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MOISTUREPROOF MATERIAL

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This application, which is a continuation-in-part of my prior application Serial No. 241,265, filed December 19, 1927, relates to moistureproof materials and the method of making the same.

5 More particularly, this invention relates to a moistureproof material resisting the action of an excess amount of moisture or water, comprising a base of a non-fibrous and smooth-surfaced material, such as a sheet or film of regenerated cellulose, a sheet or film formed of a cellulose derivative, such as the ester and ether, or a sheet or film formed of an albuminous material, such as gelatin, agar-agar and the like, having a coating resulting from a varnish, such as one containing a drying oil and/or a synthetic resin having drying characteristics and a wax.

By the term "moistureproof" or its equivalent used herein is meant the ability to resist the diffusion of a water vapor to an extent at least as great as or exceeding that displayed by ordinary waxed papers employed as wrappers and having the ability to resist the penetration of water vapor therethrough to a substantial degree for a substantial period of time, depending on the article being wrapped and/or being approximately at least 7 times or more as effective as the uncoated sheets or films when tested in accordance with the test described in the Journal of Industrial & Engineering Chemistry on page 575, vol. 21, No. 6 (June 1929). Sheets or films of the type above described and constituting the base when coated in accordance with this invention will not only show 7 but 10, 25, 50, 100 or even several hundred times the resistance to the passage of moisture or water vapor as will the uncoated sheets when tested under the same conditions. It is therefore evident that the minimum figure set forth in the above definition is in no wise limiting in respect to the higher degrees of moistureproofing that can be obtained.

There has recently appeared on the market a new material which has attained extensive and widespread use as a wrapping tissue. In one modification, this material consists of a sheet of regenerated cellulose coated with a cellulose derivative lacquer containing a wax. This wrapping tissue, because of its desirable characteristics of moistureproofness, flexibility and transparency, has been largely used for the wrapping of foodstuffs, for example, those which suffer from a gain or loss in moisture. The success which has attended this material has resulted in its use in other increasing fields and it has at times been used for purposes not primarily contemplated, with the result that the excellent re-

sults secured in other fields were not duplicated. For example, when this wrapping tissue was used for the packaging of very moist or even wet materials, such as lettuce, butter and eggs, it was not entirely satisfactory. The coating became loosened and the effectiveness of the material was substantially decreased. Again, the prior material, in view of its many excellent properties, has been extensively used in the recently developed quick freezing processes and has shown the limitation of not being sufficiently flexible at low temperatures. This is a very important factor, since in many of the quick freezing processes the goods are wrapped prior to freezing.

I have found that by coating a sheet of a non-fibrous and smooth-surfaced material, such as a sheet or film of regenerated cellulose, a sheet or film composed of a cellulose derivative, a sheet or film formed of an albuminous material, with a varnish containing a drying oil and/or a synthetic resin having drying characteristics and a wax, subjecting the coated material to a temperature at least equal to the crystallization point of the wax in the composition, and preferably also humidifying the base before the coating operation and/or after the heating operation, there is provided a non-tacky and preferably also transparent material which is not only moistureproof within the meaning of the term hereinafore defined but also markedly waterproof in that it does not become loosened upon prolonged contact with substances containing an excessive quantity of moisture and indeed water, said material also being flexible without losing its moistureproofness during all ranges of temperature up to 45° C. and notably even at very low temperatures such as below 0° C.

It is therefore an object of this invention to provide a flexible moistureproof and preferably transparent material which is markedly waterproof in that it does not lose its effectiveness when subjected to materials containing a large percentage of moisture or are indeed wet.

Another object of this invention is to provide a material which, in addition to being moistureproof, transparent and non-tacky, is also flexible even at low temperatures.

Another object of this invention is to provide a moistureproof article of manufacture possessing the properties immediately hereinbefore set forth and comprising a sheet of a non-fibrous and smooth-surfaced material and preferably also transparent, such as a sheet or film of regenerated cellulose, a sheet or film formed of a cellulose derivative, a sheet or film formed of an al-

buminous material, having a coating preferably transparent and resulting from a varnish, such as one containing a drying oil or a synthetic resin having drying characteristics and a wax.

5 Another object is to provide a method of preparing materials having the characteristics previously enumerated.

Additional objects will appear from the following description and appended claims.

10 In accordance with the principles of this invention, a suitable base is coated with a moisture-proofing composition and treated as more fully explained hereafter.

