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PROCESS OF PRODUCING MATERIAL FOR USE IN THE CASTING OF PHOTOGRAPHIC FILM SUPPORT

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This application is a continuation-in-part of our co-pending application Serial No. 5,174, filed January 29, 1948, now abandoned, and the latter application is a division of our application Serial No. 734,830, filed March 14, 1947, now abandoned.

This invention relates to a process for the manufacture of photographic film support.

It is an object of this invention to produce cellulose lower fatty acid ester layers, which have been saponified to a depth especially suitable for the casting of films or sheets; for instance, photographic film supports.

More particularly it is an object of this invention to provide the drum or belt of a casting machine with a layer, the so-called casting layer, which consists of a cellulose lower fatty acid ester having an outer portion down to a substantial depth of de-esterified cellulose.

In the manufacture of cellulose ester sheets for photographic film supports, it is known to pour the solution of a film-forming compound on a support, called the carrier, which may be either a metal surface having a very high gloss, such as a nickel or silver surface or may be the surface of an endless metal band (belt) covered with a layer of a high-polymeric surface, called the casting layer.

Hitherto, this casting layer consisted of gelatin or of a cellulose ester. However, since these materials do not possess the necessary properties to form sheets having a very high gloss, and since sheets cast on cellulose ester often stick to the casting layer, it has been proposed to superficially change the substance of the cellulose ester forming the casting layer by treating its surface with a de-esterifying liquid, for instance an aqueous solution of potassium-hydroxide.

However, in the practice of this method great drawbacks are encountered. It is very difficult, if not impossible to preserve the high gloss of the casting layer by applying the saponifying liquid directly on this layer. Furthermore, due to salt formation, the penetration of the alkali into the casting layer is limited to a depth of about 10 μ . For instance if cellulose acetate is saponified with potassium hydroxide, potassium acetate is formed which cannot be removed completely in the known processes and hinders penetration of the alkali to a sufficient depth.

In many cases, for instance when preparing casting layers for the manufacture of photographic film support of cellulose derivatives, this penetration to 10 μ is altogether insufficient. If, when casting film support, the solvent of the film-forming product also is a solvent for the unsaponified cellulose ester of the casting layer, this solvent might diffuse, by the capillary action of impurities present in the casting layer, into unsaponified cellulose ester in the inner part of the casting layer and might cause the cast film support to adhere to the casting layer.

According to the present invention, these disadvantages

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can be avoided, if the surface of the casting layer, composed of a cellulose ester, and preferably of a lower fatty acid ester, is coated with a hydrophilic colloid, preferably gelatin, and the saponifying liquid, preferably an aqueous alkali metal hydroxide, is spread on this hydrophilic colloid layer. The liquid then penetrates by diffusion into the cellulose ester layer, saponifying it to a certain depth. After the saponifying process has thus been carried through to the desired depth, the colloid layer is removed.

We have now found that so-obtained saponified cellulose ester layers are completely satisfactory as a casting layer in the manufacture of films or sheets.

Since the saponifying liquid is not spread directly on the surface of the layer to be saponified, this surface is not damaged and its high gloss remains intact. Consequently the film formed on it possesses a very high gloss.

Further, in performing the saponification in the above described manner, no screening salt layer is formed on the surface of the casting layer, because the salts that may be formed, immediately diffuse into the water-containing layer. The saponifying process may thus be guided at will to any desired depth and even through the entire thickness of the cellulose ester layer, by either applying the saponifying liquid or by applying it repeatedly.

In this manner, the adhesion of the cast film on the cellulose casting layer may be avoided, and the films are stripped off without damaging the high gloss. If the casting layer is a composite layer formed of several layers made of the same or of different cellulose esters, it is convenient to saponify completely through the top layer or layers into the region of an underlying layer, for instance where the cellulose lower fatty acid ester coating is composed of three layers each having a thickness of 0.06 mm. (total thickness 0.18 mm.) a depth of saponification of 0.15 mm. may be reached.

In practicing the process of the present invention the belt of a casting machine is provided with a lower fatty acid ester layer. This coating may be produced by dissolving a suitable ester as for example, a cellulose acetate, propionate, butyrate and/or mixtures thereof such as aceto-butyrate in a suitable organic solvent therefore and applying the solution in a known manner to the metal belt. After the casting layer has dried it is covered with a solution of gelatin in warm water. Preferably the gelatin solution also contains an agent capable of stabilizing against alkali, the gelatin layer to be formed. This stabilizing agent is preferably a sugar or sugar-like substance of the type already known as modifying agent for gelatin. Preferably the sugar or sugarlike substance is a hexitol such as sorbitol, or a hexose or pentose such as glucose, fructose and arabinose or a mixture of monosaccharide such as invert sugar which contains both glucose and fructose, or a disaccharide such as sucrose.

