

## UNITED STATES PATENT OFFICE

2,176,903

## MANUFACTURE OF NONFIBROUS FILM

Emmette F. Izard, Kenmore, N. Y., assignor to  
E. I. du Pont de Nemours & Company, Wil-  
mington, Del., a corporation of Delaware

No Drawing. Application October 22, 1936,  
Serial No. 107,054

12 Claims. (Cl. 260—32)

This invention relates to the production of nonfibrous film, such as by casting a film-forming solution onto a surface, for example, a metal casting wheel. More particularly, it relates to the production of such film by dry or evaporative methods.

In the dry method of casting film, a suitable solution of a film-former is spread or flowed upon a casting surface and the solvents removed therefrom by evaporation. One of the most commonly employed methods is to dissolve a sufficient amount of film-former in appropriate solvents to secure a solution or dope of the proper composition and viscosity and to feed this dope from a hopper, regulated to give the desired thickness, upon the surface of a slowly rotating casting wheel. The dope flows out upon the surface of the wheel as the latter rotates a current of air or other suitable evaporative medium is brought in contact with the film thus formed to evaporate the solvent therefrom. Before the wheel has rotated through a complete revolution most of the solvents have evaporated and the film is sufficiently self-sustaining to be stripped from the surface of the wheel and to be subjected to a curing treatment to further reduce its residual solvent content and to bring its shrinkage characteristics within the desired range. The cured film is finally wound on a mandrel to form a mill roll of suitable size.

In dry casting, however, depending upon the character of the particular film-former and upon the nature of the given casting surface, a film is formed which adheres relatively tenaciously to the casting surface. In commercial casting, this adherence or cohesion of the film to the casting surface, which is particularly tenacious in the case of certain film-formers, has been the source of a number of direct and indirect difficulties. Thus, this cohesion makes it somewhat difficult to strip the films from the casting surface and often necessitates the exertion of a strong pull which produces an excessive strain on the films to such an extent that sometimes thin films tear and interrupt the casting operation. In the case of thick film or relatively thick plastic sheets, the resistance to stripping exerts a stretching action which produces undesirable irregularities in the thickness of the film. Again, the tenacious adherence in certain cases has a tendency to tear off minute particles of metal from the casting surface which eventually results in the formation of irregularities on the casting surface with corresponding imperfections in the films cast thereon. However, of all the difficulties caused

by the adhesive tendency of the film towards the casting surface, "strip chattering" is probably the most important and of the most concern. "Strip chattering" is a term employed to denote a type of film defect distinguished by characteristic transverse markings or lines appearing at regularly or irregularly spaced intervals along the length of the film. Strip chattering naturally detracts from the appearance of the film and renders it undesirable as a first quality product. Strip chattering is apparently caused in a great many cases by the film being stripped from the casting surface in a jerky or spasmodic manner due to the above mentioned strong adhesive power of the film for the casting surface.

It is therefore an object of the present invention to secure films which may be stripped from a casting surface without marring the films or said casting surface.

Another object is to improve the stripping quality of the film to the extent that strip chattering defects are substantially eliminated.

A further object of the invention is to improve the stripping characteristics of films without substantially impairing the transparency, gloss and clarity thereof.

Other objects are disclosed hereinafter.

These objects are accomplished by incorporating into a film-forming dope a suitable amount of a waxy amine or salt thereof.

To facilitate clear understanding of the invention a few examples will now be given, but it is to be understood that they are illustrative only and are not to be considered limitative.

*Example I*

Twenty-five grams of octadecyl amine (commonly called stearylamine) are thoroughly and uniformly incorporated into a casting dope of the following composition:

|                        | Grams |
|------------------------|-------|
| Cellulose acetate..... | 1,000 |
| Dibutyl phthalate..... | 250   |
| Acetone.....           | 3,750 |
| Water.....             | 75    |

The resulting solution is delivered by means of a metering pump to a casting hopper which is maintained at a suitable temperature. By means of the hopper, a thin layer of the composition is deposited on the highly polished surface of a casting wheel. As the latter revolves, the layer is smoothed to a uniform thickness by a doctor knife, which latter may, if desired, be

one of the edges of the hopper. Alternatively, the hopper may be provided with an extrusion orifice in the shape of an elongated slit of adjustable width, serving to deposit a predetermined amount of casting composition on the surface of the wheel, which is caused to rotate at a peripheral speed commensurate to the linear extrusion speed. In either case, the wheel surface is maintained at a temperature of about 32 to 35° C.

