

March 25, 1952

E. H. LAND
METHOD OF FORMING FILMS

2,590,186

Filed April 24, 1948

2 SHEETS—SHEET 1

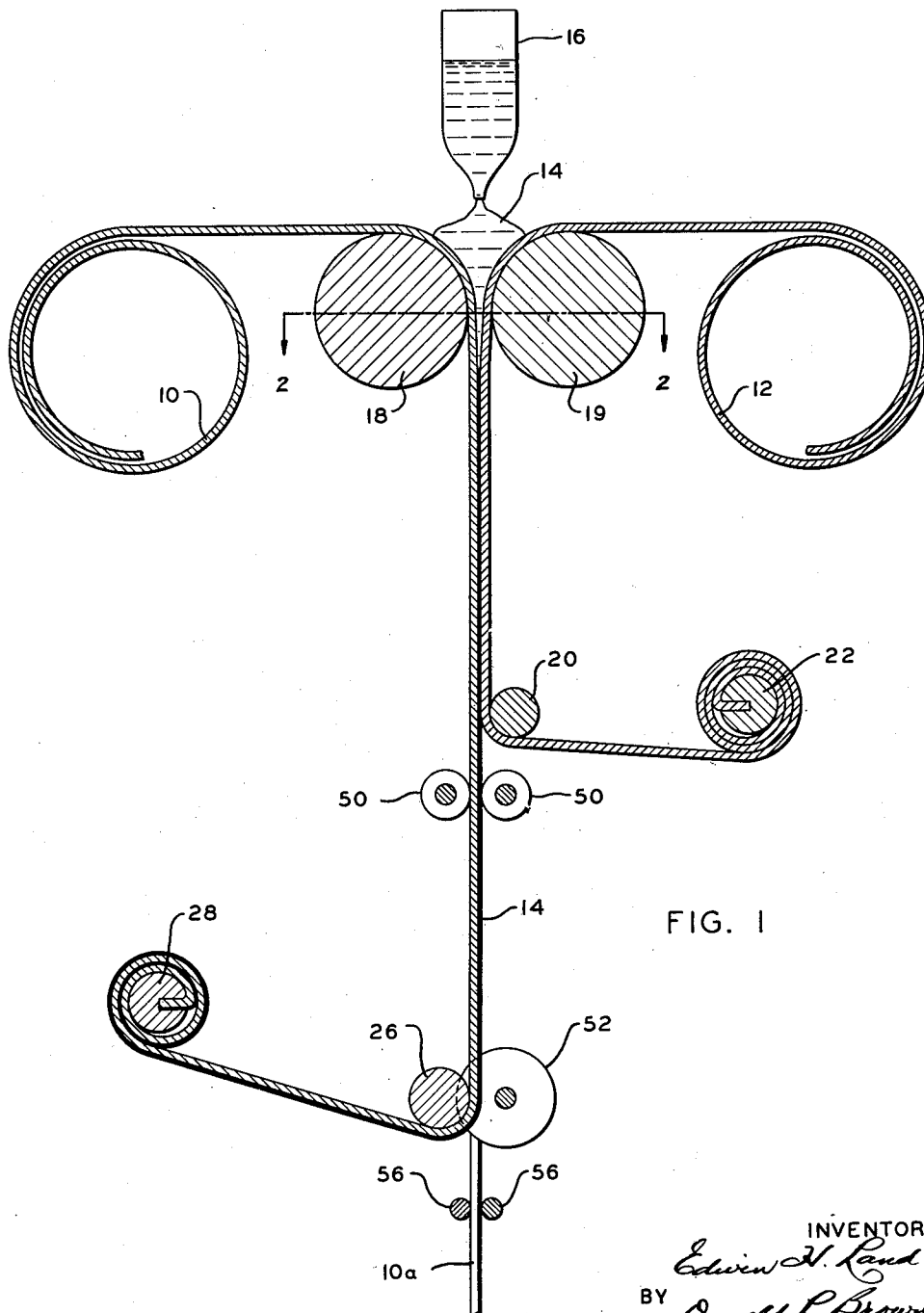


FIG. 1

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2 SHEETS—SHEET 2

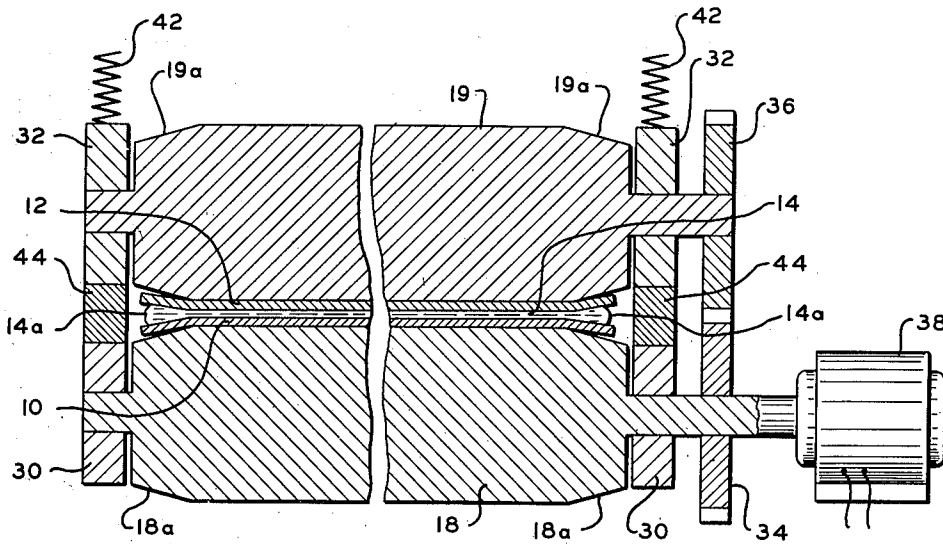


FIG. 2

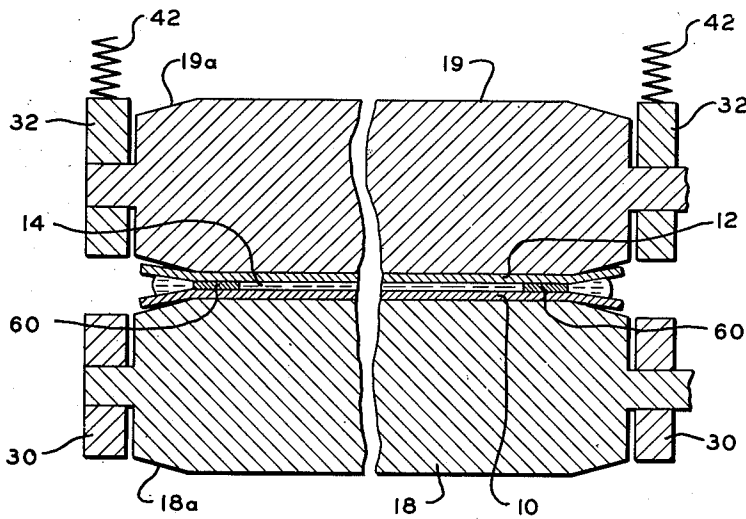


FIG. 3

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2,590,186

METHOD OF FORMING FILMS

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Application April 24, 1948, Serial No. 23,081

5 Claims. (Cl. 18—57)

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This invention relates to film-forming processes and more particularly to such processes wherein a solid film is formed on the surface of a sheet-like material from a viscous liquid mass of the film-forming material. This application is in part a continuation of my copending application Serial No. 576,254, filed February 5, 1945, now abandoned, and in part a continuation of my copending application Serial No. 7,795, filed February 12, 1948.

A principal object of the invention is to provide such processes wherein an accurate control of the final formed film is achieved.

Another object of the invention is to provide such processes which give improved coatings comprising the formed film.

Still other objects of the invention are to provide film-forming processes capable of high speed operation which do not require expensive casting belts and drums, and wherein the film thickness controlling surfaces do not contact the solution of film-forming material.

These and other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Figure 1 is a diagrammatic schematic sectional view of a device embodying the present invention and illustrating the various steps of the novel process;

