Patented July 19, 1938 2,123,883

UNITED STATES PATENT OFFICE

2,123,883

ARTICLE OF MANUFACTURE

Deane C. Ellsworth, deceased, late of Wilmington, Del., by Joseph F. Haskins, administrator, Wilmington, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application April 15, 1937, Serial No. 137,119

16 Claims. (Cl. 91—68)

This invention relates to transparent sheet material especially suitable for use as a wrapping tissue, and more particularly to the manufacture of a glass-clear, moisture-proof and water-insensitive sheet material capable of resisting the diffusion of moisture therethrough to a substantial degree for a substantial period of time.

It is a desire of manufacturers and vendors that numerous products, such as food-stuffs, drugs, candy, vegetables, tobacco products and the like, reach the consumer in their original fresh state. This goal may be achieved by wrapping the products in sheet materials which effectively prevent the passage of water therethrough.

For years waxed paper was the only material available for the purposes abovementioned. At best it was a very unsatisfactory wrapping material. As is generally known, to make an attractive package and expose the contents, the wrapper must be made of a transparent material. Waxed paper is opaque. The noisome property that many waxed papers have of being or becoming greasy-surfaced is extremely objectionable. The lack of flexibility and consequent cracking of a waxed paper upon folding or creasing, is such a well known detriment to its extended use that mention thereof is hardly warranted. Such products are of necessity stiff and relatively thick.

Recently there has appeared on the market a moisture-proof material which consists of a base of regenerated cellulose thinly coated with a moisture-proofing composition, said composition comprising, in its preferred form, a wax combined with other ingredients capable of giving a strong, flexible, transparent, non-tacky, non-greasy, odorless and colorless film. Such products are disclosed in United States Patent 2,737,187 issued November 26, 1929 and United States Patent 1,997,583 issued April 16, 1935. Processes of coating and apparatuses for carrying out the coating are also mentioned in United States Patents 1,826,696—7—8—9, issued October 6, 1931.

It has been found that when very moist or wet materials, such as butter, cheese and the like are packaged in wax composition coated regenerated cellulose sheets such as those above described, the moisture-proofing coating becomes detached or loosened from the base. As a consequence the effectiveness of the coating, so far as the prevention of the diffusion of the water vapor is concerned, is seriously impaired. Such coatings are detached from the base film in approximately one hour when the wrapping is in actual contact with water.

Many efforts have been made along various lines to correct or overcome these last-mentioned disadvantages. In the early moisture-proofing coatings, the wax was combined with a cellulose derivative. One effort to secure better anchorage of the moisture-proofing film was to replace the cellulose derivative in such compositions with rubber, as will be clear from United States Patent 2,051,944 issued August 25, 1936. Another effort is disclosed in United States Patent 2,022,490 issued November 26, 1935, wherein the use of a varnish for coating the regenerated cellulose film was proposed. A still further development involved the use of an intermediate anchoring film, as set out in United States Patent 1,962,338 issued June 12, 1934, according to which the regenerated cellulose sheet was coated with an anchoring film over which the moisture-proofing composition film was applied.

Still another effort to produce a superior moisture-proof wrapping material has involved the replacement of the regenerated cellulose with a film of a non-water-sensitive cellulose derivative, such as the more expensive cellulose acetate. This advance in the art is disclosed in United States Patent 1,997,857 issued April 16, 1935.

While each of the aforementioned improvements (as well as the original proposals to moisture-proof regenerated cellulose film) can truthfully be said to have materially advanced the art, it is well known that there is still a considerable field for improvement in this type of product.

This invention has for an object the preparation of strong, flexible, transparent, glossy, non-tacky, non-greasy, odorless, colorless, water-insensitive and moisture-proof sheet material capable of resisting the passage of water, either liquid or vapor, therethrough to a substantial degree for a substantial period of time. Another object was to devise a moisture-proof coated sheet material, whose moisture-proofing coating could not easily be detached from the base sheet material even when immersed in water for several hours or even days. Still another object was to prepare a water-proof coated sheet material. A general advance in the art and other objects which will appear hereinafter are also contemplated.

While the art was proceeding along the lines indicated above, namely, the development of different coating compositions, the utilization of intermediate anchoring coats and the employment

of expensive cellulose derivatives less sensitive to water than regenerated cellulose, the surprising and apparently irrational discovery was made that a slight etherification of the cellulose caused wax coating compositions to adhere to the extent necessary to produce a desirable water-proof wrapping tissue. This discovery was all the more incredible because it was known at the time that partially etherified cellulose was more water-sensitive than regenerated cellulose itself.

Described in more specific terms, the present invention, which accomplishes the aforementioned objects and according to which a transparent moisture-proof and water-proof wrapping tissue having the aforementioned desirable properties is produced, has resulted from the discovery that wax coating compositions adhere to lowly etherified cellulose films in the presence of water much more tenaciously than they do to ordinary transparent films having a base of regenerated cellulose.

The aforementioned objects and related ends are accomplished in the manner set out in the following description, in which are disclosed details of what is believed to be the best mode for carrying out the invention. Quantities are given in parts by weight throughout the application unless otherwise indicated.

Example I

One part of sulfite wood pulp was steeped in 18% caustic (sodium hydroxide) for one hour at 25° C., pressed to a ratio of 2.5, shredded for two hours at 25°–30° C. and set aside to age for 48 hours at 25° C. The resulting aged alkali cellulose was then placed in a baratte (a conventional tumbling device equipped for the introduction of reagents) and ethylene oxide allowed to vaporize into the baratte in the proportion of 3 parts for each 100 parts of alkali cellulose. After a two hour reaction period at 20° C., the glycol cellulose was removed from the reaction container, placed in a mixer of the type well known in the viscose art, and mixed with such a quantity of water and caustic soda that a 7% solution of glycol cellulose in 6% sodium hydroxide resulted. The mixer was cooled to —7° C. with the result that a viscous fiber-free solution was obtained. After warming to room temperature, the solution was filtered, evacuated free of bubbles and cast on a machine of the type commonly used for casting cellulose sheeting by the wet process from viscose. Glycerin was used as a softener.

The resulting transparent, lustrous film was moisture-proofed by coating it with the lacquer coating composition obtained by dissolving

	Per cent
Nitrocellulose	56.7
Dewaxed damar	14.0
Dibutyl phthalate	23.5
Paraffin wax	4.1
Zinc stearate	1.3

in a solvent consisting of ethyl acetate 55.1%, denatured ethyl alcohol (23–A formula) 3.5%, and toluene 41.4%.

When the lacquered film was immersed in water the base held to the moisture-proofing layer quite tenaciously, a period of eight days elapsing before the lacquer could be detached from the sheet by rubbing between fingers.

Example II

One part of sulfite wood pulp was steeped in 18% caustic (sodium hydroxide) for one hour at 25° C., pressed to a ratio of 2.5, shredded for two hours at 25°–30° C. and set aside to age for 48 hours at 25° C. The resulting aged alkali cellulose was then placed in a baratte and ethylene oxide allowed to vaporize into the baratte in the proportion of 6 parts for each 100 parts of alkali cellulose (0.56 mol. per glucose unit of cellulose). After a two hour reaction period at 20° C., the glycol cellulose was removed from the reaction container, placed in a mixer of the well-known type, and mixed with such a quantity of water and caustic soda that a 7% solution of glycol cellulose in 6% sodium hydroxide resulted. The mixer was cooled to —7° C. with the result that a viscose fiber-free solution was obtained. After warming to room temperature, the solution was filtered, evacuated free of bubbles and cast on a machine of the type commonly used for casting cellulose sheeting. The film was softened with glycerin in the well known manner.

The resulting transparent, lustrous film was moisture-proofed by coating it with the lacquer coating composition of Example I.

