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COATING PROCESS FOR THE PREPARATION OF A FILM CASTING SURFACE AND RESULTANT ARTICLE

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Fig. 1.

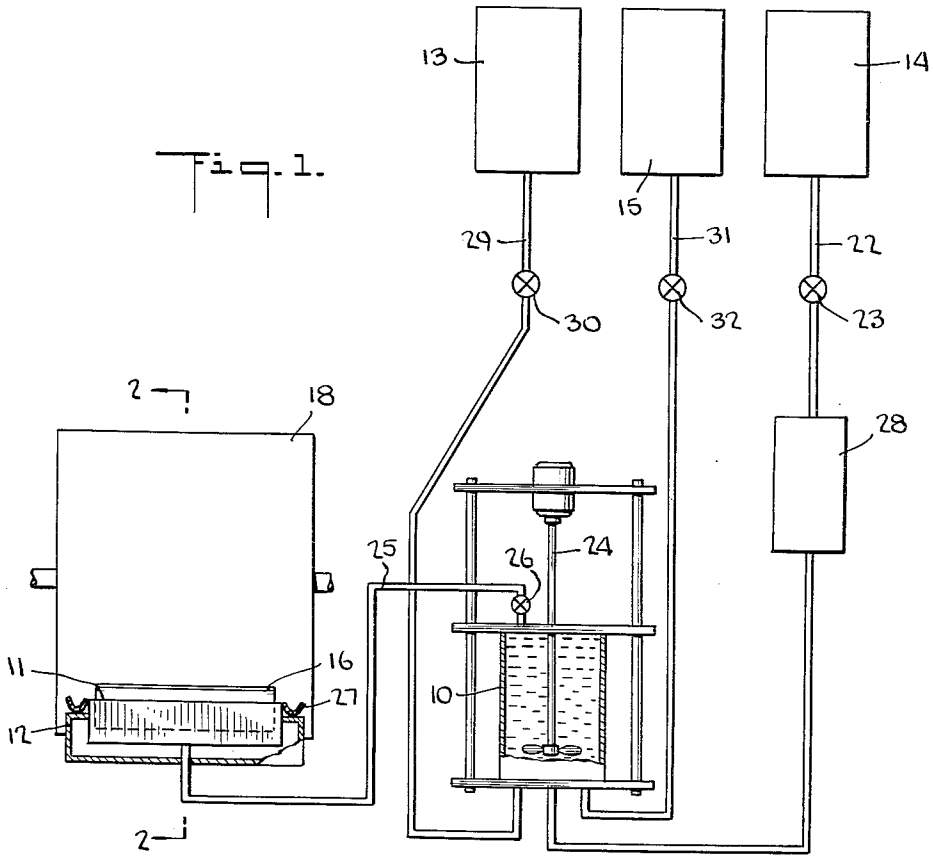
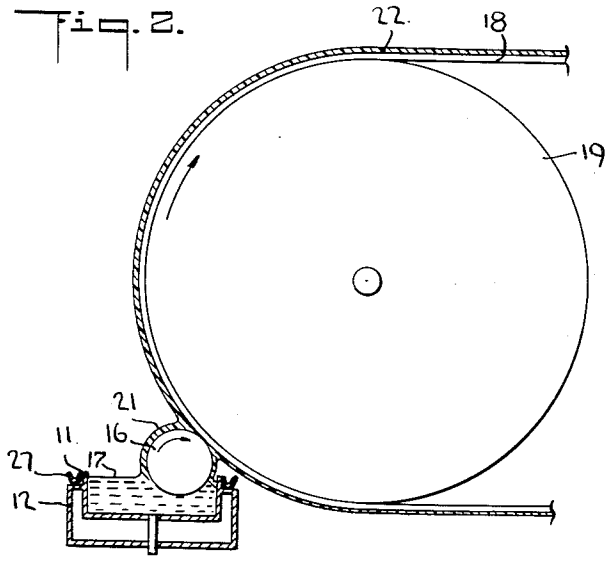


Fig. 2.



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COATING PROCESS FOR THE PREPARATION OF A FILM CASTING SURFACE AND RESULTANT ARTICLE

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This invention relates to film casting surfaces and more particularly to a novel process for preparing film casting surfaces that will produce films free from defects.

