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FILM

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This invention relates to the stripping of poly-
vinyl alcohol films cast by the evaporation
method, especially continuous webs, from the
casting surface. More particularly it appertains
to the incorporation of long chain fatty acid
salts, such as ammonium stearate, in water sol-
uble polyvinyl alcohol casting dopes, to facilitate
separation of the cast film from casting wheels.

The conventional details of the evaporative
casting of continuous films of organic solvent
soluble cellulose substitution derivatives are dis-
closed in U. S. A. Patents Nos. 1,458,592 (Olson)
and 2,176,903 (Izard). In general such proce-
dures involve the laying of a film of dope (solu-
tion of the cellulose derivative) on to a casting
wheel mounted for rotation and arranged for the
removal of the solvent from the dope during its
rotation. The means for the solvent removal may
include heating the surface of the wheel or sur-
faces adjacent thereto, together with devices such
as fans for carrying the solvent or solvent-laden
atmosphere away from the film. Ordinarily the
speed of the wheel and the degree of heating
are adjusted so that the desired amount of sol-
vent is removed in somewhat less than one revo-
lution of the casting wheel. Nickel, chromium,
stainless steel and other metals and alloys are
generally used for surfaces of the casting wheels.

In attempting to carry out a continuous cast-
ing operation of this type with dopes consisting
of polyvinyl alcohol and a solvent therefor, it
was found that the adhesion between the par-
tially dried polyvinyl alcohol film and the cast-
ing surface was a frequent source of trouble.
It caused the film to break or tear at the place
where the film was being stripped from the wheel.
This action was especially troublesome at the
edges of the film. Even when the film did not
tear or break, distortion and deformation were
quite common due to the high tension required
for pulling the film away from the casting
surface.

A type of material has now been discovered
which greatly decreases the adhesion between
such partially dried film and the metal casting
surface. With the preferred members of the
group the adhesion is reduced to such an extent
that only a very slight tension is required to
strip the film from the casting surface.

This invention had for an object the manu-
facture of transparent, strong and flexible poly-
vinyl alcohol sheets or films which were un-
deformed and/or undistorted and/or unmarred,
and the production of compositions of matter
suitable for the casting thereof. A further ob-

ject was to dry cast water soluble polyvinyl alco-
hols into thin, strong, smooth, flexible sheets
capable of being easily stripped from the casting
wheel while retaining 5% to 15% of the solvent
of the casting dope. Further objects were to
devise a means of decreasing the adhesion be-
tween a dry (or evaporative process) cast, water
soluble, polyvinyl alcohol and the casting sur-
face, to facilitate the removal of partially dried,
dry cast, polyvinyl alcohol from casting wheels
and belts, and to find materials which could be
added to polyvinyl alcohol dry casting solutions
to make removal of the film easy when only a
small proportion of the solvent remains. A gen-
eral advance in the art, and other objects which
will appear hereinafter, are also contemplated.

It has now been discovered that the salts of
fatty acids containing more than 6 carbon atoms
may be incorporated in casting dopes with the
result that the film formed therefrom can be
easily and satisfactorily removed from the cast-
ing surface.

From the following description and specific
examples, in which are disclosed certain embodi-
ments of the invention as well as details of what
is believed to be the best mode for carrying out
the invention, it will be apparent how the fore-
going objects and related ends are accomplished.
The parts are given by weight throughout the
application, unless otherwise specified.

Example I

To a solution containing 20% polyvinyl alcohol
dissolved in water, was added 3% (based on the
polyvinyl alcohol present) sodium oleate. Film
was cast from this solution onto a nickel sur-
face and dried thereon. It possessed only a
slight adhesion to the nickel surface, as compared
to film cast from a similar polyvinyl alcohol solu-
tion to which no sodium oleate had been added.
The sodium salts of lauric, myristic, palmitic,
and stearic acids, singly and in combination,
gave similar results.

Example II

A film was prepared from a dope consisting of
19% of polyvinyl alcohol (hydroxyl 95%, acetyl
5%), and 81% of water. Into this dope there
was uniformly incorporated 2.5% (based on the
solids content of the dope) potassium oleate.
The resulting material was cast on a stainless
steel casting wheel, and all but 5% of the non-
solids (the water) was evaporated, and the re-
sulting film stripped from the casting wheel. It
stripped very easily compared with a similar film

containing no stripping agent. The film obtained was highly transparent and durable. Similar results were obtained with the potassium salts of lauric acid, dodecanesulfonic acid, myristic acid, palmitic acid and stearic acid.