As the wheel revolves, the smooth uniform layer of casting composition emerges from the casting chamber into a drying chamber which encloses the casting wheel. Air passing through the drying chamber, at a temperature of about 70–80° C. or higher removes the solvents from the composition so that after approximately four-fifths of a revolution of the wheel, a film is secured which is fairly well set. The cellulose acetate film, containing approximately 1.7–2.0% by weight of stearylamine, is stripped with considerable ease from the wheel surface and is carried over suitable rolls to a conditioning chamber through which air is passed at a suitably elevated temperature and relative humidity to effect substantially complete removal of any residual solvent. The film is led from the conditioning chamber over one or more rolls and wound on a suitable core or mandrel. Optionally, it may be cut off at predetermined intervals to produce a "cut-to-size" sheeted stock.

#### Example II

One kg. of polymerized vinyl acetate in the form of a colorless resin is introduced into a container provided with an agitation system. To this is added one liter of water, 200 grams of ethyl alcohol, and 2 kg. of hydrochloric acid of 22–23° Baumé. The mixture is permitted to set for a period of approximately 5 hours, at the end of which time the mass becomes thoroughly homogeneous. Five hundred grams of paraldehyde are then added and the thickened mass is rendered homogeneous by agitation. The mass is again permitted to set for approximately 5 hours, after which the polyvinyl acetal condensation product is precipitated by the gradual addition of water. The precipitated product is washed in the cold and dried in the open air at low temperature. The product may be bleached if necessary and is soluble in the usual solvents, particularly alcohol, methyl acetate and chloroform.

Seventeen hundred eighty-five grams of a polyvinyl acetal condensation product, prepared as above, are thoroughly agitated with 9 grams of stearylamine, 200 grams of dibutyl phthalate, and 9,000 grams of a solvent mixture consisting of methylene chloride, benzene and methyl alcohol. The thoroughly mixed solution is converted into film by a procedure analogous to that of Example I, except the casting surface is maintained at a temperature of about 40 to 60° C. The resulting film contains approximately 0.3 to 0.4% by weight of stearylamine and strips readily from the casting surface.

#### Example III

Six hundred grams of potassium hydroxide are dissolved in 500 grams of ethyl alcohol in a vessel equipped with a stirrer. To this solution are added, with thorough agitation, 800 grams of ground polymerized vinyl acetate prepared by polymerizing vinyl acetate with the aid of benzoyl peroxide. After agitating about ½ hour, the polyvinyl acetate saponifies and precipitates as polyvinyl alcohol, which is separated on a filter, washed with ethyl alcohol, and dried. Two thou-

sand grams of polyvinyl alcohol, prepared in the above manner, and 13 grams of stearylamine acetate are added to a composition consisting of 8,000 grams of water, 260 grams of glycerin and 3 grams of acetic acid. The mixture is heated to a temperature of 90–97° C. and while at that temperature, is thoroughly agitated for a period of 3 hours. The solution is filtered and delivered by means of a metering pump to a casting hopper which is maintained at a suitable temperature.

The solution is converted into film by a method comparable to that of Example I, except that the casting surface is maintained at a temperature of 85 to 90° C. while the air passing through the drying chamber is kept at a temperature of approximately 200° C. The resulting film contains approximately 0.4–0.5% by weight of stearylamine acetate, and strips without difficulty from the casting surface. The presence of stearylamine acetate also facilitates wetting of the casting surface by the aqueous film-former and thereby enhances the ease of securing a thin film of uniform gage.

In the above examples, the films have been formed by what is commonly known as a wheel casting method. A continuous band casting method can be used if appropriate consideration is given to the required casting conditions and similarly, a discontinuous plate casting method can be utilized advantageously for certain purposes.

