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COATED CELLULOSIC PELLICLES AND METHODS OF PRODUCING THE SAME

William G. Grantham, Wilmington, Del., assignor to American Viscose Corporation, Philadelphia, Pa., a corporation of Delaware

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This invention relates to improved cellulosic pellicles, and more particularly to cellulosic pellicles comprising an anti-sticking agent and having improved surface slip characteristics. The invention is particularly applicable to regenerated cellulose sheeting or film which can be rolled upon itself or stacked without caking or sticking.

Transparent regenerated cellulose sheeting is produced commercially by regeneration of cellulose from, for example, viscose, followed by washing, bleaching and otherwise purifying the sheets, impregnating the wet or gel sheets with an aqueous solution of a suitable plasticizer, and finally drying the plasticized sheets over a plurality of heated rolls. In order to preserve the toughness and plasticity of the sheets, it is necessary to maintain a predetermined moisture content therein. The best results are obtained when the sheet contains moisture in equilibrium with the surrounding atmosphere having a relative humidity of approximately 35 per cent, i. e., approximately 5 per cent to 8 per cent moisture, and during manufacture of the sheets such a moisture content is obtained during drying of the sheets by careful control and constant supervision and analysis. The plain sheets as manufactured, that is sheets which have not been coated with a moistureproofing composition, are extremely sensitive to humidity changes, and the amount of moisture absorbed thereby varies over a wide range in response to variations in the humidity of the surrounding atmosphere. Glycerol or some other hygroscopic plasticizing or softening agent is incorporated in the gel sheet to insure absorption of moisture adequate for plasticity at low relative humidity of the atmosphere to which the sheets are exposed. However, because of the inherent hydrophilic character of the regenerated cellulose and the presence of the glycerol or other hygroscopic agent therein, the sheets absorb more moisture than is required for workable plasticity when they are subjected to high relative humidities, with the result that the surfaces of the sheets tend toward tackiness. Surface tackiness or the tendency to cohere when the sheets are assembled in stacks or rolls increases with increase in moisture content above the maximum needed for retention of workable plasticity and leads to caking or "blocking" of the stacked or rolled sheets so that they cannot be readily separated for use in wrapping or packaging.

It has been suggested heretofore to eliminate this difficulty by treating the surface of the film with an anti-sticking, or "slip" agent. "Slip" as used herein refers to the amount of friction, or lack of it, between adjacent surfaces of superimposed regenerated cellulose films or sheets and is designated quantitatively by the coefficient of friction of two surfaces of film when subjected to a load of approximately one lb. per sq. inch and acted on by a force at right angles to the applied load. Various agents of different types have been proposed for use as "slip" agents, but most of the materials previously suggested have had one or more defects which detract from their usefulness on a practical commercial scale. They may not impart the desired "slip" to the sheets, as is the case with soluble and insoluble silicates and albuminous substances; they may be effective only in relatively large amounts so that use thereof increases the manufacturing cost of the sheet too greatly; or they may fail to give good "slip" at the higher temperatures to which the sheet is subjected when it is exposed to heat developed by friction in an automatic wrapping machine. Heretofore, resinous materials generally have not been found satisfactory as anti-sticking agents. In general, the resinous materials have been found to greatly reduce the cohesion-resistance property of the sheets and to impair the capacity of the sheets to be glued with aqueous adhesives. It has been found, for instance, that melamine-formaldehyde resins do not prevent caking of regenerated cellulose sheets treated with it even when the resin is used in the form of a colloidal solution or dispersion.

It is an object of this invention to provide cellulosic sheets and films having good slip characteristics over a wide range of relative humidity and temperature conditions. Another object of the invention is to provide new "slip" or anti-sticking agents for non-fibrous cellulosic sheets and films. A further object is to provide cellulosic sheets and films having superior "slip" characteristics and comprising a resinous anti-sticking agent, which sheets can be glued by means of aqueous adhesives if desired.

