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METHOD OF SUPERFICIALLY SAPONIFYING A CELLULOSE ESTER FILM

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This invention relates to an improved method of making cellulosic films and more particularly to cellulosic films which are to be subsequently impregnated with a light-sensitive system containing a diazonium compound.

Fatty acid esters of cellulose films containing from 1.5 to 3.0 molecules of fatty acid per glucose unit were saponified in order to regenerate a cellulosic outer layer which can be readily impregnated with aqueous solutions. Such films had the undesirable feature that the outer layer swelled in aqueous solution while the unsaponified portion of the film did not swell, resulting in stresses in the film with subsequent peeling of the outer layer.

An object of the invention, therefore, is to provide a method to shrink the outer layer and to prevent its subsequent peeling.

This and further objects of our invention will appear as the specification progresses.

According to the invention, the cellulose strip after superficial saponification thereof is immersed in one or more after-treatment baths. One of the after-treatments contains an anti-peeling agent which shrinks an intermediate partially saponified layer such that upon subsequent immersion of the strip in an aqueous solution, for instance when impregnating the strip with a water-soluble light-sensitive system no stresses are created in the saponified layer which would cause it to peel from the underlying unsaponified portion of the strip.

The invention is particularly applicable to cellulose diesters which are subject to peeling after saponification. For example, a fatty ester of cellulose containing more than 1.5 and less than 3.0 fatty acid molecules per glucose residue after superficial saponification, i. e. by immersion of a strip of this material in a saponifying bath for a given period of time to saponify at least one side of the strip to a desired depth, is immersed in a bath containing an anti-peeling agent which is capable of shrinking a layer intermediate the outer surface of the strip and the unsaponified portion of the strip which contains 0.5 to 1.5 fatty acid molecules per glucose residue.

Anti-peeling agents suitable for the aforesaid purposes are salts soluble in water and having polyvalent anions such as sulphates, e. g., ammonium sulphate, phosphates, sulphites, thiosulphates, carbonates, tartrates and citrates. In addition water-soluble salts of organic carbonic acids having a molecular weight equivalent of not more than 100, such as acetates and lactates are likewise suitable for use in the method according to the invention. Substances having small inorganic anions, such as the fluorine ion and to a less extent the chlorine ion are serviceable. However, substances having a large monovalent anion such as the iodide ion, the nitrate ion and the rhodanide ion are unsuitable.

In addition, aqueous solutions of acids having a tri-basic acid function are suitable and some non-electrolytes also have a favourable shrinking effect, more particularly primary, saturated alcohols having a main chain of from 4 to 11 carbon atoms, such as butanol-1 and in addition a chain carbon compound having 3 to 6 hydroxyl groups, such as solutions of glycerol, glucose and other monosaccharides.

The anti-peeling agents enumerated hereinbefore may be used combined, provided that side reactions, such as the formation of insoluble or volatile substances, do not occur. It may often be advantageous to use an after-treatment bath containing both an ion-forming and a non-

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ion-forming anti-peeling agent. Immediately after saponification, an after-treatment bath may be used containing a solution of an organic carbonic acid, readily soluble in water, in a primary, saturated alcohol having a main chain of from 4 to 11 carbon atoms. Polyvalent alcohols are preferably also used in conjunction with other ion-forming anti-peeling agents. After treatment baths containing toluol and/or tetrahydronaphthalene and/or benzol and/or a liquid ether may be alternately used.

