Jan. 9, 1934. S. E. SHEPPARD ET AL 1,942,840

MANUFACTURE OF FILMS FROM CELLULOSIC MATERIALS

Filed July 2, 1928

FIG. 1.

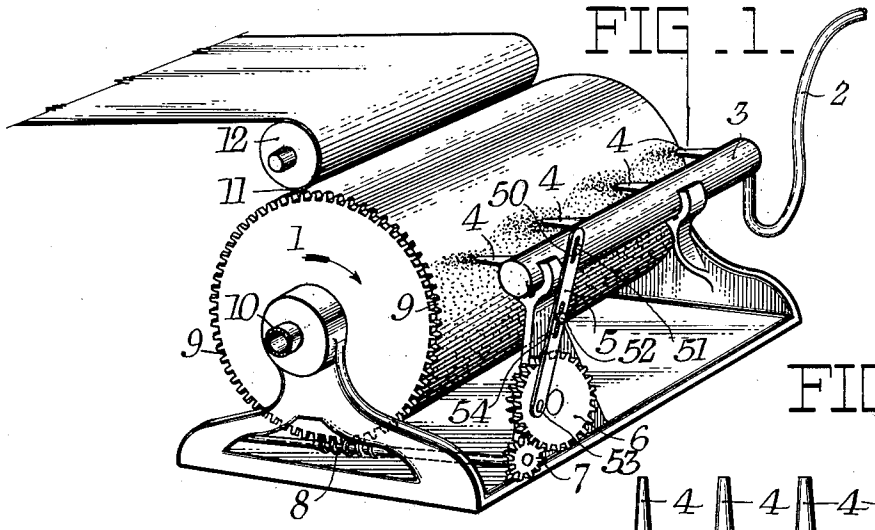


FIG. 2.

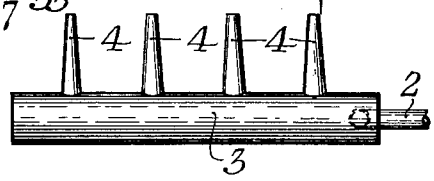


FIG. 3.

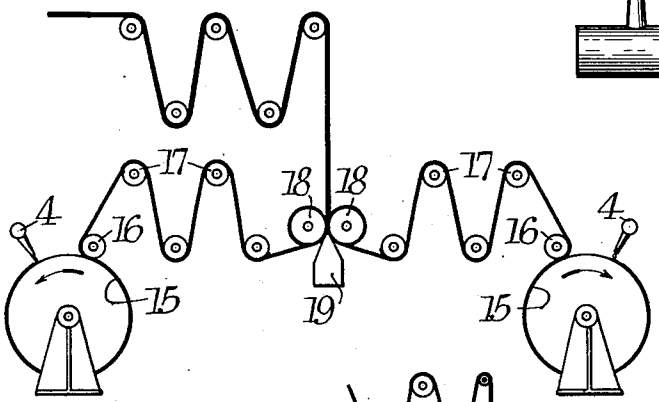
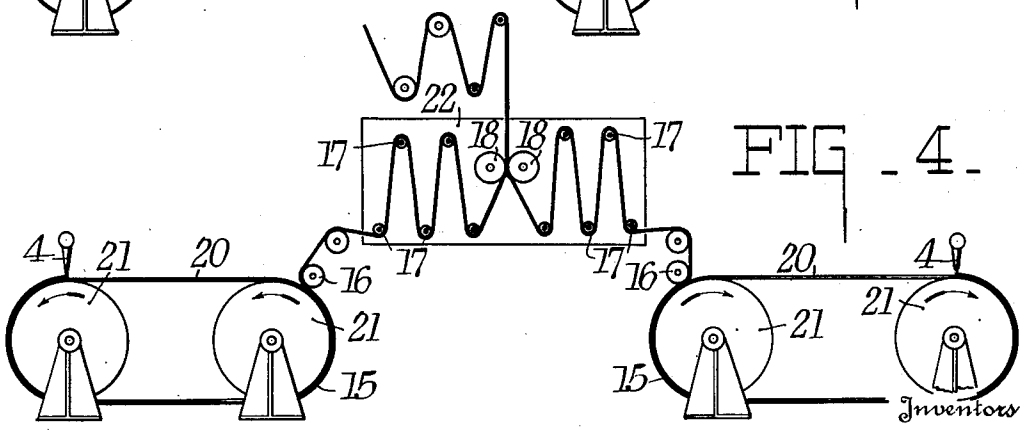


FIG. 4.