Example III

A dope was prepared consisting of 15.8% of polyvinyl alcohol (hydroxyl 99%, acetyl 1%) and 84.2% of water. To this dope there was added 3% (based on the non-volatile materials in the dope) of triethanolamine stearate. A thin layer of this dope was cast on a nickel casting wheel and the volatile solvent evaporated. A glass-clear, transparent film .001 inch thick, especially suitable for purposes which require sewing with a close stitch such as 10, 20, 30 or more stitches to the inch, without substantially weakening or tearing the film resulted. It was easily stripped from the casting surface. Similar results were obtained with other alkyl-amine acid salts such as the triethanolamine, laurates, myristates, palmitates and oleates. The corresponding monoethanolamine and diethanolamine salts were also very satisfactory.

Example IV

A dope consisting of 17% of polyvinyl alcohol (hydroxyl 97%, acetyl 3%) and 83% of water was cast in a continuous manner upon the polished surface of a large diameter chromium-surfaced drum. Before casting 3% (based on the film-forming material (of benzyl-trimethyl ammonium myristate was incorporated in the dope. Upon evaporation of the solution a highly transparent and durable film was obtained, which was easily (compared with the same composition when no stripping agent was present) stripped from the casting drum. Similar results were obtained with other alkylamine fatty acid salts, such as benzyl-trimethyl ammonium laurate, palmitate, oleate and stearate.

Example V

Six hundred (600) parts of potassium hydroxide were dissolved in 500 parts of ethyl alcohol in a vessel equipped with a stirrer. To this solution was added, with thorough agitation, 800 parts of ground polymerized vinyl acetate prepared by polymerizing vinyl acetate with the aid of benzoyl peroxide. After agitating for about one-half hour, polyvinyl acetate saponified and precipitated as polyvinyl alcohol. This was separated on a filter, washed with ethyl alcohol and dried. Two thousand (2000) parts of polyvinyl alcohol prepared in the above manner, and 13 parts of lithium palmitate (ammonium palmitate gives excellent results also) were added to a composition consisting of 8000 parts of water, 260 parts of glycerin. The mixture was heated to a temperature of 90°-97° C., and while at that temperature was thoroughly agitated for a period of 3 hours. The solution was filtered and delivered, by means of a metering pump, to a casting hopper maintained at a suitable temperature.

The solution was converted into a film by flowing the dope onto the polished nickel surface of a rotating casting wheel 6 feet in diameter, maintained at 85°-90° C. As the casting wheel revolved, the layer of dope was smoothed to a uniform thickness by a doctor knife. With continued turning of the wheel the smooth uniform layer of casting composition emerged from the casting chamber into a drying chamber (which enclosed a portion of the casting wheel). Air passing

through the drying chamber at a temperature of approximately 200° C. removed the solvent from the composition, so that after approximately $\frac{1}{2}$ of a revolution of the wheel a film, which was fairly well set, was secured. The resulting film containing the stripping agent stripped without difficulty from the casting surface, and was wound into a mill roll for further processing.

Example VI

A film was prepared by evaporating the solvent from a composition consisting of 18% polyvinyl alcohol (hydroxyl 92%, acetyl 8%) and water 82%, to which had been added lithium oleate. The film, which stripped easily from the polished metal casting surface, was found to be extremely durable and not to tear readily under a wide variety of temperature. Similar results were obtained with the lithium salts of lauric, myristic, palmitic and stearic acids.

Example VII

A dope consisting of:

	Per cent
Polyvinyl alcohol (Example II type)-----	10
Polyvinyl alcohol (Example III type)-----	5
Water -----	85

in which had been incorporated 2% (based on the polyvinyl alcohol) sodium stearate, was cast continuously on the polished surface of a rotating nickel cylinder six feet in diameter. The volatile materials were evaporated, and the resulting film stripped from the surface of the casting wheel. The film, which had a thickness of .00088 inch, was very clear, could be satisfactorily sewed, and had excellent tear resistance. It was undeformed, unmarred, and undistorted. It was stripped from the casting wheel very easily. Similar results were obtained with corresponding amounts of sodium laurate, sodium myristate, sodium oleate, sodium palmitate, ammonium stearate, ammonium oleate and ammonium palmitate.

Example VIII

A mixture of 3 grams of paraffin wax (M. P. 61°-63° C.), 10 grams of the modified rosin described and defined in U. S. A. Patent No. 2,017,866 (Morton), and 6 grams of monododecyl phthalate was melted at 120° C. and stirred until a clear melt was obtained. To this melt at a temperature of 85°-95° C. was added slowly, with stirring, 10 cc. of concentrated ammonium hydroxide. The mixture was diluted with water until the total weight was 100 grams, and then passed through a colloid mill at 65°-75° C. until the particle size of the dispersed wax had been reduced to less than 1.5 microns. After the dispersion had cooled to room temperature and the foam had been removed, the dispersion was added to a solution of 80 grams of polyvinyl alcohol and 4 grams of ammonium stearate in 480 grams of water. This mixture was stirred until uniform and then allowed to stand until the bubbles had disappeared, when it was ready for casting into sheets or films.