Although the base film is more water sensitive than the product of Example I, the coated film showed an even greater resistance to the loosening of the moisture-proofing layer by water.

Example III

One part of sulfite wood pulp was steeped in 18% caustic (sodium hydroxide) for one hour at 25° C., pressed to a ratio of 2.5, shredded for two hours at 25°–30° C. and set aside to age for 48 hours at 25° C. The resulting aged alkali cellulose was then placed in a baratte and propylene oxide allowed to vaporize into the baratte in the proportion of 8 parts for each 100 parts of alkali cellulose. After a two hour reaction period at 20° C., the cellulose ether was removed from the reaction container, placed in a mixer of the well known type, and mixed with such a quantity of water and caustic soda that a 7% solution of propylene glycol cellulose in 6% sodium hydroxide resulted. The mixer was cooled to —7° C. with the result that a viscous fiber-free solution was obtained. After warming to room temperature, the solution was filtered, evacuated free of bubbles and cast on a machine of the type commonly used for casting cellulose sheeting. Glycerin was used as a softener.

The resulting transparent, lustrous film was moisture-proofed by coating it with the lacquer coating composition of Example I.

The resulting films (base film and wax composition layer) remained unseparated in the presence of water for an even longer time than the product of Example II.

Example IV

In an excess of 20% sodium hydroxide solution, one molar weight (162 parts) of oven dried cellulose (spruce sulfite pulp) in the form of sheets is steeped for 2 hours at 28° C. This is pressed out until its weight is three times that of the starting cellulose. The sheets are shredded or torn to crumbs in a shredder of suitable type at a temperature not exceeding 25° C. for 2 hours. The alkali cellulose so prepared is allowed to age or ripen in a covered can for 24 hours at 28° C. before reacting upon it with a solution of 0.6 mol. (70 parts) of sodium chloroacetate in a little water. Such a solution is conveniently prepared by dissolving 56.5 parts of chloroacetic acid in 61 parts of water and neutralizing this with 50 parts of sodium bicarbonate. The reaction can

best be carried out in an apparatus of the mixer or shredder type, equipped with a means for circulating warm and cold water through the jacket of the mixer. The sodium chloroacetate solution is kneaded in, and then the shredder is sealed air tight and the contents are warmed to 40°–42° C., at which temperature reaction is maintained for 20 hours.

The product, which resembles the original alkali cellulose in appearance and contains approximately 0.1 to 0.2 glycolic acid residues per glucose unit, is dispersed in 1836 parts of 6% sodium hydroxide, in which at room temperature it makes only an imperfect (fibrous) dispersion but which dispersion, after being cooled to −6° to −10° C. and being again warmed to room temperature, is a clear and transparent, colorless or pale straw colored solution of moderate viscosity similar to that of spinning viscose. It is fiber-free but should be filtered to remove any extraneous matter if its application is to be in preparation of threads or films. This solution, after freezing, is stable at 30°–35° C. for 3 weeks or more without jelling or undergoing any appreciable change in clarity or in viscosity.

For films the solution is evenly spread upon glass plates to a depth of about 0.1 inch. These are immersed in a coagulating bath (7% $(NH_4)_2SO_4$+5% H_2SO_4 is very suitable) for a period sufficient to ensure thorough coagulation. This is very rapid and 5 minutes is adequate, while much shorter times can safely be used in most cases. The film is removed from its supporting plate and washed acid free. In this stage it may be quite weak and must be handled carefully. It may be softened, using a softener bath, such as glycerin or glycol in aqueous solution. Since the derivative is more readily softened by a small amount of glycerin than is a regenerated cellulose film, a softener bath of not more than 2% glycerin is adequate. The film may then be spread out upon a glass plate and dried at 65° C. for about 20 minutes, and then stripped from the plate.

The finished film is strong, flexible, and soft. The elasticity is surprising. The clarity and luster are unexcelled by that of any regenerated cellulose film. When first cast the film is weak and tender, on wetting out after drying it has very good wet strength.

If the film, made as above, is washed free of glycerin and analyzed, it will be found to contain 6.7% OCH_2COOH on the dry basis. This corresponds to one $—O.CH_2COOH$ group per 6.7 $C_6H_{10}O_5$ groups.

The films thus prepared are coated with a composition comprising a synthetic resin and a wax, preferably with the addition of a plasticizer. This can be accomplished according to the teachings of French Patent No. 718,440, by using for example:

	Parts by weight
Polymerization products resulting from 60% vinyl chloride and 40% vinyl acetate	15
Tricresyl phosphate	7
Refined paraffin	3

These components are dissolved in 100 to 200 parts of toluene, and the film is coated in any suitable manner such as by immersion. After the excess coating has been removed the solvents are evaporated at an elevated temperature, whereupon a film is produced having at least the same transparency and flexibility of the original base sheet but having in addition the ability to resist penetration of moisture or water vapors.

Example V

Sulfite cellulose (160 parts) was steeped in 2000 parts of 18% sodium hydroxide at 25° C. for one hour. The resulting alkali cellulose was pressed to 400 parts, placed in a shredder, shredded for ½ hour at 25° C. and 30 parts of dry solid sodium chloroacetate added. The shredding was then continued for two more hours, when the reaction mixture was removed from the shredder and allowed to age for 48 hours at 25° C. The aged product was dissolved in 7% caustic soda to a 7% solution by cooling to −7° C. Films were cast from the solution by the method commonly used in the casting of viscose.

(*a*) Some of the resulting film was lacquered in the manner described in Example IV. After three days soaking in water at room temperature, the lacquer coating had not become loosened. This product is especially suitable for milk bottle hoods (stock).

(*b*) Another portion of this film was also moisture-proofed by coating it with the lacquer coating composition of Example I. Excellent adherence on immersion in water was also obtained in this instance.

Example VI

Sulfite cellulose (160 parts) was steeped in 2000 parts of 18% sodium hydroxide for one hour at 30° C. The resulting alkali cellulose was then pressed to a weight of 400 parts and shredded for one-half hour at 25° C. Thereafter, 63 parts of dimethyl sulfate (0.5 mol. per glucose unit of cellulose) were sprayed into the shredder. After shredding for two more hours the reaction mixture was removed and aged for 48 hours at 25° C. Washing to produce a caustic-free product was then accomplished by drowning in a large excess of warm water, followed by rinsing until only a faint color was given by phenolphthalein. A 6% solution of the resulting ether was made in 7% caustic soda by cooling to −7° C. with good stirring. The solution was then filtered and cast into films. Films of the product were then coated with the lacquer coating composition of Example I.

The lacquered films could be immersed in water at room temperature for several days without the lacquer separating from the base.

Example VII

Sulfite cellulose (160 parts) was steeped in 2000 parts of 18% sodium hydroxide for one hour at 30° C. The resulting alkali cellulose was then pressed to a weight of 400 parts and shredded for one-half hour at 25° C. Thereafter, 30 parts of dimethyl sulfate were added to the shredder. After shredding for two more hours the reaction mixture was removed and aged for 48 hours at 25° C. Washing to produce a caustic-free product was then accomplished by drowning in a large excess of warm water, followed by rinsing until only a faint color was given by phenolphthalein. A 6% solution of the resulting ether was made in 7% caustic soda by cooling to −7° C. with good stirring. The solution was then filtered and cast into films. Films of the product were then coated with the lacquer coating composition of Example I.

When the lacquered film thus obtained was steeped in water at room temperature, it was found to exhibit a slightly lower tendency to hold the lacquered coating than was the case with the material prepared in Example VI.