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MANUFACTURE OF FILMS FROM CELLULOSIC MATERIALS

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3 Claims. (Cl. 18—57)

This invention relates to a process for the manufacture of sheets of cellulosic materials by spraying such material on a sheet-forming surface. One object of this invention is to provide an emulsion of cellulosic materials which can be formed into a continuous sheet by spraying upon a moving surface. Another object of this invention is the elimination of the fire and explosion hazards attendant on the usual film manufacturing processes. Still another object is the economies effected by the use of aqueous emulsions rather than organic solvent solutions of the cellulosic materials. Other objects will hereinafter appear.

We have found that a suspension or emulsion of cellulosic materials, such as cellulose esters, commonly used for the manufacture of films for photographic or other purposes, may be sprayed at a suitable pressure against a moving surface, such as a rotating drum or a metallic belt carried on revolving pulleys. A thin continuous sheet is obtained which may subsequently be laminated with similar or other sheets for use in the photographic or allied industries. The thin sheets may be used for other purposes, as for example, wrapping tissue, without the necessity of laminating.

By this system of film formation we have realized numerous advantages over the methods ordinarily used. The employment of aqueous suspensions or emulsions eliminates the hazards of fire and explosion that are present when cellulosic materials dissolved in highly volatile organic solvents are coated on heated surfaces. Other desirable economies are also effected by our process,—less solvent is required in the cellulosic solution prior to film coating, and hence there is less solvent to be recovered after the film has been formed.

We shall now describe two embodiments of our invention for the purpose of illustration, but it will be understood that the invention is not limited to these examples, or the details thereof, except as indicated in the appended claims.

Example I

A. A mixture of 15–25 parts of acetylene tetrachlorid and 85–75 parts of water is added to $\frac{1}{10}$ of 1% of Turkey red oil. This mixture is emulsified by agitation.

B. A second emulsion is made as in "A" of 20–50 parts of acetone, 80–50 parts of water, the whole containing $\frac{1}{10}$ of 1% of Turkey red oil.

C. 12 parts of comminuted cellulose acetate are ground in a suitable tube or ball mill with 88 parts of water until sufficiently finely divided. The particles should be of the order of 5–10 μ.

Equal parts of "B" and "C" are then mixed together with agitation and then equal parts by volume of "A" and the mixture of "B" and "C". A stable emulsion is thus formed, which separates slowly, but by moderate agitation the material is kept in the dispersed phase.

This emulsion when sprayed on a plate or drum heated to or above the boiling point of water gives coherent nearly transparent films, using a pressure of 50 pounds per square inch in the spray.

Example II

An emulsion or suspension of 50 parts nitrocellulose, plasticized with 150 parts of amyl acetate, butyl acetate or like high boiler, with or without the addition of camphor, may be prepared by a modification of the procedure described in the U. S. Patent No. 1,589,332 to the present inventors, granted June 15, 1926. In this process it is best, however, to add less than 1 part of glue or gum arabic; this mixture is vigorously agitated in 1000 parts of water containing 15 parts of an emulsifying agent like Turkey red oil.

The resulting emulsion is then sprayed, as in the first example,—a pressure as high as 700 pounds per square inch may be found necessary for uniform coalescence of the sprayed particles.

In general, however, procedures involving the emulsification of these bodies directly from solutions are less advantageous, economically, than procedures in which suspensions are prepared by grinding the already partly comminuted material in water in ball, tube or rod mills, or colloid mills, as further described in the patent to Beal and Eberlin, No. 1,589,328, granted June 15, 1926.

Cellulose acetate solutions, as in acetic acid, may be spray dried by a method similar to that described in U. S. Patent No. 1,516,225, Webb, granted November 18, 1924. A cellulose acetate hydrolyzed or unhydrolyzed to acetone solubility may be used. Prior to the above spraying, a small amount of high boilers and/or softeners may be added, but not sufficient to cause the particles formed to stick together.

The spray-dried material is then washed and ground in water, during which process the water may be removed and renewed to leach out undesirable salts. When comminution has been carried to the desired point, i. e., particles of the order of 1 to 5 μ, there may be added small amounts of a low or high boiling solvent, or mixtures, to swell the particles slightly.

In all of the above described processes there is formed an aqueous emulsion of particles which may be sprayed at high pressure on a slowly moving, heated, smooth surface, whereupon they form a smooth, uniform, coherent film. This is considered to be due to the particles tending to flow slightly upon impact against the surface and to weld together, while the water runs off.

Other cellulosic materials than those described in the foregoing examples are suitable for use in our process, especially those of the water insoluble types of ethers, esters, or dissolved cellulosic compounds.

