

1

2,721,150

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

No Drawing. Application December 12, 1952, Serial No. 325,713

10 Claims. (Cl. 117—145)

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 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 of the surfaces to cohere when the sheets are assembled in stacks or rolled upon themselves increases with increase in moisture content above the maximum needed for retention of workable plasticity and results in 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

2

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, resins greatly reduce the cohesion-resistant property of the sheets and also tend to impair the capacity of the sheets to be glued with aqueous adhesives. It has been found, for instance, that melamineformaldehyde resin, which is of the thermosetting type, does 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 of the precondensate.

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 of vinylidene chloride and vinyl chloride containing a preponderant proportion of vinylidene chloride in the molecule are very 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 the particulate copolymer of vinylidene chloride and vinyl chloride is deposited in or on the cellulosic sheet from an aqueous dispersion or emulsion of the copolymer. 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 other 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 copolymer of vinylidene chloride and vinyl chloride 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, from 60 per cent to 95 per cent of vinylidene chloride and, conversely, from 40 per cent to 5 per cent of vinyl chloride. Preferably the copolymer is a copolymer of 75 per cent to 85 per cent vinylidene chloride and 15 per cent to 25 per cent vinyl chloride, and most desirably it is a copolymer of about 80 per cent vinylidene chloride and about 20 per cent vinyl chloride. Aqueous emulsions or latices comprising the copolymers are available commercially, and such prepared com-

mercial products may be used in practicing the invention either as such or after suitable dilution with water. For example, a commercially available latex or emulsion of saran (a vinylidene chloride-vinyl chloride copolymer marketed by Dow Chemical Company) may be used. Or a latex may be prepared by any of the well-known methods used to obtain dispersions or latices, such as specific emulsifying agents, stabilizing agents, or other substances which 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 tradename "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 thermoplastic vinylidene chloride-vinyl chloride 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 moisture-proofing composition if such is applied to the finished sheet. However, the application of moisture-proofing or water-proofing 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 moisture-proofing 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 applied conjointly with moisture-proofing compositions or subsequently to the application of such compositions, 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 any drying thereof. The copolymer of vinylidene chloride and vinyl chloride may be applied to the cellulosic sheet during impregnation of the latter 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 0.1 per cent to 2.0 per cent solids based on the water content of the bath. The gel cellulosic film or sheet is then treated 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 blades, 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 0.1 per cent and 0.5 per cent is generally sufficient to prevent sticking of the dried sheets.

The cellulosic pellicle will usually be transparent and colorless, 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 moisture-proofing 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 vinylidene chloride and vinyl chloride 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 a practical application of the invention in the production of transparent, highly softened, non-sticking cellulosic pellicles. In the example the gel sheet treated comprises regenerated cellulose, but it will 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 of by weight about 80 per cent vinylidene chloride and about 20 per cent of vinyl chloride (or the product marketed commercially by the Dow Chemical Company under the trade name Dow Latex 744). The compositions of the baths are given in the following table.

Water	Glycerol	Copolymer Emulsion	Percent Solids (Copolymer)
1,895.....	100	5	0.125
1,890.....	100	10	0.25
1,885.....	100	15	0.375
1,880.....	100	20	0.50

On leaving the baths the pellicles were passed through squeeze rolls to remove excess solution and then dried to a moisture content of about 5 to 8 per cent by passing them over drier rolls. The sheets were stacked and stored under a pressure of about 1 lb. per sq. inch in an oven at 115° F. for 16 hours without exhibiting any tendency to stick or cake.

In contrast, when a gel regenerated cellulose sheet was passed through a bath containing by weight 1093.5 parts of water, 53 parts of glycerol, and a sufficient quantity of the product obtained by colloiddally dispersing a melamine-formaldehyde resin precondensate in aqueous lactic acid to give a bath containing by weight 23.5 parts of the melamine-formaldehyde resin precondensate and 5 parts by weight of lactic acid (lactic acid concentration in the bath in percent by weight 0.425) the sheets, after drying thereof, during which the resin was brought to fully condensed, thermoset condition, exhibited a definite tendency to cake when stacked and stored under the same conditions as the sheets which were treated in the softener baths containing the softener and the thermoplastic particulate vinylidene chloride-vinyl chloride copolymer.

