April 7, 1936. J. B. WELLS 2,036,377

PROCESS OF TREATING CELLULOSE DERIVATIVE SHEETS

Filed May 26, 1933

Fig. 1.

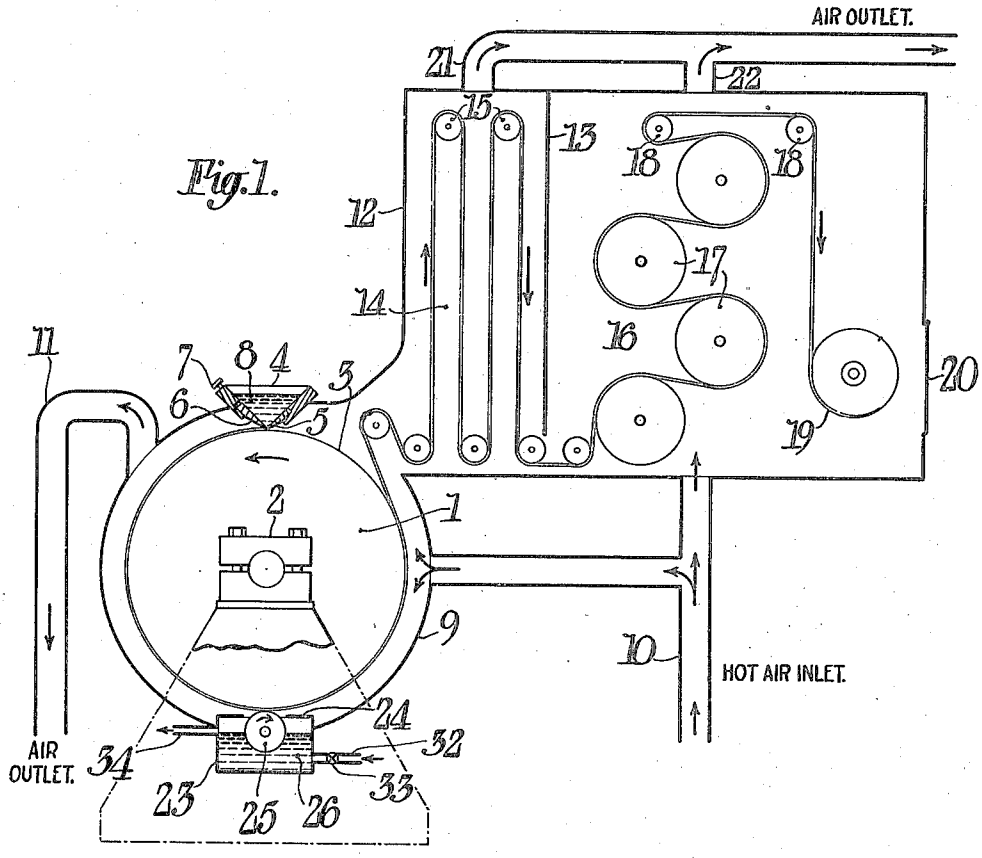



Fig. 3.

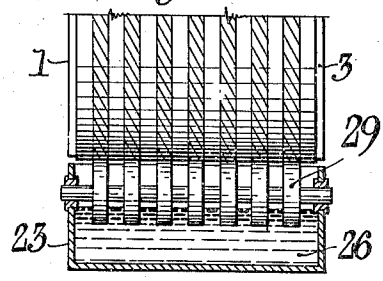



Fig. 4.

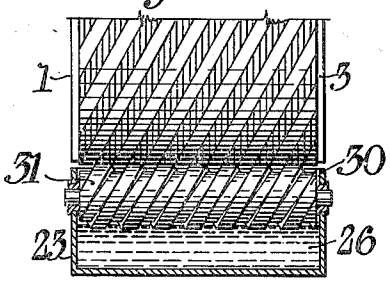
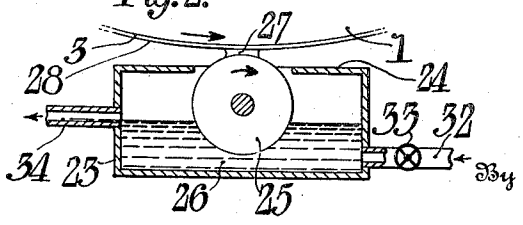



Fig. 2.