Example VIII

Sulfite celluose (160 parts) was steeped in 2000 parts of 18% sodium hydroxide for one hour at 30° C. The resulting alkali cellulose was then pressed to a weight of 400 parts and shredded for one-half hour at 25° C., whereupon 77 parts of diethyl sulfate were sprayed into the shredder. After shredding for two more hours the reaction mixture was removed and aged for 48 hours at 25° C. Washing to produce a caustic-free product was then accomplished by drowning in a large excess of warm water, followed by rinsing until only a faint color was given by phenolphthalein. A 6% solution of the resulting ether (which was substituted to the extent of 0.35 ethyl groups per glucose unit of the cellulose) was made in 7% caustic soda by cooling to —7° C. with good stirring. The solution was then filtered and cast into films. Films of the product were then coated with the moisture-proofing composition disclosed in Example XI.

These moisture-proofed films exhibited a pronounced resistance to loosening of the moisture-proofing layer by water. Almost a month's immersion at room temperature was required to effect the aforesaid loosening.

Example IX

One hundred and sixty (160) parts of wood cellulose were steeped in 2000 parts of 18% caustic for one hour at 250° C. The alkali cellulose obtained was pressed to 400 parts, shredded for two hours at 35° C., aged for 30 hours at 25° C., placed in a baratte, and treated with 11 parts of ethylene oxide over a two hour period. Fifty (50) parts of carbon disulfide were then added, and after a xanthation period of four hours at 25° C., the resulting xanthate was dissolved to give a solution containing 7% of the cellulosic body in 6% caustic soda. The solution was cast to transparent sheeting in the manner usually used for casting ordinary viscose, and the resulting film coated with the lacquer of Example I.

After steeping the lacquer film in water at room temperature for one week, the coating could not be removed by rubbing briskly between the fingers.

Example X

One hundred and sixty (160) parts of wood cellulose were steeped in 2000 parts of 18% caustic for one hour at 25° C. The alkali cellulose obtained was pressed to 400 parts, shredded for two hours at 35° C., aged for 30 hours at 25° C., placed in a baratte, and treated with 6 parts of ethylene oxide over a two hour period. Fifty (50) parts of carbon disulfide were then added, and after a xanthation period of four hours at 25° C., the xanthate obtained was dissolved to give a solution containing 7% of the cellulosic body in 6% caustic soda. The solution was cast to transparent sheeting in the manner usually used for casting ordinary viscose, and the resulting film coated with a lacquer.

The lacquer utilized was that disclosed in Example XI.

The resulting products had a lacquer anchorage in the presence of water only slightly lower than the product of Example IX.

Example XI

One hundred and sixty (160) parts of wood cellulose were steeped in 2000 parts of 18% caustic for one hour at 25° C. The alkali cellulose obtained was pressed to 400 parts, shredded for two hours at 35° C., aged for 30 hours at 25° C., placed in a baratte, and treated with 3 parts of ethylene oxide (0.07 mol. per glucose unit of cellulose) over a two hour period. Fifty (50) parts of carbon disulfide were then added, and after a xanthation period of four hours at 25° C., the cellulose xanthate ether was dissolved to give a solution containing 7% of the cellulosic body in 6% caustic soda. The solution was cast to transparent sheeting in the manner usually used for casting ordinary viscose, and the resulting film coated with a lacquer.

The lacquer utilized was obtained by dissolving the following materials in the proportions indicated:

	Per cent
Nitrocellulose	54.8
Dewaxed damar	18.7
Dibutyl phthalate	20.5
Paraffin wax	4.5
Zinc stearate	1.5

in a solvent consisting of ethyl acetate 63.8%, toluene 32.2%, and denatured alcohol (formula 23–A) 4%.

Although the cellulose ether film of this example contains only about half as many glycol groups as the film obtained in Example X, the moisture-proofing lacquer coated film had to be soaked in water for considerably longer than half the period (required to loosen the lacquer from the film) of Example X, in order to detach the moisture-proofing coating.

Example XII

One hundred and sixty (160) parts by weight of cotton linter pulp was steeped in 2000 parts of 18% caustic (sodium hydroxide) at 25° C. for one hour and the resulting cellulose pressed to 400 parts. The pressed product was placed in a shredder and 30 parts of sodium chloroacetate in solid form added to the mass while shredding. The shredding was continued for two hours at 25°–35° C., after which the reaction mixture was removed, placed in aging cans, and allowed to age for 48 hours at 25° C. The cellulosic body reaction mixture was then put into a baratte and treated with 50 parts of carbon disulfide. The xanthation was conducted at 25° C. over a four hour period, the xanthate product dissolved to give a 7% solution in 6% caustic soda, and after filtration and ripening, the solution cast into transparent film in the usual way. The film was coated in the customary manner with the coating composition utilized in Example I. A product was obtained which would seperate into the base layer and the moisture-proofing layer only after soaking in water for more than three days at 20° C.

Example XIII

One hundred and sixty (160) parts by weight of cotton linter pulp was steeped in 2000 parts of 18% caustic (sodium hydroxide) at 25° C. for one hour and the resulting cellulose pressed to 400 parts. The pressed product was placed in a shredder and 15 parts of sodium chloroacetate (0.12 mol. per glucose unit of cellulose) in solid form added to the mass while shredding. The shredding was continued for two hours at 25°–35° C., after which the reaction mixture was removed, placed in ageing cans, and allowed to age for 48 hours at 25° C. The cellulosic body reaction mixture was then put into a baratte and treated with 50 parts of carbon disulfide. The

xanthation was conducted at 25° C. over a four hour period, the xanthate dissolved to give a 7% solution in 6% caustic soda, and after filtration and ripening, the solution cast into transparent film in the usual way. The film was coated with the coating composition described in Example I. The resultant moisture-proof film was only slightly inferior to the product of Example XII in its resistance to separation of the moisture-proofing layer when in contact with water.

Example XIV

One hundred and sixty (160) parts by weight of cotton linter pulp was steeped in 2000 parts of 18% caustic (sodium hydroxide) at 25° C. for one hour and the resulting cellulose pressed to 400 parts. The pressed product was placed in a shredder and 63 parts of dimethyl sulfate sprayed into the mass while shredding. The shredding was continued for two hours at 25°–35° C., after which the reaction mixture was removed, placed in ageing cans, and allowed to age for 48 hours at 25° C. The cellulosic body reaction mixture was then put into a baratte and treated with 50 parts of carbon disulfide. The xanthation was conducted at 25° C. over a four hour period, the xanthate dissolved to give a 7% solution in 6% caustic soda, and after filtration and ripening, the solution cast into transparent film in the usual way. The film was coated with the coating composition utilized in Example I. When coated as described, the product had to be soaked in water for more than a week at room temperature before the moisture-proofing layer could be easily detached, although the uncoated methyl cellulose base film was quite water sensitive.

Example XV

One hundred and sixty (160) parts by weight of cotton linter pulp was steeped in 2000 parts of 18% caustic (sodium hydroxide) at 25° C. for one hour and the resulting cellulose pressed to 400 parts. The pressed product was placed in a shredder and 30 parts dimethyl sulfate sprayed into the mass while shredding. The shredding was continued for two hours at 25°–35° C., after which the reaction mixture was removed, placed in ageing cans, and allowed to age for 48 hours at 25° C. The cellulosic body reaction mixture was then put into a baratte and treated with 50 parts of carbon disulfide. The xanthation was conducted at 25° C. over a four hour period, the xanthate dissolved to give a 7% solution in 6% caustic soda, and after filtration and ripening, the solution cast into transparent film in the usual way. The film was coated with the coating solution of Example XI.

After removal of the solvent, the moisture-proofed film was soaked in water at room temperature, and appeared to be unchanged after 5 days.