The layers formed by our invention are generally more or less translucent or partially opaque from the precipitation or occlusion of water within the sheet during the drying operation. They are also thin and although they may be used for some purposes, such as wrapping tissue, they are not sufficiently thick for photographic or other manufactured products requiring greater strength and rigidity. Both of these disadvantages may be obviated at one and the same time by laminating the sheets in the manner disclosed in the patent to Van Derhoef, No. 1,540,822, granted June 9, 1925 and by using a cement containing a volatile solvent of the cellulosic material, or passing the formed sheet through a chamber containing the vapors of such a solvent. If an acetone soluble cellulose acetate sheet is to be laminated, a cement containing acetone may be used; if a nitrocellulose sheet, a cement containing, for example, methyl alcohol would have the desired cementing and dehazing effect.

In order further to explain our invention, reference will now be made to the accompanying drawing in the several figures of which the same reference characters denote the same parts and in which,—

Fig. 1 is a perspective view of an apparatus which may be employed in our improved process;

Fig. 2 is a plan of the spray nozzles;

Fig. 3 is a diagrammatic view of the apparatus which may be used for the lamination of the film;

Fig. 4 is a modification of Fig. 3.

Figure 1 shows one form of the apparatus in which our process may be conveniently carried out, the relative sizes of the parts being exaggerated for the sake of clearness. The drum 1 rotates in a clockwise direction, being rotated by suitable means not shown. The emulsified cellulosic material is fed under pressure through the flexible pipe or hose 2 to the header 3 from which a plurality of nozzles 4 extend. The header 3 is oscillated parallel to the drum axis by means of the lever arm 5, which is slotted at 50 and 54 and engages pin 51 on header 3, and the fixed pivot 52 with a slidable pivoted engagement. It is actuated by the gear 6 through the pivot 53, gear 6 being actuated in turn by the gear train 7 and 8,—the latter gear meshes with the teeth 9 on the periphery of the drum and is driven thereby. The drum rotates on hollow trunnions 10 through which steam, or other heating media, may be forced into the drum for more rapidly vaporizing the water from the sprayed emulsion. The resulting sheet is stripped from the drum at 11 over the roller 12 and may then be further cured by passing over other heated drums or wound up by means not shown. After curing, the sheet may be fed to laminating machines, such as those disclosed in U. S. patents to Van Derhoef, Nos. 1,540,822 and 1,641,403.

Figure 3 shows the two drums 1, similar to the drum shown in Figure 1 having the spray nozzles 4. The film 15 is stripped from the drums which rotate in the direction indicated by the arrows, over the rollers 16. The film is then drawn over the rollers 17 to the laminating apparatus. Just prior to the film passing between the pressure rollers 18 a suitable amount of cement containing, if the film is to be rendered transparent, a volatile solvent of the film. This is fed to the film from a suitable feeder 19. The film may then be directly conducted to winding reels or the curing rolls not shown.

Figure 4 shows a modification of our laminating apparatus. The aqueous emulsion is sprayed through the nozzles 4 upon the moving metallic belts 20, which are carried on the pulleys 21 rotating in the direction indicated by the arrows. The formed film 15 is stripped from the drum by the rollers 16,—the film then passes into the chamber 22, which is charged with a vapor of a solvent of the film to be laminated. The film passes over the rollers 17 in this vapor atmosphere, loses any haze or opacity that it may have and becomes slightly plastic. In this condition it is passed between the pressure rolls 18,—this cements the layers together. They are then drawn from the chamber and conducted to wind up reels or to a second cementing and laminating chamber or to a curing apparatus.

We contemplate as included in our invention all such modifications and equivalents as fall within the scope of the appended claims.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. The process of forming transparent continuous cellulosic films from thin sheets of light obstructive cellulosic material formed by spraying cellulosic particles on a smooth surface, which comprises simultaneously rendering the film transparent and adhesive with a cement containing a volatile solvent of said cellulosic material and subsequently laminating a plurality of said sheets.

2. The process of forming transparent continuous cellulose acetate films from thin sheets thereof which are formed by spraying cellulosic particles against a surface and which are light obstructive, which process comprises simultaneously rendering the film transparent and adhesive with a cement containing a volatile solvent of said cellulosic material and subsequently laminating a plurality of said sheets.

3. The process of making a transparent film of cellulosic material which process comprises spraying aqueous emulsions of plastic cellulosic materials against heated, moving, smooth film-forming surfaces, whereby there are formed thereon coherent films having a tendency to be light obstructive, stripping said films from said surfaces, submitting said films to the action of a volatile solvent whereupon they are rendered transparent and adherent and at once laminating said films together.

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