

## UNITED STATES PATENT OFFICE

2,177,645

## MOISTUREPROOF COATED SHEET

Robert B. Flint, Wilmington, Del., and James A. Mitchell, Kenmore, N. Y., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application September 8, 1937,  
Serial No. 162,904

11 Claims. (Cl. 91—68)

This invention relates to the production of coated structures. More particularly, it relates to moistureproofing coating compositions containing a new type of slip agent and the use of such coating compositions in the production of thin, non-fibrous, transparent sheets and films suitable for wrapping tissue having a coating which is non-tacky, slippery and non-adherent at elevated temperatures.

Thin, transparent sheets and films of non-fibrous cellulosic materials containing moistureproof coatings are well known as wrapping tissue. In general, the coatings of such sheets and films comprise a film-forming constituent, such as a cellulose derivative or a resin, a moistureproofing agent such as a wax, a blending agent such as a resin, and a plasticizer. Such moistureproofing coating compositions and methods for compounding and applying the same are disclosed in detail in the United States Patent No. 1,737,187 to Charch and Prindle and French Patent No. 718,440 to Charch.

Difficulty has long been experienced in the handling and storing of such sheets and films because of their lack of slipperiness and the adherence of contiguous sheets to each other. These difficulties are due to at least two factors. One factor is that some of the constituents of the moistureproofing composition may be inherently tacky. A second factor is that the surfaces of these sheets are so smooth that, when they lie in close juxtaposition, they have a tendency to exclude air from between them, thus causing a vacuum action which renders it very difficult to separate the sheets, and at the same time to increase the area of contact thus increasing the coefficient of friction. This smoothness is not overcome and in fact is accentuated by the ordinary constituents of the moistureproofing composition, particularly the moistureproofing agent, since it apparently forms a smooth continuous phase in order to prevent the passage of moisture.

Furthermore, it has been observed that these difficulties are greatly augmented by a slight rise in temperature. A sheet which proves perfectly satisfactory as to surface conditions at ordinary room temperatures may become very tacky and unmanageable when stored in heated places or when subjected to abnormally high room temperatures. Similar conditions have been found to arise in the use of automatic wrapping machinery. As long as such wrapping tissue is manually applied to packages, a slight degree of stickiness and frictional resistance, while an inconvenience, is of no considerable consequence. It becomes

of extreme importance, however, when such adherence and frictional resistance is increased by the transmission of heat or the heat developed by friction in an automatic machine. It is found actually that a difference of 1° or 2° may even cause a sticking of the material to some part or other of the machine and completely foul its operation. Furthermore, due to the high speeds developed in such automatic machinery, normal adherence and frictional resistance, even of the same degree as can be tolerated in manual operation, are objectionable even in the absence of a temperature rise.

An attempt has been made to overcome the adhesive tendency inherent in these films by the use of a thin layer of talcum powder. This method has the disadvantage, however, that while it lessens the adhesion of the sheets, it stains the film.

It has been suggested to incorporate small amounts of finely divided, insoluble materials, such as kaolin, aluminum hydroxide, titanium oxide, etc. in the moistureproofing coating compositions which are to be applied to the film. Since this solid matter is in a very finely divided form and since the coating bath is of relatively high viscosity, it is possible to disperse these solid particles in the bath and apply evenly to the surface of the film. The presence of such solid matter produces numerous points of separation between contiguous sheets in stacked relation, or between the surface of the sheet and other smooth surfaces, and thus insures good surface slip. However, the introduction of insoluble matter into the bath composition has several disadvantages. For one thing, it is very difficult to adequately disperse such solid materials without prolonged stirring and agitation and the dispersion may not be stable over long periods of time or in all conditions of operation, so that pipe lines and apparatus may become clogged with sediment. Furthermore, it is not possible to filter the bath composition once the solid, insoluble material has been added, and filtration is often necessary for the production of coating baths of the highest quality.

Another film defect from the use of such solid insoluble slip agents used heretofore has been a lowering of the moistureproof quality which is perhaps caused by interference with the continuity of the wax surface.

It is therefore an object of the present invention to produce a moistureproofing coating composition in which all constituents are in solution and which contains a solvent soluble slip

agent which will be somewhat incompatible with the other constituents of the coating in its final dry state.

It is another object of this invention to produce a transparent, non-fibrous sheet or film containing a moistureproofing coating comprising a solvent soluble slip agent, which sheet or film will be substantially non-adherent at elevated temperatures.

Other objects of the invention will appear hereinafter.

