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TREATMENT OF CELLULOSIC MATERIALS

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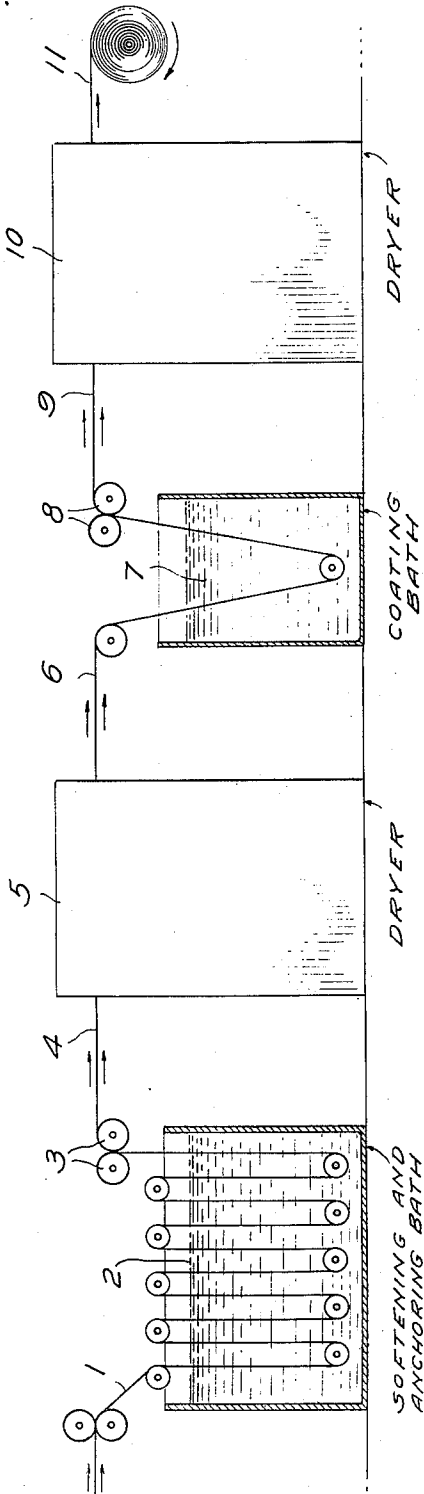


Fig. 1.

Fig. 2.

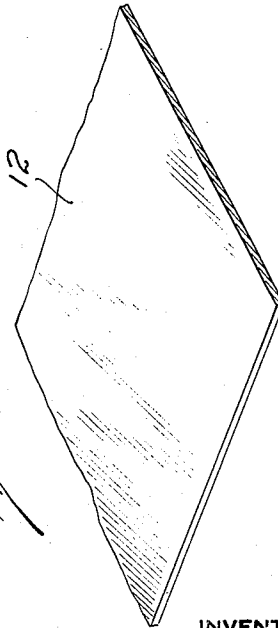
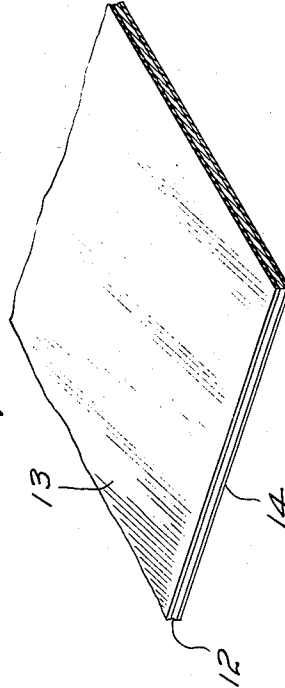


Fig. 3.



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TREATMENT OF CELLULOSIC MATERIALS

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This invention relates to improvements in non-fibrous cellulosic films and the like. More particularly, it relates to the treatment of non-fibrous cellulosic bodies in sheet, tube or filament form with aminotriazinealdehyde condensation products whereby subsequently applied coating compositions are anchored more firmly thereto. The invention includes the treated cellulosic body and the process by which it is made.

Although non-fibrous, transparent films have many outstanding properties and have enjoyed wide-spread use as wrapping material etc., it is well-known by those in the art that conventional untreated cellulosic films, particularly of regenerated cellulose, possess poor water resisting characteristics. Regenerated cellulose products, and even some of the cellulose esters and ethers now on the market in film form, have unreacted hydroxyl groups which are hydrophilic in character. As a result, these products absorb water readily when in contact with moist bodies and become swollen and weak. It has also been found that water vapor readily passes through thin films of these materials making them relatively ineffective in preventing loss of moisture from the product wrapped with them.

Attempts have been made to improve the water repellent characteristics and impermeability of cellulosic wrapping material by treatment with water repellent waxes, aluminum soaps, and the like, usually incorporated in a film-forming substance which is applied to the cellulosic body. Cellulosic sheets thus treated retain their transparency and other advantageous properties and have greatly improved water repellency and impermeability. However, when these treated sheets remain in prolonged contact with water; as is the case when they are used to wrap moist foods such as fish, meat, butter, cheese, vegetables, etc., water penetrates the top-coating, the cellulosic material swells, and the water repellent film is loosened and sloughs off. Unless special steps are taken to bond the water repellent coating to the cellulosic sheet failure of the bond between the two may occur within a few minutes after immersion of the coated cellulosic sheet in water. Obviously, the utility of such cellulosic sheets is greatly reduced by the inability of the water repellent coating to remain firmly attached to its cellulosic base under adverse conditions.

To correct the difficulties caused by separation of the water repellent coating composition from the cellulosic film, it has been proposed to treat the cellulosic film with a bonding material intended to anchor the water repellent coating

more firmly to the cellulosic film. These anchoring treatments have, however, generally necessitated the use of organic solvents in their application. The initial cost of the solvent, the necessity of special equipment for its application, the dangers and the inconvenience of its use, and other disadvantages are, of course, apparent. Some of the anchoring agents proposed have also been relatively expensive. Furthermore, of considerable importance is the fact that some types of anchoring materials are of limited effectiveness and will not prevent loosening of the water repellent coating upon prolonged contact with water. Some anchoring materials also fail to anchor some types of film-forming coating compositions to cellulosic bodies. My invention avoids all of these difficulties by employing an anchoring composition which can be applied from aqueous solution and at the same time firmly anchor all types of film-forming coating compositions to cellulosic bodies.

