Patented May 5, 1942

2,281,589

UNITED STATES PATENT OFFICE

2,281,589

MOISTUREPROOF WRAPPING MATERIAL

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No Drawing. Application June 8, 1940, Serial No. 339,493

9 Claims. (Cl. 91—68)

This invention relates to moistureproof sheet wrapping material, especially transparent moistureproofed cellulosic web. More particularly it appertains to the anchoring of moistureproofing coatings to 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 film having a moistureproofing coating. The moistureproofing coating ordinarily employed comprises essentially a film former, for example, nitro-cellulose, and a moistureproofing agent, for example, a waxy material such as paraffin wax. The coating usually contains, in addition, a blending agent for the various ingredients. Frequently a plasticizer, for the coating, is also present.

The manufacture of such a base sheet is described in U. S. A. Patent No. 1,548,864 (Brandenberger), and the coating thereof with a typical moistureproofing coating composition is described in U. S. A. Patent No. 1,737,187 (Charch & Prindle).

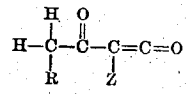
Other moistureproofing coatings are well known in the art.

When products containing considerable water (butter, cheese, fish, fresh vegetables, etc.) are packaged in the conventional moistureproof sheet wrapping material, the coating comes loose from the surface of the base sheet in a few hours. As a result, the effectiveness of the wrapping is very appreciably reduced. A way of avoiding or overcoming this failing has recently been discovered, and is described in U. S. A. Patent No. 2,022,490 (Charch). It involves incorporating in the moistureproofing coating composition a substance which, after the coating operation, anchors the coating to the base. In spite of the very great advance described in this patent, there is still considerable room for improvement.

It has now been found that an intermediate (between the base sheet and its moistureproofing coating) coating of ethenone material will securely adhere a moistureproof coating to regenerated cellulose film, and that the resulting moistureproof sheet wrapping material is superior to the products heretofore known.

It was an object of this invention to produce improved non-fibrous sheet wrapping materials having anchored moistureproof coatings. Another object was the production of a flexible, substantially odorless, colorless, transparent, moistureproof sheet wrapping material comprising a regenerated cellulose film having a moistureproof coating which adheres tenaciously thereto even when in direct contact with water for prolonged periods of time. Further objects were to devise a simple process, applicable to existing and conventional equipment, for anchoring moistureproof coating to regenerated cellulose and like film, to improve the anchorage of moistureproof coatings comprising a film former (binder), a moistureproofing agent, and optionally, a blending agent and/or a plasticizer, to regenerated cellulosic film, and to anchor a moistureproof coating to a regenerated cellulose and other non-fibrous film with ethenone material. A general advance in the art, and other objects which will appear hereinafter, are also contemplated.

The objects of this invention are obtained, in general, by applying to the base sheet a coating or a sizing of an ethenone of the general formula:



in which R and Z represent aliphatic hydrocarbon radicals which may be substituted, and then applying over the ethenone material layer a moistureproofing coating.

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.

Example I

A web of regenerated cellulose, which had been cast from viscose, desulfured, bleached, washed free from impurities, softened (impregnated with glycerol) and dried in the conventional manner (U. S. A. Patent No. 1,548,864 to Brandenberger), was passed through a bath consisting of:

	Per cent
Hexadecylketene dimer	5
Carbon tetrachloride	95

The excess solution was removed by means of doctor knives, and the carbon tetrachloride evaporated. There resulted a transparent film having a very thin layer of hexadecylketene dimer deposited upon the surface. A drying time of 3 minutes at 100° C. was found ample.

The resulting sheet of softened regenerated cellulose coated or sized with an insoluble deposit of the ketene dimer was, after conditioning to bring it to the desired moisture content, coated with a moistureproofing composition of the following formulation:

	Parts
Nitrocellulose	60
Paraffin wax (M. P. 60° C.)	3
Ester gum	7
Dicyclohexylphthalate	20
Dibutyl phthalate	10
Toluene	245
Ethyl acetate	450
Ethyl alcohol	35

by passing it therethrough. The excess of the moistureproofing coating composition was removed by scraping, and the coated sheet dried at a temperature above the melting point of the wax. The finished web was again conditioned to bring it to the desired moisture content.

