

UNITED STATES PATENT OFFICE

2,122,433

COATED FILMS AND METHOD OF MAKING
THE SAME

Frederick Madison Meigs, Wilmington, Del., assignor, by mesne assignments, to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application June 17, 1936,
Serial No. 85,769

16 Claims. (Cl. 91—68)

This invention relates to coated sheets or films and it particularly pertains to regenerated cellulose film coated with a moistureproofing composition which tenaciously adheres to or is anchored to the base film even when in direct contact with water for prolonged periods of time or when used as a wrapping tissue directly in contact with products containing large amounts of water or moisture. The invention also pertains to methods for producing such coated sheets or films.

Ordinary sheets or films of regenerated cellulose have been rendered moistureproof by coating with a moistureproofing composition comprising in its preferred form a flowable solution of a cellulose derivative, a wax or wax-like material, a blending agent and a plasticizer. These coated sheets or films are very effective as a wrapping material for such products as bread, cake, candy, or the like which it is desired to maintain in substantially their original fresh condition without any change in moisture content. Such coated sheets or films, when used as a wrapping material which is directly held in contact with products having an exceedingly high water or moisture content, such as butter, cheese, wet or frozen fish, ice cream or the like, and when such articles are kept over long periods of time in storage, have the disadvantage that the moistureproof coating tends to loosen and/or flake off from the sheet of regenerated cellulose and to thereby lessen the moistureproof quality of the wrapping material.

It is an object of this invention to provide a flexible, substantially odorless, non-fibrous cellulosic sheet or film having a surface coating which will adhere tenaciously to the cellulosic sheet or film. A further object comprises the production of films of this character having a moistureproofing coating comprising a cellulose derivative, a wax or wax-like material, a blending agent and a plasticizer. A still further object of the invention comprises a simple, workable process, directly applicable to existing equipment, such as is used for the manufacture of regenerated cellulose sheets or films, for producing products having the characteristics described.

A further object of the invention resides in the production of transparent, flexible, non-fibrous, cellulosic sheets or films prepared by precipitation from an aqueous cellulosic dispersion, coated and/or sized with an amine-phenol-aldehyde resin, and having a moistureproof surface coating which remains firmly anchored to the cellulosic

sheet or film even when in direct contact with water over a long period of time.

Other objects of the invention will appear from the following description.

The objects of the invention are accomplished in general by forming a cellulosic sheet or film, applying directly to the cellulosic base, a coating and/or sizing of an amine-phenol-aldehyde resin which is insoluble in water and soluble in dilute aqueous mineral or organic acid, and then applying to said coated and/or sized sheet or film a surface coating having moistureproofing characteristics. Some of these resins are soluble in dilute aqueous caustic solution, in acetone and in certain other solvents as set forth hereinafter.

The following examples illustrate modes of applying the principles of the invention.

Example I

A sheet of regenerated cellulose in the gel state, which has been cast from viscose, desulfured, bleached, and washed free from impurities in the usual manner on the casting machine and is ready for the glycerin treatment, is passed through an aqueous glycerin bath prepared by dissolving 2% of a phenol-formaldehyde-dimethylamine resin (prepared as described in Example A below) in an aqueous solution containing 1.5% acetic acid and 6% glycerin. The excess solution is removed from the sheet by means of squeeze rolls which reduce the water content of the sheet to between three and four times the weight of the cellulose, after which the sheet of regenerated cellulose, wet with the solution, is ready to be dried. The treated film is dried for thirty minutes at 120° C., the regenerated cellulose film being left with a transparent coating or sizing of the resin thereon.

The acetic acid is used to render the resin soluble in the form of its acetate salt. During drying, the resin acetate becomes converted into the water-insoluble resin and acetic acid, the volatile acetic acid being removed in the drying air.

The drying of the sheet of regenerated cellulose which has been treated with the aqueous glycerin solution containing the size, may be carried out according to the usual method for drying regenerated cellulose sheeting on the casting machine by bringing the sheet directly from the squeeze rolls into contact with heated rolls which dry the sheet at temperatures preferably between 50 and 90 degrees centigrade. However, there may be a tendency for the size to be deposited on the dryer rolls when they become

wet with the solubilized resin from the wet film passing over them. This deposit, resulting from the heat acting on the soluble size, may flake off from time to time on the fresh film passing over the dryer rolls, thereby imparting a faintly mottled appearance to the finished film.