I have discovered that solid, finely divided copolymers resulting from the copolymerization of vinyl chloride and lower alkyl esters of alpha,beta-unsaturated polycarboxylic acids, e. g., the lower alkyl esters of alpha,beta-unsaturated dicarboxylic acids, such as the dimethyl-, diethyl-, dipropyl-, dibutyl-, and diamyl esters of maleic, fumaric, citraconic, etc., acids, are particularly effective anti-sticking agents for cellulosic films and sheets and can be used in comparatively small amounts to prevent surface tackiness of the films and sheets throughout the range of temperatures and relative humidities normally encountered in handling, processing and using the sheets. The above objects and other objects which will clearly appear hereinafter are accomplished, therefore, by the present invention in accordance with which a particulate copolymer as defined above is deposited in or on the cellulosic sheet in the form of an aqueous dispersion or emulsion of the copolymeric resin. Although the invention is particularly applicable to sheets or films of regenerated cellulose produced by the cuprammonium or viscose processes, it is also applicable generally to cellulosic pellicles which are smooth, non-fibrous and substantially non-porous, especially water-sensitive cellulose pellicles, such as those made from solutions of cellulose in organic or inorganic solvents, denitrated cellulose nitrate, water-insoluble cellulose ethers including water-insoluble alkali-soluble hydroxyalkyl cellulose and carboxy alkyl cellulose, mixed ethers of that class, cellulose ether xanthates, cellulose thiourethanes and cellulose xantho fatty acids.

The copolyer of vinyl chloride and the selected lower alkyl diester of the alpha,beta-unsaturated dicarboxylic acid may be produced by heating the monomers at temperatures between about 50° C. and about 150° C. under appropriate conditions of polymerization, i. e., in the presence of suitable diluents and such catalysts as are known to promote the polymerization of unsaturated compounds, using the monomers in any suitable relative proportions. The copolymers should contain, by weight in the polymer molecule, at least 50 per cent of vinyl chloride and at least 5 per cent of the alpha, beta-unsaturated dicarboxylic acid diester. Those copolymers in which the vinyl chloride predominates in the molecule are especially satisfactory. Preferably, the copolymer contains, by weight in the molecule, from 80 per cent to 95 per cent of vinyl chloride and from 5 per cent to 20 per cent of the ester. Aqueous emulsions or latices comprising copolymers of this type are available com-

mercially, and such prepared commercial products may be used in practicing the invention either as such or after suitable dilution with water. Or a latex may be prepared by any of the well-known methods used to obtain dispersions or latices and employing the usual assistants, such as specific emulsifying agents, stabilizing agents, or other substances designed to produce stable dispersions. Suitable emulsifying agents include sodium lauryl sulfate, sodium dioctyl sulfate, alkaryl acids, sulfonic acids and their salts, and the like. The emulsion may also contain a plasticizing agent for the copolymer which may be, for example, of the plasticizing resin type, i. e., a "soft" resin such as a polymerized unsaturated hydrocarbon, for instance, polymerized isobutylene commonly sold under the trade name "Vistanex," a soft alkyd resin, or an organic plasticizer, such as dibutyl sebacate, dibutyl phthalate, and the like or mixtures of those plasticizers. Protective colloids may also be added to the emulsion of the copolymer, and as suitable protective colloids there may be mentioned casein, glue, a water-soluble cellulose ether such as methyl cellulose, or a gum such as arabic, karaya, or tragacanth.

The emulsion of the finely divided copolymer may be applied to a finished cellulosic sheet, after initial drying thereof, provided that the sheet is re-wet before the emulsion is applied to it. Also, the particulate copolymer may be dispersed in a moistureproofing composition if such is applied to the finished sheet. However, the application of moistureproofing or waterproofing compositions to the sheets invariably results in products which cannot be glued with commercial aqueous adhesives, and it is frequently desirable to avoid the use of such moistureproofing compositions and to use the plain regenerated cellulose sheet as manufactured for purposes which involve gluing by means of aqueous adhesives and for other purposes, for example, in the production of envelopes having a cellophane "window." Although the anti-sticking agent of the invention may be used with sheets which also comprise a moistureproofing agent or composition, the invention is particularly concerned with the treatment of plain cellulosic sheets and, generally speaking, the best results are obtained by applying the particulate solid copolymer to the sheet in the gel state; that is, after the sheet has been purified in the course of its manufacture but prior to initial drying thereof. The copolymer is preferably applied to the cellulosic sheet during impregnation of the sheet with the hygroscopic plasticizing agent by adding the aqueous latex or dispersion of the copolymer to the plasticizer bath on the casting machine in sufficient quantity to produce a concentration in the bath of 0.05 to 0.35 per cent solids. The gel cellulosic film or sheet is impregnated by passage through the bath, the excess anti-sticking agent as well as the excess softener solution being removed by means of squeeze rolls, scraper rods, wiper plates, or the like before it enters the drier in which it is dried in the usual manner. The treated cellulosic sheet does not adhere to the drier rolls, and the shrinkage which normally takes place during initial drying of a regenerated cellulose film is not affected. The amount of copolymer which is applied to the gel sheet is controlled by adjusting the concentration of the copolymer in the plasticizing bath or by varying the amount of excess removed. The copolymer is effective to completely eliminate any tendency of the sheets to stick or block in small quantities and a concentration of the copolymer latex in the bath sufficient to give a solids concentration in the bath of between 0.05 per cent and 0.35 per cent is sufficient to prevent sticking of the dried sheets.

