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PROCESS OF SAPONIFYING TEXTILE MATERIALS

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The present invention relates to a process of saponifying hydrolyzable textile materials and films. More particularly the invention consists in adding to the liquid containing the hydrolyzing agent a guanidine or biguanidine with an aliphatic carbon chain of more than 6 carbon atoms and effecting saponification with this liquid.

It is an object of the invention to provide means by which the saponifying process may be substantially accelerated and the saponification rendered more uniform.

Further objects will appear from the detailed specification following hereafter.

This application may be regarded as a continuation in part of my copending application Ser. No. 17,339 filed April 19, 1935, Pat. No. 2,144,202 which discloses the use of organic onium compounds of capillary active character as accelerators of the saponification of cellulose esters.

U. S. patent application Ser. No. 17,339 describes a process for markedly accelerating the alkaline saponification of cellulose esters, for example cellulose acetate, in the form of artificial silk by adding to the saponifying agent, for example an aqueous dye bath or a printing paste, a base or the salt of a base containing pentavalent nitrogen, phosphorus, arsenic or antimony or tetravalent sulfur, of which the cation is capable of being adsorbed by capillary attraction or has another specific affinity for the goods to be saponified. Especially suitable cations are those having aliphatic or aromatic residues of high molecular weight, for example dodecyltrimethylammonium bromide and para-methoxy-aceto-phenone-omega-trimethylammonium bromide.

This invention is based on the observation that there can advantageously be used for this purpose compounds which are derived from guanidine. Of such compounds, only those are strongly effective which are capable of existing in alkaline solution as ammonium bases containing pentavalent nitrogen. The isothiourea ethers and iso-urea ethers, though similar to guanidine, are not effective, since in alkaline solutions they exist in the form of anhydro-bases with trivalent nitrogen or, in the case of fully alkylated compounds, are hydrolyzed to the corresponding tetraalkylurea or thiourea (cf. Lecher & Graf, Liebigs Annalen, vol. 438, pages 158 and 159).

Aryl guanidine and aryl biguanidine, which are evidently incapable of existing as bases having pentavalent nitrogen, are also not useful.

Common guanidine and biguanidine, which have a certain affinity for acetate silk, is effective and can, for example, be used with advantage in alkaline printing pastes and padding solutions if saponification of the acetate silk or other cellulose ester is intended by printing with preparations containing for example a naphthol or naphtholate. Even in dilute aqueous solution the action of the guanidine is quite noticeable. The alkyl guanidines are more effective, especially those having an aliphatic or hydrocyclic residue with 6 or more, preferably 8 to 14 carbon atoms. Examples of such compounds are cyclohexylguanidine, isohexylguanidine and dodecylguanidine. With longer chains the effect may decrease because the substance penetrates the goods less deeply and has a smaller solubility in the alkaline bath. The effect obtained with guanidines is also obtained with biguanides, for example cyclohexylbiguanide, isoheptylbiguanide or dodecylbiguanide. The guanidine derivatives may also contain hydroxy-alkyl groups as substituents, whereby the range of solubility is extended.

The guanidine and biguanidine derivatives can be used in manner similar to that in which the bases of the aforesaid prior process are used, namely in combination for example with the following saponifying agents: alkali or alkaline earth hydroxides, alkali carbonates, borates or silicates, trialkali silicates, or organic bases such as triethanolamine or ethylene diamine.

For saponifying in aqueous baths, substances having 8 to 14 carbon atoms are the most suitable. In printing pastes substances of lower molecular weight and greater solubility are preferable, especially those with hydroxyalkyl groups. The action of the reagent is also dependent on the conditions of operation. The ion content of the solution is of considerable importance. In dilute alkali lyes with only a small content of electrolyte, substances with a higher molecular weight may be used in a given saponification, than when a more highly concentrated alkali carbonate solution is used. It is known that many polar substances which are capable of capillary adsorption in concentrated solutions of electrolytes are practically incapable of such adsorption in dilute solutions. This behaviour has been studied particularly in connection with mercerizing assistants.

The effectiveness in any given conditions of

operation of a compound included in the invention is easily determined by a preliminary test. For example a small sample of an acetate silk fabric is saponified at 60° C. with the quantity of N/20—N/40 lye necessary for a 10 per cent saponification (calculated as decrease in dry weight) until a quarter of the alkali has been consumed; this is compared with an experiment in which the substance to be tested is added in the form of a neutral salt, preferably a hydrochloride, in ⅕ of the quantity equivalent to the alkali hydroxide. The consumption of alkali is determined titrimetrically, and the material thoroughly freed from the catalyst by treating with 1/40 N hydrochloric acid at 40° C. is dyed with 2 per cent Diamine Pure Blue.

Textile materials of hydrolyzable artificial organic polymerides, for example polyvinyl esters or polyacrylic acid esters, can be wholly or partially saponified in a manner similar to that used for cellulose acetate or other cellulose esters.

The textile materials may have the form af artificial silk, staple fiber, filaments, foils, films, ribbons, bristles, artificial horse- and rabbit-hair, fabrics, and the like. The acceleration of the saponification does not only shorten the time of procedure, but it also ensures that the material is considerably less apt to be damaged, especially in those cases where mixtures with animal fibers are treated.