Example XVI

One hundred and sixty (160) parts by weight of cotton linter pulp was steeped in 2000 parts of 18% caustic (sodium hydroxide) at 25° C. for one hour and the resulting cellulose pressed to 400 parts. The pressed product was placed in a shredder and 15 parts dimethyl sulfate (0.12 mol. per glucose unit of cellulose) sprayed into the mass while shredding. The shredding was continued for two hours at 25°–35° C., after which the reaction mixture was removed, placed in ageing cans, and allowed to age for 48 hours at 25° C. The cellulosic body reaction mixture was then put into a baratte and treated with 50 parts of carbon disulfide. The xanthation was conducted at 25° C. over a four hour period, the xanthate dissolved to give a 7% solution in 6% caustic soda, and after filtration and ripening, the solution cast into transparent film in the usual way. The film was coated with the moisture-proofing lacquer described in Example I. The resultant moisture-proof film was only slightly less stable to water than the product of Example XV.

Example XVII

One hundred and sixty (160) parts by weight of cotton linter pulp was steeped in 2000 parts of 18% caustic (sodium hydroxide) at 25° C. for one hour and the resulting cellulose pressed to 400 parts. The pressed product was placed in a shredder and 38 parts of diethyl sulfate sprayed into the mass while shredding. The shredding was continued for two hours at 25°–35° C., after which the reaction mixture was removed, placed in ageing cans, and allowed to age for 48 hours at 25° C. The cellulosic body reaction mixture was then put into a baratte and treated with 50 parts of carbon disulfide. The xanthation was conducted at 25° C. over a four hour period, the xanthate dissolved to give a 7% solution in 6% caustic soda, and after filtration and ripening, the solution cast into transparent film in the usual way. The film was coated with a moisture-proofing lacquer.

The lacquer utilized was that of Example XI.

The resulting film was soaked in water for more than two weeks without the coating becoming sufficiently loosened from the base to be detached by rubbing between the fingers.

Example XVIII

The sodium salt of a cellulose glycolic acid containing 0.8 glycolic acid ether groups per glucose unit was dissolved in water to give a 7% solution.

Ten (10) parts of the resultant solution were mixed with 90 parts of a viscose solution containing 7% cellulose and 6% sodium hydroxide. The solution obtained was cast into films in the usual way and coated with a moisture-proof lacquer of the following composition:

	Parts
51½ second pyroxylin dissolved in 836.4 parts of ethyl acetate	796.5
Damar solution composed of 44% dewaxed damar, 22.4% toluene, and 33.6% ethyl alcohol	1111.5
Denatured alcohol (formula 23–A)	190.5
Acetone	33.0
Dibutyl phthalate	349.5
Paraffin wax dissolved in 4045 parts toluene	97.5

The resulting film had to be soaked in water for at least three days before the lacquer coating could be detached by rubbing gently with the fingers.

Example XIX

Twenty-five (25) parts of the sodium cellulose glycolate solution prepared in the manner described in Example XVIII, were mixed with 75 parts of a viscose containing 7% cellulose and 6% sodium hydroxide. The combined solution was ripened and cast into films. After moisture-proofing in the same way as described in Example XVIII, a product was obtained which had to be kept covered with water at room

temperature for almost a week before the moisture-proofing layer could be easily separated from the base.

Example XX

One hundred sixty (160) parts of sulfite cellulose were steeped in 2000 parts of 18% caustic at 25° C. After one hour the alkali cellulose was pressed to 400 parts and shredded for two hours at 35° C. It was then treated with 22 parts of ethylene oxide at 25° C. over a period of two hours. The reaction mixture was allowed to age for three days at 25° C., after which it was dissolved at 10° C. in 7% sodium hydroxide to give a 7% solution of glycol cellulose. The resultant solution was mixed with three times its weight of viscose containing 7% cellulose and 6% sodium hydroxide, and the combined solution ripened and cast into films.

The resulting film was moisture-proofed by coating it with the lacquer coating composition of Example I.

The resulting product exhibited a marked resistance to separation into the base layer and lacquer coating layer when immersed in water.

Example XXI

One hundred sixty (160) parts of sulfite wood pulp were steeped in 1600 parts of 18% caustic for one hour at 25° C. After pressing the resulting alkali cellulose to 400 parts, and shredding it for two hours at 30° C., it was treated with 11 parts of ethylene oxide at 25° C. for two hours. The reaction mixture was aged for 20 hours at 30° C. and then dissolved to form a 7% solution in 7% sodium hydroxide by cooling to —6° C. The solution was then filtered.

Fifty (50) parts of the filtered glycol cellulose solution were mixed with 50 parts of a 7% solution of viscose (in 6% sodium hydroxide). The mixture was filtered and cast into films. The wet film was almost as strong as cellulose film regenerated from viscose. It was coated with the coating composition utilized in Example XX. The resulting film, after being soaked in water at room temperature for 5 days, still retained the lacquer coating.

Example XXII

Twenty-five (25) parts of glycol cellulose solution prepared as described in Example XXI were mixed with 75 parts of a viscose solution containing 7% cellulose and 6% sodium hydroxide. This mixture was cast into films in the usual way and coated with a lacquer in the manner described in Example XXI. There was obtained a coated film which could be immersed in water for several days without the lacquer layer becoming sufficiently loosened to be easily detached by rubbing gently between the fingers.

Example XXIII

One hundred sixty (160) parts of oven-dry sulfite pulp were steeped in 1600 parts of 20% caustic for 2 hours at 25° C. The alkali cellulose obtained was pressed to 400 parts, placed in a shredder with 60 parts of sodium chloroacetate and shredded for three hours. The reaction mixture was then removed from the shredder and aged for 40 hours at 25° C. The cellulose glycolic acid obtained in this manner was made into a 7% solution in 7% caustic by cooling to —8° C.

Fifty (50) parts of the aforementioned solution were mixed with 50 parts of viscose containing 7% cellulose and 6% sodium hydroxide. The mixture was filtered, ripened and cast into films. After coating with the moisture-proofing lacquer composition of Example XX, a product was obtained which showed great resistance to loosening of the moisture-proofing layer by water. Five days at 25° C. were required before the coating could be easily removed by rubbing between the fingers.

Example XXIV

Twenty-five (25) parts of the cellulose glycolic acid solution prepared as described in the first paragraph of Example XXIII were mixed with 75 parts of the viscose solution described in Example XXIII. The resultant was filtered, ripened, cast into films and coated with the moisture-proofing lacquer described in Example XXIII. There was obtained a coated film which was somewhat less resistant to breakdown by water than the product of Example XXIII.

Example XXV

The films prepared according to the procedure set out in Example IV were coated by immersing in the composition given below, which is disclosed in Canadian Patent No. 359,728:

	Parts
Candelilla wax	33
Paraffin (melting point 62° C.)	16
Zinc resinate	5
Toluene	500 to 1000

The excess of the coating compostion was removed and the solvent evaporated at an elevated temperature. The resulting coated film was glass clear in transparency, was flexible, and was distinctly moisture-proof.

Example XXVI

Eighty (80) parts of oven dried wood pulp were steeped for one hour at 25° in 20% sodium hydroxide solution. The sheets were then pressed to 243 parts, after which they were shredded for two hours and aged at room temperature for 23 hours. The alkali cellulose was then put into a shredder and 16 parts of dimethyl sulfate dissolved in 200 parts diethyl ether were allowed to drop slowly into the shredder, which was maintained at 27° C. As soon as all of the dimethyl sulfate was added the shredder was sealed tightly and the mixture allowed to react with shredding for 18 hours. The product (which was substituted to the extent of 0.23 methyl groups per glucose unit of the cellulose) was removed and dispersed in 1316 parts of 6% sodium hydroxide to make a solution containing 5% cellulose based on the weight of the starting cellulose. The mixture formed a smooth dispersion at room temperature, but after freezing was perfectly soluble, filtering through cotton batting without difficulty.

