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MANUFACTURE OF LAMINATED FILMS

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Fig. 1

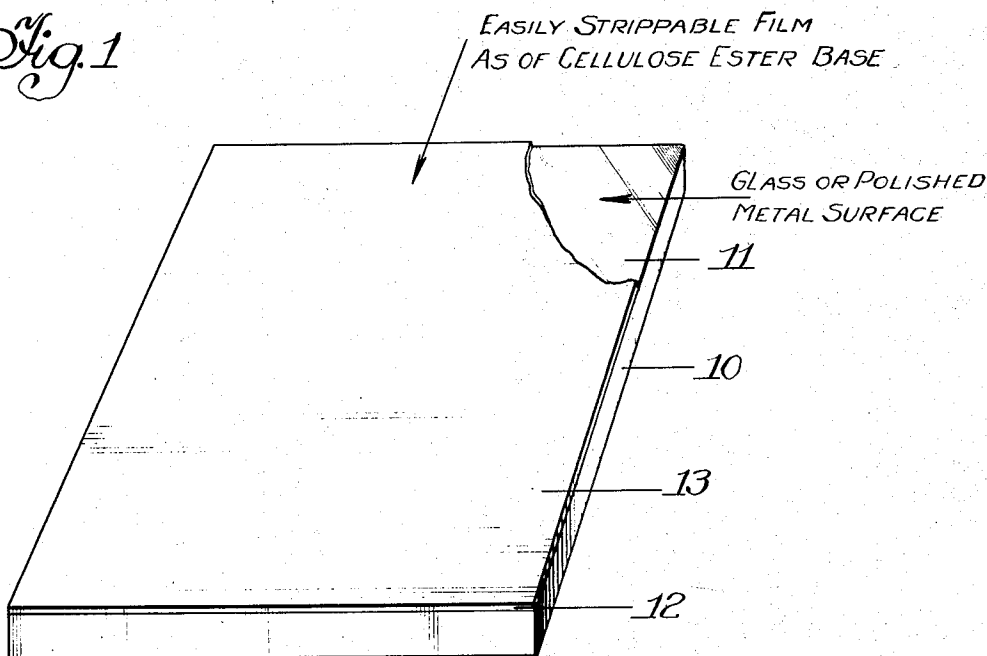


Fig. 2

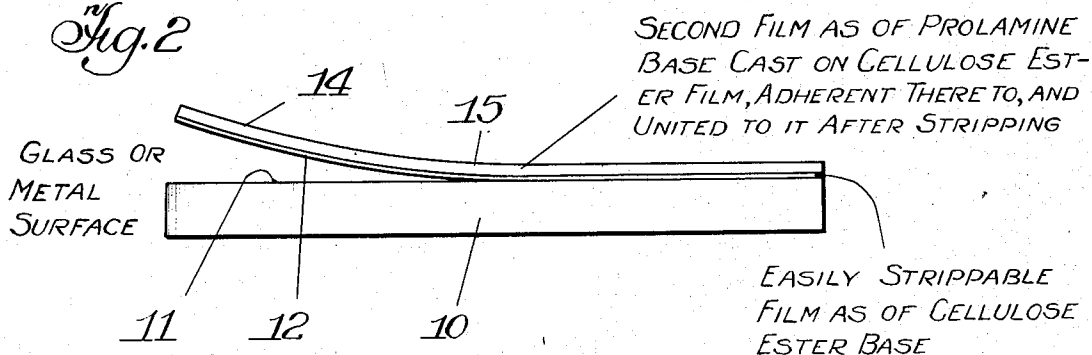
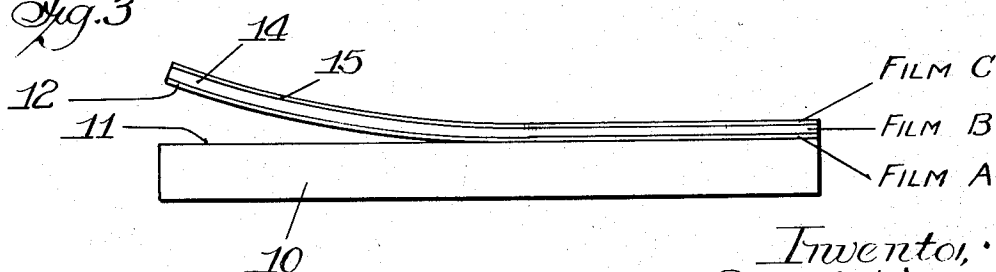