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Patented Apr. 7, 1936 2,036,377

# UNITED STATES PATENT OFFICE

2,036,377

## PROCESS OF TREATING CELLULOSE DERIVATIVE SHEETS

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Application May 26, 1933, Serial No. 673,037

12 Claims. (Cl. 18—61)

This invention relates to processes of manufacturing cellulose ester products and more particularly to processes for treating cellulose ester sheet material with various solutions or suspensions to impart improved properties thereto. Specifically, the invention relates to the treatment of sheeting particularly thin sheeting, probably while it is in a relatively plastic condition and contains a considerable proportion of solvent and in all events before it has been removed from the surface upon which it was originally cast.

In the manufacture of cellulose derivative sheeting a suitable solution of a cellulose ester is spread or flowed upon a casting surface and the solvents removed therefrom by evaporation. One of the most commonly employed methods is to make up a cellulose ester solution or dope of the proper composition and viscosity by dissolving the cellulose ester in appropriate solvents and feeding this dope from a hopper, regulated to give the desired thickness, upon the surface of a slowly rotating casting wheel. The solution flows out upon the surface of the wheel and as the latter rotates a current of air or other suitable evaporative medium is brought in contact with the sheet thus formed, causing the solvent to be evaporated therefrom. Before the wheel has rotated through a complete revolution most of the solvents have evaporated and the sheet is then in a condition in which it may be stripped from the surface of the wheel and subjected to curing treatment to further reduce its residual solvent content and bring its shrinkage characteristics within the desired range.

It is often desired to treat sheeting produced in this manner to impart to it certain properties, such as to impart color or to treat the material with various solutions for the purpose of coating or lubricating it and for many other purposes. It has heretofore been the practice to carry out such treatment, either after the sheet has been completely cured, or at some stage of the curing operation, that is, after the sheet has been removed from the casting surface. Such treatment has been attended with varying degrees of success, depending somewhat upon the nature and thickness of the sheet and the nature of the solution or liquid applied thereto. However, the results obtained, for example, in applying solutions or suspensions of colored material to cellulose derivative sheeting have not been wholly satisfactory due to lack of proper penetration of the coloring or other solution into the cured sheet and to the very marked tendency of the material to wrinkle. So marked has been this wrinkling tendency, particularly with the thinner types of cellulose derivative sheeting designed for wrapping purposes, that it has been practically out of the question to apply coloring or other types of treating solutions to this type of material.

It is the principal object of the present invention to overcome the above mentioned difficulties and to provide processes in which cellulose derivative sheeting may be treated with various impregnating solutions or suspensions and in which no wrinkling or other adverse distortion of the material takes place. A specific object of the invention is to provide a process for coloring thin cellulose derivative sheeting by application of a solution or suspension of coloring matter. Other objects will hereinafter appear.

The invention is more fully set forth in the following description taken in connection with the accompanying drawing in which like numerals are applied to like parts and in which,

Fig. 1 is a diagrammatic sectional elevation of an apparatus for the manufacture and treatment of cellulose derivative sheets in accordance with the invention, a portion of the apparatus being broken away to more clearly show the internal structure.

Fig. 2 is a fragmentary sectional elevation of a portion of the apparatus shown in Fig. 1 illustrating the application of an impregnating or coating solution to the cellulose derivative sheeting.

Figs. 3 and 4 are fragmentary elevational views in partial section looking toward the wheel and in a direction at right angles to that of Figs. 1 and 2, illustrating the lower part of a casting wheel and the method by which a striped product may be produced in accordance with specific embodiments of the invention.

Although relating primarily to the coloring or dyeing of cellulose ester sheeting, considered in its broader aspects, the invention includes treating a cellulose derivative sheet with a solution or suspension to impart color or anti-static or other desired properties thereto. When using an apparatus such as that illustrated in Fig. 1, I have discovered that this treatment of the cellulose derivative material may be best accomplished by applying the solution to the sheet at about the point where it has been carried through one half of a revolution on the casting wheel, although I do not limit myself to application of the solution at any particular point in the rotation of the wheel, specifying only that the solution is to be

applied to the sheet before removal from the casting surface.