One presently practiced method for forming films and sheeting includes broadly (1) formation of a solution of a plastic film-forming material together with such additives as plasticizers, dyes or other coloring material in a suitable solvent; (2) flowing of the solution of dope onto a casting surface such as a rotating wheel or an endless belt supported in a generally horizontal plane by at least two large pulleys; (3) conversion of the layer of cast material to a self supporting form, generally by the removal of solvent therefrom; and (4) stripping of the self-supporting film or sheeting from the casting surface.

To obtain films free from defects it has been necessary that the casting surface itself be free from discontinuities or imperfections. Since the plastic dope intimately contacts the casting surface and therefore reproduces the exact surface configuration, it is important that the casting surface have a highly polished and glossy finish and that it be devoid of any defects such as pits, scratches, splice lines or matte areas.

In addition it is required that the casting surface be formed of material possessing the necessary chemical inertness to the constituents of the plastic dope and that it retain a polished physical surface even after considerable use, or in the alternative, that the surface finish be readily susceptible to renewal to produce a finish from which the cast material strips easily without appreciable adhesion.

Prior art casting surfaces which have been used include both metallic and non-metallic materials. For example, cylindrical casting drums 10 to 18 feet or more in diameter have been provided with the desired inert, smooth, glossy film supporting surface by plating chromium, nickel or other corrosion-resistant metal thereon. The plating of drums this size is both awkward and expensive and is often required to be repeated because of scratches or other blemishes accidentally made on the surface during handling and installation of the drum.

To avoid the difficulties associated with the use of metallic casting surfaces it has been proposed to coat a metallic support with a synthetic resin such as a phenol-aldehyde or urea-aldehyde resin which is rendered insoluble by baking to yield a durable surface which is resistant to both physical and chemical alteration in use. It has also been proposed to use plural layers of cellulose acetate including a saponified outermost layer which is resistant to the solvent in the casting solution.

It has been found that in applying the coating materials in accordance with the procedures taught in the prior art, a noticeable start and end-line is usually left on the finished surface. Procedures have been developed to minimize the mark left on film by end-lines, commonly styled splice lines.

The splice lines are evidence of irregularities in the thickness of the applied coating with the resin thickness being greater at the area last in contact with the resin applicator. To minimize the splice lines, it has been the practice to grind the thicker areas down to the level of the thinner areas at the splice line so that the change in thickness is gradual rather than abrupt and then polishing the ground area. Such procedures are expensive and are of only limited effectiveness since the change in resin thickness is perceptible, even if gradual, so that a slight waviness is visible at the splice line of the casting surface and at corresponding areas of the film cast from such a surface.

Another disadvantage of the composite coatings, mentioned above is that only the outermost thin surface layer is completely inert to the casting solvent. Any damage, however slight, inflicted on the casting surface, exposes the lower portions of the coating to chemical attack by the material being cast, and particularly by the solvents in said composition which usually cause the lowermost portions of the coatings to swell, eventually destroying the coating by physically separating it from the metal support on which it is supported. Furthermore, when composite layers are used, airborne contaminants such as fibers present in the outer layer often convey the solvent by capillary action to the lower layer of the casting surface with the same disastrous results.

One object of this invention is to provide a new process for the production of film casting surfaces that will enable the production of films free from splice marks, spots and other objectionable surface defects in the finished cast film.

A further object of this invention is to provide a casting surface which can be easily repaired, should any damage be inflicted to it during use.

These and other objects are achieved with the production of a casting surface which is inert to solvents throughout its entire thickness and which has a completely "spliceless" surface by the practice of a novel method of coating.

Briefly, in accordance with the present invention, a casting surface is formed on a suitable support by maintaining contact between a supporting surface and a contact liquid, moving said supporting surface relative to said contact liquid continuously and repetitively so that said contact liquid is applied to successive portions of said supporting surface, gradually changing the composition of said contact liquid during the course of said contact, said composition comprising a solution of a film-forming material at one stage of said contact and comprising a non-solvent for said film-forming material at a subsequent stage of said contact and breaking contact between said supporting surface and said contact liquid when said contact liquid is a non-solvent for said film-forming material.

A preferred embodiment is shown in the drawings, of which FIGURE 1 is an end view, of a device for applying film-forming material to an endless belt with a semi-schematic showing of the liquid flow and FIGURE 2 is a sectional view on the plane 2—2 of FIGURE 1.

