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Method of Coating Cellulose Derivative Sheetting

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This invention relates to the manufacture of sheets from cellulose derivatives and thermoplastic resins and more particularly to the elimination of the tendency of such sheets to stick together when superimposed as when the sheets are stacked up as in a flat package.

When thin sheets of these materials are produced in the conventional manner such as by flowing a film forming solution onto a film forming surface, it is found that they have a pronounced and almost uncontrollable tendency to stick together if they come in contact for any length of time. This sticking tendency is particularly troublesome when the sheets are pressed together, as normally occurs in cutting a plurality of sheets to size or in packaging. This troublesome effect is more accentuated in thin sheets and often makes separation of these sheets extremely difficult or impossible.

After some study it was discovered that if two sheets are stacked so that their outer surfaces are together, i.e., the surface opposite that coming in contact with the film forming surface, they are so smooth there is optical contact between them. It is due to this condition that the adjacent sheets often tenaciously stick together.

There was considerable less sticking tendency between sheets if the inner sides, i.e., the side resting on the film forming surface during forming came into contact. This was found due to the fact that the film forming surface although very smooth still had microscopic indentations in it which caused a microscopic roughening of the inner sheet surface and prevented optical contact. The outer side of the same sheet, however, apparently due to a surface tension forms a very smooth surface.

This invention, therefore, has for an object a process for producing sheets of cellulose derivatives and thermoplastic resins having substantially no tendency to stick together. Another object is a process for producing such thin films and sheets which may be stacked and subjected to pressure and still remain easily separable. Another object is an improved film or sheet coating apparatus for forming sheets and films with a microscopically roughened surface particularly on the side opposite the coating surface. Other objects will appear hereinafter.

In accordance with the invention these objects are attained by coating a solution of cellulose organic acid ester or thermoplastic resin onto a film forming surface and inducing incipient precipitation of the ester or resin on the surface of a heated moist atmosphere. It appears that this moist atmosphere dilutes the upper surface of the solution sufficiently so that the solvent in this upper surface is unable to retain the ester in solution. This condition is also enhanced by vaporization of the solvent from the surface layer by the hot air contacting the ribbon of solution.

This incipient precipitation causes a microscopic roughening of the surface. At a subsequent stage of the coating process heated air usually of high temperature and of very low moisture content is brought into contact with the sheet and this effect curing out of residual solvent from the lower layer of the material in the sheet which passes thru the sheet to the upper or surface layer. As this residual solvent enters the surface layer it effects a resolution of the major portion of the previously precipitated ester, but nevertheless leaves a slightly roughened or microscopically undulated surface on the outer side of the material caused by the residue of undissolved ester or resin particles. At this stage of the process, the sheet is stripped from the forming surface and may be further cured in conventional drying apparatus as required. The roughened surface, though of microscopic character, permits entrance of air between such sheets when they are stacked up and overcomes the optical contact sticking effect that occurs when two smooth surfaces are superimposed.

The invention will be more clearly understood by reference to the following detailed description and accompanying drawing which is a sectional view in elevation of the apparatus I prefer to employ in the operation of my invention. The invention is described in connection with the making of a cellulose ester sheet, but it will be understood that the invention is not limited by this description and comprehends making sheets from other types of materials.

As shown in the drawing 10 represents the preferred form of a coating apparatus comprising a coating wheel 11 which is rotatably mounted on a shaft 12 which engages a supporting member 13. As is apparent from the drawing the coating wheel is engaged with a casing 14 having three parts 15, 16 and 17 thru which gases may pass to and from the casing as will hereinafter be explained. In an opening 18 adjacent the top of the coating wheel 11 is mounted a typical coating hopper 19, the more essential parts of which comprise slanting walls 21 and 22 which are separated at their apex to form a coating slot 23. A sliding blade 24 is mounted on wall 21 and, by means of screw 25, can be raised or lowered to regulate
the width of the coating slot 23. An end wall of the hopper is shown at 26. Coating solution 27 is shown partially filling the hopper 19 and this is added to the hopper from supply tank 28 thru pipe line 29. Above the left quadrant of the coating wheel 11 is mounted a long jet 31 thru which a gas can be caused to impinge into the atmosphere surrounding the wheel in that vicinity. The wheel 11 is heated by conventional means not shown, to expel, at an even rate, the low boiling solvents contained in the coating solution coated thereon. The coating solution 27 flows from coating slot 23 onto the wheel 11 and as the wheel turns, in the present apparatus in a counterclockwise direction, the solution, owing to evaporation of the solvents from the heated wheel surface into the atmosphere in the encased space 32 gradually becomes a more or less self-sustaining sheet 33 which may be removed by stripping roll 34 and wound up in a roll 35 after being subjected to a further drying operation, not shown. For convenience in description different sections of sheet 33 are numbered at 32a, 32b, and 32c.