Films were cast by spreading the solution on a glass plate and dipping into a bath composed of 10% sulfuric acid and 15% sodium sulfate. The films were clear and of excellent transparency. They were washed with water until acid free, dipped in a 2% glycerin bath and dried under tension.

The films were moisture-proofed with a composition prepared by dissolving 796.5 parts of 51.5 second pyroxylin in 8364 parts of ethyl acetate and mixing the same with 1111.5 parts of damar solution composed of 44% dewaxed damar, 22.4% toluene and 33.6% ethyl alcohol, 190.5 parts of denatured alcohol (formula 23—A), 33.0 parts of acetone, 349.5 parts of di-

butyl phthalate and 97.5 parts of wax (paraffin) dissolved in 4045 parts of toluene. This lacquer composition was applied to the sheets at a temperature of 45°–40°, the excess being scraped off by means of a steel doctor rod and the coated sheets dried at a temperature above the melting point of the wax (90°–100° C.). The coated sheet was tested by immersion in water at room temperature and examined periodically for adherence of the moisture-proofing coating by rubbing between thumb and forefinger to determine when the coating on the sheet had become loosened therefrom. The coating could not be detached from the sheet until one day had elapsed whereas the same moisture-proofing coating when applied to regenerated cellulose remained anchored to the cellulose under the same conditions for less than one hour.

Example XXVII

Forty-one (41) parts of oven dried wood pulp were steeped for one hour at room temperature in 20% sodium hydroxide, after which the sheets were pressed to 245 parts and shredded for 2 hours at 28° C. The alkali cellulose was then aged for 16 hours, placed in a shredder and 28.2 parts of chloracetic acid (1.2 mols per glucose unit of cellulose) neutralized with 25.2 parts of sodium bicarbonate in 30.6 parts of water were added and shredding continued for 20 hours at 35°–40° C. The reaction mixture was removed and dispersed with the aid of freezing in 1918 parts of 6% sodium hydroxide. This made an excellent solution which filtered quickly through cotton batting leaving very little undissolved material. The solution was quite clear. Films were coagulated from the solution by casting on a glass plate with a steel rod and immersing the resultant in a bath containing 7% ammonium sulfate plus 5% sulfuric acid. The sheets were then washed acid free and steeped in a bath containing 1% glycerin after which they were dried under tension. The sheets were moisture-proofed in the same manner as those described in Example XXVI. The moisture-proofing coating remained anchored to the sheet when immersed in water for one day.

Example XXVIII

One hundred sixty-two (162) parts of oven dried cotton linter pulp were steeped for one hour in 19% sodium hydroxide solution at room temperature after which the sheets were pressed to 486 parts. The pressed material was shredded in a Werner-Pfleiderer shredder for an hour and a half at 28° C. after which it was allowed to age for 21.5 hours at 28° C. The alkali cellulose was then placed in a small baratte and 11 parts of ethylene oxide were allowed to vaporize slowly into the mixture. The baratte was tumbled for a total of 20 hours at 28° C. The reaction product was dispersed in 1828 parts of 7% sodium hydroxide to make a 7% dispersion. The mixture was dissolved by cooling to −6° C. and filtered. The filtered solution was allowed to stand until all bubbles had broken after which it was cast into films by spreading on glass plates with a steel rod and coagulated by dipping in 15% sodium sulfate followed by washing with water and steeping in a 4% glycerin bath. By following this procedure films were produced which adhered to a moisture-proofing composition of the same composition as that in Example XXVI for 2–3 days compared to an anchorage time of less than one hour for regenerated cellulose when treated in the same manner.

Example XXIX

One hundred and sixty-two (162) parts of oven dried cotton linter pulp were steeped for one hour in 19% sodium hydroxide solution at room temperature, after which the sheets were pressed to 486 parts. The pressed material was shredded in a Werner-Pfleiderer shredder for an hour and a half at 28° C., after which it was allowed to age for 21.5 hours at 28° C. The alkali cellulose was then placed in a small baratte and 11 parts of ethylene oxide were allowed to vaporize slowly into the mixture. The baratte was tumbled for a total of 20 hours at 28° C. The reaction product was dispersed in 1828 parts of 7% sodium hydroxide to make a 7% dispersion. The mixture was dissolved by cooling to −6° C. and filtered. The filtered solution was allowed to stand until all bubbles had broken after which it was cast into films by spreading on glass plates with a steel rod and coagulated by treatment with 15% sodium sulfate followed by treatment with 10% sulfuric acid. After washing, steeping in 4% glycerin bath and drying films were obtained which possessed essentially the same anchorage characteristics as those of the product described in Example XXVIII.

Example XXX

One hundred sixty-two (162) parts of oven dried cotton linter pulp were steeped for one hour in 19% sodium hydroxide solution at room temperature after which the sheets were pressed to 486 parts. The pressed material was shredded in a Werner-Pfleiderer shredder for an hour and a half at 28° C., after which it was allowed to age for 21.5 hours at 28° C. The alkali cellulose was then placed in a small baratte and 11 parts of ethylene oxide were allowed to vaporize slowly into the mixture. The baratte was tumbled for a total of 20 hours at 28° C. The reaction product was dispersed in 1828 parts of 7% sodium hydroxide to make a 7% dispersion. The mixture was dissolved by cooling to −6° C. and filtered. The filtered solution was allowed to stand until all bubbles had broken after which it was cast into films by spreading on glass plates with a steel rod and coagulated by immersion in 10% sulfuric acid. After washing, steeping in a 4% glycerin bath and drying on a drying frame, films were obtained which had the same anchorage characteristics for the moisture-proofing layer as those of the product described in Example XXVIII.

Example XXXI

One hundred sixty (160) parts of oven dry wood pulp were steeped for 2 hours in 19% sodium hydroxide at room temperature. The sheets were pressed and then shredded for 2 hours, after which the product was aged for 24 hours at about 30° C. The alkali cellulose was then transferred to a baratte and treated with 11 parts of ethylene oxide in vapor form. The reaction was allowed to proceed at 28° C. for 20 hours. The product was dispersed in 1828 parts of 6% sodium hydroxide to make a solution containing about 8% sodium hydroxide and 7% cellulose. It was frozen to complete solution. It filtered very well.

Films were cast by coagulating in 15% sodium sulfate sulfate and softening with 4% glycerin; by coagulating in 15% sodium sulfate and softening in 2.67% glycerin; and by coagulating in a mixture of 7% sodium sulfate and 5% sulfuric acid followed by treatment with 3.5% glycerin. After drying under tension all of the films when

coated with a moisture-proofing lacquer of the same composition as that used in Example XXVI were found to anchor the moisture-proofing layer for a period of 2–3 days, whereas ordinary regenerated cellulose when moisture-proofed in the same manner anchored the moisture-proofing layer for less than one hour.

Example XXXII

Eighty-one (81) parts of oven dry wood pulp were steeped for one hour at room temperature (28° C. in this case) in 20% sodium hydroxide solution. The steeped sheets were pressed to 243 parts, shredded 2 hours at 28° C. and then aged for 24 hours at 28° C. The aged alkali cellulose was transferred to a baratte and treated with 3 parts of ethylene oxide in vapor form, the reaction being allowed to proceed for 20 hours. The product was removed and dispersed in 918 parts of 6% sodium hydroxide. After freezing of this dispersion a fairly viscous solution which filtered very well was obtained. Films were cast by spreading the solution on a glass plate by means of a glass rod followed by dipping in an acidified solution of sodium sulfate. The coagulated films were washed with water and softened by steeping in 3% glycerin. The films after drying were moisture-proofed with a lacquer of the same composition as that used in Example XXVI. Upon soaking the crude films in water and testing occasionally by rubbing the films between the thumb and first finger to determine if the wax film had become loosened it was found that a period of two to three days was required before the moisture-proofing layer could be detached.

