United States Patent Office

2,727,836

Patented Dec. 20, 1955

2,727,836

ANTI-STICKING CELLULOSE PELLICLES AND METHOD OF MAKING

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No Drawing. Application August 1, 1949, Serial No. 108,057

11 Claims. (Cl. 117—144)

This invention relates to improvements in smooth, non-fibrous, non-porous sheets and films. More particularly, the invention relates to the production of cellulosic pellicles which have been treated with an anti-sticking agent. The invention will be described in terms of regenerated cellulose film, but it should be understood that this is intended merely to be illustrative and not limitative.

In the manufacture of regenerated cellulose film, such as cellophane, prepared from an aqueous alkaline solution of sodium cellulose xanthate, it is necessary, in order to produce a tough plastic film, to maintain a certain pre-determined moisture content in the film. Regenerated cellulose film will absorb moisture from the surrounding atmosphere and thereby render itself plastic when the relative humidity is sufficiently high. It is generally the practice, in order to render the regenerated cellulose film plastic at all relative humidities, to incorporate therein a hygroscopic plasticizing compound such as glycerol and the like. However, at high relative humidities the amount of moisture absorbed by the film is more than necessary to attain the desired plasticity and superimposed sheets have a tendency to stick together.

Heretofore this difficulty has been overcome by impregnating the film, while in the wet gel state, with an anti-sticking or "slip" agent. "Slip" as used herein designates 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 pound per square inch and acted on by a force at right angles to the applied load. It has been suggested that to effect the desired result, regenerated cellulose film be impregnated with stearamide, which is usually applied in conjunction with the plasticizer, just prior to the drying operation.

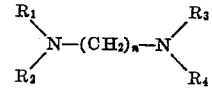
The use of stearamide is disadvantageous in that owing to its high melting point, and poor solubility, it is very difficult to prepare an emulsion or dispersion of it in water, even with the most efficient emulsifiers available. In order to obtain a stable emulsion, a relatively high temperature is necessary. Also the emulsifiers employed are eventually affected by the hardness formers found in normal water thus leading, after a certain period of operation, to an undesirably streaked film.

The aforementioned difficulties and disadvantages are overcome by the use of the present invention and further there are produced smooth non-fibrous, non-porous sheets and films having improved resistance to sticking together when superimposed.

Other advantages and features of this invention will be apparent from the description hereinafter.

This invention contemplates impregnating the regenerated cellulose film, while in the wet gel state, with an aqueous solution or dispersion of a plasticizer and an acylated polyalkylene polyamine or a salt thereof. It has been found that these compounds or their salts, which are readily soluble or dispersible in aqueous media impart excellent "slip" qualities to cellophane.

The preferred group of acylated polyalkylene polyamines are those having the generic formula:



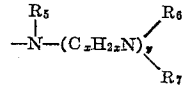
where:

n is an integer from 1–10,

R_1 is an acyl group of 2 to 18 C atoms, and preferably 12 to 18 C atoms,

R_3 is H, an alkyl radical of 1 to 7 C atoms, or an acyl group of 2 to 7 C atoms, and

R_2 and R_4 are H, alkyl radicals of 1 to 7 C atoms, acyl groups of 2 to 7 C atoms, or omega-amino polyalkylene polyamino groups having the formula:



where:

x is an integer from 1–10,

y is an integer from 1–100,

R_5 is H, or an alkyl radical of 1 to 7 C atoms, and

R_6 and R_7 are H, alkyl radicals of 1 to 7 C atoms, or acyl groups of 2 to 7 C atoms.

Compounds having the above-identified generic formula may be prepared by heating together a polyalkylene polyamine and a fatty acid in any proportion within the limit of 1 mol of polyamine to 1–1.7 mols of fatty acid. The preferred temperature range is from 105–140° C. As the temperature is decreased, the reaction time is increased, namely, for each 10° C. drop in reaction temperature (down to 105° C.) the reaction time is approximately doubled. However, the clarity of the resulting product, when dissolved at operating concentration, is improved by lowering the temperature, but in the temperature range given the "slip" of the impregnated regenerated cellulose film is not materially affected. The reaction may be carried out in the presence or absence of an inert solvent such as toluene or xylene or the like, until an equivalent molecular portion of water has been removed, then removing the solvent, if any was used, by the usual means, such as distillation with or without vacuum.