A dip or beading pan **11**, having a water jacket **12**, is maintained in connective relation to a homogenizer **10**, which in turn is in connective relation to three reservoirs, **13**, **14** and **15** so that liquid may be fed to the homogenizer from any of the reservoirs. Beading, or applicator roll **16**, a relatively small cylinder, 3 to 4 inches in diameter, is mounted and driven to rotate on horizontal axis so that the lower portion of the roll dips into the liquid **17**, in the dip tank. The supporting surface to be coated, belt **18**, is mounted and driven to rotate on a pair of horizontal rollers, **19** (of which only one is shown in the drawings) so that it passes within a few mils of the applicator roll but does not touch it or touch the liquid in the dip pan. The applicator roll **16** is parallel to rollers **19** and long enough to contact the belt across its entire width.

The liquid film of contact liquid on the applicator roll is shown as **21** and the partially liquid and partially solid film on the belt is shown as **22**. Both films are exaggerated in thickness for purposes of clarity.

Reservoir **13** contains a liquid solution of a resinous film-forming material in suitable solvent. The concentration of resin in this solution is at least as high as the highest resin concentration desired for application to the supporting surface. Reservoir **14** contains solvent, but no resin. Preferably, a gelling agent for the resin is also present in the liquid in reservoir **14**. Reservoir **15** contains a liquid which is a non-solvent for the resin and which is miscible with the solvent.

The initial liquid fed into the dip pan is the solvent (and gelling agent) from the reservoir **14**. The solvent is fed to the bottom of homogenizer **10** through line **22** and controlled by valve **23**. There is a heat exchanger **28** in the line for heating the solvent and gelling agent to a desired temperature, as will be explained below. Homogenizer **10** is always full of liquid during operation since withdrawal is from the top through line **25**, controlled by valve **26**. The contents of homogenizer **10** are agitated constantly by stirrer **24**.

Withdrawal of liquid from the beading pan is principally by film formation onto the applicator roll. However, the liquid flow into the beading pan is maintained at a slight excess over the rate of withdrawal by film formation so that a small amount of liquid overflows the pan into overflow channels **27**, through which it is withdrawn from the system.

After the belt is wetted by contact with the solvent from reservoir **14**, resin solution from reservoir **13** is gradually introduced into the homogenizer and thence into the beading pan. The resin solution is passed to the homogenizer through line **29** and controlled by valve **30**. Introduction of resin solution into the solvent-gelling agent mixture begins the application of a resin coating on the belt by application of the dilute resin solution thereto.

The resin concentration in the contact liquid in the dip pan is gradually built up to the desired maximum and maintained at this level for several passes of the supporting surface or until the desired resin thickness is almost reached. The resin concentration in the contact liquid is then gradually reduced by the introduction of solvent from the reservoir **14** until there is substantially no resin left in the dip pan.

Then non-solvent from the reservoir **15** is gradually introduced through line **31** and valve **32** and replaces the solvent until the contact liquid contains substantially no solvent. At this point the beading roll is swiftly removed from the supporting surface and contact broken.

The following specific example will serve to further illustrate the practice of our invention to form a casting surface of polyvinyl alcohol. In the process described by way of example polyvinyl alcohol is gelled by Congo red and the final liquid applied is acetone. It will be understood, however, that other film-forming materials may be substituted for the polyvinyl alcohol, including gelatin, for example, without departing from the intended scope of our invention, and that with the use of such other materials, the use of Congo red as the gelling agent may be rendered unnecessary or other suitable gelling agents may be substituted. Similarly, although acetone has been indicated as the final wash, other volatile liquids which are equally inert toward the freshly formed casting surface may be employed instead of the acetone. The choice of such liquids is clearly related to the materials in the system.

Example

Three reservoirs contained respectively: (1) an 8% solution of Du Pont Elvanol 72–60 a polyvinyl alcohol hydrolyzed to 99–100% and having a viscosity of 55–65 centiposes in a 4% by weight aqueous solution at 20° C., (2) a 0.2% solution of Congo red in deionized water and (3) technical grade acetone.

The supporting surface was an endless belt 20 feet in length and moved at the rate of 2 feet per minute. The applicator roll was 3 inches in diameter and dipped into the contact liquid at its lowermost portion to a depth of about 7/8 inch. It rotated at about 5 r.p.m. The distance between the belt and the applicator roll at their closest points was about 7 mils.