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 intermediate layer or sizing of the ketene dimer, the moistureproofing coating adhered very tenaciously to the sheet when in direct contact with water for very substantial periods of time (3 days or more). In a similar product coated with the same moistureproofing coating composition but omitting the intermediate layer of ketene dimer, the moistureproofing coating was found to loosen and flake off in a period of 6 hours when subjected to contact with water. The product having the anchored coating served as a very satisfactory wrapping for products containing large amounts of water or moisture, such as butter, cheese, wet fish, frozen fish, ice cream and the like, even when in direct contact therewith.

Example II

A film prepared as described in Example I and softened with ethylene glycol, was treated with a solution comprising:

	Per cent
Hexadecylketene dimer	2
Carbon tetrachloride	98

The excess sizing material was removed by means of doctor knives, and the film dried for 5 minutes at 100° C. After this the film was coated with the moistureproofing coating composition of Example I, giving a highly transparent, flexible, moistureproof sheet wrapping material which retained its coating in a firmly adherent condition in excess of 1 week when subjected to direct contact with water.

Example III

Regenerated cellulose film, softened with glycerol and dried in the manner described in U. S. A. Patent No. 1,606,824 (Brandenberger) was sprayed with a solution comprising:

	Per cent
Linseed oil acids ketene dimer	5
Toluene	95

After drying for 1 minute at 100° C., the film was coated with the moistureproofing coating composition of Example I to give a highly transparent moistureproof product. The moistureproofing coating was found to be firmly adherent even when immersed in water for a period of 1 week, or longer.

Example IV

Regenerated cellulose softened with a mixture of ethylene glycol and glycerol was coated by passing through a solution containing:

	Per cent
Linseed oil acids ketene dimers	5
Ethyl cellulose	0.5
Toluene	94.5

After drying for a period of 1 minute at 100° C., the film was found to be transparent and completely tack-free. It could be stored for considerable periods of time without exhibiting any tendencies for adjacent sheets to stick together. Rolls of such web material did not become solidified or stuck to such a degree that it was difficult to unroll the material.

This material was coated with a moistureproofing composition of the following formulation:

	Parts
Ethyl cellulose	71
Paraffin wax, M. P. 60° C	4
Sulfurized castor oil	5
Dibutyl phthalate	10
Dicyclohexylphthalate	10
Toluene	580
Ethyl alcohol	150

After removal of the solvent from the moistureproofing coating composition in the usual fashion, a highly transparent and moistureproof product resulted. The coating remained firmly adherent to the base sheet even when immersed in water for periods in excess of 1 week.

Example V

A regenerated cellulose film, softened with glycerol, was coated, by means of spraying, with a solution comprising:

	Parts
Ethyl ketene dimer	5
Toluene	95

After drying for 1 minute at 100° C., the film was coated with the moistureproofing composition of Example I. After removal of the solvent, the moistureproofing coating was found to adhere firmly to the base sheet even when submerged in water for a period of time considerably greater than that required to loosen the coating from a similar sheet coated with the same moistureproofing composition in which the intermediate layer of ketene dimer had been omitted.

Example VI

A regenerated cellulose film, softened with glycerol, was coated by passing it through a solution containing:

	Parts
Oleic acid ketene dimer	5
Toluene	95

After drying for a period of 2 minutes at 100° C., the film was coated with a moistureproofing composition consisting of:

	Parts
Butyl methacrylate polymer	95
Paraffin wax (M. P. 60° C.)	5
Toluene	730

The moistureproofing coating, after removal of the solvent, was found to adhere firmly to the base sheet even when submerged in water for a period of time much greater than that required to loosen a similar coating from a similar base sheet in which there was no intermediate layer of ketene dimer.

Example VII

A regenerated cellulose film softened with glycerol, was sized by passing through a solution of:

	Parts
Linoleic acid ketene dimer	5
Toluene	95

After a period of 3 minutes at 100° C. the film was coated with a moistureproofing coating composition consisting of:

	Parts
Chlorinated rubber (67% Cl)	60
Paraffin wax (M.P. 60° C.)	6
Damar resin	10
Dicyclohexyl phthalate	12
Dibutyl phthalate	12
Toluene	730

After removal of the solvent, the moistureproofing coating was found to adhere firmly to the base sheet even when submerged in water for a period of time considerably greater than that required to loosen the coating from a similar sheet coated with the same moistureproofing composition in which the intermediate layer of ketene dimer had been omitted.