Cellulosic films used as wrapping materials, masking tape, adhesive tape, etc., are also commonly coated with pressure and/or heat sensitive adhesive compositions. Although the adhesive qualities of the seating composition to itself or to some other body may be adequate, if it will not firmly adhere to its cellulosic base it is quite obvious that its value as a sealing agent is greatly diminished. Accordingly, it is frequently desirable that the sealing composition be made to adhere more firmly to its cellulosic base. It is one of the advantages of my invention that film-forming adhesives can be made to adhere more firmly to a cellulosic film when the film has been treated with aminotriazine-aldehyde condensation products of the kind and type to be hereinafter disclosed.

Frequently letters and designs are printed on cellulosic sheets. Although the sheets and printing need not be water repellent, it is nevertheless desirable that the printing material stay on its base sheet if accidentally placed in contact with water. It is another advantage of my invention that printed matter, when the printing ink contains film-forming matter of the type hereinafter disclosed, can be made to adhere more firmly to cellulosic sheets when the latter are treated with aminotriazine-aldehyde condensation products in accordance with my invention.

From the foregoing it will be seen that, broadly speaking, the principal object of my invention is to improve non-fibrous cellulosic products particularly of the type commonly used as wrapping material. Another object of my invention

is to provide a treated cellulosic sheet which can be coated with a film-forming substance whereby the latter is firmly anchored to its cellulosic base and is resistant to the loosening effects of water. Another object of my invention is to provide a sheet of water repellent regenerated cellulose of improved water resistance. Other objects of my invention are to provide a simple, inexpensive and practical method of applying an anchoring composition to cellulosic films which requires no special equipment or material changes in conventional processes of preparing cellulosic films. Still other objects of my invention will appear from what has been previously said and from what appears hereinafter.

The aforesaid objects of my invention are attained by treating non-fibrous cellulosic sheets, films, pellicles, tubing, filaments, etc., of regenerated cellulose, cellulose esters and cellulose ethers with aqueous solutions of aminotriazine-aldehyde condensation products, particularly those having hydrophilic, cationic properties. The cellulosic films to be treated may be of regenerated cellulose prepared from solutions of cellulose xanthate, cuproammonium cellulose, cellulose acetate, cellulose nitrate, etc. The cellulosic films may also be of a cellulose ester or ether such as cellulose acetate, cellulose nitrate, ethyl cellulose, methyl cellulose or similar cellulosic material containing unreacted hydroxyl groups and hence being hydrophilic in character. The treated cellulosic body may be freshly prepared and still wet or it may have been previously prepared, dried and stored. It may contain softeners, dyes, pigments, and other modifying agents or not.

The aminotriazine - aldehyde condensation products which I employ in my new process are, for the most part, known compounds. They are prepared by reacting an aldehyde; such as formaldehyde, acetaldehyde, propionaldehyde, or other aliphatic aldehyde, as well as furfural, etc., with an aminotriazine containing one, two or three reactive amino groups; such as for example, melamine, ammeline, ammelide, formoguanamine, acetoguanamine, propionoguanamine, 4-methyl-2 - acetoguanamine, etc. These condensation products are prepared by heating 1 mole of the aminotriazine with from 2 to 10 moles of the aldehyde, preferably, in an alkaline medium. Preparation of typical aminotriazines will be illustrated in the specific examples. Aminotriazine-aldehyde condensation products suitable for use in my process may also be prepared by other methods which need not be described here.

For reasons of economy and because of their greater effectiveness, I prefer to use those aminotriazine-aldehyde condensation products prepared by the reaction of melamine with aldehydes and particularly with formaldehyde. The condensation product preferred is a methylol melamine, containing approximately 3.3 moles of formaldehyde combined with 1 mole of melamine. Other condensation products containing from 2 to 6 moles of formaldehyde per mole of melamine are also suitable for use in my invention. These condensation products are unpolymerized or only partially polymerized; that is, they are uncured. They are soluble in water, with heating if necessary, or soluble in dilute solutions of strong acids.

Although regenerated cellulose films can be treated with freshly prepared aqueous solutions of melamine-formaldehyde condensation products, the anchoring effect obtained by such treatment is not particularly good as will be seen from the specific examples. While a cellulosic film

thus treated possesses some advantages over an untreated cellulosic film, the treatment by no means provides the benefits obtainable by the use of certain aqueous solutions containing cationically active, hydrophilic, partially polymerized melamine - formaldehyde particles. Solutions containing the melamine-formaldehyde material in this particular form are obtained by dissolving a methylol melamine condensation product in acid solution and allowing the solution to age until it attains the desired properties but not so long as to convert it into a hydrophobic gel.

To prepare aqueous solutions of methylol melamine having these particular properties, I dissolve a substantially uncured methylol melamine condensation product having from 2 to 6 moles of combined aldehyde per mole of melamine in an aqueous solution of an acid. As acids, I may use strong mineral or organic acids such as hydrochloric, sulfurous, phosphoric, acetic, formic, and the like. The amount of methylol melamine to be dissolved may vary from about 0.1 to 4.0 moles of acid per mole of methylol melamine. In most cases the pH of the solution is above 0.5 but below 3.0 and always less than 4.0. The amount of acid depends somewhat upon the concentration of the resinous solution. For example, in a solution containing 12% of methylol melamine, I may use from about 0.7 to 1.4 moles of hydrochloric acid per mole of methylol melamine. As the concentration of the methylol-melamine in the aqueous solution is decreased, I may use a lower molecular proportion of acid. Thus, for example, in an aqueous solution containing 3% of methylol-melamine, an amount of acid corresponding to about 0.4 mole per mole of methylol-melamine has resulted in the formation of aged solutions satisfactory for use in my process.

After the methylol-melamine has been dissolved in the acid solution, it is allowed to age until the methylol melamine has acquired certain properties which have proven to be particularly desirable in treating cellulosic films. The aging period varies with a number of factors and it is not possible to give the exact aging period for all conditions. At room temperatures at a resin concentration of 12% and a molecular methylol-melamine-acid ratio of 1:1, the aging period may be from 24 to 48 hours. At refluxing temperature the aging may be reduced to 4 or 5 hours. Again, at room temperatures using a methylol-melamine-acid ratio of 1:0.8 the aging period may vary from 5 to 24 hours for optimum results. Of course, if the solution is used before it has reached its optimum aging period, for example after 2 hours, it will nevertheless give greatly improved results over those solutions which have not been aged at all.