Among polyalkylene polyamines which are suitable as starting materials may be mentioned: ethylenediamine, diethylenetriamine, triethylene tetramine, tripropylene tetramine, tributylene tetramine, hexamethylene diamine; the suitable fatty acids are butyric, caproic, caprylic, capric and preferably the higher acids such as lauric, myristic, palmitic, stearic, oleic and linoleic.

The resulting compound, prepared as outlined above, is added slowly with stirring to water containing a predetermined amount of an organic acid, such as acetic, propionic, maleic, fumaric, lactic, succinic, etc., to neutralize a major portion of the unreacted amine groups. In this way it is possible to prepare solutions or stable emulsions of salts of acylated polyalkylene polyamines containing up to 50% solids which may be diluted to any desired concentration by simply pouring slowly into water with agitation. The acylated polyalkylene polyamines, prepared as generally outlined in U. S. Patent No. 2,345,632, are also readily dispersible in water and aqueous solutions.

The dispersion of the acylated polyalkylene polyamine or its salt is added to the plasticizer bath on the casting machine in sufficient quantity to produce a concentration in the bath of 0.05–2.00% solids. The regenerated cellulose wet gel film is then impregnated by passage through the bath, removing the excess by means of squeeze rolls, wiper blades, or the like, and dried in the usual manner.

If desired, the anti-sticking agent may be applied subsequent to the addition of plasticizer to the regenerated cellulose film and prior to the drying step by means of dip rolls, sprays, or the like. When this method of application is employed, a higher solids content of anti-sticking agent must be employed in the bath due to the shorter contact time of the film with the bath. That is to say that the percent solids in the bath would more closely approximate 1.0–2.0% solids.

The anti-sticking agent may also be applied after the film has been completely dried but preferably before it has been dried below 60% moisture content. However, here the film must be re-wet and then dried resulting in an extra step.

In a preferred embodiment of the invention, 1 mol of triethylene tetramine was condensed with 1.3 mols of stearic acid, i. e. 30 mol percent of diacylated material and 70 mol percent of monoacylated. The initial condensation was carried out in xylene at approximately 140° C. until the theoretical amount of water had been removed. The xylene was removed by distillation. The resulting compound N (β-aminoethyl), N' (β-stearamidoethyl) ethylene diamine was then added to water containing 2 mols of succinic acid with stirring and a 5–10% dispersion was prepared which in turn was added to the plasticizer bath in such quantity so as to produce the optimum concentration of 0.15% acylated polyalkylene polyamine salt. Regenerated cellulose film, while in the wet gel state, was passed through this bath, then through squeeze rolls, to remove the excess solution, and dried in the usual manner.

In another preferred embodiment of the invention, 1 mol of stearic acid was condensed with 1 mol of diethylene triamine in the same manner as outlined above. The resulting compound was then further reacted with acetic acid to form the acetylated amide. A 5–10% dispersion of the amide was prepared which in turn was added to the aqueous plasticizer bath so as to produce optimum concentration of 0.15% amide. Regenerated cellulose film was then suffused with the amide in the manner outlined in the above preferred embodiment.

Good results have also been obtained by condensing equi-molecular proportions of triethylene tetramine and stearic acid, removing water of reaction and solvent (if used) and then adding the condensation product to water containing 4 mols of acetic acid.

The same procedure was followed using lauric acid in place of stearic acid and forming both the succinate and acetate of the resulting condensation products. The application of these products to the regenerated cellulose film, in the manned described above, produced very desirable results.

The succinate of N(β-aminoethyl), N'(β-stearamidoethyl) ethylene diamine is not affected by the calcium and magnesium salts in hard water which tend to cause the film to become streaky when anti-sticking agents previously suggested are employed. The succinate is cationic in nature and therefore exhibits incompatibility with anion-active materials, such as soaps and monopole oil.

Film prepared according to the present invention have very satisfactory slip and anti-sticking properties. The film also exhibits remarkably good printing properties, that is, it is more conducive to printing than ordinary regenerated cellulose film.