The objects of the invention may, generally, be attained by the use of a moistureproofing coating composition containing a solvent soluble organic compound containing a metal substituted for an enolic hydrogen, said compound being completely soluble in the liquid composition but not completely compatible with the other constituents of the composition in its final dry state and which will therefore be present in a distinct phase from that of the main body of the coating.

Although any organic compound containing a metal substituted for an enolic hydrogen can be used provided it has the above solubility and compatibility requirements, the following test sets forth a convenient method for determining the requisite characteristics of the most useful substances:

First, test the solubility of the substance in toluene at room temperature, or approximately 25° C. To function as a slip agent in the sense of this invention, it must be soluble to the extent of 1% or more. Second, place 0.5 gram of the material in a test tube, add 25 cc. of acetone, place a stopper in the tube and shake. In this test also the temperature of the solvent should be approximately 25° C. To function as a slip agent, the material must be partially or completely insoluble. If it is completely soluble, it will not function as a slip agent.

It is desirable that the slip agents separating in a distinct phase from the coating composition upon the removal of the solvent shall have approximately the same optical characteristics as the coating composition itself. It therefore should preferably be substantially colorless (or at least colorless in the concentration present in the final film) and have approximately the same index of refraction as the coating composition, such that the resulting product will appear transparent. The materials of the present invention are well suited for this purpose. The following examples which are to be considered illustrative and not limitative will assist in an understanding of the invention.

The solvent soluble slip agents of the present invention should preferably have the characteristic of raising the "stick temperature" (defined in detail below) of the coating composition above 55° C.

For the purposes of comparison and definition, the following test is used to determine the stick temperature: A web of the material to be tested is moved across a table top and below a brass block with a surface of contact measuring 3½x1¼ inches, and weighing 500 grams, at the uniform rate of 2 meters per minute. The temperature of the brass is slowly raised at the rate of about 7° C. per minute, and the frictional drag upon the film observed. This frictional drag at low temperatures is about 50-100 grams; at some elevated temperature it increases suddenly to several thousand grams, and the temperature at which this occurs is taken as the stick temperature.

As the enolic compounds of the present invention the metal substituted beta-diketones aluminum acetyl acetone, zinc acetyl acetone, calcium ethyl acetoacetate, aluminum ethyl acetoacetate, and aluminum ethyl malonate may be used.

The following table gives the compositions of coating baths containing enolic compounds which have been found to give excellent surface conditions and transparency when applied to transparent regenerated cellulose film. In each case the stick temperature, as above defined, will be found given. Parts are parts by weight.

Table

| Material                                  | Example number |     |     |       |     |
|-------------------------------------------|----------------|-----|-----|-------|-----|
|                                           | 1              | 2   | 3   | 4     | 5   |
| Zinc acetylacetone.....                   | 2              |     |     |       |     |
| Aluminum acetylacetone.....               |                | 10  |     |       |     |
| Calcium ethylacetoacetate.....            |                |     | 1   |       |     |
| Aluminum ethylacetoacetate.....           |                |     |     | 2, 3  |     |
| Aluminum ethyl malonate.....              |                |     |     |       | 4   |
| 11.6 percent nitrogen nitrocellulose..... | 52             | 48  | 52  | 52    | 52  |
| Paraffin wax.....                         | 3              | 3   | 3   | 3     | 3   |
| Dibutyl phthalate.....                    | 15             | 13  | 15  | 15    | 15  |
| Dicyclohexyl phthalate.....               | 15             | 13  | 15  | 15    | 15  |
| Modified rosin.....                       | 13             | 13  | 14  | 12, 7 | 11  |
| Ethyl acetate.....                        | 440            | 440 | 440 | 440   | 440 |
| Toluene.....                              | 271            | 271 | 271 | 271   | 271 |
| Ethyl alcohol.....                        | 22             | 22  | 22  | 22    | 22  |
| Stick temperature, ° C.....               | 75             | 79  | 81  | 75    | 80  |

The material which is added as a slip agent to the coating composition may also contribute other valuable properties to the coating. For instance, aluminum acetyl acetone may contribute to the body of the coating and serve to a certain extent as a blending agent for the wax and the nitrocellulose. In other cases the slip agent added may aid in softening and plasticizing the coating. Advantage may be taken of such properties to so modify the coating composition as to effect a saving in some of the other ingredients such as resin, blending agent, and plasticizer.