Therefore, in this preferred example, the regenerated cellulose sheet, wet with a solution of glycerin and the size, after passing through the squeeze rolls and before coming in contact with the drier rolls, is first given a preliminary partial drying out of contact with any surface by passing the sheet through air heated to an elevated temperature of means of any suitable arrangement, whereby the moisture content of the sheet is reduced to any desired extent, for instance, from one-tenth to one-half of its initial water content before coming in contact with the drier rolls of the casting machine to complete the drying operation in the usual manner.

The resulting sheet of regenerated cellulose coated or sized with an insoluble deposit of resin may be conditioned if necessary to bring it to the desired moisture content and is then coated with a moistureproofing composition of the following formula:

	Parts by weight
Pyroxylin.....	6.75
Gum damar.....	1.64
30 Dibutyl phthalate.....	2.80
Paraffin M. P. 60-61° C.....	0.48
Zinc stearate.....	0.15
Ethyl acetate.....	56.34
Toluene.....	28.53
35 Alcohol.....	3.20
Acetone.....	0.11

The sheet is passed through the moistureproofing composition, the excess of which is removed by scraping or any suitable means, and the coated sheet is dried at a temperature above the melting point of the wax, after which the finished sheet may be conditioned if necessary to bring it to the desired moisture content. The resulting product is a sheet of regenerated cellulose with a moistureproofing coating, which is substantially odorless, transparent, flexible, and moistureproof, and to which, by virtue of the sheet being coated or sized with the resin, the moistureproof coating adheres or is anchored very tenaciously when the sheet is in direct contact with water or is used as a wrapping directly in contact with products containing large amounts of water or moisture such as butter, cheese, wet or frozen fish, ice cream, or the like, for very substantial periods of time, for example, for a month or more.

Example II

A meta-cresol - dimethylamine - formaldehyde resin similar to the resin described in Example A (below) but prepared from a chemically equivalent amount of meta-cresol instead of phenol is dissolved in dilute acetic acid containing 5-6% glycerol to form a solution containing 2% of the resin. When used as the anchoring agent, as in the preceding example, the results obtained are comparable to those obtained by the procedure of Example I.

The glycerin solution may, in addition to the resin, be combined with another size suitable for use as an anchoring agent. Thus, a 1% aqueous solution of the resin of Example II containing also about 5-6% glycerol, together with 1% of de-acetylated chitin which is solubilized by the acetic acid in the bath, results in an anchorage which is somewhat better than that obtained with

either the resin or the de-acetylated chitin when used alone in 2% concentration in the aqueous acetic acid-glycerol bath. The use of de-acetylated chitin, solubilized to the acetate salt by means of acetic acid has been disclosed in Gladding and Bateman application, Serial No. 731,603, filed June 21, 1934.

This invention contemplates, as a base, any smooth, dense, non-porous, non-fibrous cellulosic sheet or film which may be precipitated from an aqueous cellulosic dispersion. Thus, the scope of the invention includes the use of sheets or films of regenerated cellulose, whether precipitated from solutions of viscose, cuprammonium cellulose, or any other aqueous solution or dispersion of cellulose, and it also contemplates the use of sheets or films of such cellulose esters and ethers as are precipitated from aqueous solutions or dispersions, such as glycol cellulose, cellulose glycolic acid, methyl cellulose and ethyl cellulose of low alkyl content, cellulose phthalate, and other cellulose products similar to those described. When any given coating composition is applied to such cellulosic sheets or films, the coating composition will not penetrate therethrough and will normally result in a surface coating. It is desired to emphasize the fact that the preferred form of the invention is directed to the treatment of regenerated cellulose sheets or films since it is in this form that the invention may be applied with the greatest advantages.

As a surface coating, the invention contemplates the use of any coating composition containing a cellulose derivative base, such as cellulose nitrate, cellulose acetate, ethyl cellulose, benzyl cellulose or the like, which may be modified as desired by the addition of blending agents, waxes, plasticizers, et cetera. In its preferred form, this invention contemplates as a surface coating a moistureproofing coating comprising a cellulose derivative, a wax or wax-like material or other moistureproofing agent, a blending agent and a plasticizer. Such moistureproofing compositions are disclosed in Charch and Prindle U. S. Patent No. 1,737,187, issued November 26, 1929.