Fig. 2 is a sectional view of the device of Fig. 1 taken along the line 2—2; and

Fig. 3 is a sectional view similar to Fig. 2 showing another modification of the invention.

In general, this invention relates to a process for forming a solid film on the surface of sheet-like material from a viscous liquid mass, such as a solution, of a film-forming material, the formed film preferably serving as a coating for the sheet-like material. In a preferred form of the invention the film is formed between the facing surfaces of the above-mentioned sheetlike material and another sheetlike material, the two sheetlike materials being fed along converging paths between a pair of sheet-guiding members. The solution of the film-forming material is prefer-

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ably of such concentration as to have a relatively high viscosity in the neighborhood of a thousand centipoises or higher. This viscous liquid is fed to the sheets adjacent the point of convergence thereof so as to provide a body of the liquid between the converging facing surfaces of the two sheets. For supporting the outer surfaces of the two sheets, the sheet-guiding members provide a pair of converging paths and space inner surfaces of the two sheets, at the point of convergence, a predetermined amount apart. This spacing predetermines the thickness of the layer of film-forming material drawn therebetween by the converging sheets. The two sheets preferably have smooth continuous surfaces and at least one of the sheets is absorbent to the solvent for the film-forming material and is thus capable of absorbing a considerable quantity of the solvent from the spread layer.

