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MOISTUREPROOF SHEET WRAPPING
MATERIAL

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This invention relates to moistureproof sheet wrapping material, especially transparent non-fibrous moistureproofed cellulosic web. More particularly it appertains to odorless, self-anchoring moistureproofing coatings on films of regenerated cellulose and the like.

Recently there has appeared in commerce a transparent moistureproof sheet wrapping material comprising a base sheet of regenerated cellulose having a thin moistureproofing coating. The moistureproofing coating ordinarily employed comprises essentially film forming (binding, cementing) material, for example, nitrocellulose, and moistureproofing material, for example, a waxy substance such as paraffin wax. The coating may also contain transparentizing (blending, homogenizing) material and/or plasticizing material.

The manufacture of a typical non-fibrous base sheet is described in U. S. A. Patent No. 1,548,864 (Brandenberger) and the coating thereof with typical moistureproofing coating compositions is described in U. S. A. Patents No. 1,737,187 (Charch & Prindle), 1,826,697 (Charch & Craigie), and 2,147,180 (Ubben).

When products containing considerable water (cheese, fish, fresh vegetables, etc.) are wrapped in the aforementioned sheet material, the surface coating loosens in a few hours. As a result, the effectiveness of the wrapping is very appreciably reduced. A way of precluding or overcoming this failing is to anchor the moistureproofing coating to the base sheet by means of an intermediate coat.

A simpler procedure in which some substance is incorporated in the moistureproofing coating composition, and applied therewith for the purpose of anchoring the coating to the base, is obviously desirable.

It was an object of this invention to produce sheet wrapping materials having self-anchoring moistureproofing coatings. Another object was the production of a flexible, odorless, colorless, transparent, moistureproof sheet wrapping material comprising a regenerated cellulose film (pellicle, foil, sheet, tissue, web) having a self-anchoring moistureproofing coating adhering tenaciously thereto even in the presence of water. Further objects were to devise a simple process applicable to existing and conventional equipment for causing moistureproofing coatings to anchor themselves to regenerated cellulose and like film, to improve the anchorage of moistureproofing coatings comprising moistureproofing material, binding material, blending material, and plasticizing material to regenerated cellulosic film, and to anchor a moistureproofing coating to a regenerated cellulose film with a dimethylol urea ether type synthetic resin. A general ad-

vance in the art, and other objects which will appear hereinafter, are also contemplated.

Surprisingly, it has now been found that resinous derivatives of a methylol urea ether will securely adhere moistureproofing coatings not containing cellulose substitution derivatives as the principal film forming material to regenerated cellulose film, and that the resulting moistureproof sheet wrapping material is greatly superior to the products heretofore known.

From the following description and specific examples, in which are disclosed certain embodiments of the invention, as well as details of what is believed to be the best mode for carrying out the invention, it will be apparent how the foregoing objects and related ends are accomplished. The parts are given by weight throughout the application unless otherwise specified.

Example I

A web of regenerated cellulose in gel condition, which had been cast from viscous, desulfured, bleached and washed free from impurities in the conventional manner (U. S. A. Patent No. 1,548,864 to Brandenberger), was led through an aqueous softening bath containing 4.33% glycerol. The gel film containing the glycerol softener was then dried in the usual manner by passage over heated rolls maintained at 60°-90° C.

After bringing the sheet material to normal humidity, it was moistureproofed by coating it with a coating composition consisting of a 20% solution of:

	Per cent
Urea formaldehyde monohydric alcohol (normal-butanol) resin (solids basis).....	16.80
Chlorinated rubber (65%-68% Cl.).....	37.0
Paraffin wax (M. P. 60° C.).....	3.0
Dibutyl phthalate.....	6.67
Dicyclohexyl phthalate.....	6.67
Di-methylcyclohexyl-phthalate.....	6.66
Rosin 2,017,866*.....	20.0
Maleic acid.....	3.2

*This is a "modified rosin" prepared by treating rosin in accordance with U. S. A. Patent No. 2,017,866. In general its properties are much the same as those of rosin, but with the difference that it has a molecular weight within the range of 5% to 400% greater than ordinary rosin in its pure state and higher than that of pure abietic acid. That it has a melting point (as determined by the capillary tube method) of about 80° C., and higher than the melting point of pure abietic acid and of purified rosin when in the resin state. That it is substantially free from combined sulfur and hardening substances held in combination, and that it has an iodine value lower than that of pure abietic acid.