Although the melamine-formaldehyde resin does not, of itself, prevent sticking of the cellulosic sheets, it may be used in conjunction with the particulate vinylidene chloride-vinyl chloride copolymer for imparting characteristics other than surface slip to the sheets, without detracting from the effectiveness of the copolymer as an anti-sticking agent. For example, if it is desired to

5

6

after-treat the sheet comprising the particulate vinylidene chloride-vinyl chloride copolymer with a moisture-proofing agent or composition, it may be desirable to incorporate the melamine-formaldehyde resin with the gel cellulosic sheet before, simultaneously with, or after incorporation of the particulate vinylidene chloride-vinyl chloride copolymer, since those melamine-formaldehyde resins, the precondensates of which form colloidal dispersions in aqueous solutions of organic acids, are anchoring agents for compositions comprising hydrophobic moisture-proofing materials and serve to bond such materials firmly to the hydrophilic cellulosic base sheet. Sheets having both the particulate vinylidene chloride-vinyl chloride copolymer and extremely small particles of a melamine-formaldehyde resin intimately associated therewith have been obtained and, on testing for adhesion when rolled and stacked, have been found to have slip characteristics comparable to those of similar sheets having the vinylidene chloride-vinyl chloride copolymer only incorporated therewith. As an example, a regenerated cellulose sheet in gel condition was passed through an aqueous bath containing both the particulate vinylidene chloride-vinyl chloride copolymer and a melamine-formaldehyde resin precondensate. The melamine-formaldehyde resin was introduced into the bath in the form of an aqueous lactic acid colloidal solution containing between 0.5 per cent and 20 per cent by weight of a partially polymerized melamine-formaldehyde condensation product in a state of polymerization less than that characterizing a gel, prepared in accordance with U. S. 2,394,009 to John D. Pollard, issued February 5, 1946, the solution having been aged after its preparation, as set forth in the Pollard patent or in Wohnsiedler and Thomas, U. S. 2,345,543, issued March 28, 1944. The bath contained by weight 1083.5 parts of water, 53 parts of glycerol, 23.5 parts of the colloidal aqueous lactic acid solution of the melamine-formaldehyde resin (0.425 per cent lactic acid) and 10 parts of Dow latex 744 (per cent solids, 0.425). Excess bath was removed from the sheets, which were then dried. During the drying the melamine-formaldehyde partial condensate was converted to fully condensed, thermoset condition. These sheets exhibited no tendency to stick or "block" when stacked under a pressure of 1 lb. per sq. inch in an oven at 115° F. for 16 hours.

Since changes and modifications can be made in the specific details as set forth above without departing from the nature and spirit 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. An article of manufacture comprising a non-fibrous cellulosic pellicle carrying on its surface discrete, finely-divided particles of a copolymer of from 60 per cent to 95 per cent of vinylidene chloride and from 5 per cent to 40 per cent of vinyl chloride.

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 particulate copolymer is a copolymer of about 75 per cent to 85 per cent of vinylidene chloride and about 15 per cent to 25 per cent of vinyl chloride.

4. An article of manufacture according to claim 1 characterized in that the particulate copolymer is a copolymer of about 80 per cent of vinylidene chloride and about 20 per cent of vinyl chloride.

5. As a new article of manufacture, a regenerated cellulose pellicle having incorporated therein a water-soluble polyhydroxy alcohol plasticizer and carrying on its surface discrete, finely-divided particles of a copolymer of 60 per cent to 95 per cent vinylidene chloride and 5 per cent to 40 per cent of vinyl chloride.

6. An article of manufacture according to claim 5 characterized in that the water-soluble plasticizer is glycerol.

7. In a method of making a non-sticking, non-fibrous cellulosic pellicle, the steps which comprise treating the pellicle with an aqueous dispersion comprising 0.1 to 2% of a finely-divided particulate copolymer of 60 per cent to 95 per cent vinylidene chloride and 5 per cent to 40 per cent of vinyl chloride, and drying the pellicle.

8. In a method of making a non-sticking, non-fibrous cellulosic pellicle, the steps which comprise treating the pellicle in the course of its production and prior to initial drying thereof with an aqueous dispersion of 0.1 to 2% of a finely-divided particulate copolymer of 60 per cent to 95 per cent vinylidene chloride and 5 per cent to 40 per cent of vinyl chloride, and drying the pellicle.

9. In a method of making a softened, plastic, non-sticking, non-fibrous regenerated cellulose pellicle, the steps which comprise 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 0.1 to 2% of a dispersed finely-divided particulate copolymer of 75 per cent to 85 per cent vinylidene chloride and 15 per cent to 25 per cent of vinyl chloride, removing excess treating medium, and drying the pellicle.

10. The method according to claim 9 characterized in that the plasticizer is glycerol and the copolymer is a copolymer of about 80 per cent vinylidene chloride and about 20 per cent vinyl chloride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,334,236	Arnold et al.	Nov. 16, 1943
2,417,014	Pollard	Mar. 4, 1947
2,570,478	Pitzl	Oct. 9, 1951
2,618,575	Oswin	Nov. 18, 1952