Thus, a substantial amount of the drying of the formed film takes place rapidly due to the absorption of this solvent by one or both of the sheets between which the viscous solution has been spread. When this drying of the spread liquid has progressed to the point where the forming film contains a substantially continuous solid phase, at least one of the sheets may be separated from the forming film and the continued drying thereof may take place due to evaporation of the remaining solvent from the exposed surface of the film. At some point thereafter the formed solid film, free of, or almost free of, contained solvent may, if desired, be separated from the second sheet. In the preferred form of the invention the formed film remains on the surface of the second sheet and serves as a coating therefor.

Referring now to Fig. 1 there is shown, schematically, the various steps of the preferred form of process. In this figure, 10 represents a sheet material such as a roll of paper having a smooth water-permeable surface. This paper 10 may comprise a hard calendered paper and preferably one which has had applied thereto a coating agent increasing its smoothness. For example, it may comprise commercial baryta paper (i. e., paper having a coating of gelatin and baryta on one surface). At 12, there is indicated another supply of sheet material which is preferably formed of a material different from the material of sheet 10. In one form of the invention, the second sheet 12 comprises a smooth sheet material such as an organic high polymer, for example cellulose acetate, having a surface relatively impervious to the solvent of the film-forming material. The viscous solution of film-forming material is indicated at 14 in a suitable feeding means 16

therefor. For bringing facing surfaces of the two sheets 10—12 into superposed facing relationship, there are provided means defining sheet-guiding surfaces and schematically indicated as a pair of rolls 18 and 19. These rolls 18 and 19 are preferably driven and their spacing preferably bears a predetermined relation to the thickness of sheets 10—12 and the desired thickness of layer of film-forming material 14, this relationship being discussed more fully hereinafter. Two guide rolls 20 and 26 are provided for guiding sheets 12 and 10, respectively, after spreading of the liquid 14, these sheets being preferably wound on spools 22 and 28, respectively, at the end of the process. Additional guide rolls, such as sheet-edge-engaging rolls 50, and other supports may be provided where needed in accordance with the requirements of any particular case. A pair of sheet-edge-trimming knives 52, cooperating with guide roll 26 are also preferably included. The trimmed margins 10a of the sheet 10 are separately advanced by rolls 56 for disposal.

Referring now to Fig. 2 there is shown in greater detail certain features of the pressure roll mounting. A pair of fixed supports 30 carry the ends of pressure roll 18 while a pair of movable supports 32 carry the ends of roll 19. The ends of the sheet-engaging portions of both rolls are preferably of reduced diameter inwardly of the supports 30 and 32 therefor, these reduced portions being indicated at 18a and 19a. Those marginal portions of the sheets 10—12 between end portions 18a—19a of the rolls are thus free for separation under pressure in liquid 14. These rolls 18 and 19 are preferably driven, such as by spur gears 34 and 36, respectively, mounted on the ends thereof. For driving gears 34—36 there is provided a suitable power source such as a motor 38. For normally urging supports 32, carrying roll 19, towards supports 30, carrying the roll 18, there is provided a pair of springs indicated at 42. For predeterminedly spacing the two rolls, by spacing the supports therefor, there is provided a pair of cams 44 between these supports. These cams are preferably tapered along a direction normal to the plane of Fig. 2 and are movable in this direction to cause an increase in separation of the rolls or to allow a decrease in this separation, depending upon the direction of movement of the cams 44.