During the aging period certain important changes take place. The methylol-melamine which may originally have been substantially monomeric in character is believed to become partially polymerized. As the resinous particles become larger in size their presence is indicated by the formation of a bluish haze in the solution. When a beam of light is passed through these aged solutions, the well-known Tyndall effect may be observed. Although, I have not been able to see these particles by means of ordinary optical microscopes, it has been shown that colloidal solutions of particles of approximately 0.1 micron in diameter exhibit haziness. It would appear, therefore, that the size of the partially polymerized methylol-melamine particles does not exceed 0.1 to 1.0 micron in diameter.

Another important distinguishing characteristic of the methylol melamine particles in the aged solution is their cationic activity. When an aged acid solution of a methylol-melamine condensation product is placed in an electrophoresis cell and direct current applied, the resinous particles, whether the solution exhibits haziness or not, migrate to the cathode. This would indicate that they are positively charged. Whether or not this characteristic influences their action on regenerated cellulose is not known at the present time but it has been observed that cellulose has a negative charge and that the aged methylol-melamine particles in the solutions appear to be preferentially adsorbed by the cellulosic film. It has also been observed that solutions of methylol-melamine polymers which are not cationic in character do not give the same results that the cationic methylol-melamine polymers do.

Another characteristic of the aged methylol-melamine particles is that they are hydrophilic in character. The acidic methylol-melamine solutions can be diluted with water to concentrations as low as 1/2% of methylol-melamine without causing precipitation of the methylol-melamine particles from solution. This is important in that I can age the acidic methylol-melamine solutions until they have optimum properties and then dilute them to very low concentrations in which condition they can be stored for weeks without undergoing substantial change. The dilute solutions also enables me to impregnate cellulosic films with very small amounts of the condensation product.

A simple test which indicates that the formation of partially polymerized cationic methylol-melamine particles has taken place and that the solution is suitable for use consists merely in the addition of concentrated hydrochloric acid to a small amount of the aged solution. If a precipitate is obtained the presence of small amounts of partially polymerized cationic resin is indicated. An unaged solution will not respond to the test.

The preparation of aged solutions of specific aminotriazine-aldehyde condensation products and the treatment of cellulosic films therewith will now be described in greater particularity by means of the following specific examples. It should be understood however, that these examples are given principally by way of illustration and are not to be construed as limiting my invention to the particular conditions described therein. All parts are by weight unless otherwise indicated.

EXAMPLE 1

Aqueous solutions of cationic acid-type aminotriazine-aldehyde condensation products suitable for use in the treatment of cellulosic film in accordance with my invention can be prepared by different methods. A preferred method employs the condensation product of 3 moles of melamine with 10 moles of aqueous 30% formaldehyde. The condensation product is prepared by heating these reactants, at a pH of 9.0 for 30 minutes, cooling, separating and drying the resulting crystals. To prepare the cationic resin solution 50 parts by weight of the crystals are dissolved in a solution of 27.6 parts of commercial 18° Bé. hydrochloric acid and 125 parts of water with heating at 120° F. until the condensation product is dissolved. The solution is then diluted to about 14% solids and allowed to age at room temperatures for 24 to 48 hours. As the solution

ages a bluish haze develops and the colloidal solution exhibits the well-known Tyndall effect when a beam of light is passed through it. The formation of the haze and the presence of the Tyndall effect indicates that the diameters of at least some of the resinous particles suspended in this solution are approaching the range of 0.1 to 1.0 micron. When a sample of the solution is placed in an electrophoresis cell and a direct current passed therethrough, the resinous particles migrate towards the cathode thus proving them to be cationic in character. Further aging of the resin solution results in the formation of a dispersible gel which soon becomes undispersible and worthless for purposes of my invention.

Cationic acid-type aminotriazine-aldehyde resins suitable for use in treating regenerated cellulose film can also be prepared by dissolving non-acid-type uncured aminotriazine resins in strong acids. Thus, for example, a water soluble melamine-formaldehyde resin prepared under alkaline conditions using 1 mole of melamine and 3.35 moles of formaldehyde is boiled with 5 times its weight of water until dissolved. After cooling, an approximately equimolecular quantity of hydrochloric acid is added to the solution. Upon standing at room temperature for several days, the solution develops a characteristic bluish haze indicative of the formation of colloidal resinous particles of ultra-microscopic size in the solution. These particles are cationically charged as evidenced by their migration to the cathode in an electrophoretic cell.

Aqueous solutions of cationic aminotriazine resins may also be prepared by reacting an aldehyde, such as formaldehyde, with a melamine salt or by condensing the melamine and aldehyde in the presence of free acid. Thus, for example, 20 parts by weight of melamine (1/3 mole) is mixed with 42 parts of 37% aqueous formaldehyde solution (1/2 mole) and diluted with about 160 parts of water. 1/6 mole of hydrochloric acid is then added together with sufficient water to dilute the mixture to a total of 420 parts by weight. The mixture is then heated at 40-50° C. for 1 1/4 to 2 1/2 hours, or until a clear solution is obtained. Upon aging this solution 24 to 48 hours at room temperature, or for a shorter time at elevated temperatures, resinous particles are formed therein having cationic properties. This solution may be diluted to 10% resin solids or less and kept at room temperature for several weeks without appreciable change in the colloidal condition of the resin.

A mixture of 1 mole of ammeline, 6 moles of 32% aqueous formaldehyde solution and 3 moles of H₃PO₄ was heated for 5 minutes at 90° C. with the addition of sufficient water to bring the final solution to 40% solids. The resulting ammeline-formaldehyde resin contained approximately 3.2 moles of combined formaldehyde and the pH of the solution (glass electrode) was 0.9. Upon aging for 24 hours at room temperature the solution developed a bluish colloidal haze, which grew stronger and deeper until a dispersible gel was formed after 7 days standing. Upon electrophoresis of the one-day old colloidal solution between platinum electrodes the resin exhibited a definite positive charge as shown by its migration to the cathode.

A second ammeline resin was prepared by refluxing 1 mole of ammeline, 10 moles of aqueous formaldehyde solution and 0.8 moles of sulfuric acid at 50% solids for 2.5 hours under atmospheric

pressure. The resulting resin solution had a pH of 0.9 and remained clear for one week. After aging for one day it was tested by electrophoresis and found to be positively charged.

A mixture of 1 mole of acetoguanamine, 3 moles of aqueous formaldehyde solution and 1 mole of HCl was refluxed at 48% solids for 1.5 hours at atmospheric pressures. The resulting solution had a glass electrode pH of 0.9, contained approximately 2.5 moles of combined formaldehyde and was stable for one week at room temperature. After aging for one day it showed a positive charge when subjected to electrophoresis.

