol monoacetate, methyl glycol mono-acetate, the acetins, dioxane and its homologues and substitution products, methylene ethylene ether and its homologues and substitution products and similar cyclic ethers, dichlorethylene, methylene chloride and the like. Such organic solvents, latent solvents or swelling agents may be applied in conjunction with any suitable diluent, for example water, benzene and its homologues, petroleum fractions or other aliphatic hydrocarbons and chlorinated hydrocarbons, for example carbon tetrachloride, which have precipitating action or at least little or no solvent action upon the cellulose acetate or other cellulose ester treated. The stretching for the purposes of the present invention may involve a very substantial extension of the filaments, yarns or other products, and in particular extensions of the order of 200, 300 or 500% or more. Such processes of stretching may be applied either to wet or to dry spun yarns. Instead of or in addition to stretching the yarn after its formation, either continuously or discontinuously with its production, the yarn may be stretched considerably during its formation. In dry spinning operations this involves a softening treatment during the dry spinning process so as to enable substantial stretch to be imparted to the materials, while in the case of wet spinning the nature of the coagulating bath or of the spinning solution may be such that a very considerable stretch may be imparted to the materials during their actual formation. Processes of this character are described in U. S. applications S. Nos. 402,785 filed 26th October, 1929, 418,414 filed 3rd January, 1930, 437,423 filed 20th March, 1930, 469,622 filed 21st July, 1930 and 601,043 filed 24th March, 1932. In general the stretching of the threads either during, continuously with or after their formation may be such as to impart to the threads an initial tenacity exceeding 1.5 grams per denier and preferably exceeding 2 or even 2.5 or more grams per denier.

Such a stretching of the materials and also the use of high viscosity esters may still further increase the dry tenacity of the saponified materials obtainable in accordance with the invention.

The materials in the form of filaments, threads, fabrics and the like may in addition to the above treatments be subjected to a treatment with shrinking agents to improve their extension or for the production of special effects, and in this connection reference is made broadly to the processes described in U. S. applications S. Nos. 607,667 filed 26th April, 1932, 609,255 filed 4th May, 1932 and 611,240 filed 13th May, 1932. Uniform shrinkage for the purpose of increasing extension is particularly advantageous in the case of stretched yarns which usually have quite low extensions. The shrinking treatment may be applied after saponification, but is preferably applied between the stretching and the saponification. When applied between the stretching and the saponification the agents specified in the specifications referred to above may be used with advantage. When the shrinking is applied subsequent to saponification the nature of the reagent will depend upon the degree of saponification. Thus, if a relatively small degree has been applied, such as up to 10 or 20% loss in weight, swelling agents for the cellulose derivative may still be effective in producing the desired shrinkage. When a high degree of saponification or substantially complete saponification has been carried out swelling agents for cellulose should be used to effect the shrinkage.

The following examples illustrate the invention but are not to be considered as limiting it in any way:—

Example 1

Dry-spun cellulose acetate yarn or dry-spun cellulose acetate yarn which has been subjected to a stretching treatment, for example has been stretched to 400–500% of its original length, in

the form of hanks is entered into an aqueous saponification bath containing 0.158 gram per litre of caustic soda and 1.36 grams per litre of lime with a bath volume of 300:1. The saponification is carried out for 24 hours at a temperature of 26° C.

Example 2

Dry-spun cellulose acetate yarn or dry-spun cellulose acetate yarn which has been subjected to a stretching treatment, for example has been stretched to 400–500% of its original length, in the form of hanks is entered into an aqueous saponification bath containing 0.079 gram per litre of caustic soda and 1.36 grams per litre of lime with a bath volume of 300:1. The saponification is carried out for 24 hours at a temperature of 26° C.

Example 3

Dry-spun cellulose acetate yarn or dry-spun cellulose acetate yarn which has been subjected to a stretching treatment, for example has been stretched to 400–500% of its original length, in the form of hanks is entered into an aqueous saponification bath containing 0.5% caustic soda and containing an excess of lime, that is to say more than will enter into solution, the bath volume being 70:1. The treatment is carried out at ordinary temperatures until the yarn undergoes no further loss in weight.