The amine-phenol-aldehyde resins contemplated as being within the scope of this invention, are preferably substantially insoluble in water, and in 5% aqueous ammonia, but soluble in 2% aqueous acetic acid. The resin is prepared by reacting a phenol having at least two free reactive positions, that is, positions ortho and para to the phenolic hydroxyl, and containing only organic groups as ring constituents, and aldehydes (particularly formaldehyde) and an organic compound, preferably of not over six carbon atoms which has at least one amino nitrogen atom joined to an aliphatic carbon atom, that is, a carbon atom which is not part of an aromatic ring, and to at least one hydrogen atom and isolating the resulting resinous reaction product.

These resins are very insoluble in water and in organic solvents, but can be made soluble by causing them to react with any one of a larger number of acids including acetic, formic, citric, glycolic, malic, maleic, succinic, adipic, phthalic, tartaric, benzoic, hydrochloric, and the like, thereby forming salts. Coatings or films, prepared from aqueous solutions of these resin salts, upon being dried, preferably at an elevated temperature, are more or less rapidly rendered insoluble in water and organic solvents. In case of salts formed by reacting with volatile acids, particularly volatile acids which are only slightly ionized like acetic acid, the conversion to insol-

bility is easily and quickly accomplished since the acid is readily dissociated from its salt and being volatile is easily removed by heat, leaving an insoluble residue. Salts formed from non-volatile and/or from the highly volatile acids and/or from the highly ionized acids are much less readily converted to insolubility, and it is therefore preferred to use salts of the resin with the volatile acids of low ionization, e. g., acetic acid. However, the salts with the highly ionized and/or non-volatile acids may be converted into the insoluble form by treatment with ammonia, e. g., gaseous ammonia.

Any suitable concentration of a resin may be employed in the aqueous solution of its salt, depending upon the method of operation used and the amount of size which it is desired to have present in the finished cellulosic sheet. In general, it is preferred to use solutions in which the concentration of the resin salt is equivalent to between 0.2 and 2.0 per cent by weight. As has been stated, however, higher or lower concentrations may be desirable at times for different effects or with different methods of applying the size. The amount of size present in the finished cellulosic sheet is controlled by the concentration of resin salt in the solution and by the amount of this solution removed from the wet sheet by squeeze rolls or by other means, prior to the drying of the sheet. In the preferred form of this invention, this amount ranges from 0.5 to 4.0 per cent of the weight of the sheet, although it may at times be desirable for certain purposes to have present in the sheet an amount of size greater or less than those included within these limits.

A preferred example of a resin having the desired solubility in acids is the reaction product of meta-cresol, formaldehyde and dimethylamine. Other phenols may be used in place of cresol, e. g., phenol itself or p-tertiary amyl phenol, and ammonia or various primary or secondary amines for the dimethylamine. It is desirable in most cases, possible in all cases, and necessary in some cases to react the amine or ammonia with a part of the formaldehyde before adding the remainder.

The resins contemplated by this invention are to be sharply distinguished from the phenol-aldehyde resins prepared in the presence of only catalytic amounts of ammonia or amines, which resins cannot be employed in accordance with the methods of this invention because they lack the preponderance of amino nitrogen which induces the proper solubility characteristics. The molal ratio of amine to phenol which is used in making the resins with which the present invention is concerned is on the order of 1:2.

The preparation of certain of the resins contemplated as anchoring agents by this invention (viz. those obtained by reaction of selected types of phenols and primary amines under certain conditions and in particular proportions) is described in the copending application of Harmon and Meigs, Serial No. 85,820 filed June 17, 1936. To illustrate still other types of aldehyde resins, the following examples are given:

Example A—Phenol-formaldehyde-dimethylamine-ammonia resin

A solution of 18 grams (0.4 mol.) of dimethylamine in 32.4 grams (0.4 mol.) of 37% aqueous formaldehyde was added with mechanical stirring and cooling to 53.5 grams (0.5 mol.) of 88% phenol. To the above mixture, a solution of 81 grams (1 mol.) of 37% aqueous formaldehyde

and 30.4 grams (0.5 mol.) of 28% aqueous ammonia was added with cooling. The resulting solution was gradually heated in a water bath to 90° C. and held at that temperature for 5 hours. The resulting resin was purified by grinding it to a uniform slurry in the presence of a little water in an ice cold mortar, followed by filtration and washing with ice cold water. After drying, it weighed 74 grams. It was a yellow material which softened slightly above room temperature. It was soluble in acetone, ethyl acetate, dioxan, 10% aqueous sodium hydroxide, 1.5% aqueous acetic acid, 3% formic acid, and 90% toluene-10% ethanol mixture.