The undercoating operation was started using only the Congo red solution. Since this solution was essentially pure water no sharp starting line was noticed. Gradually, polyvinyl alcohol solution was introduced into a homogenizer and mixed thoroughly with the Congo red solution prior to its entry into the dip pan. Congo red is a gelling agent for polyvinyl alcohol, but the gel thus formed is thermally reversible. To prevent premature gelling of the polyvinyl alcohol solution the Congo red water solution was passed through a heat exchanger and the temperature regulated so as to avoid gelling of the polyvinyl alcohol and the Congo red solution prior to its application on the supporting surface. As the concentration of the polyvinyl alcohol was built up, the temperature of the solution was raised accordingly. The temperature at the initial low polyvinyl alcohol concentration was 85° F. and the temperature at maximum concentration was 125° F. The buildup period was about 40–60 minutes. Almost instantaneous gelling of the solution deposited on the supporting surface prevented the runbacks of coating solution. Finally when the highest concentration was reached (approximately 5% polyvinyl alcohol), it was maintained for several revolutions of the supporting surface, all other conditions such as concentration and temperature being held constant. The procedure was then reversed, that is the concentration of polyvinyl alcohol was gradually decreased until the solution consisted essentially of pure water and Congo red. The temperature was lowered during this state to 90° F. The dilution period was about 40 minutes. At this point, acetone was slowly fed into the homogenizer and from there into the beading pan. The concentration of acetone was increased gradually until the solution picked up by the applicator roll consisted almost entirely of acetone. When this condition was reached, after about 10 minutes the applicator roll was swiftly removed from the surface and contact broken. At this time the solution did not contain any polyvinyl alcohol nor any appreciable amount of water. Since acetone is a non-solvent for polyvinyl alcohol, the coating was ended without any visible splice line.

The resulting polyvinyl alcohol undercoating was usually approximately one and one-half to two-thousandths inches thick. If necessary, seasoning, or hardening, of the coating can be accelerated by installing several infrared heaters above the surface. However, in normal application complete seasoning is generally obtained by merely permitting the undercoating to age for approximately 24 hours. The final application of acetone to the coating also accelerates the seasoning by extracting traces of water from the polyvinyl alcohol coating.

Film dopes containing cellulose acetate, plasticizer and the conventional solvents (ketones, chlorinated hydrocarbons, lower alcohols) were cast on the polyvinyl alcohol surfaces prepared as described above and the resulting film was stripped easily and exhibited a high gloss and no waviness.

If the metallic surface on which the casting surface is to be supported has a relatively smooth finish the polyvinyl alcohol coating can be applied directly to the metal, (after it has been cleaned, by treatment with acetone) and will adhere tenaciously to the support. In some cases, however, it may be desired to first apply from a hopper a coating of cellulose acetate or other suitable material, four to five thousandths of an inch in thickness, smoothing out any splice lines or noticeable irregularities in same and thereafter apply a coating such as the polyvinyl alcohol coating one and one half to two thousandths inches thick as described in the example.

While the invention has been described with respect to its preferred aspect it is to be understood that various modifications may be made, if desired. In the prior art processes the finish splice line is much more objectionable than the starting splice line, particularly if the coating is relatively thick. It is therefore within the scope of this invention to eliminate the resin concentration build up step in the process and to start the coating with a solution of maximum resin concentration.

It is not essential, in accordance with the broad aspect of this invention to reduce the resin concentration in the contact liquid to zero before introducing non-solvent into the system. Non-solvent may be introduced into the contact liquid while it contains resin, provided that the amount of non-solvent is insufficient to cause precipitation of the resin at the resin concentration prevailing in the contact liquid.

While the solidification step specifically described above involves gel formation, it is to be understood that other solidification methods, such as evaporation, may also be used.

While the invention has been described particularly with respect to the formation of film casting surfaces, it is to be understood that it is applicable to the formation of any resinous surface which is ordinarily formed by the application of a liquid phase resin-containing mixture to a supporting surface and in which splice lines would be objectionable.

The invention may be used, for example, in the resin coating of belt-type bakery dryers where splice lines tend to collect flour and dust. The invention is also useful in the resin coating of belt surfaces on which foamed rubber sheet and foamed plastic sheet is made. Here, as in the case of film casting, it is desirable to avoid splice lines because of their effect on the appearance of the product. This invention is useful in the application of the resinous coatings usually used on such belts, including silicone resins and fluorinated resins which may be used for providing ease of strippability. In each case the resin is applied in its usual solvent system, but by the general procedure specified above.