in a solvent consisting of normal-butanol 15% and toluene 85%. The web was passed continuously through the bath of the aforementioned composition maintained at 35° C., the excess coating material removed by scraping, and the coated sheet dried (the volatile solvents removed)

at a temperature above the melting point of the wax. The base sheet was 450 gauge and the coating on the final product was in an amount proportional to two pounds for each 3,000 sq. ft. base sheet surface (this quantity includes coating on both sides of the film). There resulted a moisture-proofed sheet of regenerated cellulose which was transparent, flexible, odorless, non-tacky and colorless. It retained its moistureproofing surface coating tenaciously even when in direct contact with water and high proportions of moisture for prolonged periods of time. It was admirably suited for wrapping material to be employed in contact with products containing large amounts of water (or moisture) such as butter, cheese, wet fish, frozen fish and the like. The wrapping material performed its desired function as a wrapper for these commodities even when stored for long periods of time.

Example II

Non-moistureproof regenerated cellulose sheet was coated in the manner described in Example I with a moistureproofing composition consisting of a 20% solution of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	16.80
Chlorinated rubber (65% Cl.)-----	37.0
Paraffin wax (M. P. 60° C.)-----	3.0
Dicyclohexyl phthalate-----	6.67
Dibutyl phthalate-----	6.67
Dimethylcyclohexyl phthalate-----	6.66
Rosin 2,017,866-----	20.0
Maleic acid-----	3.2

in a solvent consisting of isobutanol 15%, and toluene 85%. The product was non-tacky and had an excellent permeability value.

Example III

Regenerated cellulose sheet was coated by the procedure of Example I, with a moistureproofing coating composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	3.24
Maleic acid-----	0.36
n-Butyl methacrylate polymer-----	7.44
Paraffin wax (M. P. 60° C.)-----	0.36
Diphenyl lauramide-----	0.60
Toluene-----	74.80
Isobutanol-----	13.20

The resulting moistureproof sheet wrapping material had superior anchorage and improved heat sealing properties. In this coating composition considerable care had to be exercised to secure compatibility of the various solids and desirable characteristics in the solvent composition.

Example IV

Regenerated cellulose sheet was coated with a moisture proofing coating composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	3.24
Maleic acid-----	0.36
Beta-naphthol modified rubber 2,158,530*-----	6.48
Paraffin wax (M. P. 60° C.)-----	0.72
Dewaxed dammar-----	1.20
Toluene-----	74.80
Isobutanol-----	13.20

*An alkylated beta-naphthol in which rubber is the alkylating agent. This product was prepared according to U. S. A. Patent 2,158,530 (Williams).

The resulting moistureproof sheet wrapping material had superior anchorage and improved heat sealing properties.

Example V

Regenerated cellulose sheet was coated with a moistureproofing coating composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	3.24
Maleic acid-----	0.36
Polyvinyl butyral* (hydroxyl 19%, butyral 80%, acetyl 1%)-----	6.48
Paraffin wax (M. P. 60° C.)-----	0.72
Dewaxed dammar-----	1.20
Toluene-----	35.20
Isobutanol-----	12.30
Ethyl acetate-----	40.50

*A polyvinyl alcohol butyraldehyde resin which may be prepared by the methods disclosed in U. S. A. Patent No. 2,162,678 (Robertson). Polyvinyl acetals of this type are also disclosed in U. S. A. Patents 2,035,939 and 2,036,092 (Morrison) and U. S. A. patent application Serial No. 307,081, filed December 1, 1939 (Hershsberger).

The resulting moistureproof sheet wrapping material had superior anchorage and improved heat sealing properties.

Example VI

Regenerated cellulose sheet was coated with a moistureproofing coating composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	3.24
Maleic acid-----	0.36
Pliolite*-----	6.48
Paraffin wax (M. P. 60° C.)-----	0.72
Dewaxed dammar-----	1.20
Toluene-----	74.80
Isobutanol-----	13.20

*"Pliolite" is a thermoplastic rubber derivative ordinarily containing up to about 1% chlorine made by condensing rubber with a catalyst such as tin tetrachloride (see Paper Trade Journal, page 96, February 23, 1939, J. I. E. C. XXVI, 125 and U. S. A. Patents No. 1,797,188, 1,846,247, 1,853,334 and 2,052,391). The chemical structure is also described in "Rubber Age," April, 1939, and J. I. E. C. XIX, 1033.

The resulting moistureproof sheet wrapping material had superior anchorage and improved heat sealing properties. The compatibility of paraffin wax and Pliolite is outstanding. Similar results were obtained when a normal amyl ether of dimethylol urea was used instead of the corresponding butyl ether.