The base comprises a sheet of a non-fibrous and smooth-surfaced material, preferably transparent, and includes such materials as a sheet or film of regenerated cellulose, a sheet or film formed of a cellulosic derivative, such as the cellulose nitrate, acetate, ether or the like, and a sheet or film formed of an albuminous material, such as gelatin, agar-agar and the like.

The coating composition comprises a varnish, such as one containing a drying oil and a wax or waxy substance with or without a gum or resin. 25 The varnish may also be composed of a modified synthetic resin having drying characteristics and a wax. It is obvious that the term "varnish" does not embrace the cellulose derivative lacquer mentioned above.

30 The degree of moistureproofness of the product may vary within wide limits. It chiefly depends upon the proportion of wax material employed, the characteristics of the particular waxy material, its melting point, the thickness of the coating, and also the method of application.

35 As the wax, a paraffin which is colorless and odorless is preferable to many other waxes. In addition to these characteristics, paraffin wax is also preferred because it can be secured at a relatively low cost. Any of the commonly available paraffin waxes may be employed, but when a high degree of moistureproofing is desired, it is preferable to use a paraffin wax having a melting point above 50° C., for example between 55°-65° C. or 45 even higher. Such a wax is free from or low in oils and low melting (at room temperatures) semi-solid fractions and will generally tend toward crystallinity of structure. It is clear, of course, that such a high melting point wax may be secured by suitable fractionation of the materials on the market. There are, however, other waxes and wax-like materials which are also suitable, and this invention is not limited to paraffin. For example, depending on the moistureproofness, 55 transparency, or lack of transparency, color, etc., waxes and wax-like materials, such as beeswax, ceresin wax, carnauba, candelilla wax, palm wax, spermaceti wax, etc., or wax-like materials, such as petroleum jelly, certain solid oils, esters of higher alcohols and higher acids, synthetic resins modified to be waxy in character, etc., may be used. These waxes and waxy-substances may be used either singly or in combination or blended with other wax-like materials, as is found desirable. 65

When several modifications of any of the waxes exist or can be produced, it will usually be found that the high melting modifications provide better moistureproofness and less tackiness, and these are preferable for certain uses, although 70 the invention is not restricted to these modifications. The term "wax" as hereinafter employed is intended to include both waxes and waxy or wax-like substances.

75 As the drying oil, any of the common varnish

oils, such as Chinawood oil, linseed oil, perilla, menhaden, sardine, etc., or combinations of such oils may be used. The invention is more practical when a very rapid drying oil is used, so therefore this type of material is preferable. The 5 treatment of the oil to make it a rapidly drying one does not form any essential part of this invention, since such oils are commonly known and may be prepared by heat treatments, by boiling, by blowing with air, by means of commercial 10 driers, etc., to modify their rate of oxidation or their drying characteristics. Oils which have been treated and rendered capable of drying in the shortest possible time are preferred, but of course the invention is not restricted thereto. 15 The treatment of the oil may be effected either before making into a varnish or during the varnish making process.

As the gum or resin, any of the common varnish gums, as is well known, may be used, although for special purposes the gums or resins may be entirely omitted. The gums or resins may be either natural or synthetic.

As examples of natural gums or resins, rosin, congo, East India, kauri, pontianac, manila, etc. 25 have been used. As examples of synthetic gums and resins, there may be mentioned the condensation products of polybasic acids and polyhydric alcohols, such as phthalic acid and glycerin respectively, particularly when these have been 30 modified by the introduction or incorporation of oils, oil acids, natural resins, or resin acids, and the condensation products of phenol and formaldehyde when modified so as to be oil soluble. It is obvious, of course, that any combinations of 35 any of the natural gums, natural resins, synthetic gums and synthetic resins may be used.

In producing the varnish, the procedure wherein the resin (natural or synthetic) is combined with the oil in a distinct operation may be followed. However, that technique wherein certain resin-forming materials, as for example glycerin and phthalic anhydride, are made to react with each other and in the presence of modifying agents such as oils, with the resulting formation 45 of a material having varnish-like characteristics may also be used.