The cellulosic pellicle will usually be transparent, but it is within the scope of the invention to treat colored or otherwise decorated pellicles. The presence of the copolymer in the pellicle does not interfere with subsequent treatments including laminating, coating, gluing, printing or the like, and the film may be provided with a surface coating, for example, a moistureproofing coating, without harmful effects due to the presence of the particulate copolymer therein.

The softening agent applied conjointly with the new anti-sticking agent will usually be glycerol, but the dispersion of the copolymer is compatible with aqueous solutions of other non-volatile cellulose softeners and such other softeners, including diethylene glycol, triethylene glycol, invert cane sugar, glucose, sorbitol, etc., or mixtures thereof, may be used if desired. The particle size of the water-insoluble resinous copolymer of vinyl chloride and alpha,beta-unsaturated dicarboxylic acid diester is preferably within the range of from about 0.1 to about 8 microns in its greatest linear dimension, and most desirably the particle size is within the range of 0.5 to 2.5 microns.

The following example, in which the quantities given are in parts by weight unless otherwise specified, illustrates practical applications of the invention in the production of transparent, highly softened non-sticking cellulosic pellicles. In the example the gel sheets treated comprise regenerated cellulose, but it is to be understood that the use of other cellulosic sheets is contemplated.

Example

Different pellicles of gel regenerated cellulose were passed through softening baths containing, in addition to glycerol as plasticizer, an aqueous emulsion of a particulate copolymer containing, by weight in the polymer molecule, about 95 per cent of vinyl chloride and about 5 per cent of ethyl maleate (or the product marketed commercially by the Goodyear Chemical Company under the trade-name "Pliovic Latex 300"). The compositions of the baths are given in the following table:

Water	Glycerol	Copolymer Emulsion	Percent Solids in Bath
1,395	100	5	0.0875
1,890	100	10	0.175
1,885	100	15	0.265
1,880	100	20	0.35
1,870	100	30	0.525
1,860	100	40	0.70
1,850	100	50	0.875

On leaving the baths, the pellicles were passed through squeeze rolls to remove excess solution and then dried to a final moisture content of about 3 to 9 per cent by passing them over drier rolls. The sheets were stacked and stored under a pressure of about 1 lb. per sq. inch for 16 hours in an oven at 115° F. without exhibiting any tendency to stick or cake.

As previously indicated other resins, such as the thermosetting melamine-formaldehyde resins, have not been found to be effective for preventing blocking of cellulosic sheets comprising them. Gel regenerated sheets which were passed through a bath consisting of by weight 1851.5 parts of water, 100 parts of glycerine, and a sufficient quantity of an aqueous, colloidal lactic acid solution of a partially polymerized melamine-formaldehyde condensation product (which solution was prepared from 40 parts of the melamine-formaldehyde precondensate and aqueous 8.52 per cent lactic acid as described in U. S. 2,394,009, issued February 5, 1946, to John D. Pollard, and aged as set forth in the Pollard patent or in Wohnseidler and Thomas, U. S. 2,345,543, issued March 28, 1944) to give a lactic acid concentration in the bath of 0.426 per cent and a melamine-formaldehyde precondensate concentration of 2.0 per cent, and then dried, during which operation the melamine-formaldehyde resin was brought to the fully condensed, thermoset condition, exhibited a definite tendency to adhere when they were stacked and subjected to a pressure of 1 lb. per square inch in an oven at 115° F. for 16 hours.

Although the melamine-formaldehyde resin does not

of itself, prevent blocking of cellulosic sheets comprising it, the melamine-formaldehyde precondensate may be incorporated with the sheet or film for purposes other than the purpose of inparting slip thereto, without adversely influencing the effectiveness of the vinyl chloride copolymer as an anti-blocking agent. Since the melamine-formaldehyde resin is receptive to, or has an affinity for, hydrophobic moistureproofing materials, it may be desirable to treat the gel cellulosic sheet, either prior to, simultaneously with, or subsequently to treatment thereof with the dispersion comprising the vinyl chloride-diester copolymer, with an acidic colloidal solution of the melamine-formaldehyde resin precondensate, when the sheet is to be provided subsequently with a coating of a moistureproofing agent or of a composition comprising such an agent. The melamine-formaldehyde resin functions as an anchor for the hydrophobic moistureproofing material and serves to bond it firmly to the cellulosic base sheet. As an illustration of this embodiment of the invention, gel regenerated cellulose sheets were passed through a bath consisting of by weight 1831.5 parts of water, 100 parts of glycerol, 20 parts of an emulsion of a copolymer of 95 per cent vinyl chloride and 5 per cent diethyl maleate (copolymer solids in bath, 0.35 per cent), and 40 parts of the aqueous lactic acid colloidal solution of the melamine-formaldehyde resin precondensate discussed above (lactic acid concentration in bath, 0.426 per cent; melamine-formaldehyde resin precondensate solids in bath, 2.0 per cent). The sheets were dried and thereafter showed no tendency to cake or block when stacked in an oven at 115° F. for 16 hours, proving that the melamine-formaldehyde resin does not adversely influence the effectiveness of the vinyl chloride-diester copolymer as an antiblocking agent.