A partially polymerized, water insoluble spray dried trimethylol-melamine condensation product, which is available on the market, may be dissolved in water with approximately equimolecular amounts of hydrochloric acid and allowed to age at room temperatures at a solids content of from 10% to 50% for a period of from 1 or 2 hours up to a week or more to yield a solution containing positively-charged, hydrophilic, partially polymerized methylol-melamine condensation products. These aged colloidal solutions are particularly useful in treating cellulosic films in accordance with the teachings of my invention.

EXAMPLE 2

A quantity of sodium cellulose xanthate solution (viscose) was prepared in standard manner and allowed to ripen to a stage suitable for plate-casting films. Using a glass rod viscose was applied to a glass plate and the plate with its coating was immersed in a sodium sulfate-sulfuric acid coagulating bath. The coagulated and regenerated sheets were then placed in hot dilute sodium hydroxide to remove precipitated sulfur and finally in a dilute sodium hypochlorite bleach solution. The purified gel sheets after thorough washing were then ready for immersion in aged aqueous solutions of cationic melamine-formaldehyde polymer anchoring composition. Cationic melamine-formaldehyde solutions used to treat the above described sheets of regenerated cellulose were prepared as follows:

25 grams of dry, powdered substantially unpolymerized methylol-melamine, containing approximately 3.35 moles of formaldehyde per mole of melamine, were dissolved in a heated solution (130-140° F.) of 10.4 ml. of 20% B6. hydrochloric acid in 100 ml. of water. The clear solution was then diluted to 204 ml. with water and allowed to age at room temperature for 24 hours. It was then diluted to a solids content of 3%. Glycerol, to serve as softener for the film, was added to the aged acid-resin solution in amounts of 8% and the solution was then ready for use. It was designated as solution Number 2.

Two more solutions of aged methylol-melamine-hydrochloric acid were prepared as just described. To one solution was added 0.0048% of maleic anhydride and to the other was added 0.0096% maleic anhydride. These solutions were numbered 3 and 4 respectively and were used in the tests to be described. Another aged acid solution of methylol-melamine was diluted to 3% methylol-melamine on a solids basis, mixed with an equal weight of polyvinyl alcohol and then diluted to 2% total solids (1% methylol-melamine and 1% polyvinyl alcohol). Eight per cent by weight of glycerol was added to the resin solution as before. This solution and the film treated with it were designated as Number 5.

25 grams of a substantially unpolymerized

methylol-melamine condensation product was dissolved in a heated solution of 18 grams of glacial acetic acid in 100 ml. of water. The clear solution was diluted to 204 ml. with water and allowed to age for 24 hours. It was then diluted to 3% solids, 8% by weight of glycerol added thereto and designated as Number 6 for use in the anchoring tests. A similar solution of the aged methylol-melamine-acetic resin was prepared and 0.0096% of maleic anhydride added thereto. This solution was designated as Number 7.

Sheets of the wet gel regenerated cellulose were immersed in the aged resin solutions for 5 minutes, removed to a flat metal plate and the excess resin solution squeezed off with a rubber window cleaner. Excess film was trimmed off the edges of the metal plate and the latter fitted into a frame, arranged so that the edges of the film could be held firmly while drying. Frame, plate and film were then placed in an oven at 200° F. for 8 minutes, allowed to cool, and the dried film removed.

To test the ability of aged, cationic methylol-melamine solutions to anchor water resistant films a nitrocellulose film-forming composition was prepared with the following formulation:

Parts by weight	
Nitrocellulose (11.6%-N, 8'-10'' visc.)	18.0
Dibutyl phthalate	11.7
Paraffin wax (M. P. 60° C.)	1.0
Damar resin	2.3
Ethyl acetate	159.0
Toluene	73.0
Ethyl alcohol	12.0

Each of the sheets of regenerated cellulose treated with cationic methylol-melamine and numbered 2 to 7 and a sheet of the dried, untreated regenerated cellulose, numbered 1, to serve as a control were immersed in the above nitrocellulose solution and the excess film-forming composition removed by passing the films between glass rods separated by a distance calculated to yield, upon evaporation of the solvent, a moisture proof top coat of desirable thickness on both sides of the film. The coated samples were then dried in a circulating hot air oven for 2 minutes at 85-90° C. The samples were then trimmed to a size of approximately 3 by 4 inches to provide three freshly cut edges. The seven films were then immersed in water at room temperature (22 to 24° C.) and examined periodically to determine whether or not the water resisting coating was firmly anchored to its base sheet. The results of this series of tests are shown in the following table.

In this table, and also in the other tables, the designation O. K. means that the water resistant coating was firmly and completely anchored at all points to its cellulosic base. The designation Bl. indicates that blisters had appeared in the film. It is pointed out that the formation of blisters is due to some extent to defects in the coating arising from the difficulty of obtaining perfect application of coating material, particularly by the hand methods used in these tests. In commercially produced sheets the formation of these blisters would not occur to such a great extent. The important consideration is, therefore, the determination of anchorage failure by separation and sloughing of the water resistant film, particularly at the cut edges. Sloughing of the film was determined by squeezing the film between the thumb and forefinger with a heavy

pressure. When the anchorage of the water repellent coating had failed it sloughed easily from its base sheet. In the table, S. Bl. indicates the appearance of small blisters. L. Bl. indicates that the blisters are large or many in number. Results of this series of tests are as follows:

acetic acid and also containing 8% of glycerol was used to impregnate sheet Number 10.

Another resin solution, used to treat sheet Number 11, contained 8% glycerol, 1% of HCl-aged methylol-melamine and 1% polyvinyl alcohol.

Table I

Film	Condition of topcoat after immersion for—							
	1 hr.	3 hrs.	8 hrs.	24 hrs.	72 hrs.	6 days	9 days	13 days
1.....	Sep. at cut edges.	Bad sep.	Coating off.					
2.....	O. K.	O. K.	O. K.	S. Bl.	Bl.	Bl.	L. Bl.	Loose at cut edges.
3.....	O. K.	O. K.	S. Bl.	S. Bl.	Bl.	Bl.	L. Bl.	Do.
4.....	O. K.	O. K.	O. K.	O. K.	S. Bl.	Bl.	L. Bl.	L. Bl. but no loose coating.
5.....	O. K.	O. K.	O. K.	O. K.	O. K.	O. K.	O. K.	O. K.
6.....	O. K.	O. K.	O. K.	O. K.	O. K.	Coating loose.		
7.....	O. K.	O. K.	O. K.	O. K.	O. K.	O. K.	O. K.	Bl., loose at cut edges.