In accordance with my invention I control the temperature and humidity of the atmosphere in the space 32 surrounding the solution and sheeting on the coating wheel, first to effect incipient precipitation of the cellulose ester in the surface layer of the solution, and second to put the major portion of the precipitated ester back in solution before the sheet is stripped from the wheel 11. This is preferably accomplished by forcing air thru port 17 and steam thru jet 31. This humid atmosphere contacts the solution adjacent to the point indicated as 33a soon after it leaves the hopper 15, while it contains a large proportion of low boiling solvent. The hot air causes some of the solvent in the upper stratum of solution to vaporize and the water vapor contacting this same stratum dilutes the remaining solvent in this stratum. These two cooperating factors so reduce the solvent concentration that the ester previously in solution in this upper stratum will precipitate out. The greater proportion of the air and steam leaves the apparatus thru outlet 35. At or soon after the solution 33a, new sheet 33b, passes outlet 18 it comes into contact with another current of highly heated and substantially dry air which it is introduced into the casing thru port 15. This heated air acting with the heated drum 11 promotes the vaporization of the solvent from the lower stratum of the sheet which in passing thru the sheet to the upper stratum increases the solvent concentration in the upper layer sufficiently to redissolve the major portion of the precipitated ester. However, there remains a sufficient amount of undisolved ester particles to cause a microscopic roughness in the outer surface of the sheet which is now stripped off the coating wheel as shown at 33c.

By suitable variations in the temperatures of the air sections or speed of the turning wheel on which the sheet is coated, and by variations in amounts of steam or steam and air various roughened surface conditions can be obtained. Also in the case of different esters and resins or solution viscosities different temperature of air and steam may be required to produce the most satisfactory product.

For best operation of my process the cellulose derivative or resins should be in a solution of solvents which are miscible with water such as acetone, methyl, ethyl and isopropyl alcohol. The process is generally applicable in cases where the action of steam or high humidity results in precipitation of the surface of the coated sheet as distinguished from a coagulative effect. It will be understood that other means than steam may be employed in accordance with the invention concept to add humidity to the apparatus, for example moist air.

My improved coating process may be employed for forming thin sheeting from cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate and cellulose acetate butyrate, as well as cellulose ethers such as methyl cellulose, ethyl cellulose, and benzyl cellulose and thermoplastic resins including polyvinyl acetate.

The following are examples of coating solutions which may be formed into continuous sheets or film support by my process.

**Example I**

A cellulose acetate of 39.5% acetyl is dissolved in 4 parts by weight of acetone and diethyl phthulate equal to 32% of the weight of the cellulose acetate is added. It is flowed onto the revolving coating wheel 11 at a temperature of 110-125°F. The coating wheel is maintained at 110-120°F. Moist steam is sprayed onto the freshly coated solution so that it is rather evenly distributed over the entire surface of the solution. The steam is preferably at about 10 lbs. gauge pressure and is supplied to the distributor at a rate of about 100 lbs. per hour, producing an atmosphere of approximately 100% relative humidity. As previously described the moisture contained in the steam dilutes the thin surface layer of the solution and causes precipitation of the acetate in that layer. As coating wheel 11 turns the solution will continue to vaporize somewhat and in the vicinity of 33b, the semi-hardened solution comes in contact with air at a temperature of 180°F, which is introduced into the apparatus thru port 15. This air is substantially dry and it removes the moisture previously introduced into the solution and further dries the solvent out of the solution which as it passes from the inner side of the solution thru the upper layer causes resolution of the major portion of the precipitated acetate. The now formed sheet is stripped of the coating as shown in the drawing and conducted away from the apparatus. It has a microscopic roughness on the outer side which will prevent optical contact.

**Example II**

A cellulose acetate butyrate of 10 to 30% acetyl and 5 to 15% butyryl with a total ester content of not more than 35% is dissolved in four parts by weight of solvent consisting of 10 to 20% water and the balance acetone. Dibutyl phthalate equal to 25% of the weight of the acetate butyrate is added. The amount of water used in the solvent would be dependent upon the total ester value of the mixed cellulose ester. The amount of water necessary to bring about solution would be inverse to the total ester value of the cellulose acetate butyrate. When a uniform solution is obtained it is flowed onto the revolving coating wheel 11 and processed in accordance with the conditions given in Example I. A transparent continuous sheet will result which has substantially uniform microscopic indentations on the side opposite that contacting the coating wheel and this sheet will not cause difficulty owing to optical contact.
Example III

A cellulose ethyl ether of approximately 45% ethoxyl content is dissolved in 4 parts by weight of methanol and triphenyl phosphate to the amount of 25% of the weight of the cellulose ether is added. After a clear homogenous solution has been obtained by mixing and filtering, it is flowed onto a coating surface and treated as in Example I.