I wish to emphasize that my process is especially characterized by this fact, i. e., that the sheeting is impregnated with a dissolved or suspended material before removal from the surface upon which it is cast and that the dissolved or suspended components of the treating liquid is deposited on or in the surface of the sheeting and remains in the finished product.

As pointed out above, the liquids usually employed for dyeing or otherwise treating cellulose derivative sheeting have a decided tendency to cause wrinkling, buckling or distortion thereof. This is particularly true of liquids having a direct solvent action on the cellulose derivative material, although certain nonsolvent liquids produce distortion due to their swelling action on the material. I have discovered that only when the treating liquid is applied to the sheet while still adhering to the casting surface can the desired properties be imparted thereto without wrinkling or buckling. Even extremely thin types of sheeting are amenable to treatment by my process without any undesirable distortion whatever.

As will be readily understood, the original sheet-forming cellulose ester solution or dope is spread upon the casting surface and immediately begins to lose solvent by evaporation. The solvent will of course evaporate from the outer surface of the dope much more rapidly than it does from that portion next to the casting surface or, in other words, it tends to "skin over", leaving that portion next to the casting surface in a relatively more highly plastic condition than the outside. This initial curing action takes place progressively as the casting surface rotates and the sheet tends to lose more and more of its solvent with the result that it shrinks to a certain extent and thereby clings very closely to the casting surface and lies perfectly flat thereon. I have found that if the treating solution is now applied to the surface of the sheet it will penetrate at least the outer portions or layers thereof, but since the sheet is then shrunk tightly onto the casting surface, it will continue to cling closely thereto and will not tend to wrinkle or buckle as would be the case if the treating liquid were applied after it had been removed therefrom. As a matter of fact, I have found that, once the thin sheet has been removed from the casting surface, it cannot be successfully treated with impregnating liquids without wrinkling or buckling.

It will be apparent from a consideration of the facts just stated, that a sheet may be readily colored by applying suitable dye solution thereto in the manner just specified. Although permeation of the sheet by the solution will be relatively more complete when employing as the solvent for the coloring matter an active solvent of the cellulose ester material, the process is, to all intents and purposes, equally successful when the solvent is merely a swelling agent for the ester. This fact enables me to employ both solvents and non-solvents, although, I prefer to employ a cellulose ester solvent rather than a non-solvent. It is of course possible to use a mixture of solvents and non-solvents and to control the solvent action of any given mixture by increasing or decreasing the amount of diluting non-solvent in the mixture. Even a non-solvent treating solution may be used where the solution adheres sufficiently well to the sheeting. Typical suitable non-solvent liquids are toluene, benzene and ligroin.

The particular solvent or non-solvent employed in making up my treating solution will of course depend largely upon the nature of the sheeting being treated, and to a certain extent, upon the added components of the treating liquid. If it is desired, for example, to dye the ordinary hydrolyzed cellulose acetate sheeting, a liquid comprising 50% acetone and 50% methyl alcohol may be employed. Other appropriate solvent liquids comprise a mixture of ethylene chloride and alcohol, ethyl acetate, ethylene chloride-tertiary amyl alcohol, acetone-methyl cellosolve (monomethyl ether of ethylene glycol), and many others. When dealing with cellulose acetate-propionate, solvent liquids include ethylene chloride, ethyl acetate, methyl ethyl ketone and others. It will of course be understood that the nature of cellulose ester material of the sheet must be taken into consideration when making up the treating liquid and the components of this liquid will be selected upon the basis of their solvent or swelling action with respect to a given cellulose ester. The solubility of these esters in various agents differ, not only with the particular solvent, but also with the degree of hydrolysis of the ester and with amount of acyl group present in the ester molecule. The effect of varying degrees of hydrolysis on the solubility of mixed cellulose esters is more fully explained in the co-pending application of C. J. Malm and C. F. Fletcher, Serial No. 551,546 filed July 17, 1931. In the case of the fully esterified mixed esters the solubility in a given solvent depends upon the ratio of the amounts of the different acyl groups in a given ester as more fully set forth in the application of C. J. Malm and G. F. Nadeau, Serial No. 659,698, filed March 6, 1933.

