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2,183,520

FILM FORMING PROCESS AND PRODUCT

Filed Feb. 15, 1936

FIG. 1.

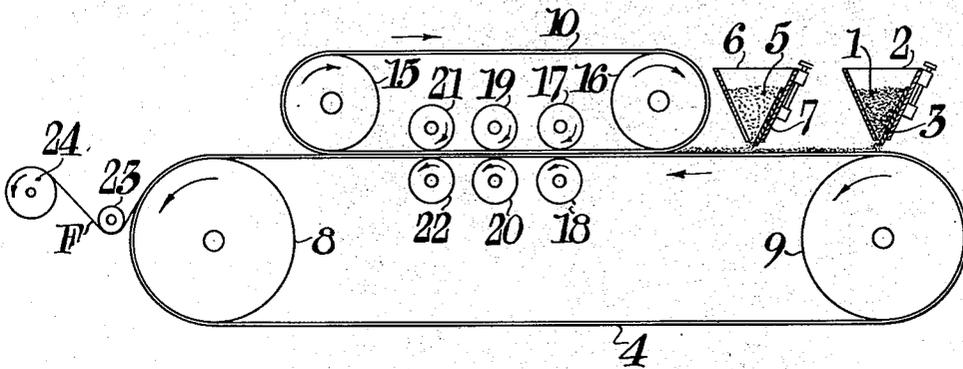


FIG. 2.

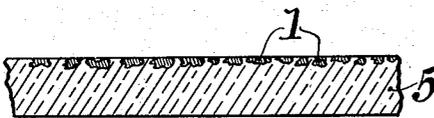


FIG. 3.

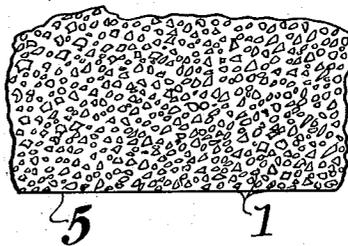


FIG. 4.

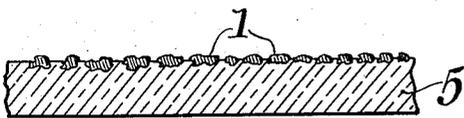
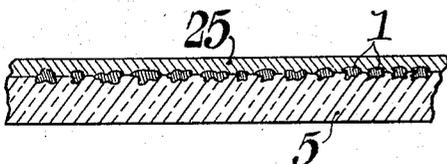


FIG. 5.



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# UNITED STATES PATENT OFFICE

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## FILM FORMING PROCESS AND PRODUCT

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by mesne assignments, to Eastman Kodak Com-  
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Jersey

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5 Claims. (Cl. 18—57)

This invention relates to the production of sheets of cellulose derivatives and similar plastic materials, and more particularly to the production of photographic film and film base.

The customary methods of forming cellulose derivative sheet material, particularly photographic film base, involves depositing in a thin layer on the surface of a slowly moving wheel or band a solution of the desired cellulose derivative in appropriate solvents, coagulation of the material by removal of solvents by evaporation, extraction or otherwise, and finally subjecting the film to a curing treatment to remove residual solvents. This method has certain disadvantages in that it involves the use of costly and somewhat dangerous solvents, necessitates a complicated and expensive solvent recovery system in order to make the method commercially feasible, and has other drawbacks. Sheet and film-makers have long sought a method whereby film might be produced without the use of solvents, but until the advent of the present invention, none has thus far been available. Furthermore, in the manufacture of photographic film, it has been necessary before application of the emulsion, to apply a thin coating or sub of gelatin to the cellulose derivative material, in order to provide a surface to which gelatin can be made to adhere. This has necessitated a separate coating or subbing operation which has involved the use of additional solvents thus adding to the disadvantages attendant on the manufacture of the base itself.

It is the principal object of the present invention to overcome the above-mentioned difficulties and to provide a process of producing sheets or films of cellulose derivatives and other thermoplastic materials without the use of solvents. Another object is the production of a flexible and durable photographic film base which is of such nature that a gelatin emulsion may be made to adhere directly thereto without subbing or other special treatment. A further object is to produce a sensitized photographic film, the sensitive layer of which is attached to the film at innumerable closely adjacent, but distinctly separated, points. A still further object is the production of photographic film having the sensitive layer firmly attached to the film base without the use of undercoats or subs, said film having a high degree of flexibility, but at the same time satisfactory emulsion adherence. Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in its broader aspects, comprises disposing a layer of finely powdered cellu-

lose derivative or other thermoplastic material between two plane surfaces, such as two endless parallel moving metallic bands, and consolidating the powdered material into a continuous sheet by colloidizing under the influence of heat and pressure. By first coating or dusting the bottom band with powdered gelatin or casein or other water-soluble or water-swellable material of a similar nature (preferably compatible with gelatin) and then depositing powdered plastic material and subjecting the whole to heat and pressure, a film base of especially desirable qualities is obtained.