When impregnating regenerated cellulose film with various organic compounds, one must be careful that such compounds do not change color, such as by yellowing with age and thereby discolor the film and reduce its salable quality. The compounds of the present invention are particularly advantageous since they do not turn yellow on prolonged aging. The compounds of this invention are also stable to hydrolysis.

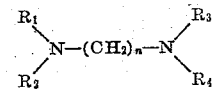
Another advantage of the present invention is that it presents a desirable method of application of anti-sticking agents from an aqueous dispersion which can be accomplished on the film-casting machine, thus attaining a considerable saving in labor, equipment and materials over the former method of application, which consisted of drying the film and coating the same with an organic solvent solution of the anti-sticking agent on a separate machine in a separate operation.

Another startling improvement in the film has been noted. The salts of acylated polyalkylene polyamines exert a marked toughening effect on regenerated cellulose film suffused with it. This is apparently due to an internal lubricating action of the "slip" agent (acylated polyalkylene polyamine salt), and a more uniform distribution of plasticizer in the film because of the wetting and penetrating action of the slip agent.

It is to be understood that the description above is merely illustrative and that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. As an article of manufacture, a regenerated cellulose film treated with a compound selected from the group consisting of acylated polyalkylene polyamines having the formula



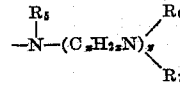
where:

n is an integer from 1 to 10

R_1 is an acyl group of 2 to 18 carbon atoms,

R_3 is selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms, and

R_2 and R_4 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, acyl groups having 2 to 7 carbon atoms, and omega-amino polyalkylene polyamino groups having the formula:



where:

x is an integer from 1 to 10,

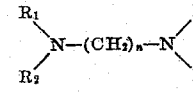
y is an integer from 1 to 100

R_5 is selected from the group consisting of hydrogen and alkyl radicals having 1 to 7 carbon atoms, and

R_6 and R_7 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms,

and salts of said acylated polyalkylene polyamines.

2. As an article of manufacture, a regenerated collulose film treated with an acylated polyalkylene polyamine having the formula



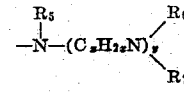
where:

n is an integer from 1 to 10

R_1 is an acyl group of 2 to 18 carbon atoms,

R_3 is selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms, and

R_2 and R_4 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, acyl groups having 2 to 7 carbon atoms, and omega-amino polyalkylene polyamino groups having the formula:



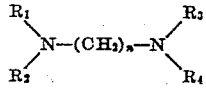
where:

x is an integer from 1 to 10,

y in an integer from 1 to 100,

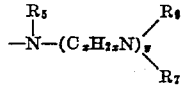
R_5 is selected from the group consisting of hydrogen and alkyl radicals having 7 to 7 carbon atoms, and
R_6 and R_7 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms.

3. As an article of manufacture, a regenerated cellulose film treated with an organic acid salt of an acylated polyalkylene polyamine having the formula:



where:

n is an integer from 1 to 10,
R_1 is an acyl group of 2 to 18 carbon atoms,
R_3 is selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms, and
R_2 and R_4 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, acyl groups having 2 to 7 carbon atoms, and omega-amino polyalkylene polyamino groups having the formula:

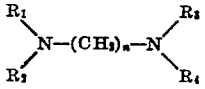


where:

x is an integer from 1 to 10,
y is an integer from 1 to 100,
R_5 is selected from the group consisting of hydrogen and alkyl radicals having 1 to 7 carbon atoms, and
R_6 and R_7 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms.

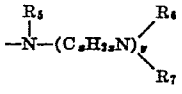
4. As an article of manufacture, a regenerated cellulose film treated with an acetylated amide from equi-molecular proportions of stearic acid and diethylene triamine.

5. As an article of manufacture, a regenerated cellulose film treated with a succinate of an acylated polyalkylene polyamine having the formula:



where:

n is an integer from 1 to 10,
R_1 is an acyl group of 2 to 18 carbon atoms,
R_3 is selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms, and
R_2 and R_4 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, acyl groups having 2 to 7 carbon atoms, and omega-amino polyalkylene polyamino groups having the formula:



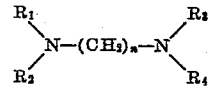
where:

x is an integer from 1 to 10,
y is an integer from 1 to 100
R_5 is selected from the group consisting of hydrogen and alkyl radicals having 1 to 7 carbon atoms, and
R_6 and R_7 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms.

