Jan. 14, 1936. M. HAGEDORN 2,027,688

MANUFACTURE OF FOILS

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Fig. 1.

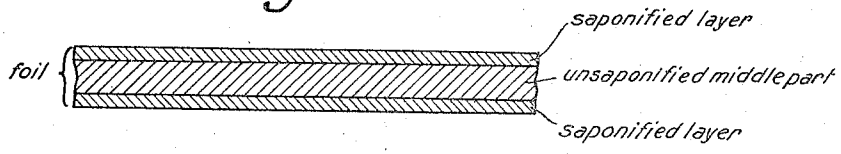
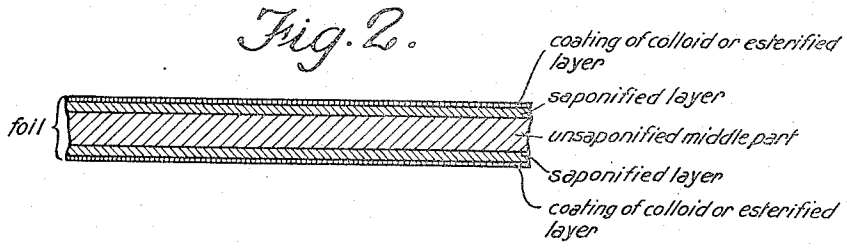


Fig. 2.



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MANUFACTURE OF FOILS

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4 Claims. (Cl. 91—68)

My present invention relates to foils and more particularly to sheets made of organic cellulose esters.

One of its objects is to provide foils having improved physical properties. Further objects will be seen from the detailed specification following hereafter. Films and sheets are made of organic cellulose esters, for instance of cellulose acetate, cellulose propionate, cellulose butyrate, cellulose nitrate acetate, cellulose acetate butyrate, with or without addition of softening agents, filling agents, etc. Furthermore it is known to superficially saponify films, made of organic cellulose esters, on one of their faces.

According to this invention improved mechanical properties can be imparted to films and foils made of cellulose esters by saponifying them superficially on both faces in such a manner that the internal portion of the foil is not attacked by the saponifying agent. The film thus obtained comprises an internal portion consisting of unsaponified cellulose ester and two external portions of cellulose which has been regenerated more or less completely. The internal portion intermixes with the external portions at point of contact, so that no well defined borders are formed and a perfect cohesion of the film is thus assured.

In the following tables the mechanical properties of sheets saponified on both faces are compared with those of sheets which have not been thus saponified. The saponification is effected with a methanolic sodium hydroxide solution of 10 per cent strength to which 10 per cent of water has been added. Aqueous solutions of sodium hydroxide can likewise be used. In this case, however, the saponification takes more time. Inorganic and organic acids in an aqueous solution or in organic solvents may likewise be used. The saponification may be effected by dipping the materials to be treated in the liquid for the time wanted or by passing them through the liquid on a sufficient length or in other known manner.

The experiments have been performed with films of 135μ to 150μ thickness. The cross section of a film after a treatment of about 10 minutes showed that the saponification with a lye of the aforesaid strength had penetrated from both sides to about $\frac{1}{6}$ of the thickness of the film, while the remaining $\frac{2}{3}$ of the film had not been saponified.

Duration of saponification	Solidity in kilos	Extension	Creasing number	Impact test by the pendulum method kilos per cc.	Elongation in water %
Films made of hydrolyzed cellulose acetate (containing 54% of bound acetic acid) having an addition of a softening agent					
Untreated	82	25	47	108	1.0
Non-saponified, extracted	85	28	46	103	3.28
Saponified for 5 minutes	84	31	113	119	3.34
Saponified for 10 minutes	92	33	122	157	3.51
Saponified for 15 minutes	96	36	175	200	3.80
Saponified for 20 minutes	96	37	245	270	4.29
Films made of hydrolyzed cellulose acetate (containing 54% of bound acetic acid) without addition of a softening agent					
Non-saponified, extracted	89	23	39	----------	3.3
Saponified for 10 minutes	94	36	122	----------	4.5
Saponified for 15 minutes	95	36	151	----------	4.5
Saponified for 20 minutes	99	47	266	----------	5.0
Films made of hydrolyzed cellulose acetate (containing 54% of bound acetic acid)					
Non-saponified	83	21.6	62	----------	----------
Saponified on one side (for 25 min.)	82.7	22.7	54	----------	----------

For the sake of better comparison the untreated material has also been extracted with the liquid used in the saponification process for dissolving the saponifying agent, in the present case methanol. The characteristics of this ma-

terial are given in the second horizontal column of the first and the second table.