Example VII

Regenerated cellulose web was moistureproofed by the procedure described in U. S. A. Patent No. 1,737,187 (Charch & Prindle), using a coating composition consisting of:

	Per cent
Dimethylol urea isobutyl ether (partially polymerized)-----	5.4
Maleic acid-----	0.6
Blond shellac-----	4.44
Gum dammar-----	1.20
Paraffin (M. P. 61° C.)-----	0.36
Ethyl acetate-----	40.5
Toluene-----	35.2
Isobutyl alcohol-----	12.3

Well anchored moistureproof coatings resulted.

Example VIII

Regenerated cellulose sheet was coated with a moistureproofing coating composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	3.24
Maleic acid-----	0.36
n-Butyl methacrylate polymer-----	1.80
Nitrocellulose (11.0% N)-----	1.80
Dewaxed dammar-----	0.84
Paraffin wax (M. P. 60° C.)-----	0.36
Diphenyl lauramide-----	3.60
Ethyl acetate-----	40.50
Toluene-----	35.20
Isobutanol-----	12.30

The resulting moistureproof sheet wrapping material had superior anchorage and improved heat sealing properties.

Example IX

A web of regenerated cellulose in gel condition, which had been cast from viscose, desulfured, bleached and washed free from impurities and softened in the conventional manner was brought to normal humidity, and moistureproofed by coating it with a coating composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	1.28
Nitrocellulose (11.05% N) 9 secs. (dry)-----	4.88
Paraffin wax (M. P. 60° C.)-----	0.35
Dicyclohexyl phthalate-----	5.61
Hydrogenated castor oil phthalate-----	0.20
Isobutyl alcohol-----	0.66
Toluene-----	28.04
Ethyl acetate-----	52.77
Isopropanol-----	2.09
Ethanol-----	4.12

in the manner described in Example I. The final sheet had a permeability value of 13.

Example X

Polyvinyl alcohol sheet of 450 gauge was coated in the usual manner with a moistureproofing composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	25.20
Nitrocellulose (11.4% N)-----	32.0
Paraffin wax (M. P.) 60° C.)-----	3.0
Dicyclohexyl phthalate-----	8.33
Dibutyl phthalate-----	8.33
Dimethyl cyclohexyl phthalate-----	8.34
Beckacite 1118*-----	10.0
Maleic acid-----	4.80

*Beckacite 1118 is an ester gum-resin and maleic acid glyceride mixture or complex having a melting range of 119°-215° F. and an acid number of 17-22. It is one of a series of related maleic anhydride modified ester gum resins commercially available.

made up as a 12% solids dispersion in a mixture consisting of ethyl acetate 46%, toluene 40% and isobutanol 14%. The product was non-tacky and had great resistance to the action of water.

Example XI

Regenerated cellulose web of 450 gauge was

moistureproofed by coating it with a composition consisting of:

	Per cent
Dimethylol urea cyclohexyl ether (partially polymerized)-----	3.2
Maleic acid-----	0.4
Diphenyl lauramide-----	3.6
Gum dammar-----	0.8
Paraffin (M. P. 61° C.)-----	0.4
Nitrocellulose (11% N)-----	3.6
Ethyl acetate-----	40.5
Toluene-----	35.2
Isobutyl alcohol-----	12.3

in the manner described in U. S. A. Patent No. 1,737,187 (Charch and Prindle). Well anchored moistureproof coatings resulted. Similar results were obtained with the corresponding amyl ether.

Example XII

Regenerated cellulose sheet of 450 gauge was coated with a moistureproof composition consisting of:

	Per cent
Dimethylol urea octyl ether (partially polymerized)-----	3.2
Maleic acid-----	0.4
Butyl phthalyl butyl glycolate-----	3.6
Gum dammar-----	0.8
Paraffin wax (M. P. 61° C.)-----	0.4
Nitrocellulose (11% N)-----	3.6
Ethyl acetate-----	40.5
Toluene-----	35.2
Isobutyl alcohol-----	12.3

by the usual procedure, the coating being carried out at 140° C. Well anchored moistureproof coatings resulted. The sheet material could be heat sealed.

Example XIII

A web of regenerated cellulose which had been cast from viscose, desulfured, bleached, washed, softened by passage through a 6% aqueous glycerol bath and dried, all in the usual manner, was coated on both sides with a coating composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin solution (65% solution in isobutanol)-----	25.2
Nitrocellulose (11.4% N)-----	49.2
Dicyclohexyl phthalate-----	9.0
Dimethyl cyclohexyl phthalate-----	9.0
Maleic acid-----	4.8
Paraffin wax-----	1.5
Dammar resin-----	1.3

The coating was applied from a 11.7% solids solution in a solvent consisting of:

	Per cent
Ethyl acetate-----	46.0
Toluene-----	40.0
Isobutyl alcohol-----	14.0

by passing the regenerated cellulose web through the bath and scraping off the excess coating composition. The dip bath was maintained at a temperature high enough to prevent separation of the wax, before and after application (35° C.). The coated sheet was dried at a temperature above the melting point of the wax (80° C.). The product was exceptionally well suited for use as a milk bottle hood.