In practicing the present invention, as illustrated in Figs. 1 and 2, a sheet 10 to be coated, comprising baryta paper for example, is suitably positioned as shown. A leading end of sheet 10 is led between rolls 18—19, between rolls 50, between knives 52 and roll 26 and secured to spool 28. The other sheet 12, which may for example be a sheet of cellulose acetate, is positioned as shown, the leading end thereof being placed between sheet 10 and roll 19, led around roll 20 and secured to spool 22. A suitable quantity of liquid 14 is placed in the feeding means 16 and the liquid in this feeding means is, for example, placed under a suitable gas pressure to assure feeding of the liquid at a rate adjusted to the speed of sheets 10—12. When a film of sodium carboxymethyl cellulose is to be formed on the surface of the baryta sheet, the liquid 14 may comprise a solution containing the following ingredients:

Example 1

Water	Grams
Sodium carboxymethyl cellulose	100
	6.3

When commercially available Hercules #1362 medium viscosity sodium carboxymethyl cellulose is used in the above proportions the viscosity of the liquid is in the neighborhood of 20,000 centipoises. With the two sheets and the liquid of the type described above, the thickness of coating depends upon the setting of the pressure rolls 18 and 19, the size of the rolls, and the angle with which the sheets converge. When the rolls 18 and 19 are relatively small, for example, having diameters on the order of $\frac{1}{2}$ inch, and the sheets converge at a relatively wide angle as shown in Fig. 1, the wet thickness of the spread layer of liquid (i. e., the thickness of the layer of the liquid while it still contains substantially all its solvent) bears a ratio of about 1 to 3 to the difference between the total thickness of the two sheets between the two rolls and the spacing between the two rolls. Thus for example, if this difference (hereinafter called the "available gap") is in the neighborhood of .006 inch, the wet thickness of the layer of spread liquid 14 will be in the neighborhood of .002 inch. After drying, this layer of film-forming material is about .0001 to .0004 inch thick. At the edges of the two sheets any liquid 14a travelling transversely of the sheets, due to pressure in the liquid being spread, is trapped between those portions of the sheet edges adjacent the tapered ends 18a—19a of the rolls. This trapping is accomplished by the pressure release in the liquid when it reaches the unsupported edges of the sheets, the liquid 14a, due to its high viscosity, ceasing to spread upon removal of the pressure thereon.

As the layer of film-forming material 14 is spread between these two layers it rapidly dries out due to the absorption of the water in the liquid by sheet 10 with a resultant decrease of thickness of the layer of liquid. As this water is absorbed by sheet 10, the sodium carboxymethyl cellulose comes out of solution and starts to form a solid film. At the end of about 5 to 20 seconds the other sheet 12 may be separated from the surface of the forming film so as to allow the drying thereof to be continued by surface evaporation of the remaining water in the forming film. If desired, layer 12 may be left in contact with the formed film for a longer time, this being desirable in those cases where a high concentration of solvent is employed in the liquid 14. On the other hand, sheet 12 may be separated from the forming film in a shorter period of time, this being possible where a relatively low concentration of solvent is employed in the liquid 14. Equally, sheet 12 may be left in contact with the forming film until this film is completely dry, for example by passing the two sheets 10—12, with the layer 14 therebetween, through an oven at about 180° F. for 1 to 2 minutes, the sheet 12 being removed at the end of this time. When the formed film is completely dried, its thickness is on the order of .0001 to .0004 inch, depending upon the initial concentration of the solvent. The drying of the film may be hastened by the use of dry hot air, infrared heat lamps, etc., which hasten the evaporation of the water from the film.

The product formed by Example 1 may be used in a number of applications wherein a smooth coating of a water-soluble plastic is desired on an opaque white paper. It is particularly useful as a base material readily adaptable for photographic processes, particularly of the type wherein the thus coated sheet is to be used as a carrier

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for a silver image formed by a silver transfer process.

When the rolls 18 and 19 have a larger diameter and the sheets are fed in the manner indicated in Fig. 1 the final wet thickness of the spread film will be greater than the .002 inch mentioned above, other conditions remaining the same. As the diameter of the rolls increases to the point where the sheets immediately adjacent the point of superposition are converging at a relatively narrow angle, the ratio of final wet thickness of spread liquid to the "available gap" increases to about 1 to 1 and may, in fact, increase to such an extent that the wet thickness of the spread layer may be greater than the "available gap."

In those cases where it is desired to provide a polyvinyl alcohol coating on a sheet of baryta paper, the liquid 14 may comprise the following solution:

Example 2

	Grams
Water	100
High viscosity polyvinyl alcohol Du Pont	
polyvinyl alcohol RH391	10

When such a film-forming solution is spread between sheets 10-12 in the same manner as described in connection with Example 1 above, a coating of polyvinyl alcohol is provided on the surface of the baryta paper. This polyvinyl alcohol coating will have a thickness on the same order as the thickness of the sodium carboxymethyl cellulose coating in Example 1 when the conditions of coating are the same.