Sheeting prepared from the above composition and formed into a film by the method hereinafter described, was found to have a moisture permeability of 250-275 when determined by the method set out in U. S. A. Patent No. 2,147,180 (Ubben). The composition was delivered by means of a metering pump to a casting hopper which was maintained at a temperature substantially equal to that of the casting composi-

tion, for example, about 80°-95° C. By means of the hopper a thin layer of the composition was deposited on the highly polished surface of the casting wheel as the latter revolved, the layer being smoothed to a uniform thickness by a doctor knife. The wheel surface was maintained at a temperature of about 80°-95° C.

The hopper was located in the casting chamber in which the atmosphere was quiescent, and was maintained at a temperature of about 80°-95° C. The advancing surface, together with the deposited layer of film-forming composition, emerged from the casting chamber into a drying chamber. Air passing through the drying chamber at a temperature of about 80°-100° C. or higher facilitated the removal of the water from the composition. After a period of 1-10 minutes, depending upon the various factors involved such as velocity and temperature of the drying air, thickness of the desired pellicle, concentration of the film-forming composition, etc., sufficient water was removed to permit the pellicle being stripped from the casting surface. After stripping, the film was carried over suitable rolls through which air was passed at a suitably elevated temperature to effect substantially complete removal of the water and to develop the moistureproof properties of the pellicle to the highest degree. The pellicle was lead from the casting chamber over cooling rolls, after which it was wound on a suitable core or mandrel. The final product had a thickness in the range 0.005 to 0.002 inch.

The dope or polyvinyl alcohol solution containing the strip agents of the invention may be handled and cast in the same manner as the dry casting dopes previously known to the art. The casting dope may contain softening or plasticizing materials such as glycol, glycerol, formamide, acetamide and the like therein.

The most marked decreased in adhesion between the film and the casting wheel surface has been noted when the casting surface was nickel.

In the preferred mode of operation the film is stripped from the casting wheel while it still contains 5% to 15% of the solvent.

This invention is not limited to the polyvinyl alcohols of the specific examples, although it peculiarly appertains thereto. In general it is, with considerable efficacy, applicable to all kinds of polyvinyl alcohols which are soluble in water. The polyvinyl alcohol may be produced in accordance with the methods known to the art, for example, by saponifying, with a 1% solution of hydrochloric acid in ethyl alcohol, a polymeric vinyl acetate, in turn prepared for example, by polymerizing monomeric vinyl acetate by means of 0.5% of sodium perborate and 5% acetic anhydride.

For convenience of consideration, the materials which decrease the adhesion between the dry cast polyvinyl alcohol film and the surface upon which the film is cast and dried (or partially dried), may be divided into two sub-generic groups, namely, alkali amine salts of fatty acids containing more than six carbon atoms, and inorganic salts of fatty acids containing more than six carbon atoms.

The alkyl amine salts of fatty acids comprehended by the present invention are those of fatty acids containing at least seven carbon atoms, and alkyl amines whose hydrocarbon groups contain fewer than eight carbon atoms. Preferably the fatty acids contain 12 to 20 carbon atoms or more. Alkyl amines containing

fewer than three aliphyl carbon atoms are preferred. Especially suitable for the purposes of the present invention are the benzyl trimethyl ammonium salts of lauric, myristic, palmitic, oleic and stearic acids. The results obtained with the triethanolamine, diethanolamine and monoethanolamine salts of the aforementioned acids are also outstanding.

The inorganic salts of fatty acids suitable for use in the operation of this invention are the alkali metal (sodium, potassium, lithium, ammonium, etc.) and like metal salts of fatty acids containing at least seven carbon atoms. Preferably the fatty acids contain from 12 to 20 carbon atoms or more. Especially suitable for the purposes of the present invention are the sodium and potassium salts of lauric, myristic, palmitic and oleic acids, and the ammonium salts of higher fatty acids, for example, ammonium stearate or ammonium palmitate. These compounds are disclosed in my earlier U. S. A. Patent No. 2,284,100.

In the preferred embodiments of the invention the stripping agent is present in an amount within the range of 0.5% to 5% by weight on the basis of the polyvinyl alcohol. Higher concentrations are not excluded, and may be used in order to secure specific results.