The slip agents of the present invention may be incorporated by any suitable method, preferably by dissolving in a suitable solvent such as toluene and then incorporating the remaining ingredients, including solvents, of the moistureproofing composition. Alternatively, the slip agents of the present invention as well as previously known insoluble slip agents may be introduced by the following method:

Cellulose nitrate in any form such as powder, flake, fiber or the like, is immersed in an aqueous solution of certain water soluble salts, such as aluminum sulfate or zinc acetate. This is then followed by treatment with a solution such as ammonium hydroxide or sodium abietate which precipitates an insoluble slip agent on the pyroxylin structure. The treated cellulose nitrate is dried or dehydrated with alcohol and used directly in preparing lacquer solutions. The method is very effective in producing moistureproof lacquers for regenerated cellulose film exhibiting good slip properties.

Still another general method of introducing silicon containing slip agents is represented by the following example. Silicon compounds, either organic such as ethyl silicate or inorganic such as silicon tetrachloride, which react with water or alcohol to precipitate silicic acid may be added to lacquers containing water and/or alcohol to produce a finely divided dispersion of silicic acid or an intermediate product of hydrolysis which is effective in producing lacquers with good slip.

The slip agents of this invention must be completely soluble in the solvent mixtures of the coating compositions, although they need not be soluble in every individual solvent of the solvent mixture. For this purpose any of the usual solvents and solvent mixtures familiar to one skilled in the art will serve. Generally speaking, the solvent will contain a cellulose derivative solvent and a wax solvent as well as a solvent for the resin and optionally a diluent. It is apparent that the same solvent may serve for two or more constituents and indeed, it may be that the cellulose derivative solvent will also be a wax solvent. The solvent mixture comprising 40-90% ethyl acetate, 10-50% toluene, and the balance ethyl alcohol will usually be found to operate satisfactorily. Depending on the amount and nature of the cellulose derivative, or the wax, or of the slip agent, etc., the amount and nature of the respective solvents will vary. Satisfactory solvents for the specific compositions are illustrated in the accompanying examples.

In the preparation of a transparent, moisture-proof wrapping tissue a suitable wax-containing composition comprising a cellulose derivative and a solvent soluble slip agent may be applied to the desired base in accordance with the methods known to the art. The solvents may be removed, and the coated material subjected to an elevated temperature at least equal to the melting point of the wax, whence a clear, transparent, moistureproof film may be obtained. The technique of this procedure is set forth in such patents as the Charch and Prindle Patent No. 1,737,187.

While this invention has been described in terms of a coating composition comprising a cellulose derivative and certain other constituents applied to a base film of regenerated cellulose or other materials, it will be understood that it is equally applicable to the preparation of self-sustaining films of cellulose derivatives which are formed by extrusion, or casting, or other means from a solution in which the desired slip agent is more soluble than in the resulting film.

Moistureproofing coating compositions may be used on various non-fibrous, transparent base sheets including sheets or films of regenerated cellulose, whether they be made by the viscose process, the cuprammonium process, or by any other manufacturing technique; cellulose ethers such as ethyl, benzyl or glycol cellulose; cellulose esters such as cellulose nitrate or cellulose acetate; lowly etherified or esterified materials such as lowly etherified ethyl cellulose, lowly etherified benzyl cellulose or lowly etherified glycol cellulose, and lowly esterified cellulose nitrate or lowly esterified cellulose acetate; gelatin, casein, or the like.

In preparing moistureproofing coating compositions comprising solvent soluble slip agents, it has been found that the best results are obtained by limiting the relative amounts of the several constituents. The amount of film-forming constituent, for example, may vary from 30-70% or more of the total solids although in most instances 50-60% is to be preferred.

The solvent soluble slip agent may be present in amounts of the order of 1-40% of the total solids, depending upon its compatibility with the rest of the constituents of the coating composition when in the final dry state. The amount of the solvent soluble slip agent used in a coating composition must be such that it will be completely soluble in the liquid coating composition but will, after removal of the solvent, separate at

least partially from the main body of the coating. Preferably it should be present in such a quantity that the separate phase will constitute only a small proportion of the total coating, such as 5% or less.

The wax content of these moistureproofing compositions may vary from 0.5%, or 1% to 10%, or more of the total solids content. Usually about 4% is satisfactory, although more or less may be found desirable for different purposes.

The amount of plasticizer may vary, of course, from none at all up to about 40 or 50% of the solids content of the composition.

The amount of solvent or solvent mixture may vary according to the composition and to the method of application, or purpose desired. The viscosity of the coating composition may be controlled by the amount or nature of the solvent and may be adjusted easily to adapt the solution for coating by brushing, spraying, dipping or any other methods familiar to the art.