Fig. 3



Witness:  
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## UNITED STATES PATENT OFFICE

2,070,596

## MANUFACTURE OF LAMINATED FILMS

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mesne assignments, to Prolamine Products  
Incorporated, Dover, Del., a corporation of  
Delaware

Application December 11, 1933, Serial No. 701,865

7 Claims. (Cl. 18—57)

The present invention relates to the manufacture of films and has particular reference to the casting of films on smooth surfaces.

It is a custom in making films to flow a liquid or viscous mixture onto a smooth surface where the mass sets, as for example by the evaporation of a solvent. Sometimes glass is used, other times polished metal, and sometimes mercury. The latter is particularly necessary where the dried or set film is adherent to solid surfaces such as glass or metal. The selection of the solid surface material is in part predetermined by the tendency of a particular film composition to adhere in the forming process.

Films so formed are thereafter frequently coated with a surfacing composition to give to the ultimate sheet certain properties which are not exhibited by the body of the film. As an example of such coating, reference is made to the practice of applying a waterproofing nitrocellulose lacquer to a regenerated cellulose to form what is commercially recognized as "waterproof cellophane".

The present invention relates to the formation of such a multiplex film, and has particular utility in casting films which have a tendency to adhere to a casting surface, or in other words which do not readily strip from a casting surface. The invention calls for the formation of a film which does strip readily from a casting surface, thus to provide by such film a new casting surface onto which another film may be cast.

The general object of the invention is the formation of a strippable film on a casting surface, and the casting on said film of a second film, and stripping the two films together from the casting surface.

A particular object of the invention is the casting of a film-forming composition, which normally adheres to a casting surface, upon a preformed unstripped cast film which is readily strippable from its casting surface.

A further object of the invention is the formation of a casting surface for films in the form of a strippable unstripped film.

Still another object of the invention is the casting of a prolamine base film onto a strippable unstripped film of cellulose ester base.

A further object of the invention is the formation of a duplex film of which one layer is a prolamine base film.

Still another object of the invention is the formation of a triplex film of which the inner layer is a prolamine base film.

Various other and ancillary objects and advantages of the invention will be apparent from

the following description and explanation of the invention.

In the accompanying drawing there is shown diagrammatically a representation of the invention and the process.

Fig. 1 represents a casting surface of cellulose ester film itself cast on and remaining unstripped from a solid smooth surfaced body.

Fig. 2 represents the cast of Fig. 1 after a second film has been cast thereon, and also shows the united films being stripped from the solid body.

Fig. 3 represents the form of Fig. 2 with a third film applied before the stripping operation.

In carrying out the invention a smooth surfaced body of glass, polished metal or stone may be employed as a solid cast. This may be flat as a plate for making sheets or curved as a cylinder for forming continuous sheets, or some suitable form from which a non-adherent film cast thereon may be stripped without destroying the continuity of the film. In the drawing a flat form 10 is illustrated. Onto the cast 10 I form a film of any suitable material, necessarily characterized by ability to strip readily from the cast 10. A very thin or thick film may be formed, and it may be formed by setting of a mass, or by the evaporation of a solvent from a solution applied to the surface 11 of cast 10. The film is designated 12 and its surface is designated 13. The coated cast 10 thus forms a new cast for the second film and a new casting surface 13.

Onto the new casting surface 13 I form a second film 14 characterized by ability to adhere to the film 12. The new film 14 may be set from a mass applied, or may be formed by applying a solution to the surface 13 and evaporating solvent from the solution. In the latter event, the solvent may be such as to soften or partially dissolve the material of film 12, but this is not necessary if adherence is otherwise obtained or naturally results from the nature of the materials.

When the new or second film 14 is dried the two films, which are now united, may be stripped as one film from the solid cast 10. The product is a duplex film with layers of different materials on the two sides.