Example *VIII*

A regenerated cellulose film softened with glycerol was coated by passing through a solution containing:

	Parts
Undecylenic acid ketene dimer	5
Toluene	95

After drying for a period of one minute at 100° C., the film was coated with a moistureproofing composition consisting of:

	Parts
Pliolite*	95
Bleached montan wax	5
Toluene	730

*"Pliolite" is a thermoplastic rubber derivative 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 Nos. 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.

After removal of the solvent, the moistureproofing coating was found to adhere firmly to the base sheet even when submerged in water for a period of time considerably greater than that required to loosen the coating from a similar sheet coated with the same moistureproofing composition in which the intermediate layer of ketene dimer had been omitted.

As base sheet material, this invention contemplates any transparent, water-sensitive, non-fibrous cellulosic sheet, especially those containing water miscible softening agents (glycerol, glycol, etc.). This includes cellulosic film regenerated or precipitated from aqueous alkaline cellulosic dispersions or solutions, for example, regenerated cellulose precipitated from viscose (solutions of cellulose xanthate), cuprammonium cellulose and cellulose ethers and esters, which ethers and esters have not been substituted to an extent or degree sufficient to cause them to loose their water sensitivity, such as glycol cellulose, cellulose glycolic acid, alkyl cellulose (preferably methyl or ethyl cellulose), and similar cellulosic products. The majority of the specific cellulose substitution derivatives just mentioned can be grouped under the generic term low or lowly substituted (not more than one mol of substitution per glucose unit) cellulose ethers and esters (see U. S. A. Patent No. 2,123,883 to Ellsworth). Some of the cellulose substitution products mentioned may be soluble in organic solvents.

Other water sensitive bases, such as polyvinyl alcohol, are within the scope of the invention.

As shown by the foregoing specific examples, anchorage of moistureproofing coatings on regenerated cellulose and like film is obtained by an ethenone material anchoring coat.

By the expression "anchor" or equivalents (anchoring, anchored, etc.) is meant the securing of the surface coating to the base in such a way that the resultant 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 when the product is directly in contact with water for appreciable and substantial periods of time (several days when immersed in water at 20° C.). Whether a substance is an anchoring agent or not is easily shown, for example, by comparing the time of immersion in water required to loosen a moistureproof coating which has been coated over a sub-layer of the substance, with the time required to bring about the same loosening with the same moistureproofing coating in the absence of the sub-layer of the substance being tested.

The preparation of the ethenones may be carried out in various ways. Preferred procedures are described in detail in U. S. A. patent applications Serial Nos. 234,843 and 234,844, now Patent No. 2,238,826, filed October 13, 1938, and 280,653, now Patent No. 2,268,169, filed June 22, 1939, by Sauer. In the interest of brevity in this application these procedures are not repeated here, but reference is made to the earlier filed specifications for details. The ethenones of these Sauer applications are of two general types, namely, aldoethenones, in which only one methylene hydrogen is replaced or substituted, and ketoethenones, in which both methylene radicals have been replaced. The more important subdivisions of the aldoethenone group are the alkylethenones and acylethenones. In the ketoethenone field the main sub-generic groups are the dialkylethenones and the acylalkylethenones.

The ethenones can be formed by the dimerization of the corresponding ketenes, and may therefore also be called "ketene dimers." Dimers in which R and Z, of the general formula shown on page 4, are chain hydrocarbon radicals such as alkyl or alkylene, are preferred. These radicals (nuclei, residues, groups) may be straight or branched chain, and in either case may be substituted as described in the patents disclosing their production. The preferred radicals are derived from propionic, butyric, caprylic, lauric, stearic, keto-stearic, undecylenic, oleic, linoleic, drying oil acids and fish oil acids. A long list of specific ethenones and their formulae are disclosed in U. S. A. patent application Serial No. 234,842, filed October 3, 1938, by Handford, to which reference is made in the interest of brevity.