Where percentages and proportions of ingredients are referred to throughout the specification and claims, they are intended to be percentages by weight, or parts by weight.

The surface conditioning agent of the present invention, when incorporated in coating compositions for use with transparent, cellulosic wrapping tissue, has been found to give a product which is eminently suited for use upon automatic wrapping machinery. For such use it is necessary that the tightly wound rolls of material supplied for use upon such machines unwind and deliver the film very smoothly and evenly through the machine. Even though rolls of such material have been tightly wound and stored at relatively high temperatures, it is found that there will be absolutely no sticking between the surfaces of the film, allowing it to unroll with great ease and freedom from tears, marred surfaces and other blemishes. It is furthermore essential that such material will pass evenly and smoothly through the whole course of the wrapping machine without adherence to various portions of said machine. Very often, certain heated elements form a part of such machines, said elements generally being used for the formation of heat seal at a certain stage of the wrapping operation. Should the adjacent parts of the machine become warm by conduction or convection of said heating elements, serious trouble may result in the operation of the machine by sticking of the wrapping tissue to these surfaces. The present invention produces a wrapping tissue which is far less likely to adhere to such surfaces than wrapping tissues previously available.

Where the coated wrapping tissue is in the form of sheets, said sheets may be stacked and stored for long periods of time without any appearance of adhesion between the sheets so stacked. Such sheets may be readily separated and handled manually or by machinery.

The method and materials of this invention produce an improved surface without adversely affecting clarity to the extent encountered in the use of the previously known insoluble slip agents.

In coating compositions giving moistureproofness, this moistureproofness is not affected so much by the solvent soluble slip agent as with previous insoluble slip agents.

The method of the invention has the very important advantage of giving a more uniform distribution of the surface conditioning agent throughout the coating bath which results in a

far more even distribution in the coating with the elimination of certain optical defects in the transparent film. Furthermore, it is possible to filter and purify the bath just before application to the film, making possible a very high grade product. Such filtration is not possible where the agent added is a dispersed solid so that large, solid particles and impurities that might occur in the bath at its later stages of preparation would remain to give trouble in the coating machinery and final product.

Not only may the use of the material be more precisely and rigidly controlled, but the disadvantages incident to sedimentation when the prepared bath solution is stored for a period of time, or transferred through pipes and under conditions which might cause the flocculation and sedimentation of a solid constituent are avoided.

Since many changes and modifications can obviously be made from the details of the above description without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited except as set forth in the following claims.

We claim:

1. A moistureproofing coating composition containing, dissolved in an organic solvent, a film-forming ingredient, a moistureproofing agent, such as a wax, and a beta-diketone of the formula  $Q-CO-CH_2-CO-R$ , in which Q and R represent alkyl or alkoxy groups, and which has a metal substituted for an enolic hydrogen, said compound having a solubility of at least 1% in toluene at a temperature of 25° C., and 0.5 gram of said compound being at least partially insoluble in 25 c. c. acetone at a temperature of 25° C., said compound being present in sufficient quantity to separate as a distinct phase after the removal of the solvent but in insufficient quantity to substantially impair the transparency of the coating.

2. A moistureproofing coating composition containing, dissolved in an organic solvent, a film-forming ingredient, a moistureproofing agent, such as a wax, and 1% to 40% (based on the solids content) of a beta-diketone of the formula  $Q-CO-CH_2-CO-R$ , in which Q and R represent alkyl or alkoxy groups, and which has a metal substituted for enolic hydrogen, said compound having a solubility of at least 1% in toluene at a temperature of 25° C., and 0.5 gram of said compound being at least partially insoluble in 25 c. c. acetone at a temperature of 25° C., said compound being present in sufficient quantity to separate as a distinct phase after the removal of the solvent but in insufficient quantity to substantially impair the transparency of the coating.

3. A moistureproofing coating composition containing, dissolved in an organic solvent, a film-forming ingredient, a moistureproofing agent, such as a wax, and a beta-diketone of the formula  $Q-CO-CH_2-CO-R$ , in which Q and R represent alkyl or alkoxy groups, and which has a metal substituted for enolic hydrogen, said compound having a solubility of at least 1% in toluene at a temperature of 25° C., and 0.5 gram of said compound being at least partially insoluble in 25 c. c. acetone at a temperature of 25° C., said compound being present in sufficient quantity to separate as a distinct phase after the removal of the solvent, but said distinct phase of the compound not exceeding 5%.