These varnish-like materials, variously referred to as "synthetic resins", modified polyhydric alcohol-polybasic acid resins, modified phenol-formaldehyde resins and modified drying oils, may, if properly modified, be used directly as the vehicle for carrying the wax. It is understood, of course, that such materials require a drying (oxidation or polymerization of the oil residue) in 55 order to become tack-free, in addition to that drying represented by the evaporation of whatever solvents may be used therewith for the facilitation of application in the coating process. Because of the fact that these "synthetic resins" 60 which are varnish-like require a secondary drying oxidation or polymerization to produce a tack-free surface, they are for all intents and purposes equivalent to a "varnish".

In certain embodiments of the invention, the 65 varnish composition may be free of volatile solvents, solvent mixtures or diluents. However, since, by the use of volatile solvents, solvent mixtures or diluents, such as toluene, gasoline, benzene, xylene, turpentine or mixtures thereof, 70 it is possible to secure the deposition of a thinner and more uniform film as well as make the process better manageable, the preferred embodiments contemplate such substances.

Substances which impart certain characteris- 75

tics to the final coating may also be incorporated in the composition. For example, a small quantity of calcium stearate may be incorporated in the composition if the feel of the final surface is to be improved.

If the coating solutions of the desired concentration are too thin, such substances as, for example, rubber or the like may be added to increase the viscosity for proper spreading without impairing the properties.

From the preceding, it is apparent that this invention contemplates the use of a mixture of drying oils with natural or synthetic resins, which resins are not tacky when the volatile solvent has been evaporated, and equally, the use of a varnish-like "synthetic resin" (synthetic resin varnish) which requires a secondary drying to produce a tack-free surface. For many purposes, I prefer the latter type, since it gives extremely rapid drying and produces brilliant surfaces.

The wax may be added to the varnish or to the varnish-like "synthetic resin" in any suitable way. For example, the wax may be added directly to the other constituents or it may be previously dissolved in a solvent which is to form a part of the final composition, and then added to the varnish at room temperature or at a slightly elevated temperature.

The degree of moistureproofness, as previously stated, depends in part on the quantity of the wax component. Satisfactory results have been secured by using amounts of the wax component up to 10%, and preferably 2%–7% (based on the film-forming ingredients), although it is obvious that if very perfect transparency is not a prime requirement, quantities in excess of 10% may be used.

When compositions containing solvents or diluents are employed, the film forming ingredients may comprise from 5% to 75% of the composition. In general, however, excellent results are obtained when the film forming ingredients constitute from 15% to 40% of the solution.

When a colored coating is desired, any suitable coloring agent, such as a dye or pigment, may be incorporated in the composition.

In order to fully describe my invention, I give herewith several examples, it being understood that my invention is not limited thereto but that other compositions are equally contemplated.

Example I

	Parts
Chinawood oil.....	50.0
Cobalt linoleate.....	0.1
Paraffin.....	3.0
Toluene.....	50.0

To prepare this composition, the varnish is preferably first prepared as by heating the Chinawood oil and the drier to the appropriate temperature, for example 425° F., and then the wax added. Finally the composition is cut with the diluent. If desired, the wax may be dissolved in the diluent or at least a portion thereof and the solution thereof added.

Example II

	Parts
Chinawood oil.....	783
Litharge.....	30
East India gum.....	500
Paraffin.....	53
Calcium stearate.....	10
Turpentine substitute.....	1375
Toluene.....	10800

In preparing this composition, the gum is melted in a portion of the oil containing the litharge by heating the mixture to 425° F., at which temperature another portion of oil is added. The addition of the oil cools the mixture and therefore it is again heated up to 425° F. The oil is added in four operations according to the preceding procedure. After the entire quantity of oil has been added and heated to 425° F., the mixture is cooled to approximately 400° F., at which time the calcium stearate is added. Subsequently, the wax is added. Before the composition has completely cooled, the turpentine substitute is added. The toluene is finally added preferably after the mixture has been further cooled.

As in the previous examples, the wax may be dissolved in either of the diluents and in this manner incorporated.

Example III

	Parts
Linseed oil.....	93
Litharge.....	6
Amberol resin.....	100
Ceresin.....	24
Calcium stearate.....	2.2
Turpentine substitute.....	200
Toluene.....	1200
Xylene.....	400

The composition may be prepared by a process similar to that employed in the preparation of Example II.

Example IV

	Parts
Linseed oil.....	150
Cobalt linoleate.....	2.5
Polyhydric alcohol-polybasic acid resin.....	100
Paraffin.....	25
Toluene.....	250

This composition is prepared in accordance with the procedure outlined in Example II.