Application of the ethenone material to the base sheet may be made by any of the conventional coating or sizing procedures, as for example, with applicator rolls, by dipping or immersing the sheet in a bath of the material, by brushing a solution on the sheet, by spraying the solution on a sheet, or any other convenient means. After application of the under-coating composition it may be smoothed and the excess

removed in any suitable manner, as for example, by doctor knives, squeeze rolls, etc.

Such organic liquids (solvents) as carbon tetrachloride, benzene, toluene and the like, which do not contain active hydrogen (that is, hydrogen detectable by the Zerewitinoff analytical method) are suitable for the formation of solutions of the ethenone material. Ester solvents such as ethyl acetate are also quite satisfactory. Mixtures of solvents and/or mixtures of ethenones can be used. The consistency of such solutions is governed by the apparatus employed, the thickness of the coating desired, the convenience of the operator, and similar factors. Solutions containing between 1% and 20% of ethenone material have been found very convenient for obtaining under-coats of the requisite thickness. A preferred concentration range is 2% to 5%. Higher or lower concentrations can be used in specific instances, and, if desired, the ethenone material may be applied in pure form as a melt.

When applying the anchoring under-coat from an organic solvent solution, the solvent is evaporated after application of the solution, preferably at temperatures above normal room temperature, but not exceeding 125° C. It is desirable that the anchoring coat set up to a hard tack-free state in three to five minutes or less at a temperature of between 70° and 110° C. if conventional apparatus and treating speeds are to be employed. These figures are for anchoring coats of less than 0.0001 of an inch in thickness.

In order to obtain anchoring layers which do not form visible cracks on cellulosic sheet when it is creased or wrinkled, ethenone material which will produce a film or size of a fair degree of flexibility, is preferred. The under-coat usually is extremely thin, being often within the range 0.00001 to 0.00003 of an inch in thickness.

In some cases it may be desirable to adjust the moisture content of the sized or coated sheet to a desired value in order to condition it for further handling.

The heat necessary (if any) to condition the ethenone treated sheet material for receiving its final moistureproofing coating, may be applied in a variety of ways, as for example, by bringing the cellulosic sheet into contact with heated drier rolls (or other heated surfaces), or by leading the sheet (or web) through a heated atmosphere in some other manner (U. S. A. Patent No. 2,115,132, Alles & Edwards).

If for any reason it is desired to modify the characteristics of any specific ethenone material or of the anchoring layer, which said ethenone material forms on the cellulosic sheet, for example, with respect to flexibility, hardness, color, and the like, certain other substances, non-reactive with the other ethenone material, may be combined therewith. These include natural resins, synthetic resins, waxes, wax-like materials, cellulose substitution derivatives such as cellulose esters, cellulose ethers and the like. Such substances serve the specific purposes of giving desirable surface characteristics, such as non-tackiness, during subsequent operations, an increase in moistureproofness of the final product, etc. Dyes and/or pigments may be added to either the intermediate or moistureproofing layer, or both.

In the preferred embodiment of the invention the moistureproofing coating composition comprises organic solvent soluble binder material from the group comprising cellulose substitution derivatives (cellulose esters, cellulose ethers, etc.), rubbery materials (rubber, balata, isoprene, neoprene, etc.), and polymerized alpha-beta unsaturated acid esters (alkyl methacrylates, etc.); moistureproofing material (waxes, waxy material, etc.); blending material and the plasticizing material, and it is applied from solution in an organic solvent.

The preferred moistureproofing coating compositions are those of U. S. A. Patents No. 1,737,187 (Charch & Prindle), 2,077,400 (Collins), 2,137,636 (Barrett), and the like.

As the moistureproofing agent, 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 blending agents should be materials which increase the compatibility of the cellulose derivative for the wax. A great variety of resins and gums are available for this purpose, as is well known in the art.

In preparing the solution type of coating compositions, the constituents are dissolved in a solvent (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 sized or coated base 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 of an 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.

The application of the moistureproofing coating may be accomplished by any suitable manner, such as application from a melt or solution in organic solvent. Passing the base film through a bath of the coating composition, spraying the composition on the base, etc., are preferred procedures.

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 in the art, and in the interest of brevity need not be reviewed here.