In those cases where a coating of hydroxyethyl cellulose on baryta paper is desired, the liquid 14 may comprise the following:

Example 3

Water	cubic centimeters..	150
Hydroxyethyl cellulose	grams..	10

One preferred type of hydroxyethyl cellulose is that sold by the Carbide and Carbon Chemical Company identified as Hydroxyethyl Cellulose (71.2CPS.). The resultant thickness of spread film-forming material will be on the same order of thickness as that of the spread film-forming materials described previously, when the conditions of spread are the same.

Where a coating of a polymethacrylic compound is desired it may be applied in accordance with the following example:

Example 4

Water	cubic centimeters..	28
Sodium hydroxide	gram..	1
High molecular weight polymethacrylic acid	do.....	1

The polymethacrylic acid is neutralized in the alkaline solution and the resultant film-forming material in the liquid comprises the sodium salt of polymethacrylic acid. This material is coated in the same manner as described in connection with Examples 1 through 3 above, sheet 12 being stripped, for example, at the end of 5 seconds after spreading of the liquid.

If a relatively white and nontransparent material is desired with any of the above-mentioned film-forming materials there may be incorporated in the film-forming liquids a suitable pigment, such as titanium dioxide, mixtures of titanium dioxide and magnesium dioxide or magnesium carbonate. The addition of titanium dioxide, equivalent to 10% and 20% by weight of

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the film-forming liquid, has given good results. These pigments may also serve as fillers for increasing the viscosity of the film-forming liquid. Among the numerous other solutions of film-forming materials which may be coated in accordance with the process of the invention are the high molecular weight polymers, particularly the highly polar compounds such as those polymers containing hydroxyl and/or carboxyl groups. These polymers may be synthetic, as exemplified in the cases listed above, or may be naturally occurring polymers such as albumen, pectin, starch, sodium alginate, gelatin, and gum arabic, and they may even be inorganic polymers such as sodium silicate (water glass).

While the above examples have been described in connection with the coating of a sheet 10 comprising baryta paper, numerous other materials may be so coated. These may, for example, comprise numerous other sheets, preferably those which are hydrophilic, such as many types of paper, particularly those which are water-permeable, regenerated cellulose, polyhydroxy alkane sheets such as polyvinyl alcohol, sodium alginate, cellulose ethers such as ethyl cellulose or their derivatives, i. e., sodium carboxymethyl cellulose, aluminum carboxymethyl cellulose and hydroxyethyl cellulose. Equally, sheet 10 may comprise proteins such as gelatin and carbohydrates such as gums and starch, and sheet 10 may be any suitable base such as metal, cloth, etc., carrying the above materials as a surface coating thereon.

The sheet 12 has been described as preferably comprising cellulose acetate although it may be formed of numerous other materials. It may comprise a sheet, preferably nonabsorbent, such as cellulose acetate butyrate, cellulose acetate propionate, cellulose nitrate, polyethylene of polystyrene, to mention a few such examples. The abovementioned materials are generally relatively impermeable to water but this is not a requisite of sheet 12. In fact, water-absorbent properties of sheet 12 may be very desirable in those cases wherein the film-forming liquid contains a high concentration of water, or where a very thick layer of the film-forming material is to be spread, or where the sheet 10 to be coated is relatively nonabsorbent to water, or is of such thinness as to be incapable of absorbing a considerable quantity of the water from the film-forming liquid. When a water-absorbent material is utilized as the sheet 12, it may comprise a paper coated with a relatively thick layer of pure gelatin such as imbibition paper, or it may comprise a paper or other water-permeable support which has, or has coated on its inner surface, a material which forms a poorer bond with the formed film than does the surface of the sheet 10.

One example of a sheet 12 which is not adherent to the formed film, but which is water-absorbent, is given below:

Example 5

A solution is prepared containing about 5 grams of polyvinyl alcohol dissolved in 100 cc. of water. A sheet of baryta paper may then be coated with this solution by utilizing the liquid-spreading technique, described in connection with the discussion of Example 1, to give a polyvinyl alcohol coating approximately .0002 inch thick. Such a coated sheet may then be used as sheet 12 in a process similar to Example 1 wherein sheet 10 comprises a plain baryta paper and the film-forming liquid 14 comprises the mixture of Example 1. When the liquid 14 is spread between plain baryta paper 10 and the polyvinyl alcohol

coated baryta paper 12, the formed film adheres to the plain baryta paper more strongly than it does to the polyvinyl alcohol coated baryta paper and the latter may be stripped after about 30 seconds from the formed film carried by the plain baryta paper. Examples of other materials which may be coated on paper, such as baryta paper, or other sheets to decrease the surface adhesion thereof with respect to a formed film of sodium carboxymethyl cellulose, for example, are cellulose acetate hydrogen phthalate, hydroxyethyl cellulose, methyl cellulose, ethyl cellulose, cellulose nitrate, sodium alginate, pectin, gum arabic, polymethacrylic acid and other plastics. Similarly, the sheet 12 may be coated for example, with an anionic surface active agent such as sodium high alkyl sulfate, or a sodium high alkyl carboxylate or a sodium alkyl aryl sulfonate. For example the surface active agent may be a soap solution coated on sheet 12 and dried, and which, when subsequently wetted by the film-forming liquid, prevents adhesion of this film-forming liquid to the surface of the sheet 12.

The adhesion of sheet 10 to the formed film may also be increased in addition to, or instead of, decreasing the adhesion of sheet 12 for the formed film. The adhesion of the formed film to the sheet 10 may be increased by providing in the sheet 10 a material capable of cross-linking the film-forming material spread in contact therewith, as set forth in the following nonlimiting example:

Example 6

Sheet 10 is dipped for 1 minute in a bath containing 45 grams of lead acetate dissolved in 100 cc. of water and then dried. When the liquid of Example 1 is spread between such a sheet 10 and another baryta sheet 12, the lead acetate is dissolved by the absorbed water and cross-links the sodium carboxymethyl cellulose in the forming film adjacent the surface of sheet 10 and thus creates a strong bond between this forming film and the surface of sheet 10. Sheet 12 in this case may be stripped from the formed film after 30 seconds.

While the process of the invention described above has been directed primarily to water-soluble film-forming materials, it is not limited thereto, and film-forming materials insoluble in water but soluble in suitable other solvents may be employed, as set forth in the following nonlimiting example:

Example 7

Liquid 14 comprises a solution of 10 grams of cellulose acetate hydrogen phthalate dissolved in 100 cc. of acetone. When such a film-forming liquid is spread between a sheet 10 of baryta paper and a sheet 12 of polyethylene, for example, the formed film adheres to the baryta paper. Similarly, cellulose nitrate, cellulose acetate, and ethyl cellulose may be coated from suitable solutions thereof. For forming such solutions suitable organic solvents may be employed. For example, in dissolving cellulose acetate the solvent may comprise a mixture of methanol, ethyl acetate and methyl Cellosolve, the proportions of these solvents being preferably in the ratio of 1:3:3 by volume respectively. For ethyl cellulose the solvent is preferably toluene, while for cellulose nitrate the solvent is preferably a mixture of methanol and ethyl acetate. In the coating of these organic solvent soluble film-forming materials between the two sheets 10-12, the sheet 12 preferably comprises a material which is not ap-

preciably dissolved by the solvent so as not to increase its adherence to the formed film. Thus for example, when a cellulose acetate solution is being spread, sheet 12, instead of being the cellulose acetate sheet mentioned as being preferable in some of the preceding examples, may comprise a sheet of polyethylene, polystyrene or imbibition paper, i. e., a heavily gelatin-coated paper to which the cellulose acetate film does not adhere as readily as to baryta paper.

In still another modification of the invention the film formed adjacent the surface of sheet 10 may be separated from sheet 10 after the film-forming is completed, thus providing an unsupported plastic film of controlled thickness which may be utilized for any purpose for which cast films of this general nature are presently employed. When the film to be formed in this manner comprises polyvinyl alcohol, the preferred method of practicing the invention is set forth in the following nonlimiting example:

Example 8

The liquid 14 comprises 5 grams of polyvinyl alcohol dissolved in 100 cc. of water. The sheet 10 comprises a sheet of imbibition paper while the sheet 12 comprises cellulose acetate. With such a modification of the invention, the solution of polyvinyl alcohol is fed between the two sheets, as shown in Fig. 1, sheet 12 being separated from the forming film after about 1 minute of drying in an oven at 180° F. The polyvinyl alcohol film is then sufficiently dried out so as to permit separation thereof from sheet 10 as well. This separation is preferably accomplished as sheet 10 passes around roll 26 of Fig. 1 and may be aided by providing another take-up spool near roll 26. With the liquid of Example 8, sheets 10-12 of the type set forth therein, with the sheets being fed substantially parallel to each other into the rolls, using a pair of rubber-coated rolls having a diameter of $\frac{3}{8}$ inch, a length of 5 inches, the rolls rotating at 40 R. P. M. and being under a total load of about 50 ounces, the final thickness of the dry film of polyvinyl alcohol is about .0002-.0003 inch.