The polyhydric alcohol-polybasic acid resin is made by heating a charge of the following ingredients in substantially the following portions in a kettle to 225° C. and holding the mass at this temperature until the acid number is 40 or less:

	Parts by weight
Glycerine.....	15.12
Phthalic anhydride.....	27.26
Rosin.....	57.62

Example V

	Parts
Polyhydric alcohol-polybasic acid resin solution.....	100
Candelilla wax.....	3
Zinc stearate.....	1
Toluene.....	100

The polyhydric alcohol-polybasic acid resin solution comprises 50 parts of the resin dissolved in an equal quantity of toluene.

The polyhydric alcohol-polybasic acid resin is made from the following ingredients in substantially the following proportions:

	Parts by weight
Glycerine.....	20.0
Phthalic anhydride.....	45.0
Perilla oil.....	35.0
Sodium hydroxide.....	0.1

The resin is prepared by heating the glycerine, oil and sodium hydroxide, the latter being dissolved in a small quantity of water, to 200° C.

The mixture is agitated and maintained at this temperature until it is homogeneous and soluble in an equal volume of 95% methyl alcohol, at which time the phthalic anhydride is added. The temperature is raised to 225° C. and maintained there until the acid number is 47±5.

The composition is prepared as explained in Example II.

Example VI

	Parts
Chinawood oil	800
Cobalt acetate.....	7
Rosin.....	75
Wax.....	50

This composition may be prepared as explained above in Example I.

Example VII

	Parts
Polyhydric alcohol-polybasic acid resin.....	25
Cobalt linoleate	0.2
Titanium oxide	30
Ceresin.....	1.0
Toluene.....	25
Xylene	25

This composition is prepared similarly to those described in Examples IV and V.

The polyhydric alcohol-polybasic acid resin is made from the following ingredients in substantially the following portions:

	Parts by weight
Glycerine.....	14.6
Phthalic anhydride.....	35.4
Linseed oil.....	25.0
Chinawood oil.....	25.0

The process by which it is made comprises charging the glycerine, phthalic anhydride and linseed oil in a kettle where it is heated to 250° C. and there kept until the violent reaction ceases. The temperature is lowered to 225° C. at which time the Chinawood oil is added. The mass is then kept at 225° C. until the mass shows an acid number of 50.

The moistureproofing composition, at either room or an elevated temperature, may be applied to the base in any convenient manner, such as by coating, spraying, immersing, etc., and the base may be treated on one or both sides. After having applied the composition to the base and the excess removed in any known manner, the resulting product is dried to remove the solvent, if any, and to dry the oil. The drying is preferably carried out at a temperature at or above the crystallizing point of the wax component in the mixture. This elevated temperature drying is preferably effected immediately after the application of the moistureproofing composition and before an initial setting has taken place. It is maintained until, at least, a surface drying has been effected, so that the sheets or films may be stacked, rolled, wound, or otherwise handled.

The drying is best carried out in warm air, which is circulating, or in the presence of an oxidizing medium, such as ozonized air or ultraviolet light. The temperature limits will usually be found to be between 35 and 100° C.

Under the aforementioned conditions, with a relatively thin film, such as .0001" to .00005" or less (1 side), the drying has proceeded sufficiently far in five to ten minutes, or even less, so that the film or sheet can be further handled. Of course, the coated sheets or films may be festooned or otherwise freely arranged and allowed

to remain so for several hours or even days to complete the drying.

It is to be understood that it is the initial or surface drying which is to be carried out at an elevated temperature and immediately after the application of the composition. Residual drying may be effected, as indicated, but in practice the sheets or films will be piled or wound and the residual drying will take place at ordinary temperatures as the product proceeds through the usual steps of counting, sorting, cutting, etc.

In applying the moistureproofing composition to bases, especially cellulosic bases, of which regenerated cellulose is an example, or gelatin, it will some times be desirable to increase the humidity or moisture content of the sheet or film before the application of the composition in order to facilitate the operation of a continuous method. In like manner, it will usually be found that the steps of applying the moistureproofing composition and of drying it have deprived the film of some of its moisture, so that it tends to be somewhat less flexible. This can be corrected by exposing the partly dried film while it is being maintained at an elevated temperature to a humidifying treatment, whereby the moisture is reintroduced, so that the film regains its normal flexibility. Incidentally, this humidifying treatment also serves the very useful purpose of removing the last traces of odor, which is a critical matter if the product is to be used for the wrapping of foodstuffs, for example.