If desired a third layer 15 may be applied to layer 14 before the stripping operation as shown in Fig. 3. The third layer may be the same or different from the first layer 12. It is preferred to make it the same as the first film so that the resulting triplex product may have a heavy middle layer as a body, and similar thin coating layers for special surface properties. In

the drawing the three layers are designated film A, film B and film C.

In actually carrying out the invention I have applied it by using as film B a prolamine base film, as of zein, hordein or gliadin. Such films may be formed from aqueous alcoholic solution and have a tendency to adhere to glass, polished metal, etc. I have found, however, that the tendency of prolamine solutions to adhere in film-formation, is dependent upon many factors, and is not easily predictable. The character of solvent, the concentration, the presence of plasticizers, the presence of anti-blushing agents and of other modifying agents, the character of the casting surface, the temperature of drying, etc., are all factors affecting this property of adherence or of stripping a formed film.

I have also found that film-forming prolamine base solutions which do and which do not strip easily have the power of adhering to other cast films, particularly to cellulose ester base films. This is more particularly true when the cellulose ester base film contains material, preferably the cellulose ester base itself, which is softened by or which is soluble in solvent material used in the film-forming prolamine solution.

In practice, therefore, I use a cellulose ester base film as a casting surface for a prolamine base film. I prefer a cellulose ester film which gives valuable surface properties to the resulting product.

The following formulas are suitable for film A:

#### Formula No. 1

|                                   | Parts by weight |
|-----------------------------------|-----------------|
| Alcohol soluble cellulose nitrate | 1               |
| Ethylene glycol monoethyl ether   | 10              |
| Ethyl alcohol                     | 90              |

#### Formula No. 2

|                   | Parts by weight |
|-------------------|-----------------|
| Cellulose acetate | 1               |
| Ethyl lactate     | 10              |
| Acetone           | 90              |

These solutions may be applied onto glass, polished metal and the like, and will dry in about 5 minutes at 125° F. The examples show quick drying solvents such as alcohol and acetone, and also slowly volatile high-boiling solvents. Upon loss of the highly volatile solvent about 10% of the original solution remains as a dry solid. It is set and non-tacky but is not a strong tenuous film, inasmuch as it has only about 10% ester in its make-up. The rest is plasticizing solvent which can be lost by seasoning or further exposure. Presence of some of this higher boiling solvent assures strippability of the film, but not until it is reinforced by the film to be cast upon it. It does not matter what composition the film has, because the essential requirement is its strippability. The solution is preferably applied to form a film about 0.00005 to 0.0001 inch in thickness. If it is too thin, it may dissolve in the solvents of the applied prolamine composition. It is to be understood that the thickness of the film above specified is given only by way of example, and is not to be considered as any essential limitation. Formula No. 1 is preferred for the prolamine compositions hereinafter given because both have the same solvents and one recovery system may be employed. Proofing agents may be added to the formulas, as by following the general disclosures of the Charch and Prindle U. S. Patents Nos. 1,826,697 to 1,826,699. Where formulas like those of Charch and Prindle are

used for proofing compositions to be applied to prolamine films already formed and stripped, it is advisable to omit ethyl alcohol or other alcohol, which is a quick solvent for zein, or it will cause the zein film to stretch and curl. Thus, where film C is to be applied to film B, it is preferred to apply the composition for film C before the stripping operation. In such case the precaution as to the alcohol need not be so fully observed.

*Prolamine film.*—For the prolamine film I may use zein, hordein or gliadin bases. Using zein, the following composition is suitable. To 75 parts by weight of 12% zein solution in a solvent consisting of 70% of ethyl alcohol and 30% of water, or to any equivalent solution, I may add a leveling solvent, preferably 10 parts by weight, such as ethylene glycol monoethyl ether. As a plasticizer I may add 2 parts by weight of dibutyl tartrate. As an anti-blushing agent, I may add on the basis of zein 2% to 3% of material such as monoethanolamine salt or monopropanolamine salt, such as an acetate or lactate salt. In addition there is added a protein fixative such as 2.5 parts by weight of 37% formaldehyde solution, or a small quantity of glyoxal. This composition may be spread to dry onto the film A, to form film B.

In the above description it is to be understood that many variations of the zein solution are permitted, and some of these are given in full in my copending application Serial No. 701,863, filed December 11, 1933. All the disclosures for prolamine base compositions therein given are hereby incorporated by reference in this application.