In carrying out the invention, various changes and modifications may be made in the specific details given in the embodiments illustrated. Thus, instead of the emulsion or dispersion of the vinyl chloride-ethyl maleate copolymer, there may be used, in like amounts and under like conditions, an emulsion or dispersion of a copolymer of vinyl chloride and diethyl fumarate or diethyl citraconate, or of a copolymer of vinyl chloride and any other dialkyl ester of an alpha,beta-dicarboxylic acid in which the alkyl groups contain from 1 to 5 carbon atoms. Since such changes and modifications can be made without departing from the spirit and scope of the invention, it is to be understood that the invention is not to be limited except as set forth in the appended claims.

I claim:

1. As a new article of manufacture, a non-fibrous cellulosic pellicle having deposited on its surface discrete, finely divided particles of a copolymer of by weight from 50 per cent to 95 per cent of vinyl chloride and from 5 per cent to 50 per cent of a lower dialkyl diester of an alpha,beta-unsaturated dicarboxylic acid.

2. An article of manufacture according to claim 1 characterized in that the pellicle comprises regenerated cellulose.

3. An article of manufacture according to claim 1 characterized in that the copolymer is a copolymer of vinyl chloride and diethyl maleate.

4. An article of manufacture according to claim 1 characterized in that the copolymer is a copolymer of by weight from 80 per cent to 95 per cent of vinyl chloride and from 5 per cent to 20 per cent of the lower dialkyl diester of the alpha, beta-unsaturated dicarboxylic acid.

5. An article of manufacture according to claim 1 characterized in that the copolymer is a copolymer of about 95 per cent vinyl chloride and about 5 per cent diethyl maleate.

6. As a new article of manufacture, a regenerated cellulose pellicle having incorporated therein a water-soluble polyhydroxy alcohol plasticizer and having deposited on its surface discrete, finely divided particles of a copolymer of by weight from 50 per cent to 95 per cent of vinyl chloride and from 5 per cent to 50 per cent of a lower dialkyl diester of an alpha, beta-unsaturated dicarboxylic acid.

7. An article of manufacture according to claim 6 characterized in that the water-soluble softener is glycerol.

8. In a method of making a non-sticking, non-fibrous cellulosic pellicle, the step which comprises treating the pellicle with an aqueous dispersion of a finely-divided particulate copolymer of by weight from 50 per cent to 95 per cent of vinyl chloride and from 5 per cent to 50 per cent of a lower dialkyl diester of an alpha,beta-unsaturated dicarboxylic acid, the total solids concentration of the dispersion being from about 0.05 to 0.35%.

9. In a method of making a non-sticking, non-fibrous cellulosic pellicle, the step which comprises treating the pellicle, in the course of its production and prior to initial drying thereof, with an aqueous dispersion of a finely divided particulate copolymer of by weight from 50 per cent to 95 per cent of vinyl chloride and from 5 per cent to 50 per cent of a lower dialkyl diester of an alpha,beta-unsaturated dicarboxylic acid, and drying the pellicle, the total solids concentration of the dispersion being from about 0.05 to 0.35%.

10. In a method of making a softened, plastic non-sticking, non-fibrous regenerated cellulose pellicle, the step which comprises treating the pellicle, after washing thereof in the course of its production and prior to initial drying thereof, with an aqueous medium containing a water-soluble polyhydroxy alcohol plasticizer for regenerated cellulose and a dispersed particulate copolymer of by weight from 80 per cent to 95 per cent vinyl chloride and from 5 per cent to 20 per cent of a lower dialkyl diester of an alpha,beta-unsaturated dicarboxylic acid, the total solids concentration of the aqueous medium being from about 0.05 to 0.35%, removing excees treating medium from the pellicle, and drying the pellicle.

11. The method according to claim 10 characterized in that the plasticizer is glycerol and the copolymer is a copolymer of about 95 per cent vinyl chloride and about 5 per cent diethyl maleate.

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