Similar results were obtained when volatile ester solvents such as isopropyl acetate and isobutyl acetate, and ketone solvents such as ethyl

butyl ketone, were substituted for the ethyl acetate. Benzene can replace the toluene satisfactorily. Methanol, ethanol, propanol, butanol and the existing isomeric alcohols may be used in place of the isobutyl alcohol, if desired.

In this type of coating composition the ethyl acetate range is preferably 35% to 70% of the solvent. The toluene range is 35% to 70% of the solvent. The toluene range is 30% to 65%, and the isobutyl alcohol range 10% to 18% on the same basis.

The sheet wrapping material of this example had excellent anchorage and odor characteristics.

Example XIV

Regenerated cellulose sheet was coated on both sides with a composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin solution (65% solution iso-butanol)-----	4.0
Para-toluene sulfonic acid-----	0.5
Nitrocellulose (high viscosity)-----	0.5
Isobutyl alcohol-----	33.25
Toluene-----	28.50
Ethyl acetate-----	33.25

Example XV

Continuous sheet regenerated cellulose in gel state, which had been cast from viscose, desulfured, bleached and washed free from impurities in the usual manner in the casting machine, was impregnated with glycerol by passing it through an aqueous bath containing 6% glycerol. The excess solution was removed from the web by means of squeeze rolls which reduced the water content of the sheet to between three and four times the weight of the cellulose. It was then dried in the usual manner upon heated rolls.

The resulting sheet material (softened with glycerol) was moistureproofed by coating it with a moistureproofing coating composition of the following formulation:

	Per cent
Urea formaldehyde monohydric alcohol (normal butanol) resin solution (60%--65% solution in normal butanol)-----	3.0
Nitrocellulose (11.4% N) 8 sec. viscosity-----	4.5
Dibutyl phthalate-----	3.0
Maleic acid-----	0.5
Dewaxed dammar-----	0.8
Paraffin (M. P. 61° C.)-----	0.3
Ethyl alcohol-----	4.0
Butyl alcohol-----	8.0
Toluene-----	28.9
Ethyl acetate-----	47.0

In applying the coating the sheet was passed through a bath of the moistureproofing coating composition, the excess coating composition removed by scraping (any other suitable means may be employed), and the coated sheet dried at a temperature above the melting point of the wax. The finished sheet was then conditioned to bring it to the desired moisture content. Conditioning (humidification or dehumidification) to bring the uncoated film to a specific moisture content is carried out just prior to coating in some instances, for example, when the film as a result of being stored for extended periods of time has a moisture content different from that desired at the beginning of the coating operation. The resulting product was a sheet of regenerated cellulose with a moistureproofing coating which was substantially odorless, transparent, flexible and

moistureproof. By virtue of the presence of the polymerized methylol urea ether resin in the coating composition, the moistureproofing coating was anchored very satisfactorily to the base sheet. When the finished product was in direct contact with water or was 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 and the like, the coating remained anchored for very substantial periods of time (a month or more).

Example XVI

The procedure of Example XV was carried out using a moistureproofing coating composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (normal-butanol) resin (50% solution in normal butanol)-----	20.0
Nitrocellulose (12.5% N) 30 sec. viscosity-----	4.3
Beckacite 1118*-----	2.0
Tricresyl phosphate-----	3.5
Salicylic acid-----	1.0
Paraffin (M. P. 61° C.)-----	0.7
Isobutyl acetate-----	39.3
Toluene-----	29.2

*Beckacite 1118 is an ester gum-rosin and maleic acid glyceride mixture or complex having a melting range of 119°-215° F. and an acid number of 17-22. It is one of a series of related maleic anhydride modified ester gum resins commercially available.

In the final product the coating was very satisfactorily anchored to the base sheet. Similar results were obtained when the normal amyl ether of dimethylol urea was used instead of the normal butyl ether.

Example XVII

The procedure of Example VIII was carried out, using a moistureproofing coating composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (normal-butanol) resin solution (60%--65% solution in normal-butanol)-----	7.2
11.4% nitrogen nitro cotton-----	4.2
Paraffin-----	0.6
Phthalic anhydride-----	0.48
Dewaxed dammar-----	1.2
Dibutyl phthalate-----	1.2
Ethyl acetate-----	57.20
Toluene-----	26.40
Ethyl alcohol-----	1.52

The moistureproof sheet wrapping material had excellent anchorage and odor characteristics.