The cyclic period for the movement of the supporting surface, or the time between successive approaches of a particular portion of the surface to the applicator roll will vary with the nature of the resin, solvent and gelling agent, if any. Where there is no gelling agent longer cyclic periods will be required. For the polyvinyl alcohol-water-Congo red system described above it is preferred to maintain the cyclic period between about 7 and about 12 minutes, depending on the length of the band being coated.

The maximum resin content in the contact liquid will depend on the nature of the resin solvent system and on the nature of the solidification system. For polyvinyl alcohol-water-Congo red, the maximum resin content will generally run from about 5.0 to about 6.5 weight percent.

The temperature in the contact liquid is adjusted to avoid solidification in the dip tank and to permit solidification on the supporting surface. The solidification temperatures for particular concentrations of resin and gelling agent are known, or easily determinable and the temperature in the dip tank is maintained from about 5 to about 10° F. above the solidification temperature so that solidification may take place on the supporting surface by natural cooling.

The period for each complete change in composition of the contact liquid in the dip tank (e.g. from zero to maximum resin concentration or from maximum to zero solvent concentration) should preferably be no less than about twice the cyclic period.

The resinous coatings produced by this invention have no visible splice line whatsoever. The coatings are uniform in thickness and have a uniform surface all of which is formed by the flow characteristics of the liquid applied. This is in contrast to the "spliceless" coatings of the prior art where the splice was ground and polished. The prior art coatings are wavy and uneven at the splice line and their surfaces, which are formed in part by grinding and polishing, have at the polished portions, the characteristic very fine scratches produced by the polishing process.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

Having described our invention what we desire to secure by Letters Patent is:

1. A process for the preparation of a spliceless resinous coating which comprises maintaining contact between a supporting surface and a contact liquid, moving said supporting surface relative to said contact liquid continuously and repetitively so that said contact liquid is applied to successive portions of said supporting surface, gradually changing the composition of said contact liquid during the course of said contact, said composition comprising a solution of a film-forming material at one stage of said contact and comprising a non-solvent for said film-forming material at a subsequent stage of said contact and breaking contact between said supporting surface and said contact liquid when said contact liquid is a non-solvent for said film-forming material.

2. A resin-coated support produced in accordance with the process of claim 1.

3. A support according to claim 2 wherein said resin comprises polyvinyl alcohol.

4. A process for the preparation of a spliceless resinous coating surface which comprises maintaining contact between a supporting surface and a contact liquid, moving said supporting surface relative to said contact liquid continuously and repetitively so that said contact liquid is applied to successive portions of said supporting surface, maintaining in said contact liquid a film-forming material in a solvent therefor, solidifying said film-forming material at successive portions of said supporting surface to which it has been applied in said contact liquid, progressively reducing the concentration of film-forming material in said contact liquid until said liquid contains substantially no film-forming material, thereafter introducing into said contact liquid a liquid material which is a non-solvent for said film-forming material but which is miscible with said solvent, progressively increasing the concentration of said non-solvent liquid in said contact liquid until said contact liquid contains substantially no solvent and thereafter terminating contact between said contact liquid and said supporting surface.

5. A process for the preparation of a film casting surface which comprises maintaining contact between a supporting surface and a contact liquid, moving said supporting surface relative to said contact liquid continuously and repetitively so that said contact liquid is applied to successive portions of said supporting surface, maintaining in said contact liquid a film-forming resin in a solvent therefor and a gelling agent for said resin, solidifying said film-forming resin by gel formation at successive portions of said supporting surface to which it has been applied in said contact liquid, progressively reducing the concentration of film-forming resin in said contact liquid until said liquid contains substantially no resin, thereafter introducing into said contact liquid a liquid material which is a non-solvent for said resin but which is miscible with said solvent, progressively increasing the concentration of said non-solvent liquid in said contact liquid until said contact liquid contains substantially no solvent and thereafter terminating contact between said contact liquid and said supporting surface.

6. A process for the preparation of a film casting surface which comprises maintaining contact between a supporting surface and a contact liquid, moving said supporting surface relative to said contact liquid continuously and repetitively so that said contact liquid is applied to successive portions of said supporting surface, maintain-

ing in said contact liquid a solvent for a film-forming resin but substantially no resin, gradually introducing into said contact liquid a film-forming resin which is soluble in said solvent, solidifying said film-forming resin at successive portions of said supporting surface to which it has been applied in said contact liquid, progressively increasing the concentration of said film-forming resin in said contact liquid until said liquid contains an optimum concentration of film-forming resin, progressively reducing the concentration of film-forming resin in said contact liquid until said liquid contains substantially no resin, thereafter introducing into said contact liquid a liquid material which is a non-solvent for said resin but which is miscible with said solvent, progressively increasing the concentration of said non-solvent liquid in said contact liquid until said contact liquid contains substantially no solvent and thereafter terminating contact between said contact liquid and said supporting surface.