In the above examples, polyvinyl acetal compounds and cellulose acetate have been cited as typical examples of the incorporation of a waxy amine in a film-forming dope, wherein a volatile, organic liquid is employed as the solvent. It will, however, be recognized by those skilled in the art that the process is broadly applicable to the dry casting of any film-former dissolved in a volatile, organic solvent wherein it is desired to facilitate the stripping operation by the incorporation of a waxy amine that does not react detrimentally with the film-former and is soluble in the solvent or mixture of solvents employed. Thus, the process may be applied in casting cellulose propionate, cellulose aceto-propionate, cellulose aceto-butyrate, cellulose aceto-stearate, cellulose crotonate, or other simple and mixed cellulose esters; also in casting ethyl, butyl, benzyl, or other cellulose ethers, and in casting resinous films, such as ether resins, polymerized vinyl compounds, interpolymerized vinyl chloride-vinyl acetate compounds, and polymerized acrylate and/or methacrylate compounds. The condition of casting and conditioning the film will, of course, be suitably regulated and adjusted to meet the needs of the individual case.

Furthermore, in the case of cellulose acetate, it is immaterial whether the combined acetic acid content of the ester is relatively high or relatively low as long as the ester is soluble in organic solvents. Thus, the stearylamine may be incorporated in a chloroform solution of cellulose acetate having a combined acetic acid content of 62.5% or in an acetone solution of cellulose acetate having a combined acetic acid content of 54% or less, with equal advantage. Likewise, stearylamine may be utilized in the case of any polyvinyl acetal condensation product that is soluble in an organic solvent. Thus, the polyvinyl acetal film-former may be one obtained by the reaction of other aldehydes, such as formaldehyde, propionaldehyde, butaldehyde, or benzaldehyde with a partially or completely hydrolyzed

polyvinyl acetate ester as exemplified in U. S. Patents Nos. 2,036,092 and 2,035,939.

In the above examples, polyvinyl alcohol has been given as a typical application of the incorporation of a stearylamine derivative in a film-forming dope wherein the solvent is water or aqueous in nature. The waxy amine derivative will produce comparably good results when incorporated into aqueous solutions of gelatin, casein, lowly etherified methyl cellulose, or other lowly etherified or esterified cellulose derivatives such as cellulose acetophthalate, cellulose acetotartrate, or other water-soluble film-formers. The conditions of casting and conditioning the film are of course suitably regulated to fit the peculiarities of the given film-former.

In the case of film-formers dissolved in organic solvents, it will be noted that stearylamine is employed as the free base. In the case of film-formers dissolved in aqueous media, on the other hand, the stearylamine is conveniently employed in the form of a water-soluble salt derivative, such as the acetate, lactate, or hydrochloride. It is thought probable that the stearylamine salt decomposes partially or completely to stearylamine during the casting and/or conditioning of the water-soluble film.

The amount of stearylamine or derivative thereof necessary for good stripping varies according to the particular nature of the film-former to be cast and the particular casting conditions to be followed. In the preferred embodiment of the invention, only a relatively small amount of a waxy amine or salt thereof is employed. Large amounts will unduly increase the cost of the product, will tend to cause haze or opacity when the film-forming material is not completely compatible with the waxy amine, may impart odor and taste to the film, and may cause the film to strip from the support in advance of the time desired. In general, amounts less than 5% based on the weight of the film are desired. In the case of cellulose acetate, an amount of stearylamine corresponding to 1.5-3.0% by weight of the film is preferably incorporated in the casting dope, but quantities of 4% or more of stearylamine may be added, if desired. In the polyvinyl acetal type of film-former, an amount of stearylamine corresponding to 0.25-0.50% by weight of the film is preferably incorporated in the casting dope, but quantities of 1% or more may be added, if desired. In the case of polyvinyl alcohol, an amount of stearylamine corresponding to 0.25-0.50% by weight of the film is preferably incorporated in the casting dope, but quantities of 1% or more may be added, depending on the ease of stripping desired.

While stearylamine (octadecyl amine) or its salts are preferred, other waxy amines and salts thereof may be used as strip agents with satisfactory results. Thus, cetyl amine and lauryl amine (dodecyl amine) and their water-soluble salts may be substituted. Generally speaking, depending of course upon the nature of the particular film-former, any waxy amine, particularly aliphatic amines, may be used satisfactorily as a strip agent provided its molecular weight is not so high that the amine is insoluble in the casting dope, nor so low that the amine is not solid at ordinary temperatures (25° C.).

