

UNITED STATES PATENT OFFICE

2,144,202

SAPONIFYING CELLULOSE ESTERS

Paul Schlack, Berlin-Lichtenberg, Germany, assignor to I. G. Farbenindustrie Aktiengesellschaft, Frankfurt-on-the-Main, Germany

No Drawing. Application April 19, 1935, Serial No. 17,339. In Germany April 21, 1934

7 Claims. (Cl. 8-130)

My present invention relates to a process of saponifying shaped articles of cellulose esters.

One of its objects is an improved process of saponifying shaped articles of cellulose esters. Further objects will be seen from the detailed specification following hereafter.

I have found that the alkaline saponification of shaped articles from cellulose esters, for instance, of artificial silk from cellulose acetate, can be considerably accelerated, if there is added to the alkaline treating liquid, padding solutions or printing pastes which may contain caustic alkali, tri-sodiumphosphate, sodium silicate or potassium carbonate as the efficient agent, an organic onium base containing pentavalent nitrogen, phosphorus, antimony, arsenic or tetravalent sulfur or the salts of these bases.

Especially such compounds enter into consideration which contain organic radicals having an affinity to the material to be treated. This may be due to suitable substituents introduced into the radicals. Furthermore there may be used compounds with a decidedly capillary active action.

The following are such compounds:

Dodecyltrimethylammoniumbromide, octadecyltrimethylammoniummethosulfate, dodecylpyridiniumsulfate, diethylbenzyl-dodecylammoniumchloride, the product of addition from dimethylsulfate and naphthalinsulfo-N-hydroxyethyl-N'-dimethyl-1,3-propylenediamine, p-methoxyphenylacetophenone- ω -trimethylammoniumbromide, products of alkylation of tertiary bases from aminoalcohols or polyamines such as of dimethylaminoethanol or as dimethylethylenediamine with alkylene oxides. The alkylene oxides react in this case by forming a polyglycol ether chain. The tertiary amines which result primarily from this reaction and which are substituted with the said polyglycol ether chain are transformed into quaternary products by the addition of alkyl esters of inorganic or mixed organic-inorganic acids.

The process is for instance applicable for the superficial saponification of films from cellulose acetate or nitrocellulose, for the superficial saponification of mixed fabrics from threads of cellulose and cellulose acetate silk for the purpose of applying a common ground color with directly dyeing cotton dyes for discharge printing, for the regular or irregular saponification of the moving thread of cellulose acetate silk, for instance, during its manufacture, for priming fabrics of cellulose acetate with an alkaline solution of a naphtholate, or in the printing of

such fabrics with color pastes whereby a local saponification shall take place, for instance, in directly printing mixed fabrics from artificial silk of cellulose acetate and viscose with directly dyeing cotton dyes.

It is also possible to print fabrics with an alkaline saponifying liquid and to dye them later with dyes dyeing regenerated cellulose or cellulose hydrate directly. Simultaneously the non-saponified parts of the fabric may be dyed with the special dyes which enter into consideration.

It is not necessary that the compounds which accelerate saponification are brought to action simultaneously with the saponifying agent; they may be applied before saponification locally or uniformly, if required in the presence of a swelling agent, and the saponification may be performed in a separate operation eventually even after an intercalated drying operation.

The quantity of onium base to be applied may vary within wide limits. In the first instance it is dependent on the method of operation and especially on the proportion of material to treating liquid. When applying an aqueous saponification liquid an addition of 0.5-3 grams of onium base per liter may be sufficient.

The following examples serve to illustrate the invention:

Example 1.—A fabric of cellulose acetate silk is saponified for 1 hour at 60° C. with a

$$\frac{n}{20}$$

solution of sodium hydroxide containing 3 grams of dodecyltrimethylammoniumbromide per liter, the proportion of material to be treated to treating liquid being 1:80. The treated fabric is dyed uniformly and intensely by direct dyes, for instance, Brilliant Benzo Blue 6 B (compare Schultz, Farbstofftabellen, 5th edition No. 424).

If the fabric is dyed without the addition of the quaternary ammonium salt the saponification progresses much slower and the dyeing is lighter and less uniform.

Example 2.—A web of cellulose acetate silk is saponified with a

$$\frac{n}{20}$$

solution of sodium hydroxide with the addition of 3 grams of p-ethoxyacetanilide- ω -trimethylammonium bromide per liter for one hour at 50° C. The proportion of material to treating liquid is 1:70. The saponification has progressed further than in a treatment under the same conditions but without the addition.

Example 3.—The operation is as described in Example 1, but the dodecyltrimethylammoniumbromide is replaced by 1 gram of diethylbenzyl-dodecylammoniumchloride. There is produced
5 a stronger saponification than when saponifying under the same conditions but without the addition.