As seen from the above table the new sheets possess improved mechanical properties. However, the elongation when wetted with water is likewise increased and that may be disadvantageous for certain uses. By the following treatment the elongation in water may be diminished while the improvements of the mechanical properties obtained by the saponification may at the same time be preserved. It consists in esterifying superficially the outer layers consisting of regenerated cellulose only to a small depth, or providing them with a thin coating of a colloid which is less sensitive to water than is regenerated cellulose; all of the known esters, mixed esters, ether-esters and ethers of cellulose, as well as natural and artificial resins are suitable for this purpose.

The following examples illustrate the invention:

Example 1.—A film of hydrolyzed cellulose acetate the two faces of which are saponified superficially is provided with a coating of 5 to 8μ thickness consisting of a solution of

	Grams
Nitrocellulose	100
Polyvinyl acetate resin	50
Phthalic acid dimethylester	30
Triphenylphosphate	20
Acetone	1700
Ethanol	300

Example 2.—A film of hydrolyzed cellulose acetate the two faces of which have been saponified superficially are treated at a temperature of 60° C. for 15 minutes with a mixture consisting of:

	Parts
Acetic anhydride	10
Butyric anhydride	10
Glacial acetic acid	40

The esterification hereby obtained penetrates by about 10μ into the film.

The sheets according to this invention are suitable for all purposes of application, for which there was hitherto made use of the unsaponified cellulose ester foils. More particularly they are suitable for use as supports for photographic emulsion layers. In this case the emulsion can directly be applied on the saponified surface of the support without the necessity of a special intermediate treatment of the support since the adhesive power of the saponified surface is strong enough. The back of the film may be provided with a layer for the purpose of protecting it from being scratched or of enhancing the gliding property. In the saponified outer skin there may be incorporated substances of any kind, such as dyestuffs, gliding agents, softening agents, filling agents etc. by bathing the material in suitable solutions or suspensions. In the case of sheets the surface of which has been subjected to a treatment preventing a too great elongation in the wet state, and if desired in the case of sheets having a saponified surface, the surface of the foils may be provided with a special preparation layer ensuring the adhesion of the photographic emulsion layer.

In the accompanying drawing:

Fig. 1 is a diagrammatic illustration,

Fig. 2 is a diagrammatic illustration of a specific embodiment of the invention.

In the accompanying drawing there are diagrammatically illustrated the two kinds of sheets, the drawing being in itself explanatory. The lines of separation seen in the drawing dividing the saponified layers and the middle part of the sheet do not exist in reality, the layers intermingling as already explained. These lines have only been drawn to give a clearer idea of the invention.

What I claim is:

1. A laminated sheet comprising an internal stratum comprising an organic cellulose ester and adjacent to said internal portion and blended therewith at point of contact on both faces external strata of regenerated cellulose bearing on their outer surfaces and firmly adhering thereto a layer of a colloid less sensitive to water than cellulose hydrate.

2. A laminated sheet comprising an internal stratum comprising an organic cellulose ester, and adjacent to said internal stratum and blended therewith at point of contact on both faces middle strata of regenerated cellulose and adjacent said middle strata and blended therewith at point of contact external strata of an organic cellulose ester.

3. A laminated sheet comprising an internal stratum comprising cellulose acetate, and adjacent to said internal portion and blended therewith at point of contact on both faces middle strata of regenerated cellulose and adjacent said middle portions and blended therewith at point of contact external strata of cellulose acetate.

4. A laminated sheet comprising an internal stratum comprising an organic cellulose ester and adjacent to said internal stratum and blended therewith at point of contact on both faces strata of regenerated cellulose bearing on their outer surface and firmly adhering thereto layers consisting of nitrocellulose, polyvinyl acetate resin, phthalic acid dimethylester, and triphenyl phosphate.

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