Apparatus suitable for use in carrying out my invention is shown in diagrammatic form in Fig. 1 of the accompanying drawing.

Fig. 2 is a fragmentary section through a thermoplastic sheet produced according to the process of my invention, the component parts thereof being shown in greatly exaggerated proportions.

Fig. 3 is a plan view of Fig. 2, illustrating the manner in which the powder particles are imbedded in the film.

Fig. 4 is a section similar to Fig. 2 illustrating the effect of application of moisture to the material.

Fig. 5 is a section similar to Fig. 4 in which a light sensitive emulsion has been applied and in which the embedded particles of gelatin are illustrated as holding the emulsion securely to the film base.

In the following examples and description, I have set forth several of the preferred embodiments of my invention, but it is to be understood that they are included merely for purposes of illustration and not as a limitation thereof.

In accordance with one form of my invention, cellulose acetate in finely powdered form having mixed therewith an appropriate plasticizer or softener is evenly spread upon a highly polished horizontally moving metal sheet or band. Another similar sheet or band having the required plane surface is disposed over the powder layer and the two sheets having the powder between them are subjected to heat and pressure which colloidizes the cellulose derivative, causing the powdered material to melt or flow together into a solid sheet. Heat and pressure are conveniently applied by passing the material between several sets of heated rollers, each successive set preferably being spaced closer together than the preceding set until the final thickness of sheet desired is obtained. After cooling the sheet is removed in any desired manner.

In order to provide a sheet or film to which a

light-sensitive emulsion will readily adhere, a finely powdered water-soluble or water-swella-  
 5 material, such as gelatin dust, is first dusted or evenly spread over the metal sheet and the powdered thermoplastic material evenly disposed  
 over it. Upon application of heat and pressure the very fine grains of gelatin are imbedded in the surface of the resulting sheet or film to  
 10 produce a material similar to that shown in Fig. 2. When a gelatin emulsion is applied to such a film, the particles of gelatin swell and protrude into the emulsion layer and the sensitive film is thus caused to adhere strongly to the film surface at a multitude of individual but closely adjacent points. This gives a film free of the  
 15 brittleness generally characteristic of films in which the emulsion is attached to the base through the medium of a continuous gelatin sub-layer, the interrupted adhesion giving a very good degree of adherence, yet avoiding brittleness. Gelatin, being transparent, of course does not adversely affect the transparency of the film. Other water-soluble or water-swella-  
 20 materials giving the same effect may be used provided they are compatible with gelatin. Where transparency is no object, opaque or translucent materials may be employed.

To aid in a clear understanding of the invention, I will now describe my process as carried  
 30 out in an apparatus such as disclosed in Fig. 1, but it is to be understood that this represents only one of the preferred methods of operation in accordance with the invention.

Referring to Fig. 1, finely powdered gelatin 1 is placed in hopper 2, provided with a suitable  
 35 gate 3 to regulate the flow of material therefrom, and is evenly and continuously spread in an extremely thin, discontinuous layer upon an endless band 4 of flexible steel, which preferably has a highly polished upper surface. Similarly, finely powdered cellulose acetate 5, in which a plasticizing agent such as diacetin, triacetin, or tripropionin has been incorporated in appropriate amount, is continuously fed through gate 7 of  
 40 hopper 6, and is evenly and continuously spread in appropriate depth over the gelatin. Band 4 is moved in the direction indicated by the horizontal arrow at a uniform speed by pulleys 8 and 9 driven by a source of power (not shown). Above band 4 is a similar but shorter continuous band 10 driven in the same direction by pulleys  
 45 15 and 16 and at the same linear speed as band 4. Upon reaching roller 16, the layer of gelatin and cellulose acetate is compressed between bands 4 and 10, and is there subjected to heat and pressure by means of a series of heated pressure rolls 17 and 18, 19 and 20, and 21 and 22, where the particles become plastic and flow together to form a continuous plastic sheet. These  
 50 rolls are adapted by controllable means (not shown) to be set at any desired distance from each other, the upper and lower rolls preferably being set at progressively decreasing distances with respect to each other in such manner that the film is subjected to greater pressure, thereby becoming progressively thinner as it passes each successive set of rolls. The adjustment of the last set of rolls determines the final thickness of the sheet. The film F is stripped from the band  
 55 4 and wound up on storage roll 24, a chilled roll 23 being interposed, between pulley 8 and the windup, if required, to harden the sheet and facilitate its removal from the band.