Example B—Phenol lignin-formaldehyde-dimethylamine resin

The crude phenol lignin used in this preparation was made as follows:

A 3-liter 3-necked flask was equipped with a hook-type mechanical stirrer, wide bore air reflux condenser and thermometer and mounted in an oil bath. The flask was charged with 900 grams of phenol, the stirrer started and 190 grams of a fine grade of spruce wood flour (100 mesh or better) were added through the condenser while the temperature of the phenol was increased from 65° to 116° C. Then 25 grams of concentrated hydrochloric acid were added all at once. After the reaction mixture had become homogeneous (about 15 minutes), 190 grams more of wood flour were added during the course of about one hour. Heating at 116–120° C. and stirring were continued for 4 hours, at which time the reaction mixture was viscous and black. It was allowed to cool, diluted with 2 liters of 95% ethanol, heated with stirring until the alcohol refluxed, filtered with suction, and the cellulosic residue was washed well with hot alcohol. The alcohol and 200 grams of phenol were removed from the filtrate by heating in a hot water bath in vacuo (2.5 mm. to take off the phenol). The remaining uncombined phenol was removed from the product by steam distilling until 6.5 liters of distillate had collected. The flask was allowed to cool, the water layer (about 1 liter) was decanted from the tarry product, about 500 cc. of distilled water was added and steam distillation was continued until test samples of the distillate were free from phenol (FeCl₃ test). The water which had collected in the flask was decanted and the residual product of crude phenol lignin was allowed to cool. It was a fused, hard, brittle, black mass and weighed 560 grams. It probably did not contain more than 5% of its weight of water.

The amine resin was made as follows from the crude phenol lignin described above:

The 560 grams of crude phenol lignin prepared as described above was dissolved in 1,900 cc. of 95% ethanol. The solution was cooled to 8° C. and an aqueous solution of 3.8 mols. of dimethylaminomethanol was added with mechanical stirring at 8° C. during the course of 15 minutes. The dimethylaminomethanol solution was made by bubbling 171 grams of dimethylamine into 308 grams of aqueous 37% formaldehyde solution while the temperature was kept below 30° C. After the addition of dimethylaminomethanol was completed the ice bath was removed and the solution was warmed to 36° C., at which temperature a mild exothermic reaction set in. Heating was discontinued. The reaction temperature stayed at 36–38° C. for 1.25 hours and then started to drop. The reaction was next heated in a water bath at 65–70° C. for 3 hours. The alcohol solu-

tion was allowed to cool and then added slowly to 12.5 liters of efficiently stirred distilled water. The resin was precipitated as a finely divided light brown, amorphous solid. It was filtered, washed well with water and dried first in the air and then in a vacuum desiccator. The dry product was light brown in color and weighed 459 grams. It was soluble in acetone, ethanol, dioxan, chloroform, hot ethyl acetate, 1.5% aqueous acetic acid, and 5% aqueous sodium hydroxide solution.