In the example above given the use of fixing agent such as formaldehyde aids in producing a strippable film, yet its use is not to assure strippability. When fixing agent is not used it is usually impossible to strip a film from the casting surface. Therefore, when a prolamine base film B is to be cast onto a strippable film A, adherence of B to A may be increased by reducing the quantity of fixing agent even to the point of omission. It is therefore readily apparent that film A need not contain substance soluble in or softened by solvent used in the forming composition for a prolamine film B.

The solutions used for prolamine contain considerable water. Since prolamines are not soluble in water or in alcohol, but only in aqueous alcohol, it is necessary to guard the solvent for prolamine from dilution to such extent that it becomes a non-solvent. Thus, the strippable film is first dried to assure that residual solvent content therein does not alter the prolamine solvent and precipitate prolamine at the interface. Another advantage of dryness for the strippable film lies in the fact that the dry film is more slowly affected or penetrated by solvent of the prolamine, compared to a still-wet strippable film.

I claim:

1. The method of forming a prolamine base film with a surface coat thereon which comprises forming a dry solid strippable film of cellulose ester base on a solid casting body with a surface from which the said film may be readily stripped, casting a prolamine base film onto said first-formed film in adhesive union thereto, and stripping the united films as a single body from the solid casting body.

2. The method of forming a prolamine base film with a surface coat thereon which comprises forming a dry solid strippable film of cellulose

ester base on a solid casting body with a surface from which the said film may be readily stripped, casting a prolamine base film onto said first-formed film in adhesive union thereto, forming  
5 a third film of cellulose ester base on said prolamine base film in adhesive union thereto, and stripping the united films as a single body from the solid casting body.

3. The method of forming a prolamine base  
10 film with a surface coat thereon which comprises forming on a surface of a solid casting body a dry solid strippable film of cellulose ester base which is softened by or soluble in an alcohol solvent, the casting surface of said body being  
15 such as to permit stripping said film without destroying the continuity thereof, casting onto said film a film-forming solution of prolamine base and alcohol solvent which is a softener or solvent for said cellulose ester base, drying out the solvent  
20 whereby to form a prolamine base film in adhesive union with the cellulose ester base film, and stripping the united film as one body from the solid casting body.

4. The method of forming a prolamine base  
25 film with a surface coat thereon which comprises forming on a surface of a solid casting body a dry solid strippable film of cellulose ester base which is softened by or soluble in an alcohol solvent, the casting surface of said body being  
30 such as to permit stripping said film without destroying the continuity thereof, casting onto said film a film-forming solution of prolamine base and alcohol solvent which is a softener or solvent for said cellulose ester base, drying out the solvent  
35 whereby to form a prolamine base film in adhesive union with the cellulose ester base film, forming a third film by casting on the prolamine base film a cellulose ester base composition con-

taining prolamine solvent, evaporating the solvent from the third film, and stripping the united film as one body from the solid casting body.

5. The method of forming a zein base film with  
5 a surface coat thereon which comprises forming a dry solid strippable film of alcohol-soluble nitrocellulose base on a solid casting body with a surface from which the said film may be readily stripped, coating an alcoholic solution of zein  
10 base film-forming composition onto said nitrocellulose film, drying out the volatile solvent of said zein composition, and stripping the resulting united films together as one body from the solid casting body.

6. The method of forming a zein base film with  
15 a surface coat thereon which comprises forming a dry solid strippable film of alcohol-soluble nitrocellulose base on a solid casting body with a surface from which the said film may be readily stripped, coating an alcoholic solution of zein  
20 base film-forming composition onto said nitrocellulose film, drying out the volatile solvent of said zein composition, casting on the zein film a third film of base composition different from the zein base film, and stripping the resulting united  
25 films together as one body from the solid casting body.

7. The method of forming a zein base film with  
30 a surface coat thereon which comprises forming a dry solid strippable film of cellulose acetate base on a solid casting body with a surface from which the said film may be readily stripped, coating a solution of zein base film-forming composition onto said cellulose acetate film, drying out  
35 the volatile solvent of said zein composition, and stripping the resulting united films together as one body from the solid casting body.

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