7. A process for the preparation of a film casting surface which comprises maintaining contact between a supporting surface and a contact liquid, moving said supporting surface relative to said contact liquid continuously and repetitively so that said contact liquid is applied to successive portions of said supporting surface, maintaining in said contact liquid a solvent for a film-forming resin and a gelling agent for said resin but substantially no resin, gradually introducing into said contact liquid a film-forming resin which is soluble in said solvent, solidifying said film-forming resin by gel formation at sucessive portions of said supporting surface to which it has been applied in said contact liquid, progressively increasing the concentration of said film-forming resin in said contact liquid until said liquid contains an optimum concentration of film-forming resin, progressively reducing the concentration of film-forming resin in said contact liquid until said liquid contains substantially no resin, thereafter introducing into said contact liquid a liquid material which is a non-solvent for said resin but which is miscible with said solvent, progressively increasing the concentration of said non-solvent liquid in said contact liquid until said contact liquid contains substantially no solvent and thereafter terminating contact between said contact liquid and said supporting surface.

8. A process for the preparation of a film casting surface which comprises maintaining a body of contact liquid, maintaining three reservoirs of liquid connected to permit flow of liquid between each of said reservoirs and said body of liquid, the first of said reservoirs containing a solution of a film-forming resin in a suitable solvent, the second of said reservoirs containing said solvent but no resin and the third of said reservoirs containing a liquid material which is a non-solvent for said resin but which is miscible with said solvent, rotating a solid supporting surface about a horizontal axis so that contact liquid from said body is applied repetitively to successive portions of said surface, maintaining as said contact liquid a resin solution which is dilute with respect to the concentration of said resin, solidifying said film-forming resin as successive portions of said supporting surface to which it has been applied in said contact liquid, progressively increasing the concentration of said film-forming resin in said contact liquid by the addition of resin solution from said first reservoir until said liquid contains an optimum concentration of film-forming resin progressively reducing the concentration of film-forming resin in said contact liquid by the addition of solvent from said second reservoir until said liquid contains substantially no resin, thereafter introducing into said contact liquid non-solvent liquid from said third reservoir, progressively increasing the concentration of said non-solvent liquid in said contact liquid until said contact liquid contains substantially no solvent and thereafter terminating application of said liquid to said supporting surface.

9. The process of claim 8 wherein said solvent is aqueous.

10. The process of claim 9 wherein said resin is polyvinyl alcohol.

11. The process of claim 8 wherein said second reservoir contains a liquid composition comprising said solvent and a gelling agent for said resin and wherein said solidification is by gelation.

12. The process of claim 11 wherein said resin is polyvinyl alcohol and said gelling agent is Congo red.

13. The process of claim 12 wherein said non-solvent liquid is acetone.

14. In a process for the preparation of a film casting surface which is extended in at least two dimensions and which defines an endless path in the direction of its motion in which a layer of film-forming material is deposited on a supporting surface by maintaining contact between said supporting surface and a contact liquid, moving said supporting surface relative to said contact liquid continuously and repetitively so that the contact liquid is applied to successive portions of said supporting surface, said contact liquid, at one stage, comprising a solution of said film-forming material, the improvement which comprises gradually changing the composition of said contact liquid while maintaining said contact until said contact liquid is a non-solvent for said film-forming material and breaking contact between said supporting surface and said contact liquid when said contact liquid is a non-solvent for said film-forming material.

15. A process for the preparation of a spliceless resinous coating which comprises maintaining contact between a supporting surface and a contact liquid within a contact period, moving said supporting surface relative to said contact liquid continuously and repetitively within said contact period so that said contact liquid is applied to successive portions of said supporting surface, gradually changing the composition of said contact liquid during the course of said contact period, said composition comprising a solution of a film-forming material at one stage of said contact period and comprising a non-solvent for said film-forming material at a subsequent stage of said contact period, and breaking contact between said supporting surface and said contact liquid when said contact liquid is a non-solvent for said film-forming material, said application of contact liquid to said surface taking place at the same location during the process, and said cycle of gradually changing the composition of said contact liquid and breaking contact between said surface and said liquid occurring only once at the end of said contact period.

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