Example C—Phenol-formaldehyde-dimethylamine resin

To a solution of 564 grams (6 mols) of phenol in 680 grams (8.4 mols) of aqueous 37% formaldehyde was added, with stirring and cooling at such a rate that the temperature remained below 10° C., an aqueous solution of 3 mols of dimethylaminomethanol made by bubbling 135 grams (3 mols) of dimethylamine into 243 grams (3 mols) of cold aqueous 37% formaldehyde. The addition of this solution to the phenol solution required about an hour. The cooling bath was then removed and the temperature of the reaction mixture was allowed to rise spontaneously to 40° C., where it was held by means of a cooling bath until the exothermic reaction was over. The reaction mixture was then heated in a boiling water bath until the resinous mass which was formed was too thick to stir mechanically. It was transferred, while hot, to a large nickel plate, cooled, and the brittle resin was ground in a cold mortar with a little cold water to a uniform slurry. The resin was filtered, washed thoroughly with water, and dried in vacuo at room temperature. After drying, the weight of light yellow, granular, resin was 900 grams. Analysis showed that the product contained 4.94% nitrogen. It was soluble in dilute (1.5%) acetic acid to the extent of at least 1 gram of resin in 99 grams of acid solution, in 5% sodium hydroxide solution, and in benzyl alcohol and pyridine. It was insoluble in aromatic hydrocarbons. A film flowed from the acetic acid was, after being baked at 100° C. for 15 hours, clear, colorless, hard, and insoluble in dilute acids. The resin was also soluble to the extent of at least 1% in 1.5% aqueous solutions of the following acids: formic, glycolic, lactic, tartaric, phosphoric, and maleic. It was soluble in 0.6% aqueous hydrochloric acid to the extent of 4.5 grams in 95.5 grams of the acid solution. Mineral acids in concentrations of 1.5% or more appear to catalyze hardening of the resin. Consequently they do not dissolve in it. The resin was insoluble in 1.5% aqueous sulfuric acid, n-caprylic acid, and hydrochloric acid.

Example D—Phenol-formaldehyde-dimethylamine resin

The above procedure was repeated except that the ratios of reactants were phenol, 1 mol.; formaldehyde 1.4 mols; dimethylaminomethanol, 1 mol. The resulting resin was a yellow amorphous powder. It was insoluble in all of the common organic solvents except methyl Cellosolve. It was soluble in the theoretical amount of 1.5% aqueous acetic acid and was also soluble in 5% sodium hydroxide solution. A suspension of this resin in ice cold water was dissolved when the water was saturated with carbon dioxide. A film flowed from a dilute (1.5%) acetic acid solution of this resin remained clear and was soluble in dilute acetic acid after prolonged baking at 100° C.

Example E—Phenol-formaldehyde-cyclohexylamine resin

A mixture of 85.5 grams (0.8 mol.) of 88% phenol and 91 grams (1.12 mols) of 37% formaldehyde was stirred mechanically and cooled in an ice bath. To this mixture at 5° C., there was added a solution made from 54.5 grams (0.55 mol.) of cyclohexylamine and 65.5 grams (0.64 mol.) of 37% aqueous formaldehyde. The ice bath was removed and the stirred reaction mixture was allowed to warm to room temperature and it was then heated gradually on a water bath up to 90° C. and was held there for 3.5 hours. The resin which formed was purified by the method outlined under Example C. It was a light yellow, granular solid and weighed 143 grams. It was soluble in 45% acetic acid, ethyl acetate, dioxan, pyridine, and 90% toluene-10% ethanol mixture.

There are, of course, numerous other amine phenol formaldehyde resins which are prepared in much the same manner as described in these specific examples which may be used with good results in improving the anchoring of coatings to base films, as for example resins prepared from symmetrical xylenol, formaldehyde and methylamine; phenol, lignin, formaldehyde and methylamine; phenol, formaldehyde and cyclohexanolamine; p-toluene sulfonamide, phenol, formaldehyde and methylamine; diphenyl cyclohexanone, formaldehyde and dimethylaminomethanol; diphenylguanidine and formaldehyde; phenol, formaldehyde and dimethylamine; m-cresol, formaldehyde and dimethylamine; xylenol, formaldehyde and dimethylaminomethanol; phenol, formaldehyde, ammonia and diethanolamine, etc.

In order that the finished cellulosic sheet may be of the desired degree of softness, a softening agent, such as glycerin, is incorporated in the aqueous solution of the size. The aqueous solution may be applied to the cellulosic sheet by immersing the sheet in the solution or by brushing or spraying the solution onto the sheet, or by applying the solution to the sheet by rollers or by any other convenient means. Moreover, the size solution may be applied either to the cellulosic sheet in the gel condition or to the finished dry cellulosic sheet by another operation. We prefer, however, to apply it to the gel sheet from the glycerin bath. In the step of drying the cellulosic sheet treated with a solution of the size, for example, the acetate salt of the resin, in which step the soluble salt is converted to an insoluble coating or sizing on the sheet, a wide range of temperature and a number of methods are possible. For example, a preliminary drying operation may be carried out with air which is at temperatures in the range 60 to 250° C., subsequent drying being preferably carried out on rolls at temperatures in the approximate range 50 to 90° C. Alternatively, the entire drying process may be carried out on rolls at 50 to 130° C. In certain cases vapors of basic compounds, such as ammonia, may be caused to act on the cellulosic sheet after drying if it is desired to facilitate the conversion of the size salt to an insoluble product. The same effect may be achieved by treating the cellulosic sheet, which has been dried or partially dried after the application of the solution of the size, with a solution of a basic compound, such as dilute ammonium hydroxide, a solution of ethylene diamine, or of triethanolamine or the like.