Example XVIII

Regenerated cellulose sheet was coated with a moistureproofing coating composition consisting of:

	Per cent
Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	3.24
Maleic acid-----	0.36
Ethyl cellulose-----	1.23
Nitrocellulose (11.0% N)-----	3.06
Dewaxed dammar-----	1.63
Paraffin (M. P. 60° C.)-----	0.36
Diphenyl lauramide-----	2.12
Ethyl acetate-----	40.50
Toluene-----	35.20
Isobutanol-----	12.30

The resulting moistureproof sheet wrapping material had superior anchorage and improved heat

sealing properties. The base sheet of U. S. A. Patent No. 2,123,883 may also be used satisfactorily.

Example XIX

Regenerated cellulose web was moistureproofed by the procedures described in U. S. A. Patent No. 2,147,180 (Ubben), using a coating composition consisting of:

	Per cent
Lauryl ether of dimethylol urea (partially polymerized) -----	3.2
Maleic acid -----	0.4
Gum dammar -----	0.8
Paraffin (M. P. 61° C.) -----	0.4
Diphenyl lauramide -----	3.6
Nitrocellulose (11% N) -----	3.6
Ethyl acetate -----	40.5
Toluene -----	35.2
Isobutyl alcohol -----	12.3

A well anchored moistureproof coating resulted. The sheet material could be heat sealed.

Example XX

Regenerated cellulose web was moistureproofed by the procedure described in U. S. A. Patent No. 2,147,180 (Ubben), using a coating composition consisting of:

	Per cent
Dimethylol urea benzyl ether (partially polymerized) -----	3.2
Maleic acid -----	0.4
Gum dammar -----	0.8
Paraffin (M. P. 61° C.) -----	0.4
Dibutyl phthalate -----	1.2
Dicyclohexyl phthalate -----	1.2
Dimethyl cyclohexyl phthalate -----	1.2
Nitrocellulose (11% N) -----	3.6
Ethyl acetate -----	40.5
Toluene -----	35.2
Isobutyl alcohol -----	12.3

Well anchored moistureproof coatings resulted.

Example XXI

Regenerated cellulose web was moistureproofed by the procedure described in U. S. A. Patent No. 2,147,180 (Ubben), using a coating composition consisting of:

	Per cent
Isobutyl ether of dimethylol urea (partially polymerized) -----	3.2
Maleic acid -----	0.4
Ethyl-phthalyl-ethyl-glycolate -----	3.6
Paraffin (M. P. 61° C.) -----	0.4
Gum dammar -----	0.8
Nitrocellulose (11% N) -----	3.6
Ethyl acetate -----	40.5
Toluene -----	35.2
Isobutyl alcohol -----	12.3

Well anchored moistureproof coatings resulted.

As shown by the foregoing-specific examples, anchored moistureproofing coatings on regenerated cellulose and like film can be obtained by incorporating in the moistureproofing coating compositions the polymerization derivative of mono- and/or di-methylol urea alkyl ether.

By the expression "anchor" or equivalents (anchoring, anchored, etc.) is meant the securing of the surface coating on the base in such a way that the resulting product will withstand the deleterious effects of water (or moisture). In other words, the surface coating will not loosen and/or flake off from the water sensitive base film when the product is directly in contact with water for

appreciable and substantial periods of time (at least two days when immersed in water at 20° C.).

Whether a substance is an anchoring agent or not is easily determined, for example, by comparing the time of immersion in water required to loosen a moistureproofing coating containing the substance, with the time required to bring about the same loosening with the coating omitting the substance being tested (but otherwise having the same proportions of ingredients).

The dimethylol urea ether component of the moistureproofing lacquer or coating composition may consist of a single ether or a mixture of different ethers. The ether type material may be in the monomeric and/or the partially polymerized form. Partial or complete polymerization may be effected after the coating has been applied to the base sheet.

The preparation of the urea formaldehyde monohydric alcohol reaction product resin solutions may be carried out in various ways. Preferred procedures are described in detail in U. S. A. Patent No. 2,191,957 dated February 27, 1940 (Edgar & Robinson). The methylol urea ethers may be prepared according to the disclosures in U. S. A. Patents No. 2,191,974 dated February 27, 1940, and 2,201,927 dated May 21, 1940, 2,213,921 dated September 3, 1940, and 2,247,419 dated July 1, 1941 (Sorenson).

The amount of methylol urea ether material in the moistureproofing lacquer is preferably in the neighborhood of 5%, 2% to 8% being a preferred range.