While I find it convenient to illustrate my invention by reference to cellulose acetate sheet, it is in no sense limited to the treatment of this material, but broadly applicable to the dyeing or other treatment of sheeting produced from a wide variety of single or mixed cellulose esters, such as cellulose nitrate, cellulose propionate, cellulose butyrate, cellulose stearate, cellulose acetate-nitrate, cellulose acetate-propionate, cellulose acetate-butyrate, cellulose acetate-stearate and many others.

It is also to be understood that the cellulose ester solutions from which the sheeting is cast may contain any suitable plasticizers. In the case of cellulose acetate appropriate plasticizers include monoacetin, triacetin, monochlornaphthalene, camphor, tricresyl phosphate, triphenyl phosphate, pentaerythritol tetracetate and many others known to those skilled in the art.

While I have just referred to the use of solutions or suspensions of coloring matter and to the coloring of cellulose ester sheeting, my invention is in no sense limited to this specific treatment as it is equally applicable to the treatment of sheet material for many other purposes as will be more fully set forth. I may, for example, wish to apply thin coatings of various solid materials to the surface of the sheeting. I may, for example, desire to apply certain lubricating materials to the surface of thin cellulose ester material designed for wrapping purposes to enable this type of sheeting to be more rapidly passed through packaging machinery, or to treat the surface of a cinematographic film support with a lubricating agent to enable it to be more easily passed through a projection apparatus.

In the case of wrapping material it has been proposed in the U. S. patent to Alfred D. Slack and Albert A. Young, No. 2,011,348, issued on application Serial No. 673,038, filed May 26, 1933. to treat this type of sheeting with a solution of an agent which will prevent the accumulation of static charges on its surface and will also lubricate the material. In this case, the sheeting is treated with a dilute solution of stearic acid in a cellulose ester non-solvent. I have found that such a process may be most effectively carried out in accordance with the invention if the solution is applied to the sheeting before it has been stripped from the casting surface. I may in this manner also employ various solutions of inorganic salts for improving the anti-static properties of the material such as Glauber's salt, lithium chloride, stannic chloride and, in fact, almost any metallic salts which increase its electrical conductivity.

The practice of my invention will best be illustrated by reference to a typical example which is included merely for purposes of illustration and in no sense as a limitation thereof.

Referring now to the drawing, the numeral 1 designates a casting wheel mounted in suitable bearings 2 and provided with a suitable coating surface 3, preferably consisting of several different metallic layers plated one on top of the other. The numeral 4 designates a hopper comprising a V-shaped container provided with a stationary blade 5 and an adjustable blade 6 actuated by a suitable device, such as thumb screw 7, for regulating the thickness of the stream of cellulose derivative solution or dope 8 flowing from the hopper onto the surface of the wheel.

The wheel 1 is completely surrounded by a casing 9 through which a current of heated air passes in the direction indicated by the arrows, the air being supplied to the casing by a blower or other appropriate means (not shown) through the hot air inlet 10, and, after passing around the casing to the opposite side is evacuated therefrom by the air outlet 11.

The numeral 12 designates a curing section directly connected to the casing 9 and, in fact, forming an extension or continuation thereof. The section 12 is divided by a partition 13 into two compartments 14 and 16. The compartment 14 is provided with a series of idle rolls 15 over which the sheet is passed after being stripped from the casting surface. The second compartment 16 of the curing section is provided with drying or curing drums 17 over which the sheet is carried after leaving the idle rolls 15 of compartment 14. Guide rolls 18 serve to convey the cured sheet to the wind-up roll 19 positioned opposite the door 20 through which the finished material may be removed when desired.

The hot air inlet pipe 10 supplies both compartments 14 and 16 of the curing section 12 with heated air which is led from these compartments by the air outlets 21 and 22, respectively.