When speaking of gelatin in relation with the present invention, we mean gelatin as such or in the presence of a stabilizing agent of the type already known and as indicated above.

In any event the gelatin solution is cooled to approximately room temperature whereupon it solidifies or jellifies. The gelatin surface is then treated with an aqueous solution of an alkali metal hydroxide as for example, sodium lithium or potassium hydroxide. Preferably a solution having a concentration of from 3 to 30% by weight of alkali metal hydroxide is used. The gelatin layer may be treated any number of times with the alkali depending on the penetration desired. Thereafter the gelatin layer is stripped from the ester layer and a perfectly smooth surface having a substantial depth of de-esterification or saponification is disclosed.

The following specific examples serve to illustrate but are not intended to limit the present invention.

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Example I

A solution of 13 kgms. cellulose acetate in 100 litres acetone is coated in three superimposed layers on the endless belt of a band-casting machine. After drying, the casting layer thus produced is covered with a solution of 15 kgms. gelatin in 30 litres water at 55° C. The solution also contained 1 kgm. of sorbitol. On cooling to 20° C. the gelatin jellifies. This gelatin is treated ten times running with a 20% aqueous potassium hydroxide solution and is then removed. The casting layer laid bare after this removal still shows a perfect high gloss. It is inert to the usual solvents, being converted into regenerated cellulose to a depth of 100 μ , and therefore is a very suitable casting layer for films support of every kind.

Example II

An endless travelling copper band is coated during three revolutions of the band with an 18% acetone solution of cellulose acetate containing 40% acetyl. The beginning and ending of this layer are shortly overlapped and after sufficient drying, the small overlap is polished in a well-known manner for obtaining high gloss. After complete drying, this layer is coated with a warm 30% gelatin solution which solidifies on cooling, so that the whole surface of the cellulose acetate layer is covered with a 4 mm. thick gelatin layer. A 20% KOH solution in 60 parts by volume methanol and 40 parts water is applied to this gelatin layer by means of a rubber roll revolving at high speed in close contiguity with the band. After 14 complete revolutions of the band, which occurs within about 4¼ hours, the saponification treatment is interrupted and the gelatin layer is washed in order to remove all residual alkali and salts, by gently dabbing it with props of cotton wool impregnated with cooled water. After 3 hours washing, the gelatin layer is dried in a moderately warm air current. After a rest period of 2¼ minutes, said layer is removed and the cellulose acetate layer is dried in a warm air current. The saponification depth is found to be about 0.10 mm.

Example III

15 parts by weight of a partially hydrolysed cellulose aceto propionate with a 5% propionyl content and a 35% acetyl content are dissolved in 100 litres acetone and coated within two revolutions onto the endless copper band of a casting machine, forming in this way a 0.16 mm. thick composite layer. After drying and polishing the overlap, a hot solution of 50 parts by weight of gelatin in 100 parts of water, stabilized by invert sugar added in an amount of 3 parts by weight is coated onto the cellulose ester layer in a thickness of about 5 mm. A 25% NaOH solution in 100 parts by volume of an equal mixture of methanol and water is applied to and removed from this gelatin layer as described in Example I. The dried cellulose ester is saponified to a depth of about 0.12 mm.

Example IV

14 parts by weight of partially hydrolysed cellulose aceto butyrate with a 10% butyryl content and a 32% acetyl content are dissolved in 100 litres acetone. This solution is coated onto the endless band of the casting machine, dried and superficially hydrolysed as described in Example I through the gelatin layer containing as stabilizer 2% arabinose on the weight of the gelatine. The saponifying liquid contains 25% of KOH in a mixture of 70 parts of water in 30% parts by volume of methanol. The dried cellulose ester layer is saponified to a depth of about 0.14 mm.

Example V

10 parts by weight of a cellulose acetate with a 43% acetyl content are dissolved in 100 litres methylene chloride and coated onto the endless band of the casting machine in three revolutions. After drying and polishing,

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this layer is further superficially hydrolysed through a gelatin layer as described in Example I. The gelatin layer contains as stabilizer 5% fructose on the weight of the gelatin and has a thickness of 5 mm. while the saponifying liquid contains 30% NaOH in 45 parts of water and 55 parts by volume of methanol. A depth of saponification of 0.15 mm. is reached.

Example VI

18 parts by weight of cellulose propionate with a 48% propionyl content are dissolved in 100 litres methyl acetate. This solution is coated only once onto the endless band of the casting machine and treated as described in Example I, with a saponifying liquid of 10% LiOH in an equal mixture of water and methanol. The saponification is completed in 10 hours and reaches a depth of 0.11 mm.

The casting layers obtained according to the above examples possess a perfect high gloss and are excellently suited to the casting of photographic film supports.