Example XXXIII

Eighty (80) parts of oven dried wood pulp were steeped for one hour at 25° C. in 20% sodium hydroxide solution. The sheets were then pressed to 243 parts, after which they were shredded for two hours and aged at room temperature for 23 hours. The alkali cellulose was then put into a shredder and 16 parts of dimethyl sulfate dissolved in 200 parts diethyl ether were allowed to drop slowly into the shredder which was maintained at 27° C. As soon as all the dimethyl sulfate was added the shredder was sealed tightly and the mixture allowed to react with shredding for 18 hours. The product (which had 0.23 alkyl residues per C_6 unit of the cellulose) was removed and dispersed in 1316 parts of 6% sodium hydroxide to make a solution containing 5% cellulosic body based on the weight of the starting cellulose. The mixture formed a smooth dispersion at room temperature but after freezing was perfectly soluble, filtering through cotton batting without difficulty.

Films were cast by spreading the solution on a glass plate and dipping into a bath composed of 10% sulfuric acid and 15% sodium sulfate. The films were clear and of excellent transparency. They were washed with water until acid free, dipped in a 2% glycerin bath and dried under tension.

The resulting films were moisture-proofed by coating with a lacquer having the following composition:

	Percent
Nitrocellulose	54.8
Dewaxed damar	18.7
Dibutyl phthalate	20.5
Paraffin wax	4.5
Zinc stearate	1.5

which has been compounded by dissolving the tabulated ingredients in a solvent consisting of ethyl acetate 63.8%, denatured ethyl alcohol (formula 23—A) 4.0%, and toluene 32.2%. These, when tested for anchorage by steeping in water at room temperature, were found to require a period of one day before the moisture-proofing layer became sufficiently loosened so it could be detached by rubbing between the thumb and first finger vigorously.

Example XXXIV

Forty-one (41) parts of oven dried wood pulp were steeped for one hour at room temperature in 20% sodium hydroxide, after which the sheets were pressed to 245 parts and shredded for 2 hours at 28° C. The alkali cellulose was then aged for 16 hours, placed in a shredder and 28.2 parts of chloroacetic acid neutralized with 25.2 parts of sodium bicarbonate in 30.6 parts of water were added and shredding continued for 20 hours at 35°–40° C. The reaction mixture was removed and dispersed with the aid of freezing in 1918 parts of 6% sodium hydroxide. This made an excellent solution which filtered quickly through cotton batting leaving very little undissolved material. The solution was quite clear. Films were coagulated from the solution by casting on a glass plate with a steel rod and immersing in a bath containing 7% ammonium sulfate plus 5% sulfuric acid. The sheets were then washed acid free and steeped in a bath containing 1% glycerin after which they were dried under tension.

The resulting films were moisture-proofed by coating with the lacquer composition of Example XV. These when tested for anchorage by steeping in water at room temperature were found to require a period of one day before the moisture-proofing layer became sufficiently loosened so it could be detached by rubbing between the thumb and first finger vigorously.

Example XXXV

One hundred sixty-two (162) parts of oven dried cotton linter pulp were steeped for one hour in 19% sodium hydroxide solution at room temperature after which the sheets were pressed to 486 parts. The pressed material was shredded in a Werner-Pfleiderer shredder for an hour and a half at 28° C. after which it was allowed to age for 21.5 hours at 28° C. The alkali cellulose was then placed in a small baratte and 11 parts of ethylene oxide were allowed to vaporize slowly into the mixture. The baratte was tumbled for a total of 20 hours at 28° C. The reaction product was dispersed in 1828 parts of 7% sodium hydroxide to make a 7% dispersion. The mixture was dissolved by cooling to −6° C. and filtered. The filtered solution was allowed to stand until all bubbles had broken after which it was cast into films by spreading on glass plates with a steel rod and coagulated by dipping in 15% sodium sulfate, followed by washing with water and steeping in a 4% glycerin bath. Similar results have been obtained by treating with 15% sodium sulfate followed by treating with 10% sulfuric acid, washing, and steeping in a 4% glycerin bath. The films were dried on a drying frame.

The resulting films were moisture-proofed by coating with the coating composition of Example XI. It was found necessary to soak these coated films in water for a period of two to three days before the moisture-proofing layer could

be loosened by rubbing vigorously between the thumb and first finger.

Example XXXVI

One hundred sixty (160) parts of oven dry wood pulp were steeped for 2 hours in 19% sodium hydroxide at room temperature. The sheets were shredded for 2 hours and then aged for 24 hours at about 30° C. The alkali cellulose was then transferred to a baratte and treated with 11 parts of ethylene oxide in vapor form. The reaction was allowed to proceed at 28° C. for 20 hours. The product was dispersed in 1828 parts of 6% sodium hydroxide to make a solution containing about 8% sodium hydroxide and 7% cellulose derivative. It was frozen to complete solution. It filtered very well.

Films were cast by coagulating in 15% sodium sulfate and softening with 4% glycerin, by coagulating in 15% sodium sulfate and softening in 2.67% glycerin, and by coagulating in a mixture of 7% sodium sulfate and 5% sulfuric acid followed by treatment with 3.5% glycerin. All films were dried under tension.

The resulting films were moisture-proofed by coating with the wax-nitrocellulose composition of Example XV. It was found necessary to soak these coated films in water for a period of two to three days before the moisture-proofing layer could be loosened by rubbing vigorously between the thumb and first finger.

Example XXXVII

Eighty-one (81) parts of oven dry wood pulp were steeped for one hour at 28° C. in 20% sodium hydroxide solution. The steeped sheets were pressed to 243 parts, shredded 2 hours at 28° C. and then aged for 24 hours at 28° C. The aged alkali cellulose was transferred to a baratte and treated with 3 parts of ethylene oxide in vapor form, reaction being allowed to proceed for 20 hours. The product was removed and dispersed in 918 parts of 6% sodium hydroxide. After freezing of this dispersion a fairly viscous solution which filtered very well was obtained. Films were cast by spreading the solution on a glass plate by means of a glass rod followed by dipping in an acidified solution of sodium sulfate. The coagulated films were washed with water and softened by steeping in 3% glycerin. The films were then dried.

The resulting films were moisture-proofed by coating with the damar-nitrocellulose composition of Example XV.

After drying of the lacquer it was found necessary to soak these coated films in water for a period of two to three days before the moisture-proofing layer could be loosened by rubbing vigorously between the thumb and first finger.

Example XXXVIII

One hundred sixty (160) parts of sulfite cellulose were steeped in 2,000 parts of 18% caustic. After one hour at 25° C. the resulting alkali cellulose was pressed to 400 parts and shredded for 2 hours at 35° C. The shredded material was then placed in a tumbling device provided with a means for vaporizing ethylene oxide into the interior, and 88 parts of ethylene oxide vaporized thereinto at 20° C. over a period of 12 hours. The resulting water soluble glycol cellulose was aged for 24 hours at 25° C., after which it was made into a 6% solution in 7% caustic.

Twenty-five (25) parts of the resulting solution were mixed with 75 parts of a viscose containing 7% cellulose and 6% caustic. After a suitable ripening period, the mixture was cast into transparent films in the usual way, and was then coated with a moisture-proof lacquer coating composition such as was used in Example XX.

The moisture-proofed film had to be soaked in water at 25° C. for 6 days before the lacquer coating could be detached by rubbing between the thumb and fingers.