Numeral 23 designates a hopper or tank, preferably positioned at the lowest point of the casting surface, and partially or wholly enclosed by the air casing 9. The hopper 23 may be provided with a suitable cover to prevent excessive evaporation of its contents and is provided with a cylindrical applicator roll 25 rotatably mounted therein and adapted to be partially submerged in a body of treating solution 26 and to convey a thin film of this solution into close proximity with the surface of the casting wheel as roll 1 rotates in the direction indicated by the arrow at the upper part of the figure, the roll 25 being driven in the direction indicated by the arrow appearing thereon. The hopper 23 is supplied with treating fluid through the inlet pipe 32 controlled by valve 33, the fluid, if desired, circulating through the hopper and being discharged therefrom through outlet pipe 34. It will of course be understood that both the casting wheel and the applicator roll are driven by appropriate mechanism, not shown.

Referring now to Fig. 2 which illustrates the method of application of the treating solution to the support or film and in which the relative sizes of the various elements have been somewhat exaggerated for the sake of clearness, it will be seen that the applicator roll 25 dipping in the solution 26 carries up a portion thereof and applies it to the surface of the film 28 in the form of a bead 27. It will thus be seen that the roll is positioned just close enough to the surface of the wheel to provide for maintaining this relatively fine bead of solution in constant contact with the film surface.

Referring to Fig. 3, the numeral 29 designates a special type of roll for applying parallel colored stripes to the cellulose derivative sheet material, the roll 29 dipping in the body of fluid 26 in the same manner as illustrated in Fig. 2 and applying the colored solution or suspension as a plurality of small beads.

In Fig. 4 there is illustrated a still different type of roll 30 for application of diagonal stripes to the sheeting. The operation of this roll 30 is in all respects similar to the operation of the roll 29 shown in Fig. 3, except that the fluid 26 is carried up along the outside of the spiral 31 in order to provide for diagonal application of the stripes. It will of course be understood that the outside surface of the spiral is relatively flat and is machined so that it is substantially parallel with the surface of the wheel 1 and, as in the two previous instances, is spaced a small distance therefrom. When employing this type of roll it is necessary that the roll turn in the direction indicated by the arrow thereon, that is, in a direction such that the treating solution roll moves at the point of contact in the same direction and at the same peripheral speed as the sheet to which it is applied.

As shown in the drawing, the hopper 23 is mounted so as to protrude into the air casing 9, but since the hopper is of less width than the width of the wheel casing 1, the air passing through the casing may pass around the hopper and is not obstructed thereby. In some cases it may be desirable to form the walls of the casing 1 so as to protrude outwardly to provide additional space on either side of the hopper 23 for the passage of the air through the casing.

Although I have shown a single hopper adapted for the application of one treating or impregnating solution at a time, I may employ a plurality of hoppers to provide for the successive application of a number of different solutions or suspensions to the sheet. For example, it may be desired to apply a plurality of colors to the sheet. In order to accomplish this, I may employ a series of hoppers each equipped with applicator rolls and containing the desired color, mounted one ahead of the other at the bottom of the wheel casing and appropriately spaced. In such an arrangement the first hopper will supply one color which will be carried up onto the surface of the sheet by means of an appropriate roll sim-

ilar to roll 25, while each succeeding hopper and its roll will supply additional colors as desired. It will, of course, be necessary to space the respective hoppers at such a distance from one another as will permit a sufficient amount of evaporation or drying out of solvent contained in the coloring liquids to take place to prevent running or smudging. Such details of construction and operation are obviously within the province of those skilled in the art.

The above described methods of striping or otherwise coloring cellulosic sheeting are to be distinguished from processes known to the photographic art, for example, covering broadly the application of dye solutions to finished film support or even emulsioned film for the purpose of edge marking and involving the use of various forms of edge marking rolls. An example of the latter process is contained in the co-pending application of K. C. D. Hickman, Serial No. 362,844, filed May 13, 1929.