As has been stated, the greatest advantages follow from the use of the resin size as an anchoring agent for moistureproofing coatings applied to regenerated cellulose or to other cellulosic films of the character described. It will be understood that it can in general be used to anchor coatings for transparent cellulosic sheeting where such coatings have less or greater moistureproofing properties than those described in the examples given above.

The present invention effects the production of flexible, substantially odorless, non-fibrous, non-porous cellulosic sheets or films having a moistureproofing coating securely anchored to the film base and resistant to deterioration when subjected to the action of liquid water over long periods of time. Further advantages are the adaptability of the process of the invention to equipment now used for the production of regenerated cellulose film and the like, without necessitating a substantial change in the design of such equipment; lower cost, minimum waste and great efficiency. Where no pigment is used, the composite films have a high degree of transparency.

In some instances the direct cellulosic sheet coated or sized with the resin anchoring agent may retain a very faint trace of the characteristic odor of the acid used in forming the water-soluble resin solution. This trace of odor may readily be removed by treating the sheet with dilute vapors or a dilute solution of a basic compound like ammonia to neutralize the acid, by volatilizing the acid by means of heat, or by a current of air or steam, or by any known deodorizing treatment. If desired, the aqueous solution of the size may be subjected to treatment with activated carbon in order to remove any undesirable odor.

While the invention has been described particularly with respect to transparent wrapping tissues, it will be understood that within its broad scope, the invention includes the anchoring of coatings to sheets which are thicker than wrapping tissues. The invention is also applicable to the anchoring of coatings to tubes, sausage casings, bottle caps and bands, molded articles, and, in general, to any articles of cellulose or similar material of the character described, where the problem of anchoring coatings arises.

The preferred form of the invention resides in the anchoring of moistureproofing surface coatings to a non-porous, non-fibrous base such as regenerated cellulose. Within its broadest scope, the invention comprehends also the coating of other bases, e. g., rayon fabric and the like, in order to anchor surface coatings thereto. Even where the coating of the base, whether it be non-porous or of other character, is discontinuous in character, such, for example, as in the printing of colors, symbols, indicia, advertisements, etc., the resin size may be used as the anchoring agent. Thus, regenerated cellulose sheets, tubes, caps, sausage casings, etc., when coated or sized with the resin size may be printed with printing ink either having a lacquer base or a drying-oil base, to give any desired indicia, and, after drying, the printing remains securely anchored to the base even after being subjected to rigid washing, boiling or other processing steps.

Additionally, the present invention may be used to improve the anchorage of various coatings to bases other than those specifically noted above, for example, paper, cotton cloth, and other

bases which are water sensitive, i. e., will absorb water, the anchoring agents improving the adhesion between the coating and base over that exhibited where the coating is applied to the base in the absence of the anchoring agent.

For the purposes of this invention, moistureproof materials are defined as those which, in the form of a thin, continuous and unbroken film, will permit the passage of not more than 690 grams of water vapor per 100 square meters per hour, over a period of 24 hours at approximately 39.5° C. $\pm 0.5^\circ$ C., the relative humidity of the atmosphere at one side of the film being maintained at least at 98% and the relative humidity of the atmosphere at the other side being maintained at such value as to give a humidity differential of at least 95%.

Moistureproofing coating compositions are defined as those which, when laid down in the form of thin, continuous, unbroken films, applied uniformly as a coating with a total thickness not exceeding 0.0005" to both sides of a sheet of regenerated cellulose of thickness approximately 0.0009", will produce a coated product which is moistureproof.

A moistureproofed regenerated cellulose sheet is capable of resisting the passage of moisture or water vapor at least ten times as effectively as the uncoated regenerated cellulose sheet.