As will be seen from these results, the water resistant nitrocellulose coating commenced to separate from its untreated base sheet within an hour after immersion in water. On the other hand, the water resistant coating remained firmly attached to those viscose sheets which had been treated with aged cationic methylol-melamine solutions for a period of days.

EXAMPLE 3

In this series of tests, commercial regenerated cellulose sheets, which had been softened and dried were used. This film was rinsed in running water for an hour to remove the softening agent and swell the regenerated cellulose. Wet swollen sheets of the regenerated cellulose were immersed in various baths, as will be designated, for 5 minutes, removed and the excess squeezed out with a wringer. The sheets were then placed on metal plates, the edges securely clamped down, and dried in an oven for 6 minutes at 90–95° C. After cooling, the resin treated sheets were cut to convenient test sizes and impregnated with a

A sheet of the regenerated cellulose was treated with a 3% solution of HCl-aged methylol-melamine resin, removed from the resin solution, thoroughly washed with running water and then treated with an 8% solution of glycerol. When dried this sheet was found to contain 1.4% of methylol-melamine resin based on the dry weight of the sheet. This sheet was designated Number 12.

Three more solutions of aged cationic methylol-melamine resin were prepared similar to the solution used to treat Number 9. However, additional amounts of glycerol were added to the sheets so that they contained 10%, 12% and 15% of glycerol and 3% of methylol-melamine. These sheets were numbered 13, 14 and 15 respectively.

After treatment with the water resistant nitrocellulose lacquer described above, and dried for 2 minutes at 85–90° C. the test sheets were immersed in water at room temperatures and examined periodically for failure of the top coat. The results of this series of observations are shown in the following table.

Table II

Film	Condition of topcoat after immersion for—					
	1 hr.	8 hrs.	24 hrs.	3 days	6 days	12 days
8.....	O. K.	Coat sloughed.				
9.....	O. K.	O. K.	S. Bl.	S. Bl.	L. Bl.	L. Bl. but no slough.
10.....	O. K.	O. K.	S. Bl.	S. Bl.	S. Bl.	Do.
11.....	O. K.	O. K.	S. Bl.	S. Bl.	S. Bl.	Do.
12.....	O. K.	O. K.	S. Bl.	S. Bl.	L. Bl.	Coat sloughed.
13.....	O. K.	O. K.	O. K.	S. Bl.	L. Bl.	L. Bl. but no slough.
14.....	O. K.	O. K.	S. Bl.	S. Bl.	L. Bl.	Do.
15.....	O. K.	O. K.	O. K.	S. Bl.	L. Bl.	Do.

nitrocellulose coating composition similar to that described in the preceding example.

The various test sheets used in this series of experiments were treated with anchoring solutions as follows. Number 8, to serve as control, was treated in an aqueous solution containing 8% glycerol. Sheet Number 9 was treated with a 3% aqueous solution of a methylol-melamine condensation product which had aged for 24 hours with an equimolecular proportion of HCl. The solution also contained 8% of glycerol as softener. After the sheet had been impregnated with the resin solution, it was found to have 2.8% of resin, dry basis, in it. Another aged methylol-melamine solution containing 3% of methylol-melamine aged for 24 hours at a solids content of 12% with an equimolecular proportion of

These results show that aged cationic methylol-melamine-acid-type condensation products can also be successfully used to bond film-forming coating compositions to regenerated cellulose which has been prepared and dried by conventional manufacturing processes. Sheet Number 12 shows that the treated regenerated film can be washed with water to remove excess anchoring bath without removing all of the resin from the sheet. The results indicate a preferential absorption of the cationic methylol-melamine polymer by the cellulosic material.

EXAMPLE 4

The series of experiments described in Example 3 were repeated with the difference that an ethyl cellulose film-forming composition was applied to the resin treated regenerated cellulose

sheet. The composition of this water resistant coating composition was as follows.

	Parts by weight
Ethyl cellulose (med. visc.)	24.0
Paraffin wax (M. P. 60° C.)	1.4
Sulfonated castor oil	1.6
Dibutyl phthalate	6.6
Toluene	193.4
Ethyl alcohol	50.0

Sheets of the resin treated regenerated cellulose were dried at 90-95° C. then impregnated with the above coating composition, and dried. They were then trimmed to expose uncoated edges and immersed in water at room temperature. This series of test sheets was numbered 16 to 20 in-

5 nated with 2.8% by weight of methylol-melamine polymer from a 3% solution of aged methylol-melamine-HCl solution. Film 23 had been impregnated with a solution of 8% glycerol and 3% of a methylol-melamine polymer which had been aged with an equimolecular proportion of acetic acid at a concentration of 12% for 24 hours. Film 24 had a treatment with a solution containing 8% glycerol, 1% of aged methylol-melamine-HCl polymer and 1% of polyvinyl alcohol. Film 25 was treated with an aged 3% methylol-melamine-HCl resin, washed thoroughly with water and then impregnated with an 8% glycerol solution prior to treatment with the chlorinated rubber coating composition. The results of the tests are shown in the following table.

Table IV

Film	Condition of topcoat after immersion for—					
	1 hr.	8 hrs.	24 hrs.	3 days	6 days	12 days
21.....	Slough ¼" at bot....	Badly sloughed edges..	Coating off....	O. K.....	O. K.....	O. K.....
22.....	O. K.....	O. K.....	O. K.....	O. K.....	O. K.....	O. K.....
23.....	O. K.....	O. K.....	O. K.....	O. K.....	O. K.....	O. K.....
24.....	O. K.....	O. K.....	O. K.....	O. K.....	O. K.....	O. K.....
25.....	¾" slough at bottom..	¾" peel all cut edges..	Same.....	Same.....	Same.....	Same.....

clusive. Number 16 was a control impregnated with an 8% glycerol solution. Sample Number 17 was impregnated with a 3% aged methylol-melamine-HCl solution. Sheet 18 was impregnated with an aged 3% methylol-melamine-acetic acid solution. Sheet 19 was impregnated with a solution containing 1% of the aged methylol-melamine resin and 1% polyvinyl alcohol and sheet 20 was impregnated with an aqueous solution containing 3% of aged methylol-melamine-HCl solution washed and then impregnated with an 8% glycerol solution. The dried sheet contained 1.4% resin on dry basis. The results of this series of tests were as follows.