Cellulosic films which initially contain ester plasticizers such as triphenylphosphate and tricresylphosphate, which upon the superficial saponification of the fatty acid cellulose ester are not saponified completely. Particularly the intermediate layer may hold or subsequently attract from the substratum by diffusion a comparatively large amount of plasticizer resulting in deposition or turbidity of particles of plasticizer on the surface of the film, foil or the like. It has now been found that the plasticizer still present after saponification in the totally saponified layer and the intermediate layer of the foil, film or the like can be removed with the use of solvents. Such solvents are, for example, solutions of so-called "dispersion agents," such as a salt of a sulphated hydroxycarbonic acid having at least 10 carbon atoms, for example, ammonium or sodium salts of ricinolic acid esterified with sulphuric acid, in addition sodium oleate, the sodium salt of p.octylbenzolsulphonic acid, cationegenous dispersion agents such as dodecylaminehydrochloride or compounds derived therefrom and in addition non-ion forming dispersion agents, such as polyethers, derived from methylene or ethylene oxide, which at the end of the chain, are esterified, for example, with a lauryl alcohol. Solutions of from 5 to 10% by weight of these ion-forming dispersion agents in water are suited to free from plasticizer saponified superficial layers of foils, films or the like made of fatty acid cellulose esters.

An after-treatment bath may contain both an anti-peeling agent for partially esterified cellulose containing from 0.5 to 1.5 molecules of fatty acid per glucose residue and a solvent for the plasticizer. It must be noted that a great number of non-ion-forming shrinking agents also have a dissolving effect on plasticizers.

Since the intermediate layer formed during saponification does not swell appreciably in the solution of the dispersion agent there is no probability of the saponified layer peeling from the non-saponified substratum. There is therefore entire liberty in regard to the choice between treating the foil, film or the like upon saponification first with the use of the dispersion agent or by treating it first with the use of the anti-peeling agent. For the sake of simplicity the shrinking agent and the solvent for the plasticizer may be combined in one after-treatment bath.

The invention will now be described in connection with the following examples:

Example 1

A film 125 μ in thickness and made of cellulose acetate containing about 2.2 molecules of fatty acid per glucose residue (that is to say having an acetic acid content of 52%) is superficially saponified, while agitating, for 70 seconds at 27.5° C. on one side or on two sides in a solution of 1.15 n-potassium hydroxide in a mixture of 45 parts by volume of methanol and 55 parts by volume of water. The film is then treated, also while agitating, for 23 seconds in a solution of 2 n sulphuric acid and 2 n ammonium sulphate in water and eventually washed in circulating water for at least 75 seconds. The thickness of the regenerated cellulose layer is 8 μ and that of the intermediate layer 2 μ . The saponified layer rigidly adheres to the substratum.

Example 2

Foils about 110 μ thick and made of cellulose acetate containing about 1.8 molecules of acetic acid per glucose unit (that is to say having an acetic acid content of 45.25%) are saponified for 1 minute at 25° C. in a solution of 1 n potassium hydroxide in methanol. The foils are then treated, while agitating, for a period of 30 sec-

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onds in a salt solution. The minimum concentration of this salt solution as required to ensure satisfactory adhesion of the saponified layer to the non-saponified substratum is ascertained at the period of treatment mentioned, that is to say in 30 seconds, the following minimum concentrations, expressed in gram molecules per litre, being found for the salts mentioned as under:

Potassium fluoride	0.12
Lithium chloride	1.0
Sodium chloride	0.6
Ammonium chloride	0.24
Magnesium chloride	0.23
Zinc chloride	0.2
(CH ₃) ₄ NCl	0.6

If the foils are inserted in water directly upon saponification the saponified layer peels.

Calcium and barium chloride do not result in adhesion. Zinc chloride in high concentrations has a swelling effect and causes the saponified layer to peel.

The same experiments are undertaken with the following salts, the concentrations thus found being mentioned as under:

Lithium sulphate	0.2
Sodium sulphate	0.2
Ammonium sulphate	0.1
Magnesium sulphate	0.9
Trisodium phosphate	0.06

Nitrates, bromides, iodides and rhodanides do not result in adhesive, but in peeling saponified layers.

An adhesive effect is procured by sodium acetate, formate, citrate, sulphite and thiosulphate.

Example 3

A piece of foil made of cellulose acetate containing about 2.3 molecules of fatty acid per glucose unit (that is to say having an acetic acid content of 53.7%) is saponified at 23° C. for 1 minute in a solution of 1 n potassium hydroxide in a mixture of 62 parts by volume of methanol and 38 parts by volume of water. The foil is then treated, while agitating, for 5 to 10 minutes in a solution of 3.8% of trisodium phosphate in water and then washed by rinsing with water. The foil may be treated after saponification with 1.4% ammonium sulphate instead of with trisodium phosphate.