It will be apparent that my invention is broadly applicable to the production of sheets and

films from a wide variety of cellulose derivatives and other plastic substances. As typical examples of powdered compositions which may be used for producing sheeting in accordance with the procedure set forth above, the following are  
 5 given:

*Example I*

	Parts by weight	
Cellulose acetate.....	100	
Dimethyl phthalate.....	40	10

*Example II*

	Parts by weight	
Hydrolyzed cellulose acetate propionate.....	100	
Dimethyl phthalate.....	40	15

*Example III*

	Parts by weight	
Hydrolyzed cellulose acetate butyrate.....	100	
Diethyl phthalate.....	40	20

*Example IV*

	Parts by weight	
"Formvar" resin.....	100	
Triphenyl phosphate.....	10	25

*Example V*

	Parts by weight	
"Alvar" resin.....	100	
Dimethyl phthalate.....	10	25

It will, of course, also be apparent that the specific film-forming composition may vary  
 30 solely, depending on the properties desired in the finished film. In general, it may be said that a high degree of flexibility is desired, a fairly high percentage of plasticizer should be employed, whereas, if a less flexible film is required,  
 35 the amount of plasticizer will be correspondingly less. It will of course be evident that a fair percentage of plasticizer is required to provide for colloidizing and molding the material into a sheet or film at moderate temperatures, the higher  
 40 the percentage of plasticizer, the lower may be the film-forming temperature. In any event, the amount of plasticizer should be sufficient to permit molding at temperatures well below the decomposition temperature of the cellulose deriva-  
 45 tive material being used. On the other hand, the percentage of plasticizer should be kept as low as is consistent with a moderate molding temperature in order that the wear, tensile strength and other properties of the film will not  
 50 be adversely affected.

Referring to the drawing, Figures 2 and 3, the sheet produced in the above manner is indicated in cross sectional and surface views, respectively, reference numeral 1 indicating the imbedded  
 55 gelatin particles and 5 a molded cellulose acetate base. In Fig. 4 the gelatin 1 is illustrated as having been swollen with water as would be the case when brought in contact with an emulsion. In Fig. 5 is shown a cross section of the  
 60 same film sensitized with a light sensitive emulsion 25, and indicating how the gelatin particles afford an excellent means for obtaining adherence of the light sensitive layer.

Although the above description refers to the  
 65 preparation of film containing imbedded gelatin, it is obvious that a film composed entirely of cellulose acetate may be prepared in the same manner by eliminating hopper 2. This method may be employed when films or sheets other than  
 70 those adapted for direct emulsion coating are to be produced. In this case it will of course be apparent that film produced in this way may be subbed and emulsion-coated in known manner, if desired. Thus, where a material such as gela-  
 75

tin is not to be imbedded in the sheet, the bands 4 or 10 or both of them may have slightly roughened or embossed surfaces to provide a film having any surface characteristics desired which will afford a slightly roughened but at the same time transparent surface suitable for holding the sensitive layer.

It is apparent that other materials than powdered gelatin or casein may be embedded in a cellulosic support for producing a multiplicity of points to which a coating may be caused to adhere. Obviously, the imbedded powder may be any material that will be so acted upon (as by swelling) by a deposited layer such as a gelatin emulsion. While water-swelling powders have been specifically mentioned as preferred materials, powders swelling in the presence of other solvents may be used as well as powders which are rendered sticky or adherent by partial solvent action. In general I prefer protein substances such as gelatin and casein and as a general rule such substances should be as nearly like gelatin as possible when the product is designed for photographic uses, in order that a satisfactory degree of emulsion adherence may be obtained.

It will also be evident that the finely defined gelatin, casein or similar materials may be applied to sheets made from various materials other than cellulose derivatives, in accordance with my invention. For example, I may apply the gelatin or casein particles to a film produced from various types of resins and the like.

While I have illustrated the application of gelatin and similar materials to sheets or films by the dry method, it is within the scope of my invention to apply this material to a cellulose derivative sheet or film produced from "dopes" of cellulose nitrate, cellulose acetate and other cellulose derivatives in the customary manner. In this variation of my process, the finely defined gelatin or equivalent substance may be dusted onto the coating wheel customarily employed for the production of sheets or films in this manner just prior to deposition of the "dope" on the wheel. In this way the finely divided material will be imbedded in the surface of the sheet as the "dope" congeals, thus producing an extremely thin discontinuous layer of imbedded particles on the finished sheet.

A still further modification of this phase of my invention consists in mixing the finely divided gelatin or its equivalent in appropriate amounts into the dope from which the film is to be made. Of course, in this case the amount of added material is kept down to a point where it will not interfere with the transparency of the film or give rise to any other adverse optical effects.

While I have found it convenient to describe my invention particularly by reference to the production of cellulose acetate films, it is broadly applicable to the production of films or sheets from other cellulose derivatives such as cellulose propionate, cellulose butyrate, cellulose acetate propionate, cellulose acetate stearate, cellulose propionate butyrate and the cellulose ethers. Of the mixed cellulose organic acid esters I prefer the hydrolyzed esters, because of their inherently greater plasticity and the fact that they may be molded or worked at relatively lower temperatures and with a relatively less amount of plasticizer than the unhydrolyzed materials.