Table III

Film	Condition of topcoat after immersion for—					
	1 hr.	8 hrs.	24 hrs.	3 days	6 days	12 days
16.....	Sep. at cut edge....	Coating off....	S. Bl.....	S. Bl.....	L. Bl.....	Slight slough.
17.....	O. K.....	O. K.....	O. K.....	S. Bl.....	Bl.....	Sloughed.
18.....	O. K.....	O. K.....	O. K.....	S. Bl.....	Bl.....	Sloughed.
19.....	Slight slough.....	Slight slough.....	¼" slough at edges..	¼" slough at edges..	Sloughed..	
20.....	¾" slough at edges	do.....	Coating off.....			

Although ethyl cellulose is a difficult top coat to anchor, these results show that cationic methylol-melamine polymers are highly effective in anchoring it to its cellulosic base.

EXAMPLE 5

A film-forming coating composition having the following formulation was prepared.

	Parts by weight
Chlorinated rubber	20.0
Paraffin wax (M. P. 60° C.)	2.0
Damar resin	3.3
Dibutyl phthalate	8.0
Toluene	243.0

Sheets of resin treated regenerated cellulose were impregnated with this coating composition and dried. They were then trimmed to expose uncoated edges and immersed in water at room temperature. The results of these tests are shown in the following table. Film Number 21 was a control which had been treated with an 8% aqueous solution of glycerol. Film 22 was impreg-

Cationic methylol-melamine polymers are shown to be highly effective in anchoring chlorinated rubber topcoats to cellulosic film.

EXAMPLE 6

A film-forming coating composition containing "Pliolite" (cyclicized rubber) as the film-forming constituent was prepared as follows:

	Parts by weight
"Pliolite"	31.4
Bleached montan wax	1.6
Toluene	243.0

40 Sheets of regenerated cellulose were impregnated with aqueous solutions of aged, cationic, partially

polymerized methylol-melamine condensation products as previously described. Sheet Number 26 served as a control and was impregnated with an 8% solution of glycerol prior to application of the top coat. Sheet Number 27 was impregnated with an aged methylol-melamine-HCl solution containing 3% resin solids. Sheet Number 28 was impregnated with an aqueous solution containing 3% of an aged methylol-melamine-acetic acid condensation product. Sheet 29 was impregnated with a solution containing 1% of aged methylol-melamine-HCl condensation product and 1% of polyvinyl alcohol. The baths used to treat sheets 27, 28 and 29 each contained 8% by weight of glycerol as softener for the regenerated cellulose. Sheet Number 30 was impregnated with an aged cationic methylol-melamine-HCl condensation product containing 3% of methylol-melamine. It was then thoroughly washed with water and then impregnated with an 8% solution of glycerol. Results of this series of tests are shown in the following table.

Table V

Film	Condition of topcoat after immersion for—					
	1 hr.	8 hrs.	24 hrs.	3 days	6 days	12 days
26.....	V. slight peel at bottom.	Coating off.....	-----	-----	-----	-----
27.....	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----
28.....	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----
29.....	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----
30.....	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----

Sheet Number 30 shows particularly well the fact that the resin treated cellulosic sheet can be washed with water to remove excess resin before application of the top coat.

EXAMPLE 7

A film-forming coating composition containing a butyl methacrylate polymer as the essential film-forming material and containing paraffin wax as the water repellent constituent was prepared having the following composition:

Parts by weight	
Polymerized butyl methacrylate.....	31.4
Paraffin wax (M. P. 60° C.).....	1.6
Toluene	243.0

melamine polymer which had been aged for 24 hours at a solids content of 12% with an equimolecular proportion of HCl. After treatment in the 3% resin solution, the sheets were thoroughly washed with running water and then impregnated with a solution containing 8% by weight of ammonium sulfamate and 2% glycerol. The sheets were then dried and coated with the nitrocellulose, the butyl methacrylate and the "Pliolite" coating compositions previously described. After drying, the sheets were immersed in water at room temperature and the anchoring effect of the cationic methylol-melamine observed. The results are given in the following table.

Table VII

Film	Condition of topcoat after immersion for—				
	1 hr.	8 hrs.	24 hrs.	3 days	6 days
Nitrocellulose.....	O. K.-----	1/4" slough.	1/4" slough.	1/4" slough.	1/4" slough.
Butyl methacrylate.....	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----
"Pliolite".....	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----

A sheet of tinted regenerated cellulose, Number 32, was impregnated with an aqueous solution containing 8% glycerol and 3% of an aged methylol-melamine-HCl polymer. Another sheet, Number 33, was impregnated with an aqueous solution containing 8% glycerol and 3% of aged methylol-melamine-acetic acid polymer. A third sheet, Number 34, of tinted regenerated cellulose was impregnated with a solution containing 8% glycerol, 1% of aged methylol-melamine-HCl polymer and 1% of polyvinyl alcohol. Another sheet, Number 31, was impregnated with an aqueous solution of 8% of glycerol but no methylol-melamine condensation product. These sheets were dried as previously described and then coated on both sides with the butyl methacrylate coating composition above. The dried sheets were then immersed in water at room temperature and observed from time to time to determine the anchoring effect of the cationic methylol-melamine. The results of these observations are shown in the following table.

Table VI

Film	Condition of top coat after immersion for—				
	1 hr.	8 hrs.	24 hrs.	3 days	6 days
31.....	Not tested.	Coating off.....	-----	-----	-----
32.....	do.....	O. K.-----	O. K.-----	O. K.-----	S. Bl. no slough.
33.....	do.....	O. K.-----	O. K.-----	O. K.-----	Do.
34.....	do.....	O. K.-----	O. K.-----	O. K.-----	Do.

EXAMPLE 8

Three sheets of dried regenerated cellulose were impregnated for 5 minutes with an aqueous solution containing 3% of a cationic methylol-

As will be seen, the aged methylol-melamine polymer does not lose its effectiveness when the treated film is subjected to a washing treatment. This observation was also made in the case of films 12, 20, 25 and 30 previously described. The results also show that the methylol-melamine polymer is compatible with softeners other than glycerol and that the softener may be subsequently applied to the methylol-melamine treated film after drying if desired.