Example XXXIX

One hundred sixty (160) parts of sulfite cellulose were steeped in 2000 parts of 18% caustic. After one hour at 25° C. the resulting alkali cellulose was pressed to 400 parts and shredded for 2 hours at 35° C. The shredded material was then placed in a tumbling device provided with a means for vaporizing ethylene oxide into the interior, and 88 parts of ethylene oxide vaporized thereinto at 20° C. over a period of 12 hours. The resulting water soluble glycol cellulose was aged for 24 hours at 25° C., after which it was made into a 6% solution in 7% caustic.

Six (6) parts of the foregoing glycol cellulose solution were mixed with 94 parts of a viscose containing 7% cellulose and 6% caustic. After a suitable ripening interval, the mixture was cast into films in a sulfuric acid-sodium sulfate bath. The film was then coated with a moisture-proofed lacquer coating composition obtained by dissolving

	Per cent
Nitrocellulose	56.7
Dewaxed damar	14.0
Dibutyl phthalate	23.5
Paraffin wax	4.1
Zinc stearate	1.3

in a solvent consisting of ethyl acetate 55.1%, toluene 41.4% and denatured alcohol (formula 23—A) 3.5%. The Internal Revenue Bureau denatured alcohol formula 23—A covers the product obtained by adding 10 gallons of C. P. acetone to each 100 gallons of ethyl alcohol.

After soaking in water at 25° C. for 2 days, the moisture-proofing layer was still tightly bound to the base. This product is especially suitable for milk bottle hoods.

As indicated before in this specification, the coating compositions used in this invention are wax types. They include wax and cellulose derivative combinations, such as wax-cellulose nitrate, wax-cellulose acetate, wax-ethyl cellulose and the like, wax and rubber combinations and wax and synthetic resin combinations such as wax-alkyd resin and the like. In some of the wax and cellulose derivative combinations, a plasticizer (softener) may be regarded as an essential ingredient if certain degrees of flexibility are to be attained. In addition to the specific coating compositions described in the examples, the particular combinations listed in the patents mentioned in the first part of the specification are suitable for coating according to this invention.

All of the low substituted cellulose ether in the base film may be of the same composition, or it may be made up of a mixture of low substituted cellulose ethers varying in degree of substitution, in substituent radical or both. The base films whether produced from solutions of low substituted cellulose ethers, solutions of xanthated low substituted cellulose ethers or solutions of mixtures of these with each other or with viscose are characterized by being insoluble

in water and organic solvents. In addition the said ethers are dissolved by 7% aqueous sodium hydroxide at least after xanthation and freezing, and have no more than one mol. of ether residue per glucose unit of the cellulose. Preferably products having not more than one-half mol. of substitution are used.

As disclosed in the examples, the cellulose ethers suitable for use in the preparation of the base film include alkyl, hydroxy-alkyl, carboxy-alkyl, xanthated alkyl, xanthated hydroxy-alkyl and xanthated carboxy-alkyl types.

Ethylene glycol and propylene glycol ethers of cellulose are mentioned in the specific examples. It is not intended to limit the invention to these specific compounds. Such compounds as butylene glycol cellulose and isobutylene-glycol cellulose are contemplated in instances where details of the specific process are compatible with the physical and chemical properties of the particular ether. Similarly the invention is not limited to the other specific cellulose ethers of the examples.

The films coated in the specific examples were of three types, as indicated by the processes of production. Those derived from solutions of low-substituted cellulose ethers substantially undissolvable in dilute aqueous caustic soda at ordinary temperature but dissolvable therein after cooling to near the freezing point theroef, are especially interesting. Those derived from solutions of xanthated low substituted cellulose ethers show that the process of film production is not responsible for the improved results obtained according to this invention. The films obtainable from solutions of mixtures of viscose and low substituted cellulose ethers indicate that the superiority of the present products is not dependent on the absence of cellulose.

The moisture-proofing coatings may be applied to the base film material by various well known apparatuses, for example, those described in United States Patents 1,826,697, 2,051,944, 2,042,589 and the like. Manual procedures such as those adaptable to laboratory work as well as the processes similar to those described in the patents mentioned earlier in the specification, are suitable for applying the coatings.

The expression "low substituted cellulose ether" is used to denote a cellulose ether having less than one mol. of substitution per glucose unit and which is insoluble in water and in organic solvents.

The term "water-proof" is used to denote the property which a material has of not losing its effectiveness when subjected to conditions where a large percentage of moisture is present, or for example, where the sheet material is actually in contact with water.

The expression "moisture-proof sheet material" is used to denote the sheet material which, in the form of continuous unbroken sheets (or films), permits the passage of not more than 690 grams of water vapor per 100 square meters per hour over a period of 24 hours at a temperature of 39.5° C.±0.5° C. (preferably 39.5° C.±0.25° C.), with a water vapor pressure differential of 50–55 millimeters (preferably 53.4±0.7 millimeters) of mercury (i. e., the relative humidity of the atmosphere at one side of the sheet material being maintained at at least 98% and the relative humidity of the atmosphere at the other side being maintained at such a value as to give a humidity differential of at least 95%).

The expression "moisture-proofing coating composition" is used to denote a substance which, when laid down in the form of a thin, continuous, unbroken film applied uniformly as a coating to both sides of an approximately 0.0009 inch thick sheet of cellulose regenerated from viscose so that the total coating thickness does not exceed 0.0005 inch, will produce a coated sheet which is moisture-proof, as defined in the previous paragraph.

Cellulose ethers disclosed as base film-material in this application, for example, low substituted glycol cellulose, are quite water sensitive, being weakened and swollen by water considerably more than cellulose sheeting regenerated from viscose. The superiority of coated films of low substituted cellulose ethers for moisture-proofing wrappings was therefore unexpected and entirely unpredictable. A satisfactory theory of this phenomena has not yet been found, but it appears that the adhesion of the base film and the wax composition coating is in some way responsible. As is apparent from the specific examples, the efforts directed toward producing an improved moisture-proof wrapping tissue, by proceeding in a manner directly contrary to that adopted by the workers in the art, were signally successful. The ultimate success of the problem confronting the art seems to be in the development of a special type of film rather than a special type of film coating composition.

This specification contains subject matter taken from the earlier applications 681,760 filed July 22, 1933 and 682,119 filed July 25, 1933.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiment thereof except as defined in the appended claims.

What is claimed is:

1. As a new article of manufacture, a moisture-proof, water-insensitive wrapping tissue comprising a base film of low substituted cellulose ether having a coating thereon selected from the group consisting of wax-cellulose derivative coating composition, wax-rubber coating compositions and wax-synthetic resin coating compositions.

2. Low substituted cellulose ether film having a wax moisture-proofing coating composition thereon.

3. As a new product alkyl cellulose, containing from 0.23 to 0.35 lower alkyl residues per C_6 unit of cellulose, said alkyl residues containing one to two carbon atoms, said product being substantially insoluble in 6% aqueous caustic alkali at room temperature but soluble in said alkali solution near the freezing point thereof, in the form of a sheet and having thereon a wax containing film which is impervious to moisture.

4. A process which comprises treating a thin film comprising substantially cellulose glycolic acid containing from .1 to .35 glycolic acid residues per C_6 unit of cellulose, said cellulose derivative being substantially insoluble in 6% caustic soda solution at ordinary temperatures but soluble in said alkali solution near the freezing point thereof, with a moisture-proof composition.

5. A thin film comprising substantially the low substituted cellulose glycolic acid obtainable by treating alkali cellulose degraded but not beyond the stage obtained by ageing alkali cellulose for 48 hours at 25° C. with an alkali metal haloacetate under non-oxidizing conditions until from .1 to .35 glycolic residues per C_6 unit of cellulose have been introduced and stopping the

etherification, treated so as to be substantially impervious to moisture.