Although the carrying out of my process will be fairly evident from a consideration of the several figures of the drawing, briefly stated, the operation is as follows. A cellulose ester dope, for example, a solution consisting of one part by weight of the acetone-soluble variety of cellulose acetate dissolved in four to six parts by weight of acetone is placed in the hopper 4 from which it is fed in suitable thickness and at an appropriate temperature to the surface of the coating wheel 1. As the wheel rotates in the direction indicated by the arrow, a thin layer of solution is continually spread upon the wheel and solvents are rapidly evaporated therefrom by the current of heated air passing around the wheel surface through the casing 9. This evaporation takes place progressively until the sheet contains, say, only a few percent of solvents in which condition it may then be readily stripped from the wheel and passed through the curing section. When the sheet reaches the lowermost position in the casing it meets solution 26 carried up by the rotating roll 25 and is readily permeated thereby. When the solution 26 contains dyes or other coloring matter, for example, these are carried well into the body of the film and, in fact, may in some cases completely penetrate the full thickness of the film. Not only is the sheet penetrated by the solution, but, due to the fact that it clings closely to the casting surface when the treating solution is applied thereto, it has no tendency to wrinkle or buckle away from the coating surface and, in fact, has exactly the opposite tendency, that is, a positive tendency to shrink closer thereto and lie perfectly flat thereon. It is this fact that makes possible the successful treatment of even extremely thin sheeting by my process.

The treated sheet, after stripping from the casting surface, is subjected to any desired curing operation, such as by carrying it through the various compartments of the curing section 12 where it is subjected to an additional current of warm air to remove any residual solvents and to give the film its proper shrinkage characteristics.

As pointed out above, the invention is of rather broad scope and includes various types of film treatment. As indicated, one of the most important applications is in the coloring of thin sheeting. A suitable solution for color treatment may comprise the following:

| | Grams |
|---|---|
| Oil red O | 50 |
| Acetone | 850 |
| Butyl acetate | 100 |

The above solution is of course only typical of many which may be employed for cellulose acetate or other types of cellulose ester thin sheeting. In addition to acetone-soluble dyes other dyes such as the following may be successfully employed.

| | Color Index No. |
|---|---|
| Fuchsin Y | 677 |
| Spirit red | 258 |
| Acid green L | 666 |
| Malachite green | 657 |
| Oil orange E | 24 |
| Methanil yellow | 138 |
| Fast wool yellow 3 g | 636 |
| Fast wool blue B | 209 |
| Spirit blue | 689 |
| Spirit nigrosine | 864 |

In addition other coloring material, such as suspensions of various finely divided vegetable and mineral coloring matters, metallic powders such as gold, silver and bronze powders, pigments such as titanium dioxide, lithopone, baryta, and other materials may be employed.

If it is desired to impregnate or coat the cellulose derivative sheeting with solid material such as stearic acid, in accordance with the procedure outlined in the above mentioned Slack and Young application, the following formula may be employed:

| | Grams |
|---|---|
| Stearic acid | 40 |
| Acetone | 700 |
| Butyl acetate | 260 |

As above indicated, in some cases it may be desirable to impregnate the sheeting in this manner with a solution of a metallic salt such as lithium or stannic chloride to give it anti-static properties. The salt may be applied in the form of a separate solution or may be added to a coloring solution. For example, when employing a separate solution for this purpose, it may contain 2% lithium chloride and 5% glycerine dissolved in a mixture of 10% water and 90% acetone.

If it is desired to render the sheeting hygroscopic, glycerine may be incorporated with a given treating solution, this being carried into the interior of the sheet and being retained thereby after curing is completed.

The invention also includes applying coatings or layers of various materials to the sheeting. It may, for example, be desired to apply a thin coating of gelatin in which case the treating solution may comprise a few percent of gelatin dissolved in a mixture of acetone and water in which the acetone preferably predominates. Coatings of cellulose esters may also be applied in accordance with the invention. For example, I may coat a sheet of cellulose acetate with cellulose nitrate by applying a dilute solution of the nitrate in methyl alcohol or in a mixture of methyl alcohol and acetone. In any of these cases, in accordance with the invention, the sheeting is treated before removal from, and therefore clinging closely to, the casting surface and the liquid is such that it slightly attacks the plastic material or at least penetrates thereinto.