Example 4

Dry-spun cellulose acetate yarn or dry-spun cellulose acetate yarn which has been subjected to a stretching treatment, for example has been stretched to 400–500% of its original length, in the form of hanks is entered into a bath made up from a mixture of 50% by weight of methyl alcohol and 50% by weight of water, to which has been added 0.5% caustic soda and a somewhat greater amount of lime than will dissolve in the mixture, the bath volume being 70:1. The treatment is carried out at ordinary temperatures until the yarn undergoes no further loss in weight.

Example 5

Dry-spun cellulose acetate yarn or dry-spun cellulose acetate yarn which has been subjected to a stretching treatment, for example has been stretched to 400–500% of its original length, in the form of hanks is entered into a bath made up from a mixture of 50% by weight of methyl alcohol and 50% by weight of water, to which has been added 5% caustic soda and a somewhat greater amount of lime than will dissolve in the mixture, the bath volume being 70:1. The treatment is carried out at ordinary temperatures until the yarn undergoes no further loss in weight.

Instead of employing the yarn in the form of hanks it may be in the form of cakes produced, for example, in a centrifugal spinning box. The cake may be treated in the centrifugal spinning box or may be removed therefrom, and the saponification liquor continuously circulated through the cake. Methods of saponifying the yarn in the form of cakes are described in my co-pending U. S. application S. No. 655,773 filed on even date herewith.

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

1. Process which comprises the step of saponifying filaments, yarns, fabrics and like materials comprising organic esters of cellulose, by means of a saponifying agent containing an alkaline compound of an alkali-metal present in insufficient quantity to effect the desired degree of saponification, and an alkali-earth-metal-compound of lower alkalinity.

2. Process which comprises the step of saponifying filaments, yarns, fabrics and like materials comprising cellulose acetate, by means of a saponifying agent containing an alkaline compound of an alkali-metal present in insufficient quantity to effect the desired degree of saponification, and an alkali-earth-metal-compound of lower alkalinity.

3. Process which comprises the step of saponifying filaments, yarns, fabrics and like materials comprising organic esters of cellulose, by means of a saponifying agent containing an alkaline compound of an alkali-metal present in insufficient quantity to effect the desired degree of saponification, and a hydroxide of an alkaline earth metal.

4. Process which comprises the step of saponifying filaments, yarns, fabrics and like materials comprising cellulose acetate, by means of a saponifying agent containing an alkaline compound of an alkali-metal present in insufficient quantity to effect the desired degree of saponification, and a hydroxide of an alkaline earth metal.

5. Process which comprises the step of saponifying filaments, yarns, fabrics and like materials comprising organic esters of cellulose, by means of a saponifying agent containing an alkali-metal-hydroxide in quantity insufficient to effect the desired saponification, and an alkali-earth-metal-compound of lower alkalinity.

6. Process which comprises the step of completely saponifying filaments, yarns, fabrics and like materials containing organic esters of cellulose, by treatment with a saponifying agent comprising an alkaline compound of an alkali-metal present in insufficient quantity to effect the desired degree of saponification, and an alkali-earth-metal-compound of lower alkalinity, until the materials undergo no further loss in weight.

7. Process which comprises the step of completely saponifying filaments, yarns, fabrics and like materials containing cellulose acetate, by treatment with a saponifying agent comprising an alkaline compound of an alkali-metal present in insufficient quantity to effect the desired degree of saponification, and an alkali-earth-metal-compound of lower alkalinity, until the materials undergo no further loss in weight.

8. Process which comprises the step of saponifying filaments, yarns, fabrics and like materials containing organic esters of cellulose, by means of a saponifying agent comprising an alkaline compound of an alkali-metal present in insufficient quantity to effect the desired degree of saponification, and an alkali-earth-metal-compound of lower alkalinity, at temperatures not substantially above atmospheric temperature.

HENRY DREYFUS.