6. Low substituted glycol cellulose ether film having a wax moisture-proofing coating composition thereon.

7. Low substituted alkyl cellulose ether film having a wax moisture-proofing coating composition thereon.

8. Low substituted cellulose glycolic acid ether film having a wax moisture-proofing coating composition thereon.

9. As a new product alkyl cellulose, containing from 0.23 to 0.5 lower alkyl residues per C_6 unit of cellulose, said alkyl residues containing one to two carbon atoms, said product being substantially insoluble in 6% aqueous caustic alkali at room temperature but soluble in said alkali solution near the freezing point thereof, in the form of a sheet and having thereon a wax containing film which is impervious to moisture.

10. A low substituted water sensitive alkyl cellulose in the form of a sheet, having thereon a wax containing film coating which is impervious to moisture, the alkyl residue of the alkyl cellulose containing not more than two carbon atoms, the said alkyl cellulose not being dissolvable in 6% aqueous caustic soda at room temperature but dissolvable therein at near the freezing point thereof, and the said alkyl cellulose having the number of alkyl residues per C_6 unit of cellulose obtainable by etherifying alkali cellulose with an etherifying agent in the proportion of 0.12 to 0.5 mols per C_6 unit of cellulose.

11. A low substituted water sensitive glycol cellulose in the form of a sheet, having thereon a wax containing film coating which is impervious to moisture, the said glycol cellulose not being dissolvable in 6% aqueous caustic soda at room temperature but dissolvable therein near the freezing point thereof, and the said glycol cellulose having the number of glycol residues per C_6 unit of cellulose obtainable by etherifying alkali cellulose with an etherifying agent in the proportion of 0.07 to 0.56 mols per C_6 unit of cellulose.

12. A low substituted water sensitive glycol cellulose in the form of a sheet having thereon a wax containing film coating which is impervious to moisture, the said glycol cellulose containing up to 0.5 mols of substitution per glucose unit of cellulose and not being dissolvable in 6% aqueous caustic soda at room temperature but dissolvable therein near the freezing point thereof.

13. A low substituted water sensitive glycol cellulose in the form of a sheet, having thereon a wax containing film coating which is impervious to moisture, the said glycol cellulose being insoluble in water and organic solvents and dissolvable in 7% aqueous sodium hydroxide at least after xanthation and freezing, the amount of substitution not exceeding one-half mol. per glucose unit of the cellulose.

14. A low substituted cellulose ether film having a wax moistureproofing composition coating thereon, the said ethers being insoluble in water and organic solvents and dissolvable in 7% aqueous sodium hydroxide at least after xanthation and freezing, the degree of substitution of the said ethers being not more than one-half mol. per glucose unit of cellulose.

15. Low substituted cellulose ether film having a wax moisture-proofing coating composition comprising candelilla wax, paraffin and zinc resinate thereon.

16. A low substituted water sensitive lower alkyl cellulose in the form of a sheet, having thereon a wax containing film coating which is impervious to moisture, the said lower alkyl cellulose being insoluble in water and organic solvents and dissolvable in 7% aqueous sodium hydroxide, at least after xanthation and freezing, the amount of substitution not exceeding one-half mol. per glucose unit of the cellulose.

JOSEPH F. HASKINS,
Administrator of Deane C. Ellsworth, Deceased.

CERTIFICATE OF CORRECTION.

Patent No. 2,123,883. July 19, 1938.

JOSEPH F. HASKINS,
ADMINISTRATOR OF DEANE C. ELLSWORTH, DECEASED.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 39, for the patent number "2,737,187" read 1,737,187; page 4, first column, line 33, Example IX, for "250°C." read 25°C.; same page, second column, line 57, Example XII, for "seperate" read separate; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 27th day of September, A. D. 1938.

Henry Van Arsdale
Acting Commissioner of Patents.

(Seal)

etherification, treated so as to be substantially impervious to moisture.

6. Low substituted glycol cellulose ether film having a wax moisture-proofing coating composition thereon.

7. Low substituted alkyl cellulose ether film having a wax moisture-proofing coating composition thereon.

8. Low substituted cellulose glycolic acid ether film having a wax moisture-proofing coating composition thereon.

9. As a new product alkyl cellulose, containing from 0.23 to 0.5 lower alkyl residues per C_6 unit of cellulose, said alkyl residues containing one to two carbon atoms, said product being substantially insoluble in 6% aqueous caustic alkali at room temperature but soluble in said alkali solution near the freezing point thereof, in the form of a sheet and having thereon a wax containing film which is impervious to moisture.

10. A low substituted water sensitive alkyl cellulose in the form of a sheet, having thereon a wax containing film coating which is impervious to moisture, the alkyl residue of the alkyl cellulose containing not more than two carbon atoms, the said alkyl cellulose not being dissolvable in 6% aqueous caustic soda at room temperature but dissolvable therein at near the freezing point thereof, and the said alkyl cellulose having the number of alkyl residues per C_6 unit of cellulose obtainable by etherifying alkali cellulose with an etherifying agent in the proportion of 0.12 to 0.5 mols per C_6 unit of cellulose.

11. A low substituted water sensitive glycol cellulose in the form of a sheet, having thereon a wax containing film coating which is impervious to moisture, the said glycol cellulose not being dissolvable in 6% aqueous caustic soda at room temperature but dissolvable therein near the freezing point thereof, and the said glycol cellulose having the number of glycol residues per C_6 unit of cellulose obtainable by etherifying alkali cellulose with an etherifying agent in the proportion of 0.07 to 0.56 mols per C_6 unit of cellulose.

12. A low substituted water sensitive glycol cellulose in the form of a sheet having thereon a wax containing film coating which is impervious to moisture, the said glycol cellulose containing up to 0.5 mols of substitution per glucose unit of cellulose and not being dissolvable in 6% aqueous caustic soda at room temperature but dissolvable therein near the freezing point thereof.

13. A low substituted water sensitive glycol cellulose in the form of a sheet, having thereon a wax containing film coating which is impervious to moisture, the said glycol cellulose being insoluble in water and organic solvents and dissolvable in 7% aqueous sodium hydroxide at least after xanthation and freezing, the amount of substitution not exceeding one-half mol. per glucose unit of the cellulose.

14. A low substituted cellulose ether film having a wax moistureproofing composition coating thereon, the said ethers being insoluble in water and organic solvents and dissolvable in 7% aqueous sodium hydroxide at least after xanthation and freezing, the degree of substitution of the said ethers being not more than one-half mol. per glucose unit of cellulose.

15. Low substituted cellulose ether film having a wax moisture-proofing coating composition comprising candelilla wax, paraffin and zinc resinate thereon.

16. A low substituted water sensitive lower alkyl cellulose in the form of a sheet, having thereon a wax containing film coating which is impervious to moisture, the said lower alkyl cellulose being insoluble in water and organic solvents and dissolvable in 7% aqueous sodium hydroxide, at least after xanthation and freezing, the amount of substitution not exceeding one-half mol. per glucose unit of the cellulose.

JOSEPH F. HASKINS,
Administrator of Deane C. Ellsworth, Deceased.

CERTIFICATE OF CORRECTION.

Patent No. 2,123,883. July 19, 1938.

JOSEPH F. HASKINS,
ADMINISTRATOR OF DEANE C. ELLSWORTH, DECEASED.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 39, for the patent number "2,737,187" read 1,737,187; page 4, first column, line 33, Example IX, for "250°C." read 25°C.; same page, second column, line 57, Example XII, for "seperate" read separate; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 27th day of September, A. D. 1938.

Henry Van Arsdale
Acting Commissioner of Patents.

(Seal)