Monohydric alcohols for use as solvents, either alone or in admixture with other solvents for the methylol urea and/or methylol thiourea condensation (or etherification) include methanol, ethanol, propanol, isopropanol, normal butanol, isobutanol, amyl alcohol, hexyl alcohol, lauryl alcohol, octyl alcohol, benzyl alcohol, cyclohexanol, and ethylene chlorhydrin. The mono ethers or esters, for example, ethylene glycol, its mono-acetate, its mon-ethyl and mono-phenyl ethers, may also be used in this process.

The urea ether material should be substantially odorless after being hardened (condensed, polymerized). In order to save time in completing polymerization it is desirable to use incompletely polymerized resinous material rather than the monomeric crystalline monohydric alcohol ether of methylol urea.

Better seat sealing is obtained with the high alkyl ethers (octyl, lauryl, etc.) of methylol urea. The heat sealing properties are improved by incorporating amides (for example, diphenyl-lauramide, dimethyl-benzoyl benzamide, acetanilide, etc.) in the moistureproofing coating.

The dimethylol ethers are preferred to the mono methylol ethers.

The moistureproofing coating compositions used to make regenerated cellulose and other non-moistureproof type sheet materials moistureproof comprise essentially moistureproofing material (one or more moistureproofing agents), binding material (one or more binding agents, and the methylol urea ether anchoring material. One or more agents for homogenizing the coating composition and one or more agents for plasticizing the coating composition, may be present if desired.

The wide variety of materials, moistureproofing agents, binding agents, homogenizing agents, plasticizing agents, catalysts, etc., for use in the coating compositions, and the characteristics which render them suitable in such a composi-

tion, are well known in the art and are described in the patent art. Certain materials being preferred warrant the special mention which follows.

The preferred binders include rubber, rubber-like materials, rubber derivatives (such as halogenated rubber, isomerized rubber, and hydrogenated rubber), ether linkage resins (resins resulting from the reaction of polyhydric phenols with aliphatic polyhalides and during the production of which ether linkages are formed), vinyl resins and like materials capable of forming thin, self-supporting films (numerous other such materials are mentioned in the patent art).

Preferably the binding material is a non-cellulosic substance such as a rubber derivative containing chlorine. The best results have been obtained with chlorinated rubber of 65%–68% chlorine content. The alkyl methacrylates, particularly the *n*-butyl methacrylates, are also very satisfactory for this purpose.

A material composed of 60% vinyl chloride and 40% vinyl acetate has been found to be suitable.

In the field of rubber derivative (that is, products made up of isoprene residues and obtained from rubber by substituting and/or cross-linking the isoprene units—see Paper Trade Journal of February 23, 1939, pages 1–3) and rubberlike material, special mention may also be made of Thermoprene (a thermoplastic unsaturated hydrocarbon described in detail by H. L. Fisher in "Industrial and Engineering Chemistry," volume 19, No. 12, page 1325), polymerized chloro-2-butadiene-1:3, Pliolite and Plioform (Pliolite and Plioform are thermoplastic rubber derivatives of substantially the same chemical composition, and either may contain traces of chlorine).

The ether linkage resin formed by the reaction of dihydroxy-diphenyl-propane and beta-beta'-di-chloro-di-ethyl ether in the presence of alkali, is preferred.

As the moistureproofing material, any wax (used generically to include waxy substances like paraffin wax, as well as true waxes which are monohydric alcohol esters of higher fatty acids) may be employed. Ordinarily paraffin wax melting above 50° C., or better, that melting at 60° C. (and above), is preferred.

The homogenizing agents should be substances which increase the compatibility of the binding material and the wax. Resins and gums are the most satisfactory substances for this purpose so far tested.

The application of the moistureproofing coating may be accomplished in any suitable manner, such as by passing the base film through a bath of the coating composition, by spraying the composition on the base, etc. After application any excess of the coating may be removed in any desired manner, such as by doctor knives, doctor rolls, etc. Various coating procedures are known to the art, and in the interest of brevity need not be reviewed here.

Clearer films are obtained when the coated film is chilled rapidly after evaporation of the solvent from the coating.

In the preferred embodiment of the invention regenerated cellulose and like materials are coated with moistureproofing coating compositions comprising waxy material, organic solvent soluble binding material, blending material, plasticizing material, and the dimethylol urea ether product, and it is applied from solution in organic solvent.

In preparing the solution type of coating compositions the constituents are dissolved in a sol-

vent (a single organic liquid or mixture of liquids as is expedient) to give a clear, homogeneous solution which may be smoothly applied to the surface of the base film (sheet, web or the like) in a layer sufficiently thin that the solids (resulting from evaporation of the solvent) will produce a layer in the neighborhood and preferably not exceeding 0.0005 inch in thickness.