The strip agents may be used singly or in any combination, and it is to be understood that the invention is not limited to the specific materials listed above or in the specific examples.

The stripping agents of this invention may be incorporated in the casting dope in any desired manner. If preferred they may be predissolved and the solvent used for dissolving the polyvinyl alcohol. Ordinarily they are incorporated into the solvent simultaneously with the polyvinyl alcohol. In some instances it has been found convenient to add the stripping agent to the solution of the polyvinyl alcohol.

Many of the advantages of the present invention will be apparent from the preceding portion of the specification. Specific mention may be made of the fact that by this invention it is possible to easily, speedily and satisfactorily remove the partially dried, dry cast polyvinyl alcohol film from a metal or alloy casting wheel at elevated temperatures, and that all danger of tearing or deforming the dry cast film at the stripping point (or line) due to the pull required to separate the film from the casting surface has been removed.

The advantage of incorporating in a casting solution a material, such as a conventional sodium or alkyl (including hydroxy alkyl and aralkyl) amine soap, which decreases the adhesion between the polyvinyl alcohol film cast therefrom and the casting surface without unduly affecting the transparency and surface characteristics of the film, will be obvious to those skilled in the art.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A film of polyvinyl alcohol containing, as a strip agent, 0.5% to 5% of a salt of a fatty acid containing at least 7 carbon atoms.
2. The product of claim 1 when the fatty acid contains 12 to 20 carbon atoms.
3. A water evaporative casting solution of

polyvinyl alcohol containing 0.5% to 5% (based on the polyvinyl alcohol present) of ammonium palmitate.

4. An evaporative process casting solution of polyvinyl alcohol containing 0.5% to 5% of salt of fatty acid containing more than 6 carbon atoms, said salt forming radical being an alkali metal.

5. The product of claim 4 when the fatty acid radical contains 12 to 20 carbon atoms.

6. An evaporative process casting solution of polyvinyl alcohol containing 0.5% to 5% of salt of fatty acid containing more than 6 carbon atoms, said salt forming radical being an alkyl amine radical containing fewer than 8 carbon atoms.

7. A film of polyvinyl alcohol containing 0.5% to 5% of an alkali metal salt of a fatty acid containing at least 7 carbon atoms.

8. A film of polyvinyl alcohol containing 0.5% to 5% of an alkali metal salt of a fatty acid containing 12 to 20 carbon atoms.

9. Sheet wrapping material approximately 0.00088 inch thick, comprising essentially polyvinyl alcohol containing 0.5% to 5.0% sodium oleate and 5%-15% water.

10. An evaporative process casting solution comprising essentially water and polyvinyl alcohol and containing 0.5% to 5% (based on the polyvinyl alcohol) of salt of fatty acid containing more than 6 carbon atoms, said salt forming radical being an alkali metal.

11. An evaporative process casting solution comprising essentially water and polyvinyl alcohol and containing 0.5% to 5% (based on the polyvinyl alcohol) of salt of fatty acid containing more than 6 carbon atoms, said salt forming radical being an alkyl amine radical containing fewer than 8 carbon atoms.

12. A water evaporative casting solution of polyvinyl alcohol containing 0.5% to 5% (based on the polyvinyl alcohol present) of salt of fatty acid, the fatty acid radical of which contains at least 7 carbon atoms.

13. A water evaporative casting solution of polyvinyl alcohol containing 0.5% to 5% (based on the polyvinyl alcohol present) of alkali metal salt of fatty acid, the fatty acid radical of which contains at least 7 carbon atoms.

14. A water evaporative casting solution of polyvinyl alcohol containing 0.5% to 5% (based on the polyvinyl alcohol present) of salt of fatty acid, the fatty acid radical of which contains 12 to 20 carbon atoms.

15. A water evaporative casting solution of polyvinyl alcohol containing 0.5% to 5% (based on the polyvinyl alcohol present) of sodium salt of fatty acid, the fatty acid radical of which contains at least 7 carbon atoms.

16. A water evaporative casting solution of polyvinyl alcohol containing 0.5% to 5% (based on the polyvinyl alcohol present) of sodium oleate.

17. A water evaporative casting solution of polyvinyl alcohol containing 0.5% to 5% (based on the polyvinyl alcohol present) of triethanol amine stearate.

18. A water evaporative casting solution containing 20% polyvinyl alcohol and 3% (based on the polyvinyl alcohol present) of sodium oleate.

19. A water evaporative casting solution containing 15.8% polyvinyl alcohol and 3% (based on the polyvinyl alcohol present) of triethanol-amine stearate.

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