The material constituting one phase of this invention is moistureproof, non-tacky and also transparent when a transparent base is used and a composition chosen which deposits a transparent film. It is, moreover, characterized by marked waterproof properties. When used to wrap substances containing large quantities of moisture, it successfully resists the loosening action of the moisture. Again, the product is not only flexible at ordinary temperatures but retains its flexibility at low temperatures, such as 0° C. or even lower.

The thickness of the coating, as is apparent, may vary within wide limits. In the case of regenerated cellulose sheeting having a thickness of 0.0009", a coating of 0.0001" on each side, gave excellent results.

These films may be made of any thickness, depending partly on their destined use. They will be moistureproof, non-tacky, waterproof, flexible and preferably also transparent.

Since it is obvious that various changes and modifications may be made in the above description without departing from the nature and spirit thereof, this invention is not restricted thereto except as set forth in the appended claims.

I claim:

1. A moistureproof article of manufacture comprising a sheet of a non-fibrous and smooth-surfaced material having a thin moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax and a film-forming substance selected from the group which consists of drying oils and synthetic resins having drying characteristics, said article being flexible without losing its moistureproofness at a temperature of 0° C.

2. A moistureproof article of manufacture comprising a sheet of a non-fibrous and smooth-

containing a wax, a resin and a film-forming substance selected from the group which consists of drying oils and synthetic resins having drying characteristics, the wax being present in an amount up to 10% by weight of the film-forming ingredients, and said article being flexible without losing its moistureproofness at a temperature of 0° C.

23. A moistureproof article of manufacture comprising a transparent sheet formed of a substance selected from the group which consists of regenerated cellulose, cellulose derivatives and albuminous substances, said sheet having a thin transparent moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax and a film-forming substance selected from the group which consists of drying oils and synthetic resins having drying characteristics, the wax being present in an amount from 2% to 10% by weight of the film-forming ingredients, and said article being flexible without losing its moistureproofness at a temperature of 0° C.

24. A moistureproof article of manufacture comprising a transparent sheet formed of a substance selected from the group which consists of regenerated cellulose, cellulose derivatives and albuminous substances, said sheet having a thin transparent moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax, a resin and a film-forming substance selected from the group which consists of drying oils and synthetic resins having drying characteristics, the wax being present in an amount from 2% to 10% by weight of the film-forming ingredients, and said article being flexible without losing its moistureproofness at a temperature of 0° C.

25. An article of manufacture comprising a sheet of regenerated cellulose having on each side thereof a thin moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax and linseed oil, said article being flexible without losing its moistureproofness at a temperature of 0° C.

26. An article of manufacture comprising a sheet of regenerated cellulose having on each side thereof a thin moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax, a resin and linseed oil, said article being flexible without losing its moistureproofness at a temperature of 0° C.

27. An article of manufacture comprising a

transparent sheet of regenerated cellulose having on each side thereof a thin transparent moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax and linseed oil, said article being flexible without losing its moistureproofness at a temperature of 0° C.

28. An article of manufacture comprising a sheet of regenerated cellulose having on each side thereof a thin moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax, a resin and linseed oil, the wax being present in an amount up to 10% by weight of film-forming ingredients, said article being flexible without losing its moistureproofness at a temperature of 0° C.

29. An article of manufacture comprising a sheet of regenerated cellulose having on each side thereof a thin moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax and China-wood oil, said article being flexible without losing its moistureproofness at a temperature of 0° C.

30. An article of manufacture comprising a sheet of regenerated cellulose having on each side thereof a thin moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax, a resin and China-wood oil, said article being flexible without losing its moistureproofness at a temperature of 0° C.

31. An article of manufacture comprising a transparent sheet of regenerated cellulose having on each side thereof a thin transparent moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax and China-wood oil, said article being flexible without losing its moistureproofness at a temperature of 0° C.

32. An article of manufacture comprising a sheet of regenerated cellulose having on each side thereof a thin moistureproof surface coating which does not become loosened upon prolonged contact with substances containing a high moisture content or water and is deposited from a varnish containing a wax, a resin and China-wood oil, the wax being present in an amount up to 10% by weight of film-forming ingredients, said article being flexible without losing its moistureproofness at a temperature of 0° C.

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