Not only should the solvents be selected to give a clear, homogeneous solution, but the solid constituents should be so blended (compounded) that a clear, transparent film results.

While it is possible in certain instances to use solvents (for the formulation of the moistureproofing lacquer) which will have a solvent action on the base sheet, this arrangement is preferably avoided. In the preferred procedures the solvents selected for the moistureproofing coating composition or lacquer ingredients are those which do not have a harmful effect upon the base sheet to which the moistureproofing lacquer is to be applied. In such cases the coating composition will not penetrate through the base sheet, and will normally result in a surface coating or covering.

Although procedures not employing polymerization catalysts are generally satisfactory, in the preferred processes an acidic condensing agent is employed in conjunction with the methylol urea ether material. In general such materials are more effective the lower the pH of their solution. Acidic condensing agents for the polymerization processes of the present invention are well known in the art, for example, acids such as phosphoric, maleic, citric, lactic, acetic, trichloroacetic, tartaric, oxalic, phthalic, and the like. Acid esters and half esters, and the like such as mono-isobutyl phosphate, dibutyl phosphate, mono-phenyl phosphate (and generically acid esters of phosphoric acid), mono-butyl phthalate, and mono-ethyl succinate, are satisfactory condensing agents, as are acid resins such as rosin and "modified rosin" (see U. S. A. Patents 2,017,866 and 2,147,180). Phosphorous pentoxide, shellac, Glyptal (alkyd) resins, and the like, may also be used.

As a base this invention contemplates any smooth, substantially non-porous, non-fibrous sheet, especially cellulosic film precipitated from an aqueous cellulosic dispersion or solution or from solution in an organic solvent (one or more organic liquids). This includes sheets of regenerated cellulose whether precipitated from viscose (solutions of cellulose xanthate), cuprammonium or any other aqueous solutions or dispersions of cellulose. It also includes sheets of cellulose ethers and esters precipitated from aqueous solutions or dispersions (U. S. A. Patent No. 2,123,883 to Ellsworth) such as glycol cellulose, cellulose glycolic acid, alkyl cellulose (preferably methyl or ethyl cellulose), cellulose phthalic acid, and other similar cellulosic products described by these terms. These specific cellulose substitution derivatives just mentioned are usually grouped under the generic term low (or lowly) substituted cellulose ethers (and esters). In the language of the art, low substituted cellulose derivatives are those in which there is not more than one mol of substitution per glucose unit.

The organic solvent soluble cellulose substitution products such as cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetopropionate, cellulose acetobutyrate, ethyl cellulose, benzyl cellulose, ethyl benzyl cellulose, and other esters and ethers of cellulose (particu-

larly the organic acid esters and the alkyl ethers of cellulose), which can be precipitated from solution of the cellulosic derivative in an organic solvent, are also included.

In addition to the cellulosic sheets or films, there may also be mentioned those from gelatin, polyvinyl alcohol, rubber hydrochloride, vinyl resins and the like.

The composition of this invention can be applied to base materials comprising cellulosic threads or fibers whether natural, such as cotton, linen, jute, ramie, hemp and the like, or synthetic fibers precipitated from aqueous cellulosic dispersions or solutions, or from solutions of cellulosic derivatives in organic solvents.

In order that the finished sheet wrapping material may be of the desired softness, a softener such as glycerol may be incorporated in the base sheet.

The base sheet may be clear or dyed in appropriate colors.

Moistureproofness, moistureproofing and moistureproof materials and expressions are defined in U. S. A. Patent No. 2,147,180 (Ubben). In the interest of brevity the definitions are not repeated here. The terms and expressions related thereto and employed herein are used in accordance with such definitions.

Heat seal bond and heat seal bond strength are defined and a standard test for their determination is given in U. S. A. Patent No. 2,147,180 (Ubben). In the interest of brevity the definitions and test description are not repeated here. The terms and expressions related thereto and employed herein are used in accordance with such definitions and description.

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 this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. Moistureproof sheet wrapping material comprising a base formed of non-fibrous base sheet coated with a moistureproofing coating composition, said coating composition comprising halogen containing rubber derivative film former, wax and dimethylol urea ether resin.

2. The material of claim 1 when the film former is chlorinated rubber.

3. The material of claim 1 when the base sheet is regenerated cellulose.

4. The material of claim 1 when the dimethylol urea ether is the butyl ether.

5. Moistureproof sheet wrapping material comprising a base formed of non-fibrous base sheet coated with a moistureproofing coating composition, said coating composition comprising chlorinated rubber film former, moistureproofing agent, blending agent, and dimethylol urea ether resin.