Example IV

A polyvinyl acetate acetal having a residual polyvinyl alcohol content of about 8% and a residual polyvinyl acetate content of about 5% is dissolved in 4 parts by weight of a solvent mixture consisting of equal parts by weight of acetone and methyl alcohol. After a clear homogenous solution has been obtained by mixing and filtering, it is flowed onto a coating surface and is treated as in Example I.

I claim:

1. In the process of forming a continuous sheet from thermoplastic material which includes flowing a film forming solution onto a film forming surface adapted to evaporate solvents therefrom to form the sheet, the step of roughening the outer surface of the sheet which comprises first precipitating a part of the thermoplastic material out of the solution on the film forming surface by exposing the solution while it contains a relative large proportion of solvent to a heated atmosphere of high humidity, and subsequently redissolving the major portion of the precipitated material in the solution by passing the solution through a higher heated atmosphere of lower humidity which is formed the while by progressive evaporation of solvents from the forming surface.

2. In the process of forming a thin continuous cellulose organic acid ester sheet which includes flowing a film forming solution containing solvents and dissolved ester onto a heated film forming surface adapted to evaporate solvents therefrom to form the sheet, the step of roughening the outer surface of the sheet which comprises first precipitating a portion of the ester out of the solution on the film forming surface by exposing the solution while it contains a relatively large proportion of solvent to a heated atmosphere of high humidity whereby microscopic indentations in the outer surface of the solution are formed, and subsequently redissolving the major portion of the precipitated ester in the solution by passing the solution on the film forming surface through a heated atmosphere of lower humidity to reduce the magnitude of the microscopic indentations while the solution contains a less amount of solvent prior to removing the sheet which is formed the while by progressive evaporation of solvents from the forming surface.

3. In the process of forming a continuous thin cellulose acetate sheet which includes flowing a film forming solution containing solvents and dissolved cellulose acetate onto a heated film forming surface adapted to evaporate solvents therefrom to form the sheet, the step of roughening the outer surface of the sheet which comprises first precipitating a portion of the cellulose acetate out of the solution on the film forming surface by exposing the solution while it contains a relatively large proportion of solvent to a heated atmosphere of high humidity whereby microscopic indentations in the outer surface of the solution are formed, and subsequently redissolving the major portion of the precipitated cellulose acetate in the solution by passing the solution through a higher heated atmosphere of lower humidity which reduces the magnitude of the microscopic indentations while it contains a less amount of solvent prior to removing the sheet, which is formed the while by progressive evaporation of solvents, from the forming surface.

4. In the process of forming a continuous thin cellulose acetate butyrate sheet which includes flowing a film forming solution containing solvents and dissolved cellulose acetate butyrate onto a heated film forming surface adapted to evaporate solvents therefrom to form the sheet, the step of roughening the outer surface of the sheet which comprises first precipitating a portion of the cellulose acetate butyrate out of the solution on the film forming surface by exposing the solution while it contains a relatively large proportion of solvent to a heated atmosphere of high humidity whereby microscopic indentations in the outer surface of the solution are formed, and subsequently redissolving the major portion of the precipitated cellulose acetate butyrate in the solution by passing the solution through a higher heated atmosphere of lower humidity which reduces the magnitude of the microscopic indentations while it contains a less amount of solvent prior to removing the sheet, which is formed the while by progressive evaporation of solvents, from the forming surface.

5. In the process of forming a continuous thin polyvinyl acetate sheet which includes flowing a film forming solution containing solvents and dissolved polyvinyl acetate onto a heated film forming surface adapted to evaporate solvents therefrom to form the sheet, the step of roughening the outer surface of the sheet which comprises first precipitating a portion of the polyvinyl acetate out of the solution on the film forming surface by exposing the solution while it contains a relatively large proportion of solvent to a heated atmosphere of high humidity whereby microscopic indentations in the outer surface of the solution are formed, and subsequently redissolving the major portion of the precipitated acetate resin in the solution by passing the solution through a higher heated atmosphere of lower humidity which reduces the magnitude of the microscopic indentations while it contains a less amount of solvent prior to removing the sheet, which is formed the while by progressive evaporation of solvents, from the forming surface.

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