6. As an article of manufacture, a regenerated cellulose film treated with a succinate of N(β-aminoethyl), N'(β-stearamidoethyl) ethylene diamine.

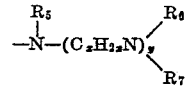
7. A method of rendering regenerated cellulose films resistant to sticking which comprises treating said films while in the wet gel state with an aqueous bath containing between 0.05% and 2.0% of a compound selected from

the group consisting of acylated polyalkylene polyamines having the formula:



where:

n is an integer from 1 to 10
R_1 is an acyl group of 2 to 18 carbon atoms,
R_3 is selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms, and
R_2 and R_4 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, acyl groups having 2 to 7 carbon atoms, and omega-amino polyalkylene polyamino groups having the formula:

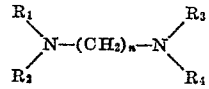


where:

x in an integer from 1 to 10,
y is an integer from 1 to 100
R_5 is selected from the group consisting of hydrogen and alkyl radicals having 1 to 7 carbon atoms, and
R_6 and R_7 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms,

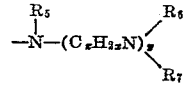
and salts of said acylated polyalkylene polyamines.

8. A method of rendering regenerated cellulose films resistant to sticking which comprises treating such films while in the wet gel state prior to any dehydration with an aqueous bath containing between 0.15% and 1.0% of a salt of an acylated polyalkylene polyamine having the formula:



where:

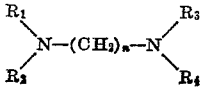
n is an integer from 1 to 10,
R_1 is an acyl group of 2 to 18 carbon atoms,
R_3 is selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms, and
R_2 and R_4 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, acyl groups having 2 to 7 carbon atoms, and omega-amino polyalkylene polyamino groups having the formula:



where:

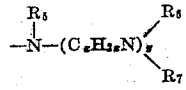
x is an integer from 1 to 10,
y is an integer from 1 to 100,
R_5 is selected from the group consisting of hydrogen and alkyl radicals having 1 to 7 carbon atoms, and
R_6 and R_7 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms.

9. A method of rendering regenerated cellulose films resistant to sticking which comprises treating such films while in the wet gel state with an aqueous bath containing between 0.15% and 1.0% of an organic acid salt of an acylated polyalkylene polyamine having the formula:



where:

n is an integer from 1 to 10,
R_1 is an acyl group of 2 to 18 carbon atoms,
R_3 is selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms, and
R_2 and R_4 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, acyl groups having 2 to 7 carbon atoms, and omega-amino polyalkylene polyamino groups having the formula:

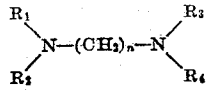


where:

x is an integer from 1 to 10,
y is an integer from 1 to 100,
R_5 is selected from the group consisting of hydrogen and alkyl radicals having 1 to 7 carbon atoms, and
R_6 and R_7 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms.

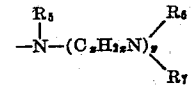
10. A method of rendering regenerated cellulose films resistant to sticking which comprises treating said films while in the wet gel state with an aqueous bath containing between 0.05% and 2.0% of an acetylated amide from equi-molecular proportions of stearic acid and diethylene triamine.

11. A method of rendering regenerated cellulose films resistant to sticking which comprises treating such films while in the wet gel state with an aqueous bath containing between 0.05% and 1.00% of the succinate of an acylated polyalkylene polyamine having the formula:



where:

n is an integer from 1 to 10,
R_1 is an acyl group of 2 to 18 carbon atoms,
R_3 is selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms, and
R_2 and R_4 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, acyl groups having 2 to 7 carbon atoms, and omega-amino polyalkylene polyamino groups having the formula:



where:

x is an integer from 1 to 10,
y is an integer from 1 to 100,
R_5 is selected from the group consisting of hydrogen and alkyl radicals having 1 to 7 carbon atoms, and
R_6 and R_7 are selected from the group consisting of hydrogen, alkyl radicals having 1 to 7 carbon atoms, and acyl groups having 2 to 7 carbon atoms.

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