We claim:

1. The process of producing a casting layer for the manufacture of photographic film support, which comprises coating the surface of a sheet of cellulose lower fatty acid ester soluble in an organic solvent with an aqueous solution of gelatin, allowing this solution to set, spreading on the thus obtained gelatin layer an aqueous solution containing from 3 to 30 percent by weight of alkali metal hydroxide, allowing the aqueous solution to diffuse through the gelatin layer, saponifying said cellulose lower fatty acid ester sheet and then removing the gelatin layer.

2. The process of producing a casting layer for the manufacture of photographic film support, which comprises coating the surface of a sheet of cellulose lower fatty acid ester soluble in an organic solvent with an aqueous solution of gelatin which contains at least one stabilizing agent selected from the group consisting of disaccharide, pentose, hexose and hexitol, allowing this solution to set, spreading on the thus obtained gelatin layer an aqueous solution containing from 3 to 30 percent by weight of alkali metal hydroxide, allowing the aqueous solution to diffuse through the gelatin layer, saponifying said cellulose lower fatty acid ester sheet, and then removing the gelatin layer.

3. The process of producing a casting layer for the manufacture of photographic film support, which comprises coating the surface of a sheet of cellulose lower fatty acid ester soluble in an organic solvent with an aqueous solution of gelatin, allowing this solution to set, spreading on the thus obtained gelatin layer an aqueous solution containing approximately from 3 to 10 percent by weight of lithium hydroxide, allowing the aqueous solution to diffuse through the gelatin layer, saponifying said cellulose lower fatty acid ester sheet, and then removing the gelatin layer.

4. The process of producing a casting layer for the manufacture of photographic film support, which comprises coating the surface of a sheet of cellulose lower fatty acid ester soluble in an organic solvent with an aqueous solution of gelatin, allowing this solution to set, spreading on the thus obtained gelatin layer an aqueous solution containing approximately from 5 to 20 percent by weight of sodium hydroxide, allowing the aqueous solution to diffuse through the gelatin layer, saponifying said cellulose lower fatty acid ester sheet, and then removing the gelatin layer.

5. The process of producing a casting layer for the manufacture of photographic film support, which comprises coating the surface of a sheet of cellulose lower fatty acid ester soluble in an organic solvent with an aqueous solution of gelatin, allowing this solution to set, spreading on the thus obtained gelatin layer an aqueous solution containing approximately from 5 to 30 percent by weight of potassium hydroxide, allowing the aqueous

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solution to diffuse through the gelation layer, saponifying said cellulose lower fatty acid ester sheet, and then removing the gelatin layer.

6. The process of producing a casting layer for the manufacture of photographic film support, which comprises coating the surface of a sheet of cellulose acetate, soluble in an organic solvent with an aqueous solution of gelatin, allowing this solution to set, spreading on the thus obtained gelatin layer an aqueous solution containing from 3 to 30 percent by weight of alkali metal hydroxide, allowing the aqueous solution to diffuse through the gelatin layer, saponifying said cellulose acetate sheet, and then removing the gelatin layer.

7. The process of producing a casting layer for the manufacture of photographic film support, which comprises coating the surface of a sheet of cellulose acetate propionate soluble in an organic solvent with an aqueous solution of gelatin, allowing this solution to set, spreading on the thus obtained gelatin layer an aqueous solution containing from 3 to 30 percent by weight of alkali metal hydroxide, allowing the aqueous solution to diffuse through the gelatin layer, saponifying said cellulose acetate propionate sheet, and then removing the gelatin layer.

8. The process of producing a casting layer for the manufacture of photographic film support, which comprises coating the surface of a sheet of cellulose acetate butyrate soluble in an organic solvent with an aqueous

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solution of gelatin, allowing this solution to set, spreading on the thus obtained gelatin layer an aqueous solution containing from 3 to 30 percent by weight of alkali metal hydroxide, allowing the aqueous solution to diffuse through the gelatin layer, saponifying said cellulose acetate butyrate sheet, and then removing the gelatin layer.

9. The process of producing a casting layer for the manufacture of photographic film support, which comprises coating the surface of a sheet of cellulose acetate soluble in an organic solvent with an aqueous solution of gelatin containing sorbitol, allowing this solution to set, spreading on the thus obtained gelatin layer an aqueous solution containing from 3 to 30 percent by weight of potassium hydroxide, allowing the aqueous solution to diffuse through the gelatin layer, saponifying said cellulose acetate sheet, and then removing the gelatin layer.

References Cited in the file of this patent

UNITED STATES PATENTS

1,988,550	Gladhorn	Jan. 22, 1935
2,092,005	Moncrieff	Sept. 7, 1937
2,116,063	Dreyfus	May 3, 1938
2,558,555	Hendricx	June 26, 1951

FOREIGN PATENTS

897,404	France	Mar. 21, 1945
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