My invention also includes the formation of

sheets or films from resinous materials such as vinyl resins, Bakelite, and others. Of the vinyl resins I have found those sold under the trade names Gelva (a polymerized form of vinyl acetate, the preparation of which is described in U. S. Patents 1,241,738, 1,586,803, and 1,710,825), Alvar (an acetal derived from the condensation of partially hydrolyzed polyvinyl acetate with acetaldehyde, the preparation of which is described in U. S. Patents 1,872,834 and 1,971,951), and Formvar (an acetal derived from the condensation of partially hydrolyzed polyvinyl acetate with formaldehyde, the preparation of which is described in British Patent 351,082), of particular value.

It will also be evident that the particular plasticizer employed in my process will depend on the particular cellulose derivative used as the basic material for making the sheeting. Inasmuch as plasticizers for the various cellulose derivatives and similar compounds are known to persons skilled in the art to which the invention relates, no extended discussion of these agents and their use is necessary.

The matter of temperature of the sheet-forming operation is also something which may vary rather widely depending upon the particular cellulose derivative or resinous material employed, the amount of plasticizer present in the composition, the speed of sheet formation, and the like. In general, it may be said that the temperature ranges from the colloidizing or melting point of the cellulose derivative or resinous composition up to the decomposition point of the material. In the case of cellulose acetate, for example, the temperature should be kept well below its decomposition point, temperatures up to about 200° C. being satisfactory. In this connection, it may also be pointed out that the resinous materials employed as film base require far less plasticizer to enable them to be molded in accordance with the principles of my invention than do the cellulose derivative materials. It will be evident that no definite ranges of temperature can be given, since the actual sheet-forming temperature depends upon so many other variables.

The herein described invention constitutes a simple, economical and effective method of producing films of thermo-plastic materials. By means of my invention, sheets or films may be produced without the use of costly solvents and the attendant danger of explosion or fire. An outstanding advantage of the invention is the economical production of a film base having a surface providing means for multi-point direct adhesion of a light-sensitive photographic emulsion. Many other advantages will be apparent to those skilled in the art.

What I claim is:

1. The process of making sheets or films having a surface to which a gelatin emulsion may be made to adhere without the use of substrata which comprises depositing an extremely thin discontinuous layer of finely divided water-soluble or water-swellaible material on the surface of one of two parallel bands disposed in close proximity to one another and moving in the same direction, depositing over the first layer a layer of thermo-plastic cellulose derivative material in finely divided form and colloidizing the material into a sheet by applying thereto a progressively increasing pressure for a predetermined length of travel of the bands and at a

temperature sufficient to colloidize the cellulose derivative.

2. The process of making sheets or films having a surface to which a gelatin emulsion may be made to adhere without the use of substrata which comprises depositing an extremely thin discontinuous layer of finely divided water-soluble or water-swellable material on the surface of one of two parallel bands disposed in close proximity to one another, and moving in the same direction, depositing over the first layer a layer of thermo-plastic cellulose organic acid ester composition in finely divided form and colloidizing the material into a sheet by applying thereto a progressively increasing pressure for a predetermined length of travel of the bands, and at a temperature sufficient to colloidize the cellulose derivative.

3. The process of making sheets or films having a surface to which a gelatin emulsion may be made to adhere without the use of substrata which comprises depositing an extremely thin discontinuous layer of finely divided water-soluble or water-swellable material on the surface of one of two parallel bands, moving in the same direction, depositing over the first layer a layer of cellulose acetate in finely divided form and colloidizing the material into a sheet by applying thereto a progressively increasing pressure for a predetermined length of travel of the bands and at a temperature sufficient to colloidize the cellulose acetate.

4. The process of making sheets or films having a surface to which a gelatin emulsion may be made to adhere without the use of substrata which comprises depositing an extremely thin discontinuous layer of finely divided gelatin on the surface of one of two parallel bands disposed in close proximity to one another and moving in the same direction, depositing over the first layer a layer of thermoplastic cellulose derivative material in finely divided form and colloidizing the material into a sheet by applying thereto a progressively increasing pressure for a predetermined length of travel of the bands and at a temperature sufficient to colloidize the cellulose derivative.

5. The process of making sheets or films having a surface to which a gelatin emulsion may be made to adhere without the use of substrata which comprises depositing an extremely thin discontinuous layer of finely divided casein on the surface of one of two parallel bands disposed in close proximity to one another and moving in the same direction, depositing over the first layer a layer of thermoplastic cellulose derivative material in finely divided form and colloidizing the material into a sheet by applying thereto a progressively increasing pressure for a predetermined length of travel of the bands and at a temperature sufficient to colloidize the cellulose derivative.

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