The invention is illustrated by the following examples:

(1) A fabric of acetate silk is handled for 30 minutes in a bath of liquor ratio 1:100 at 55–60° C., which contains per liter 1 gram of sodium hydroxide, 10 grams of sodium acetate and 1.1 gram of dodecylguanidine hydrochloride. The saponified fabric can be dyed a medium depth with Diamine Pure Blue FF (Schultz Farbstofftabellen, 7th ed., vol. I, page 209), whereas fabric treated in like manner, but without the addition of the guanidine derivative, is dyed only weakly and unevenly. The dodecylguanidine is obtained by warming dodecylamine with an alcoholic solution of S-methylisothiourea methosulfate.

Similar effects as the one described may also be obtained with substantially smaller quantities of dodecylguanidine.

(2) The dodecylguanidine hydrochloride of Example 1 is exchanged for dodecylbiguanide mono-hydrochloride or bromide. The saponification is approximately the same.

The dodecylbiguanide mono-hydrobromide is obtained by warming dodecylamine in an alcoholic solution with 3-ethyl-guanylisothiourea hydrobromide. The hydrochloride is obtained by heating dicyandiamide with dodecylamine hydrochloride.

(3) Acetate silk is saponified by sodium hydroxide in the presence of ⅕ mol of γ-phenoxy-β-hydroxypropyl-guanidine reckoned on the alkali used.

The γ-phenoxy-β-hydroxypropyl guanidine is obtained by splitting phenoxypropene oxide with an execss of ammonia and treating the primary hydroxyamine so formed with S-methylisothiourea.

(4) An acetate silk containing 10 per cent of nitrocellulose is de-nitrated with a solution containing 120 grams of sodium hydrosulfide and 2 grams of dodecyl-guanidine per liter for ½ hour at 60° C. The silk so treated no longer gives the diphenylamine reaction, and can be dyed with many direct dyestuffs, for example Sirius Blue BB.

(5) Acetate silk is saponified as in Example 1, except that the accelerating agent is μ-dodecylethylene guanidine.

(6) An acetate silk fabric is saponified at 75° C. in a bath containing 80 grams of sodium carbonate and 3 grams of cyclohexylbiguanidine hydrochloride. The saponifiation proceeds more quickly than without the additon of the biguanide.

(7) A cellulose acetate film is saponified at 75° C. in $n/10$ caustic soda lye containing 10 grams of sodium chloride and 2 grams of dodecylguanidine per liter until it can be dyed uniformly with a medium tone by a direct dyestuff. This effect is obtained considerably more quickly with the addition of the accelerating agent than without it.

(8) A satin fabric of cellulose acetate silk is printed with a paste of the following composition:

	Grams
Cyclohexylguanidine acetate	50
Water	370
Potassium carbonate	80
Tragacanth, 60:100	500

The fabric is steamed for 20 minutes in the round steamer, washed and dyed with 6 per cent of its weight of Direct Black VT (Schultz Farbstofftabellen, 7th ed., vol. I, page 271). The printed parts are more deeply colored than if they had been printed with a paste not containing the guanidine derivative.

In the claims following hereafter the term "aliphatic" comprises substituted alkyl radicals such as hydroxyalkyl and aralkyl.

What I claim is:

1. A process of saponifying artificial textile materials or films mainly consisting of cellulose esters, polymerized vinyl esters, polymerized acrylic acid esters, which process comprises performing the saponification with a solution of mineral alkali containing as a saponification catalyst a relatively small amount insufficient to cause saponification of a guanidine compound selected from the group consisting of guanidinium and biguanidinium bases and their salts, said guanidine compound containing in its molecule a radical selected from the group consisting of aliphatic and hydrocyclic radicals with at least six carbon atoms.

2. A process of saponifying textile materials or films consisting mainly of organic cellulose esters, which process comprises performing the saponification with a solution of mineral alkali containing as a saponification catalyst about one fifth of the amount equivalent to the mineral alkali employed of a guanidine compound selected from the group consisting of guanidinium and biguanidinium bases and their salts, said guanidine compound containing in its molecule a radical selected from the group consisting of aliphatic and hydrocyclic radicals with at least six carbon atoms.

3. A process of saponifying textile materials or films consisting mainly of organic cellulose esters, which process comprises performing the saponification with a solution of mineral alkali containing as a saponification catalyst a relatively small amount insufficient to cause saponification of a guanidine compound selected from the group consisting of guanidinium and biguanidinium bases and their salts, said guanidinium compound

containing in its molecule an aliphatic radical of 8 to 14 carbon atoms.

4. A process of saponifying textile materials or films consisting mainly of organic cellulose esters, which process comprises performing the saponification with a solution of mineral alkali containing as a saponification catalyst about one fifth of the amount equivalent to the mineral alkali employed of a guanidine compound selected from the group consisting of guanidinium and biguanidinium bases and their salts, said guanidinium compound containing in its molecule an aliphatic radical of 8 to 14 carbon atoms.

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