EXAMPLE 9

Three sheets of dried regenerated cellulose were impregnated for 5 minutes with an aqueous solution containing 4% of glycerol, 4% of urea, and 3% of methylol-melamine polymer which had been aged for 24 hours at a solids content of 12% with an equimolecular proportion of HCl. The treated cellulosic sheets were dried in an oven for 8 minutes at 200° F. and then coated on both sides with the nitrocellulose, the butyl methacrylate and the "Pliolite" coating compositions previously described. After drying, the sheets were immersed in water at room temperature and the anchoring effect of the cationic methylol-melamine observed. The results are given in the following table.

Table VIII

Film	Condition of topcoat after immersion for—				
	1 hr.	8 hrs.	24 hrs.	3 days	6 days
Nitrocellulose.....	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----
Butyl methacrylate.....	O. K.-----	O. K.-----	O. K.-----	O. K.-----	O. K.-----
"Pliolite".....	Slight slough at bottom.	Same.	Same.	Same.	Same.

These results also show that the cationic methylol-melamine polymer is compatible with plasticizers such as glycerol and urea in the same impregnating bath. The "Pliolite" treated film showed some tendency for sloughing early in the test but by far the greater proportion of the film was anchored firmly to its cellulosic base after 6 days' immersion in water. The initial sloughing may have been due to imperfections arising from coating technique.

EXAMPLE 10

The anchoring efficiency of cationic methylol-melamine polymers was compared with that of non-cationic melamine-formaldehyde and urea-formaldehyde condensation products. One anchoring bath contained 3% of a cationic methylol-melamine polymer which had been aged for 24 hours at a solids content of 12% with an equimolecular proportion of HCl. Another solution contained 3% of an aqueous solution of methylol-melamine unaged and noncationic. An aqueous solution of a methylated methylol-melamine was also included in this group. Other aqueous baths were made up containing 3% of a urea-formaldehyde resin and 3% of a methylated urea-formaldehyde resin. Sheets of regenerated cellulose were impregnated in these baths for 5 minutes, then dried for 8 minutes at 200° F. and then coated on both sides with the nitrocellulose lacquer described above. The coated films were dried for 2 minutes at 90-95° C., trimmed to provide 3 freshly cut edges and then immersed in water at room temperature. The results of this series of tests are shown in the following table.

Table IX

Film	Condition of topcoat after immersion for—				
	1 hr.	8 hrs.	24 hrs.	3 days	6 days
Control.....	Coating off.....				
Aged methylol-melamine.....	O. K.....	O. K.....	O. K.....	O. K.....	O. K.....
Unaged methylol-melamine.....	O. K.....	Bad slough.....			
Methylated methylol-melamine.....	Slough at bottom.....	do.....			
Urea-formaldehyde.....	Slough at edge.....	do.....			
Methylated urea-formaldehyde.....	do.....	do.....			

As will be seen methylol-melamine was the only material that gave any substantial anchoring effect to the nitrocellulose coating composition. While the unaged methylol-melamine polymer gave better results than any of the other polymers tested, it was much inferior to the aged cationic methylol-melamine polymer. The latter gave perfect anchorage for more than 6 days whereas the others all failed within eight hours.

In commercial production of cellulosic films using cationic methylol-melamine polymers in accordance with my invention the process will normally be substantially continuous. A typical anchoring and coating process may be exemplified by the accompanying drawing in which:

Figure 1 is a sectional elevation showing one way of applying the cationic methylol-melamine polymer to regenerated cellulose film and thereafter applying a water-repellent coating;

Figure 2 is an isometric view of a section of the methylol-melamine impregnated cellulosic base sheet; and

Figure 3 is an isometric view showing the water repellent coating anchored to the regenerated cellulose base sheet.

In carrying out my invention, according to Fig. 1, a sheet of purified and washed gel regener-

ated cellulose 1 is passed through a softening agent and cationic methylol-melamine polymer. Excess bath is removed by means of a suitable doctoring device such as rolls 3, or knives, air jet, water spray, etc. (not shown). The impregnated film 4 is then dried by passing through a suitable drier 5 which may be of the loft, tower, heated drum type or the like. In this drier the impregnated film is heated for a period of time ranging from 2 or 3 seconds to 20 minutes or more, at temperatures of about 60° to 150° C., or higher, to cure the methylol-melamine to a substantially water insoluble stage. The dried and cured film 6 may then be wound up and stored, or shipped, for further treatment or it may be directly treated, as shown, with a coating bath 7. The coating material may be applied, of course, by means of sprays, rolls, or other conventional type of coating apparatus (not shown). The excess coating material is removed by means of a doctoring device 8. The coated film is then passed through a drier 10 to dry the coating composition. The finished product 11 may then be wound in rolls and is ready for use. Since the coating or cellulosic films and drying thereof is well known in the art, further discussion of this part of the process is unnecessary.

The cellulosic film 12 impregnated with the cationic methylol-melamine is illustrated in Fig. 2. So far as I have been able to determine the methylol-melamine is uniformly dispersed throughout the cellulosic body. This is an important advantage of my invention since some of the previously described anchoring processes yield a sheet of cellulose with a film of anchoring material on it as a separate body and under cer-

tain conditions the anchoring film may separate from its cellulosic base.

Figure 3 shows the cellulosic film 12 with top coats 13 and 14 firmly anchored thereto.

From the foregoing examples and discussion of my process, it will be evident that many modifications may be made therein without departing from its fundamental principles. For example, the softening agent can be applied in a separate bath. Also, if desired the impregnated film can be washed with water to remove excess methylol-melamine. Instead of coating the treated film on both sides it may be coated on only one side, or, if desired, it may be treated in discontinuous areas as when printing designs or letters thereon. Also, it may be desirable to coat the treated film with adhesive compositions of known type.

The amount of cationic methylol-melamine polymer incorporated in the sheet may vary from about 0.5 to 10%, or more, by weight. The amount of the polymer picked up by the sheet can be readily governed by controlling the concentration of the resin in the anchoring bath. I have used an anchoring bath containing about 3.0% by weight of methylol-melamine and found that the impregnated sheet contained about 2.3% by

weight of the methylol-melamine polymer. Using 1% of methylol-melamine in the bath gave a sheet containing about 1% of the polymer. Control of the amount of resin in the sheet may also be had by means of the doctoring device.

Although no curing catalyst for the cationic methylol-melamine is generally necessary, my experiments have shown that the acid curing catalysts can be incorporated in the anchoring bath without impairing the anchoring efficiency of the methylol-melamine.

The methylol-melamine polymer is odorless, tasteless, non-poisonous, colorless, transparent, heat and light stable and accordingly is an ideal compound for use in the treatment of cellulose films intended for wrapping foods.