Parts, proportions and/or percentages referred to throughout the specification and claims are to be construed as parts, proportions and/or percentages by weight unless indicated otherwise.

Since the invention is capable of considerable modification and variations of the details given above, any change which conforms to the spirit of the invention is intended to be included in the scope of the appended claims.

I claim:

1. An article of manufacture comprising a water-sensitive base, a surface coating and an intermediate coating comprising an aliphatic amine-phenol-aldehyde resin substantially insoluble in water and in 5% aqueous ammonia but soluble in 2% aqueous acetic acid.

2. An article of manufacture comprising a water-sensitive non-fibrous base, a surface coating and an intermediate coating comprising an aliphatic amine-phenol-aldehyde resin substantially insoluble in water and in 5% aqueous ammonia but soluble in 2% aqueous acetic acid.

3. A composite film suitable for use as a wrapping tissue comprising a water-sensitive, non-fibrous base, a surface coating and an intermediate coating comprising an aliphatic amine-phenol-aldehyde resin substantially insoluble in water and in 5% aqueous ammonia but soluble in 2% aqueous acetic acid.

4. A composite film suitable for use as a wrapping tissue comprising a water-sensitive, non-fibrous base, a moistureproofing coating and an intermediate coating comprising an aliphatic amine-phenol-aldehyde resin substantially insoluble in water and in 5% aqueous ammonia but soluble in 2% aqueous acetic acid.

5. In a process for producing an article comprising a water-sensitive base and a surface coating which adheres tenaciously to the base even when in contact with water over long periods of time, the steps which comprise applying to the base an intermediate coating comprising an aliphatic amine-phenol-aldehyde resin substantially insoluble in water and in 5% aqueous am-

monia but soluble in 2% aqueous acetic acid, then applying a surface coating.

6. In a process for producing an article comprising a water-sensitive non-fibrous base and a surface coating which adheres tenaciously to the base even when in contact with water over long periods of time, the steps which comprise applying to the base an intermediate coating comprising an aliphatic amine-phenol-aldehyde resin substantially insoluble in water and in 5% aqueous ammonia but soluble in 2% aqueous acetic acid, then applying a surface coating.

7. A composite film suitable for use as a wrapping tissue comprising a non-fibrous cellulosic sheet, an intermediate coating comprising an aliphatic amine-phenol-aldehyde resin substantially insoluble in water and in 5% aqueous ammonia but soluble in 2% aqueous acetic acid, and a surface coating, said sheet and said surface coating exhibiting an adhesion greatly improved over that exhibited between a similar sheet and surface coating when in direct contact with each other, said adhesion being tenacious even when the composite film is subjected to contact with water over a long period of time.

8. The product described in claim 7 characterized in that the sheet is regenerated cellulose.

9. The product described in claim 7 characterized in that the sheet is regenerated cellulose and the surface coating comprises a moisture-proofing composition.

10. In a process for producing an article comprising a water sensitive base and a surface coating which adheres tenaciously to the base even when in contact with water over long periods of time, the steps which comprise treating the base

with an aqueous solution of a salt of an aliphatic amine-phenol-aldehyde resin substantially insoluble in water and in 5% aqueous ammonia but soluble in 2% aqueous acetic acid, converting said salt of said resin to an amine-phenol-aldehyde resin substantially insoluble in water, and applying a surface coating thereto.

11. The process of claim 10 characterized in that said water sensitive base is non-fibrous.

12. The process of claim 10 characterized in that said water sensitive base is regenerated cellulose and the coating applied thereto is a moisture-proof coating.

13. The article of claim 1 characterized in that said aliphatic amine contains from 1 to 6 carbon atoms.

14. The article of claim 4 characterized in that said aliphatic amine contains from 1 to 6 carbon atoms.

15. The article of claim 1 characterized in that said aliphatic amine is of the general formula:



wherein R represents an aliphatic group containing from 1 to 6 carbon atoms, and R' is hydrogen or an aliphatic group containing from one to six carbon atoms.

16. The article of claim 4 characterized in that said aliphatic amine is of the general formula:



wherein R represents an aliphatic group containing from 1 to 6 carbon atoms, and R' is hydrogen or an aliphatic group containing from one to six carbon atoms.

FREDERICK MADISON MEIGS.