Still another method of forming a film, which is not supported by a base, is accomplished by the process as set forth in the following nonlimiting example:

Example 9

The liquid of Example 8 is replaced by a solution containing 100 cc. of water and 7.5 grams of hydroxyethyl cellulose. The other conditions remaining the same, a solid strippable film .0002-.0003 inch thick of hydroxyethyl cellulose is formed when the hydroxyethyl cellulose is spread between the sheet of imbibition paper and the sheet of cellulose acetate.

While one preferred schematic form of apparatus suitable for practicing the invention has been shown in Figs. 1 and 2 above, such apparatus is susceptible of considerable modifications. For example, the liquid 14 may be pumped from supply 16, fed by gravity or in any other suitable manner. The liquid-spreading rolls 18 and 19 may be replaced by other members which are nonrotatable and which provide converging surfaces between which the two sheets 10-12 are advanced with the supply of film-forming material adjacent the point of superposition of the two sheets. Examples of such other liquid-spreading surfaces are given in the copending application of Edwin H. Land, Murry N. Fairbank, and David S. Grey, Serial No. 790,064, filed December 6, 1947, now

Patent No. 2,483,014. When such other surfaces are employed, suitable propelling means may be provided such as by driving spools 22 and 28 and/or by driving other suitable rolls such as the edge-engaging rolls 50. Equally, rolls 18 and 19 may be idler rolls and the two sheets may be drawn therepast by suitable propelling means. In the preferred mounting of rolls 18 and 19, shown in Fig. 2, these rolls are predeterminedly fixedly spaced apart and these surfaces are non-resilient. However, these rolls may be resiliently mounted and may have resilient surfaces. Where the rolls are resiliently mounted or have resilient surfaces the thickness of the spread film will be dependent on a number of factors such as the loading of the rolls, the viscosity of the film-forming material, the speed of the sheets and the resilience of these roll surfaces.

In another form of the invention, the "available gap," in which the layer of film-forming material is spread between the two sheets, is maintained constant despite wide variations in the thicknesses of the two sheets. One preferred method of practicing this aspect of the invention is shown in Fig. 3 where like numbers refer to like elements of the preceding figures. In this modification of the invention, the minimum separation of the two sheets between the rolls is controlled by a pair of relatively incompressible edge strips 60, preferably secured to margins of one of the sheets inwardly of the edges thereof. These strips may comprise hard calendered paper, cellulose acetate and the like. In such a modification of the invention, the "available gap" is maintained constant and substantially equal to the thickness of strips 60, despite wide variations of thickness in the two sheets 10-12 between which the liquid is spread, since these strips maintain the rolls spaced apart a distance equal to the sum of the thickness of the two sheets and one strip. The springs 42 in this modification preferably urge roll 19 towards roll 18 under a force greater than the force generated in the viscous liquid during the spreading thereof. The wet thickness of the spread liquid will bear a ratio to this "available gap" depending upon the angle at which these sheets converge, as discussed previously in connection with Fig. 1.

While the invention has been described in terms of the use of a viscous liquid mass comprising a solution of the film-forming material, this viscous liquid may equally comprise an emulsion of the film-forming material which, upon drying out, is capable of forming a substantially continuous solid film. For example the water-soluble film-forming materials may be emulsified with organic solvents while the water-insoluble film-forming materials may be emulsified with water, the water in the latter case, and the organic solvent in the former case, being absorbed by one or both of the sheets after spreading, thus leaving the solid film on one of the sheets.