6. Moistureproof sheet wrapping material comprising a base formed of non-fibrous base sheet coated with a moistureproofing coating composition, said coating composition comprising chlorinated rubber film former, moistureproofing agent, plasticizer, and dimethylol urea ether resin.

7. A method of forming moistureproof sheet wrapping material which comprises incorporating an incompletely polymerized dimethylol urea ether in a moistureproofing coating composition and coating a non-fibrous base sheet with the coating composition.

8. Moistureproof sheet wrapping material comprising a regenerated cellulose base sheet coated with a moistureproofing coating composition consisting of:

	Per cent
5 Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	16.80
Chlorinated rubber (65% Cl)-----	37.0
Paraffin wax (M. P. 60° C.)-----	3.0
10 Dicyclohexyl phthalate-----	6.67
Dibutyl phthalate-----	6.67
Dimethylcyclohexyl phthalate-----	6.66
Modified rosin-----	20.0
Maleic acid-----	3.2

15 said modified rosin having the same general properties as rosin, but with the difference that it has a molecular weight within the range of 5% to 400% greater than ordinary rosin in its pure state; that it has a melting point, as determined by the capillary tube method, above 80° C. and higher than the melting point of pure abietic acid and of purified rosin when in the resinous state; that it is substantially free from combined sulfur and hardening substances held in combination; that it has an iodine value lower than that of pure abietic acid; and that it has a molecular weight higher than that of pure abietic acid.

9. A method of forming moistureproof sheet wrapping material which comprises incorporating an incompletely polymerized dimethylol urea ether in a moistureproofing coating composition and coating a regenerated cellulose base sheet with the coating composition.

10. A method of forming moistureproof sheet wrapping material which comprises incorporating an incompletely polymerized dimethylol urea ether in a moistureproofing coating composition and coating a polyvinyl alcohol base sheet with the coating composition.

11. A method of forming moistureproof sheet wrapping material which comprises incorporating an incompletely polymerized dimethylol urea ether in a moistureproofing coating composition including chlorinated rubber as cementing material and coating a non-fibrous base sheet with the coating composition.

12. A method of forming moistureproof sheet wrapping material which comprises incorporating an incompletely polymerized dimethylol urea ether in a moistureproofing coating composition including butyl methacrylate polymer as cementing material, and coating a non-fibrous base sheet with the coating composition.

13. A method of forming moistureproof sheet wrapping material which comprises coating a regenerated cellulose base sheet with a coating composition consisting of:

	Per cent
60 Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	16.80
Chlorinated rubber (65% Cl)-----	37.0
Paraffin wax (M. P. 60° C.)-----	3.0
Dicyclohexyl phthalate-----	6.67
65 Dibutyl phthalate-----	6.67
Dimethylcyclohexyl phthalate-----	6.66
Modified rosin-----	20.0
Maleic acid-----	3.2

70 said modified rosin having the same general properties as rosin, but with the difference that it has a molecular weight within the range of 5% to 400% greater than ordinary rosin in its pure state; that it has a melting point, as determined by the capillary tube method, above 80° C.

and higher than the melting point of pure abietic acid and of purified rosin when in the resinous state; that it is substantially free from combined sulfur and hardening substances held in combination; that it has an iodine value lower than that of pure abietic acid; and that it has a molecular weight higher than that of pure abietic acid.

14. A method of forming moistureproof sheet wrapping material which comprises coating a regenerated cellulose base sheet with a coating composition consisting of:

	Parts
Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	3.24
Maleic acid-----	0.36
n-Butyl methacrylate polymer-----	7.44
Paraffin wax (M. P. 60° C.)-----	0.36
Diphenyl lauramide-----	0.60

15. A method of forming moistureproof sheet 20

wrapping material which comprises coating a polyvinyl alcohol base sheet with a coating composition consisting of:

	Per cent
5 Urea formaldehyde monohydric alcohol (iso-butanol) resin (solids basis)-----	25.20
Nitrocellulose (11.4% N)-----	32.0
Paraffin wax (M. P. 60° C.)-----	3.0
10 Dicyclohexyl phthalate-----	8.33
Dibutyl phthalate-----	8.33
Dimethyl cyclohexyl phthalate-----	8.34
Beckacite-----	10.0
Maleic acid-----	4.80

15 said Beckacite being an ester gum-rosin and maleic acid glyceride mixture or complex having a melting range of 119°-215° F. and an acid number of 17-22.

DANIEL D. LANNING.