After saponification the piece of foil may be treated with highly satisfactory results first for 1 minute with butanol-1 and then for 1 minute in a solution of 3.8% of trisodium-phosphate or 1.4% of ammonium sulphate. After the treatment in a solution of trisodiumphosphate or ammoniumsulphate the piece of foil is washed in water and eventually skimmed and dried. The adhesion of the saponified superficial layer to the substratum is excellent.

Example 4

A mechanically moved web 130μ thick and made of cellulose acetate containing about 2.3 molecules of acetic acid per glucose unit is saponified at 24° C. for 45 seconds on two sides in a solution of 1 n potassium hydroxide in a mixture of 66 parts by volume of methanol and 34 parts by volume of water, shrinking then taking place for a period of 45 seconds in a mixture of 1 part by volume of butanol-1 and 1 part by volume of toluol. The web then passes during a period of 45 seconds through a stopper bath of 0.6 n acetic acid in butanol-1. Eventually the web is washed in circulating water for 2.5 minutes and after spraying with water and skimming dried with the use of warm air of about 90 to 100° C.

The thickness of the regenerated cellulose layer is 10μ and that of the intermediate layer 4μ. The adhesion of the saponified layer to the non-saponified substratum is excellent. The butanol-toluol mixture may be replaced with equally satisfactory results by a mixture of butanol-1 with benzol or with tetrahydronaphthalene or with a liquid ether for example diethylether or by diethylether without butanol-1. As an alternative, an ether bath may be used after a treatment with an aqueous liquid.

Example 5

A piece of foil 135μ thick and made of cellulose acetate having an acetic acid content of 53.5% is saponi-

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fied mechanically at 23° C. on two sides for a period of 62 seconds in an 1 n solution of potassium hydroxide in equal parts by volume of methanol and butanol-1. The web then passes through a bath of 30 parts by volume of methanol on 30 parts by volume of water on 30 parts by volume of glycerol, then through a bath of 60 parts by volume of butanol-1 and 40 parts by volume of ethanol and eventually through a bath of 800 parts by volume of ethanol, 1900 parts by volume of methanol, 68.50 parts by volume of butanol-1 and 443 parts by volume of concentrated acetic acid. In each of these baths the time of treatment is 62 seconds. After successive washing in circulating water for 130 seconds, spraying with water and skimming for a period of 30 seconds the web is dried at 85° C. with the use of a warm flow of air.

The thickness of the regenerated cellulose layer is 10μ and that of the intermediate layer 4μ. The adhesion of the saponified layer to the substratum is excellent.

Composition and order of the baths should be such that unwanted crystallization and/or turbidity is avoided.

Example 6

A web 140μ thick and made of cellulose acetate having an acetic acid content of 53.3% is passed mechanically at 23.5° C. at the rate of 60 seconds per bath in succession through the following baths:

- (a) 1-n potassium hydroxide in 66% methanol
- (b) Butanol-1
- (c) Butanol-1
- (d) 2 n phosphoric acid in water
- (e) Circulating water
- (f) Circulating water

use being made with advantage of the difference in specific gravity between butanol-1 and water so that the film upon immersion in bath (d) repels the alcohol.

The web is then sprayed with water for 30 seconds and after skimming at 90° C. dried with a warm flow of air. The thickness of the regenerated cellulose layer is 10μ and that of the intermediate layer 3μ. The adhesion of the saponified layer to the substratum is excellent.