Example 4.—Cellulose acetate silk is treated at the spinning machine on its way to the winding device with an aqueous solution containing per liter
10 30 grams of trimethyldodecylammoniumbromide and 30 grams of methylglycol. The dried threads are twisted together with similar threads, however, which have been treated with olive oil.
15 After the yarn obtained has been made into a fabric the latter is treated with a saponifying agent. After dyeing with directly dyeing dyes powerful effects are produced.

The threads which should resist saponification, for instance, in printing with alkaline pastes may be treated with resisting agents, for instance, with cresolsulfonic sodium, preferably in the presence of a protective colloid insoluble under the conditions of saponification, for instance, methylcellulose.
25

Example 5.—A crape fabric from viscose and cellulose acetate silk is treated with a liquid containing 80 grams of sodium carbonate and 5 grams of dodecyltrimethylammoniumchloride per liter for 15 minutes at 55° C. The uniformly saponified piece can be dyed intensely with directly dyeing dyes which are capable of being etched, for instance, Cotonerol A (Schultz Farbstofftabellen, 7th edition, Vol. II, page 64). When suitably selecting the dyes the dyeing can easily be etched to a pure white. The acetate character of the fabric will be conserved.
35

The content of acetic acid of the cellulose acetate has been reduced from 54.7% to 46.4% in the present instance, whereas in the case of saponifying without the addition of dodecyltrimethylammoniumchloride the content of acetic acid has been reduced to only 52.35%. The same effect is obtained with a reduced addition of onium base but operating at a higher temperature.
40

Example 6.—A cellulose acetate satin is printed with a printing paste consisting of 100 grams of dodecyltrimethylammoniumthiocyanate, 320 parts of water, 80 parts of potassium carbonate and 500 parts of tragacanth 60:1000, and subjected for 20 minutes to the action of steam. After rinsing the printed parts are intensely dyed by Direct Black AT (Schultz Farbstofftabellen, 7th edition, suppl. vol. page 88) (6%). When operating in the same manner but without the addition of trimethyldodecylammoniumchloride the dyeings will be considerably weaker.
45 50

Example 7.—A knit fabric from cellulose acetate is saponified in the manner described in Example 5 by means of sodium carbonate where-
60 by the dodecyltrimethylammoniumchloride is replaced by 3 grams of methylethylcetyl-sulfonium-methosulfate. The saponifying treatment lasts 25 minutes at 55 to 60° C.; the material is dyed with 3% of Sirius Light Green BB (Schultz Farbstofftabellen, 7th edition, suppl. vol. page 131). The dyeing can be provided with a white etching or color etching.
65

Example 8.—The operation is as described in

Example 7 however, the methylethylcetyl-sulfonium-methosulfate is replaced by the equivalent amount of cetyltrimethylphosphoniumiodide.

Example 9.—A spinning solution containing 20 parts of cellulose acetate with a content of 54%
5 of acetic acid, 2.5 parts of dodecyltrimethylammoniumchloride and 77.5 parts of acetone is spun to artificial threads according to the dry spinning system. The threads thus obtained are more quickly saponified by sodium hydroxide or alkali carbonate than are similar threads without the addition of onium base.
10

The term "organic onium base" used in the specification and the claims is intended to include such bases which as to their strength are equal or approximately equal to that of the alkalies. This, as known from literature, holds true for bases containing pentavalent sulfur, pentavalent phosphorus, pentavalent arsenic or pentavalent antimony.
15 20

What I claim is:

1. A method of saponifying shaped articles made from cellulose esters which comprises performing the saponification with a solution of an inorganic alkali in the presence of the product of addition from dimethylsulfate and naphthalinsulfo-N-hydroxyethyl-N'-dimethyl-1,3-propylenediamine.
25

2. A process of saponifying shaped articles from cellulose esters, which comprises performing the saponification with an aqueous medium containing inorganic alkali and an organic onium compound, capillary active and soluble in said medium.
30

3. A process of saponifying shaped articles from cellulose esters, which comprises performing the saponification with an aqueous medium containing inorganic alkali and an organic pentavalent ammonium compound, capillary active and soluble in said medium.
35 40

4. A process of saponifying artificial fibrous material from cellulose esters which comprises performing the saponification with an aqueous medium containing inorganic alkali and an organic pentavalent ammonium compound soluble and capillary active in said medium and containing in its molecule an aliphatic carbon chain of from 12 to 16 carbon atoms.
45

5. A process which comprises saponifying cellulose acetate artificial silk with an aqueous solution of sodium hydroxide containing dodecyltrimethyl-ammonium bromide.
50

6. A process which comprises saponifying artificial silk from cellulose acetate by immersing said material in a solution containing trimethyldodecyl-ammonium bromide, and treating the material with an aqueous alkaline saponifying agent.
55

7. A process which comprises saponifying artificial fibrous material from cellulose acetate with an aqueous solution of an inorganic alkali containing the capillary active product of reaction of a compound selected from the group consisting of amino alcohols and polyamines with an alkylene oxide, said product being alkylated by means of a reactive alkyl ester to yield a quaternary ammonium compound.
60 65

PAUL SCHLACK.