Typical procedures are disclosed in U. S. A. Patents No. 1,826,696-7-8-9. Clearer films are obtained when the coated film is chilled rapidly after evaporation of the solvent from the coating.

Although the invention has been described particularly with respect to the anchoring of moistureproofing surface coatings, to non-porous, non-fibrous base material such as regenerated cellulose in the preparation of transparent sheet wrapping material, it is broader. The ethenone material will satisfactorily anchor coatings to sheet material thicker than wrapping tissue, and may also be used satisfactorily with tubes, sausage casing, bottle caps and bands, molded articles, and in general to any articles of cellulose or similar material of the character described, when the problem of anchoring coatings arises.

The invention comprehends the coating of still other bases, such as rayon fabrics and the like, in order to anchor surface coatings thereto.

Additionally, the present invention may be employed to improve the anchorage of various coatings to bases other than those specifically mentioned heretofore, for example, paper, cotton

cloth, and the like, which are water sensitive. In other words, with bases which will absorb water, the ethenone material improves the adhesion between the coating and the base.

The ethenone material sizes may be used satisfactorily where the final coating is of a discontinuous character, as for example, in the printing of colors, symbols, indicia, advertisements, etc. Thus regenerated cellulose sheets, tubes, caps, sausage casings, etc., when coated or sized with the ethenone material, may be printed with printing ink either having a lacquer base or a drying oil base for giving any desired indicia, and after drying, the printing adheres securely to the base even after being subjected to rigid washing, boiling and other process steps.

The present invention effects the production of flexible, substantially odorless, non-fibrous, non-porous, cellulosic sheet material having a moistureproofing coating securely anchored thereto, which is resistant to deterioration when subjected to the action of liquid water over long periods of time.

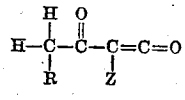
A further advantage is the adaptability of the process of the invention to the equipment now used in the production of regenerated cellulose film and the like, without necessitating a substantial change in the design of such equipment. Still further advantages are lower cost, minimum waste and greater efficiency. The composite films of the present invention, in the absence of pigments, have a high degree of transparency.

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.

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:

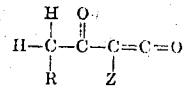
1. A moistureproof wrapping material sheet comprising a regenerated cellulose base sheet having a moistureproofing coating adhered thereto with a layer of ethenone material of the formula:



in which R and Z are aliphatic groups.

2. The product of claim 1 when the ethenone is hexadecylketene dimer.

3. The process which comprises coating self-supporting water sensitive film with a layer of a ketene dimer of the formula:

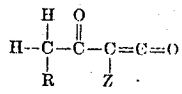


in which R and Z are aliphatic groups, and thereafter overcoating the ketene dimer layer with a moistureproofing coating.

4. The product of claim 1 when the ethenone is linseed oil acids ketene dimer.

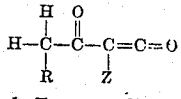
5. The product of claim 1 when the ethenone is oleic acid ketene dimer.

6. The process which comprises coating self-sustaining water-sensitive film from the group consisting of transparent, non-fibrous, cellulosic sheet and polyvinyl alcohol sheet, with a layer of ketene dimer of the formula:



in which R and Z are aliphatic groups, and thereafter over-coating the ketene dimer layer with a moistureproofing coating.

7. The process which comprises coating transparent, water-sensitive, non-fibrous cellulosic sheet with a layer of ketene dimer of the formula:



in which R and Z are aliphatic groups, and thereafter over-coating the ketene dimer layer with a moistureproofing coating.

8. The process which comprises spraying regenerated cellulose sheet softened with glycerol, with a solution comprising essentially:

	Per cent
Linseed oil acids ketene dimer	5
Toluene	95

drying, and thereafter coating with a moistureproofing coating composition.

9. The process which comprises spraying regenerated cellulose sheet softened with glycerol, with a solution comprising essentially:

	Per cent
Oleic acid ketene dimer	5
Toluene	95

drying, coating with a moistureproofing coating composition comprising essentially:

	Parts
Butyl methacrylate polymer	95
Paraffin wax	5
Toluene	730

and removing the solvent from the coating.

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