Example 7

A web 135μ thick and made of cellulose acetate having an acetic acid content of 53.5% and containing about 17% of triphenyl phosphate as a plasticizer is superficially saponified by mechanical means at 23° C. for 1 minute in a solution of 1.16 n potassium hydroxide in a mixture of 62 parts by volume of methanol and 38 parts by volume of water. The web is then treated for 1 minute with a solution of 5% by weight of the ammonium salt of sulphated ricinolic acid (so called Turkey-red oil) in equal parts of water and methanol, then for 1 minute in circulating water and next for 1 minute in a solution of 2 n phosphoric acid in water. Subsequently the web is washed in circulating water for two minutes, then sprayed with water for 30 seconds and, upon superficial skimming, dried at 90 to 100° C. with the use of filtered warm air and wound.

Highly satisfactory results are obtained if in addition, say, 3.8% sodium phosphate is dissolved in the Turkey-red oil bath.

The thickness of the regenerated cellulose layer and that of the intermediate layer are measured with a microscope in a cut. The thickness of the first-mentioned layer is 13μ and that of the last-mentioned layer 3 to 4μ. The dry web is glossy and bright and upon subsequent rinsing with water no longer gives up plasticizer. The resultant web superficially saponified on two sides is eminently suited to be sensitized with an aqueous solution of a diazo compound and, if desired, a metal salt. Such photographic material may be used after exposure, for example with a mercury vapour lamp, to develop, with the use of a physical developer, a highly satisfactory contrast constituted by metal which is contained in the thin, saponified layer. The separating power of such materials is very high and they are specially suited for microdocumentation or for registration of sound tracks.

The adhesion of the saponified layers to the substratum is excellent.

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Example 8

A piece of foil 135 μ thick and made of cellulose acetate containing about 2.3 molecules of fatty acid per glucose unit (or in other words having an acetic acid content of 53.6%) is saponified at a temperature of 23° C. for 1 minute with the use of a solution of 1 n potassium hydroxide in a mixture of two parts by volume of methanol and one part by volume of water.

The foil superficially saponified on two sides is treated for 0.5 to 1 minute with a solution of 3 n phosphoric acid in water and eventually washed in water. The thickness of the layer of regenerated cellulose is from 14 to 15 μ , whereas the intermediate layer has a thickness of from 3 to 4 μ . Even after long treatment of the foil with water or aqueous solutions the saponified layers do not peel from the substratum but rigidly adhere thereto.

Example 9

Cellulose diacetate foil was superficially saponified for 1 minute in a solution of 1 n-potassium hydroxide in a mixture of 2 parts by volume of methanol and 1 part by volume of water at 25° C. The web was then immediately inserted in a solution obtained by diluting 10 ccs. of 89% phosphoric acid with 300 ccs. of butanol-1 (this solution is about 1.5 n). After immersion in this bath for 1 minute at 25° C. the foil was rinsed in water for 30 minutes and then dried in air. The saponified layer adheres most satisfactorily and the surface is smooth. It is preferred that the concentration of phosphoric acid should not be excessive since otherwise the surface of the saponified layer, which in itself is readily adhesive, tends to become slightly shrivelled.

Satisfactory results are also obtained if the solution of phosphoric acid in butanol-1 is replaced by a 10%-

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solution of citric acid in fermentation-amyl alcohol (methyl-3 butanol-1). This solution is about 1.5 n in citric acid.

While the invention has been described with reference to specific examples and applications thereof, other modifications will be readily apparent to those skilled in the art without departing from the spirit and scope of the invention as defined in the appended claims.

What we claim is:

1. A process of superficially saponifying a strip of cellulose ester containing between 1.5 and 3.0 molecules of fatty acid per glucose residue, which comprises the steps of immersing said strip in a saponifying bath containing at least a 0.1 normal solution of an alkali hydroxide and an alcoholic solvent to effect rapid saponification of said strip for a time sufficient to produce a partially-saponified intermediate layer in said strip containing between 0.5 and 1.5 fatty acid molecules per glucose residue, and thereafter immersing said strip for at least 30 seconds in an aqueous stopping bath containing at least 0.12 gram molecules per liter of a water-soluble anti-peeling agent consisting of a water-soluble fluoride to prevent peeling of the saponified layer.
2. A process as claimed in claim 1 in which the anti-peeling agent is potassium fluoride.

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