The methylol-melamine polymer is compatible with many different kinds of softeners, plasticizers, synthetic and natural resins, gums, cellulosic esters and ethers, rubber and rubber like materials, waxes, oils, dyes, pigments, etc. The water soluble or dispersible materials of this group may be incorporated in the aqueous methylol-melamine resin solution if desired.

The cationic methylol-melamine polymers appear to be effective in anchoring all types of film-forming coating compositions to cellulosic base sheets. Coating compositions containing, as the film-forming constituent, compounds such as cellulose acetate, cellulose nitrate, ethyl cellulose, methyl cellulose, deacetylated chitin, rubber, chlorinated rubber, rubber hydrochloride, cyclized rubber, synthetic rubbers of different types, methacrylate polymers and other conventional film-forming coating materials may be employed to coat my treated cellulosic sheets. To obtain water repellent effects, waxes such as paraffin wax, scale wax, beeswax, montan wax, carnauba wax, candelilla wax and compounds such as aluminum stearate may be incorporated in the coating composition. Plasticizers, gums, pigments, etc., may also be added thereto.

I claim:

1. A process of treating non-fibrous cellulosic films which comprises the steps of impregnating a non-fibrous cellulosic film of regenerated cellulose with an acidic, aqueous, colloidal solution containing from about 0.5% to 20% by weight of partially polymerized melamine-formaldehyde condensation product, said product being in a state of polymerization less than that characterizing a gel, being water-dilutable, colloidal in nature, and having positively charged, hydrophilic particles of less than about one micron in diameter, washing the impregnated cellulosic film with water to remove excess melamine-formaldehyde condensation product, introducing a plasticizing agent into the cellulosic film, drying the film and thereafter applying a water-repellent coating composition thereto.

2. A process of preparing non-fibrous, cellulosic films having a water-repellent coating anchored firmly thereto which comprises the steps of dissolving one molecular equivalent of a melamine-formaldehyde condensation product in an aqueous solution containing from about 0.1 to 4.0 mols of acid per mol of condensation product to obtain a solution having from about 10% to 50% resin solids by weight, allowing the solution to stand at approximately room temperature for a period of time from between about two hours to forty-eight hours until the melamine-formaldehyde condensation product has become polymerized to a state at which the particles thereof are hydrophilic, positively charged, less than

about one micron in diameter, but being polymerized to a state less than that characterizing a gel, adjusting the resin content of said solution to a solids content of about 0.5% to 20% by weight, impregnating non-fibrous, cellulosic films with said solution, removing excess solution from the film by washing with water, incorporating a plasticizing agent in the film, drying and thereafter applying a water-repellent coating composition thereto.

3. A process of treating non-fibrous cellulosic films which comprises the steps of impregnating a film of regenerated cellulose with an acidic, aqueous solution containing from about 1% to 3% by weight of a hydrophilic, positively charged methylol-melamine partial polymer having particles within the colloidal range, said solution resulting from the aging of an acidic, aqueous solution containing from about 10% to 50% by weight of methylol-melamine at a pH within the range of 0.5 to 4.0 until the said methylol-melamine has become hydrophilic, water-dilutable, and having positively charged colloidal particles but has not attained the state of polymerization characterizing a gel, thereafter washing the impregnated cellulosic film with water to remove excess methylol-melamine from the surface, introducing a plasticizing agent thereinto, drying and thereafter applying a surface coating of a water-repellent material thereto.

4. A process of treating non-fibrous cellulosic films which comprises the steps of impregnating a film of regenerated cellulose with an acidic, aqueous solution containing from about 1% to 3% by weight of a hydrophilic, positively charged methylol-melamine partial polymer having particles within the colloidal range, said solution resulting from the aging of an acidic, aqueous solution containing from about 10% to 50% by weight of methylol-melamine at a pH within the range of 0.5 to 4.0 until the said methylol-melamine has become hydrophilic, water-dilutable, and having positively charged colloidal particles but has not attained the state of polymerization characterizing a gel, thereafter washing the impregnated cellulosic film with water to remove excess methylol-melamine from the surface thereof, introducing a plasticizing agent thereinto, drying and thereafter applying a film-forming adhesive composition thereto.

5. A process of treating non-fibrous cellulosic films which comprises the steps of impregnating a film of regenerated cellulose with an acidic, aqueous solution containing from about 1% to 3% by weight of a hydrophilic, positively charged methylol-melamine partial polymer having particles within the colloidal range, said solution resulting from the aging of an acidic, aqueous solution containing from about 10% to 50% by weight of methylol-melamine at a pH within the range of 0.5 to 4.0 until the said methylol-melamine has become hydrophilic, water-dilutable, and having positively charged colloidal particles but has not attained the state of polymerization characterizing a gel, thereafter washing the impregnated cellulosic film with water to remove excess methylol-melamine from the surface thereof, introducing a plasticizing agent thereinto, drying and thereafter applying a film-forming printing composition in discontinuous areas thereto.

6. A process of preparing non-fibrous, cellulosic films having a water-repellent coating anchored firmly thereto which comprises the steps of dissolving one molecular equivalent of a melamine-

formaldehyde condensation product in an aqueous solution containing from about 0.1 to 4.0 mols of acid per mol of condensation product to obtain a solution having from about 10% to 50% resin solids by weight, allowing the solution to stand at approximately room temperature for a period of time from between about two hours to forty-eight hours until the melamine-formaldehyde condensation product has become polymerized to a state at which the particles thereof are hydrophilic, positively charged, less than about one micron in diameter, but being polymerized to a state less than that characterizing a gel, adjusting the resin content of said solution to a solids content of about 0.5% to 20% by weight, impregnating non-fibrous, cellulosic films with said solution containing also a plasticizing agent, removing excess solution from the film, drying and

thereafter applying a water-repellent coating composition thereto.

7. A process of treating non-fibrous cellulosic films which comprises the steps of impregnating a non-fibrous cellulosic film of regenerated cellulose with an acidic, aqueous, colloidal solution containing a plasticizing agent and from about 0.5% to 20% by weight of a partially polymerized melamine-formaldehyde condensation product, said product being in a state of polymerization less than that characterizing a gel, being water-dilutable, colloidal in nature, and having positively charged, hydrophilic particles of less than about one micron in diameter, removing the excess of said impregnating solution from the surface of the impregnated cellulosic film, drying the film, and thereafter applying a water-repellent coating composition thereto.

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