The present invention provides for obtaining accurately dimensioned solid coatings or films from viscous liquids containing the film-forming material. These viscous liquids can have a very high viscosity, in the neighborhood of several hundred thousands centipoises, thus permitting the use of a small amount of solvent. The process permits the use of rapid drying of the forming film and allows an extremely accurate control of the film thickness. The apparatus using the process may be relatively simple and inexpensive in relation to usual coating or casting machines and the film-thickness-controlling sur-

faces of the apparatus do not contact the liquid being spread.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The method of forming a continuous solid film which comprises guiding a sheet material into substantially parallel relation with another sheet, said sheets travelling along converging paths to provide a converging space between facing surfaces of said sheets, at least one of said sheets being absorbent to portions of a viscous liquid mass containing a film-forming material capable of forming said solid film, feeding a bulk of said liquid into said space between converging inner surfaces of said sheets, said bulk of liquid being of greater thickness than the desired thickness of spread liquid, supporting outer surfaces of said sheets during convergence to confine said bulk of liquid, maintaining inner surfaces of said sheets predeterminedly spaced at the point of convergence thereof by liquid pressure created in said bulk of liquid at the point of convergence by passage of said inner surfaces past and in contact with said bulk to thereby create a substantially uniform layer of said film-forming liquid between said sheets, maintaining said two sheets in substantially parallel relation with said layer of film-forming material therebetween at least until such time as said absorbent sheet has removed from said layer a sufficient quantity of said portion of said liquid absorbable by said sheet so that said layer includes a substantially continuous solid phase of said film-forming material, removing one of said sheets, and drying said formed film.

2. The method of forming a substantially uniform, continuous solid film of an organic high polymer which is soluble in an aqueous liquid, comprising simultaneously advancing two individual sheets, at least one of which is of a water-absorbent material, lengthwise of themselves in substantially flat condition towards each other along converging paths while feeding an aqueous liquid solution of said polymer, which has a viscosity greater than 1000 centipoises, between the converging inner surfaces of said sheets and applying pressure to said sheets and the liquid therebetween by passing said sheets between pressure-applying members which apply pressure to the outer surfaces of said sheets to act transversely of said sheets except for a small marginal portion adjacent each edge of each sheet and which bring said sheets into substantially parallel relation with respect to each other whereby to spread the viscous liquid solution of said high polymer in a layer between and in contact with the inner surfaces of said sheets as said sheets are brought into said substantially parallel relation, continuing the lengthwise advance of said sheets, without interruption, while maintaining said sheets in said substantially parallel relation with the layer of viscous liquid therebetween until said absorbent sheet has removed sufficient water from said viscous liquid layer to substantially solidify said layer and provide said polymer in a substantially continuous solid phase, stripping one of said sheets from said solid polymer film, and continuing the drying of said film of polymer carried on the other sheet, at least partially by surface evaporation, until substan-

tially all of said water is eliminated from said solid polymer film.

3. In a method of forming a substantially uniform, continuous solid film of an organic high polymer which is soluble in an aqueous liquid, the steps of simultaneously advancing a base sheet material and another sheet material lengthwise of themselves in substantially flat condition and in a direction towards each other along converging paths, at least one of said sheets being water-absorbent, introducing said polymer in an aqueous liquid solution having a viscosity greater than 1000 centipoises between the converging inner surfaces of said moving sheets and bringing said moving sheets into substantially parallel relation with their inner surfaces substantially parallel to but separated from each other by applying pressure transversely across the outer surfaces of said sheets to press said sheets towards each other while limiting the separation of said sheets to a predetermined minimum by causing said applied pressure to work against substantially incompressible members carried by one sheet adjacent each edge thereof whereby to effect the spreading of said viscous solution between said sheets in a substantially uniform layer having a minimum thickness substantially equal to said minimum separation, continuing the lengthwise advance of said sheets, without interruption, while maintaining said sheets in said substantially parallel relation with said layer of viscous liquid therebetween until said absorbent sheet has removed sufficient water from said viscous liquid layer to substantially solidify said layer and provide said polymer in a substantially continuous solid phase, stripping one of said sheets from said solid polymer layer, and continuing the drying of said layer of polymer carried on the other sheet, at least partially

by surface evaporation, until substantially all of said water is eliminated from said solid polymer layer.

4. A method of forming a substantially uniform, continuous solid film of an organic high polymer as defined in claim 3 wherein pressure is applied to the outer surfaces of said sheets by a pair of pressure-applying members operatively aligned with each other and between which said sheets are moved and wherein said pressure-applying members when applying pressure to said sheets are substantially maintained in spaced-apart relation by a distance substantially equal to the sum of the thickness of each sheet and the thickness of one incompressible member.

5. A method of forming a substantially uniform, continuous solid film of an organic high polymer as defined in claim 3 including the step of applying pressure to said sheets and the liquid therebetween by passing said sheets between pressure-applying members which apply pressure to the outer surfaces of said sheets to act transversely thereof except for a marginal portion adjacent each edge of each sheet and extending at least from each said edge to the incompressible member associated with each said edge.

EDWIN H. LAND.

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