The invention is to be distinguished from known processes involving the application of solutions as suspensions to the surface of sheeting to build up a thin layer thereon as in such processes, not only is a definite and distinct layer or stratum built up by such treatment, but there is no appreciable penetration or permeation of

the sheet by the liquid. Furthermore, in these cases the sheet is not treated until the sheet is stripped from the wheel whereas according to the present invention the treatment can be carried out only before the sheet is stripped from the casting surface.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent of the United States is:

1. The process which comprises casting a cellulose ester solution in the form of a sheet on an appropriate surface, allowing the sheet to set by evaporation of solvent therefrom, and treating the sheet before removal from the casting surface and while the sheet contains an appreciable amount of residual solvent with a dye solution.

2. The process which comprises casting a cellulose ester solution in the form of a sheet on an appropriate surface, allowing the sheet to set by evaporation of solvent therefrom, and treating the sheet, before removal from the casting surface and while the sheet contains an appreciable amount of residual solvent with a dye dissolved in a liquid containing an active solvent of the cellulose ester.

3. The process which comprises casting a cellulose ester solution in the form of a sheet on an appropriate surface, allowing the sheet to set by evaporation of solvent therefrom, and treating the sheet, before removal from the casting surface and while the sheet contains an appreciable amount of residual solvent with a dye dissolved in a liquid containing an active solvent of the cellulose ester and a non-solvent.

4. The process which comprises casting a cellulose ester solution in the form of a sheet on an appropriate surface, allowing the sheet to set by evaporation of solvent therefrom, and treating the sheet before removal from the casting surface and while the sheet contains an appreciable amount of residual solvent with a solution of a lubricating agent.

5. The process which comprises casting a cellulose ester solution in the form of a sheet on an appropriate surface, allowing the sheet to set by evaporation of solvent therefrom and treating the sheet before removal from the casting surface and while the sheet contains an appreciable amount of residual solvent with a solution of stearic acid.

6. The process which comprises casting a cellulose acetate solution in the form of a sheet on an appropriate surface, allowing the sheet to set by evaporation of solvent therefrom, and treating the sheet, before removal from the casting surface and while the sheet contains an appreciable amount of residual solvent with an acetone solution of dye.

7. The process of applying color in the form of stripes to cellulose derivative sheeting which comprises applying a dye solution thereto in the form of a plurality of beads before the sheeting is removed from the surface on which it is cast and while the sheeting still contains an appreciable amount of residual solvent.

8. The process of coloring cellulose acetate sheeting which comprises applying to the sheeting before removal from the surface on which it is cast and while still containing an appreciable amount of residual solvent, a colored solution which contains a liquid which substantially penetrates the body of the sheeting and permanently deposits the color within the structure thereof.

9. The process of making a cellulose ester sheeting having a permanent gelatin coating thereon which comprises casting a cellulose ester solution in the form of a sheet on an appropriate surface, allowing the sheet to set by evaporation of solvent therefrom, and applying to the sheet before removal from the casting surface and while the sheet contains an appreciable amount of residual solvent, a gelatin solution containing a liquid which penetrates into the body of the sheet.

10. The process of making a cellulose organic ester sheeting having a permanent gelatin coating thereon which comprises casting a cellulose organic ester solution in the form of a sheet on an appropriate surface, allowing the sheet to set by evaporation of solvent therefrom, and applying to the sheet before removal from the casting surface and while the sheet contains an appreciable amount of residual solvent, a gelatin solution containing a liquid which penetrates into the body of the sheet.

11. The process of making a cellulose nitrate sheeting having a permanent gelatin coating thereon which comprises casting a cellulose nitrate solution in the form of a sheet on an appropriate surface, allowing the sheet to set by evaporation of solvent therefrom, and applying to the sheet before removal from the casting surface and while the sheet contains an appreciable amount of residual solvent, a gelatin solution containing a liquid which penetrates into the body of the sheet.

12. The process of making a cellulose acetate sheeting having a permanent gelatin coating thereon which comprises casting a cellulose acetate solution in the form of a sheet on an appropriate surface, allowing the sheet to set by evaporation of solvent therefrom, and applying to the sheet before removal from the casting surface and while the sheet contains an appreciable amount of residual solvent, a gelatin solution containing a liquid which penetrates into the body of the sheet.

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