The film-forming dopes in addition to stearylamine or its salts may have also present other modifying agents such as plasticizers, pigments and dyes. The dyes may be selected either for the purpose of coloring the films or for the pur-

pose of improving the transparency of the films by neutralization of any coloration that may be present. In certain cases, suitable deodorizing substances may be added to mask any undesirable odor that may be present. With polyvinyl alcohol, water soluble dimethylolurea or urea formaldehyde in an amount of 15 to 20% by weight of the finished film may be incorporated in the film-former, with beneficial results.

The advantages of the invention are obviously many. The fact that the film strips easily and readily from the casting surface means that the highly undesirable strip chattering defects are substantially eliminated. In the dry casting of thick film at relatively high rates of speed, the film peels so readily from the casting surface that substantially no undesirable stretching occurs, even though the film retains considerable solvent and is plastic. Film, and particularly thick film, can be cast at higher rates of speed. Another distinct advantage of the invention is that waxy amines are soluble in most organic solvents customarily used to dissolve film-forming compositions. Likewise, waxy amine salts are soluble in water, and can therefore be used as strip agents for film cast from aqueous solution. Furthermore, these waxy amines and salts thereof do not interfere with the good transparency, gloss and clarity of the film, which are essential requirements for a commercial article.

Under certain conditions, the waxy amine or salt thereof may be applied directly to the casting surface, such as by means of a brush or other spreading device. Care must be taken, however, that uniform distribution in the proper quantity is secured and that proper precautions be taken to replenish the supply of strip agent as it is removed from the support.

Any other variation or modification of the invention as described, which conforms to the spirit of the invention, is intended to be included within the scope of the claims.

I claim:

1. A solution comprising polyvinyl alcohol, water and a salt of octodecyl amine.
2. A solution comprising a polyvinyl alcohol, water, and octodecyl amine acetate.
3. A solution comprising essentially 2,000 parts polyvinyl alcohol, 8,000 parts water, 260 parts glycerin, 3 parts acetic acid and 13 parts octodecyl amine acetate.
4. A solution comprising cellulose acetate, an organic solvent and octodecyl amine.
5. A solution comprising essentially 1,000 parts cellulose acetate, 3,750 parts acetone, 250 parts dibutyl phthalate, 75 parts water and 25 parts octodecyl amine.
6. A solution comprising polyvinyl acetal, an organic solvent, and octodecyl amine.
7. A solution comprising essentially 1785 parts polyvinyl acetal, 9000 parts organic solvent therefor consisting of methylene chloride, benzene and methyl alcohol, 200 parts dibutyl phthalate, and 9 parts octodecyl amine.
8. A solution capable of being dry-cast to form a solid self-sustaining film, said solution containing a substance taken from the class consisting of normally solid primary alkyl amines of high molecular weight hydrocarbons and salts thereof, said substance being soluble in said solution, said substance being present in sufficient quantity to improve the stripping characteristics of the film, but in insufficient quantity to materially affect the transparency of the resultant film.
9. An aqueous solution capable of being dry-

cast to form a solid self-sustaining film, said solution containing a water-soluble salt of a normally solid primary alkyl amine of a high molecular weight hydrocarbon, said salt being present in sufficient quantity to improve the stripping characteristics of the film, but in insufficient quantity to materially affect the transparency of the resultant film.

10. An aqueous solution capable of being dry-cast to form a solid self-sustaining film, said solution containing a water-soluble salt of octodecyl amine, said salt being present in sufficient quantity to improve the stripping characteristics of the film, but in insufficient quantity to materially affect the transparency of the resultant film.

11. An organic solvent solution capable of being

dry-cast to form a solid self-sustaining film, said solution containing octodecyl amine, said amine being soluble in said solvent, said amine being present in sufficient quantity to improve the stripping characteristics of the film, but in insufficient quantity to materially affect the transparency of the resultant film.

12. An organic solvent solution capable of being dry-cast to form a solid self-sustaining film, said solution containing a normally solid, primary alkyl amine of a high molecular weight hydrocarbon, said amine being soluble in said solvent, said amine being present in sufficient quantity to improve the stripping characteristics of the film, but in insufficient quantity to materially affect the transparency of the resultant film.

EMMETTE F. IZARD.