4. A moistureproofing coating composition

containing, dissolved in an organic solvent, a film-forming ingredient, a moistureproofing agent, such as a wax, and zinc acetyl acetone, said zinc acetyl acetone being present in sufficient quantity to separate as a distinct phase after the removal of the solvent but in insufficient quantity to substantially impair the transparency of the coating.

5. A thin, flexible, slippery, non-fibrous, transparent sheet provided with a moistureproofing coating containing a film-forming ingredient, a moistureproofing agent, such as a wax, and, as a slip agent in a phase separate from the main body of the coating, a solvent-soluble beta-diketone of the formula  $Q-CO-CH_2-CO-R$ , in which Q and R represent alkyl or alkoxy groups, and which has a metal substituted for enolic hydrogen, said compound having a solubility of at least 1% in toluene at a temperature of 25° C., and 0.5 gram of said compound being at least partially insoluble in 25 c. c. acetone at a temperature of 25° C., said compound being present in insufficient quantity to substantially impair the transparency of the sheet.

6. A thin, flexible, slippery, non-fibrous, transparent sheet provided with a moistureproofing coating containing a film-forming ingredient, a moistureproofing agent, such as a wax, and, as a slip agent in a phase separate from the main body of the coating, a solvent-soluble beta-diketone of the formula  $Q-CO-CH_2-CO-R$ , in which Q and R represent alkyl or alkoxy groups, and which has a metal substituted for enolic hydrogen, in an amount not exceeding 5% of the coating, said compound having a solubility of at least 1% in toluene at a temperature of 25° C., and 0.5 gram of said compound being at least partially insoluble in 25 c. c. acetone at a temperature of 25° C.

7. The method of producing a thin, flexible, slippery, high-stick temperature, transparent, moistureproof sheet which comprises applying to a transparent, non-fibrous base sheet, a moistureproofing coating composition containing in solution a film-forming ingredient, a moistureproofing agent, such as a wax, and a beta-diketone of the formula  $Q-CO-CH_2-CO-R$ , in which Q and R represent alkyl or alkoxy groups, and which has a metal substituted for enolic hydrogen, said compound being present in sufficient quantity to separate as a distinct phase after the removal of the solvent but in insufficient quantity to substantially impair the transparency of the coating, and drying said coating composition whereby to cause said compound to separate as a distinct phase from the main body of the coating.

8. The method of producing a thin, flexible, slippery, high-stick temperature, transparent, moistureproof sheet which comprises applying to a transparent, non-fibrous base sheet, a moistureproofing coating composition containing in solution a film-forming ingredient, a moistureproofing agent, such as a wax, and 1% to 40% (based on the solids content) of a beta-diketone of the formula  $Q-CO-CH_2-CO-R$ , in which Q and R represent alkyl or alkoxy groups, and which has a metal substituted for enolic hydrogen, said compound having a solubility of at least 1% in toluene at a temperature of 25° C., and 0.5 gram of said compound being at least partially insoluble in 25 c. c. acetone at a temperature of 25° C., and drying said coating composition whereby to cause said compound to

separate as a distinct phase from the main body of the coating in an amount not exceeding 5%.

9. A moistureproofing coating composition containing, dissolved in an organic solvent, a film-forming ingredient, a moistureproofing agent, such as wax, and organic compound containing a metal substituted for enolic hydrogen, said compound being from the group consisting of aluminum acetyl acetone, zinc acetyl acetone, calcium ethyl aceto acetate, aluminum ethyl aceto acetate and aluminum ethyl malonate and being present in sufficient quantity to separate as a distinct phase after the removal of the solvent but in insufficient quantity to substantially impair the transparency of the coating.

10. A thin, flexible, slippery, non-fibrous, transparent sheet provided with a moistureproofing coating containing a film-forming in-

redient, a moistureproofing agent such as a wax, and organic compound containing a metal substituted for enolic hydrogen, said compound being from the group consisting of aluminum acetyl acetone, zinc acetyl acetone, calcium ethyl aceto acetate, aluminum ethyl aceto acetate and aluminum ethyl malonate and being present in an amount not exceeding 5% of the coating.

11. A thin, flexible, slippery, non-fibrous, transparent sheet provided with a moistureproofing coating containing a film-forming ingredient, a moistureproofing agent such as a wax, and, as a slip agent in a phase separate from the main body of the coating, zinc acetyl acetone in an amount not exceeding 5% of the coating.

ROBERT B. FLINT.  
JAMES A. MITCHELL.