CONTAINER WITH CLEAVABLE COATING ON INTERIOR SURFACE

Filed June 6, 1956

Fig. 1

Fig. 2

Fig. 3

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CONTAINER WITH CLEAVABLE COATING ON INTERIOR SURFACE

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This invention relates to cleavable release coatings and particularly pertains to coating compositions for application to the inside walls of fiber board containers, and to such containers having coatings on the inner walls.

A general object of the invention is to provide improved release coatings and coating compositions, and specific objects include the provision of coatings and coating compositions which are less costly, which are effective in decreased thickness, which are highly heat resistant, both in that the coating itself is not adversely affected by high temperatures and in that the container itself is protected from damage from high temperatures of the contained material by the coating, which do not crack or peel away from the container wall material, which are more easily applied to the container wall material, which permit rolling or stacking of coated material on itself with minimized sticking of the coated face to the next layer of material, which do not undesirably contaminate the product which it is desired to package in the container, and which cleave within the coating to release the product from the container.

The invention finds special applicability to the art of packaging asphalt, and other materials which present similar packaging problems, for example, resins and bitumens generally, latex, and the like, such as may be termed meltable gummy solids, and which are ordinarily melted at elevated temperatures for pouring into the containers and thereafter permitted to cool and solidify.

While fiber board cartons and drums seem presently to offer the most satisfactory and economic containers for asphalt and similar products, it will be understood that the coatings of this invention may be used on wooden barrels or on containers made of other materials and of other types of construction.

Many release coating mixtures have been heretofore proposed, among which are, for example, wax emulsions containing, typically, bentonite, emulsifying agents and graphite, and various starch-containing mixtures. The coatings formed of such prior art mixtures, however, have left much to be desired, in that clays of acceptable quality are expensive, in most instances considerable thickness of the coating has been necessary, the resistance to cracking and peeling away of the coating has been low, necessitating great care in handling of the coated containers, the coatings have been difficult and expensive to apply and often ineffective for the intended purpose, or the coating was itself destroyed by hot materials or proved ineffective to protect the container from damage from hot materials. A particularly difficult problem has been the provision of a coating which will stand up and which will protect the container when the container is filled with hot dead-level asphalt.

The novel features which are believed to be characteristic of this invention are set forth with particularity in the appended claims. The invention itself, however, both as to its organization and method of operation, together with further objects and advantages thereof, may best be understood by reference to the following description taken in connection with the accompanying drawing, in which:

FIG. 1 is an isometric view of a container of a type useful in this invention;

FIG. 2 is a fragmentary sectional view of a portion of a container wall having a coating thereon in accord with this invention; and

FIG. 3 is a fragmentary sectional view of a portion of a container wall having a double coating thereon in accord with a modification of this invention.

As seen in FIG. 1, container 1 comprises a kraft fiber box or carton adapted to contain asphalt or the like. In accord with the invention, the inner walls 2 of the container are coated with a cleavable coating, whereby the container may be torn away from a contained hard block of asphalt when it is desired to use the asphalt, as at a construction site. End wall top flaps 3 and side wall top flaps 4 are also preferably coated with the cleavable coating.

The container is typically formed of a double wall flute kraft board 5 as seen in FIG. 2 and carries a coating 6 comprising, as later described in detail, a synthetic resin binder material having small solid particles dispersed therein. The exposed coating surface 6' has characteristic tackiness, at least at elevated temperatures, and bonds or adheres to the material to be contained by the container.

FIG. 3 discloses a modification of the invention wherein solid kraft fiber board wall 7 carries a base or bottom coat 8 of a synthetic plastic in which are dispersed small solid particles and, in overlying relation to the base coat, a top coat 9 of a synthetic resin having an exposed surface 9' which is presented to the material to be contained in the container of which the walls are formed of board 7.

The surface 9' is preferably non-tacky and hard at room or atmospheric temperatures, but becomes tacky at elevated temperatures.

It has been found that certain substances hereinafter employed in release coating formulations can be profitably employed in the present invention, but certain important departures from previous teachings have resulted in a much improved coating, which can be deposited at a rate as low as six pounds per one-thousand square feet and yet function effectively, which is substantially less costly than the most nearly comparable coating, and which will, in accord with preferred embodiments of this invention, operate satisfactorily not only to release hot dead-level asphalt poured into the container at about 400° F. but also to protect the container from damage from the high temperature of the contained asphalt.

Either of two systems may be employed in practicing this invention, a single coat system, as shown in FIG. 2, or a double coat system, as shown in FIG. 3. In the former, a single coat 6 may be spread by any of several methods on the surface of the wall material, which may be, typically, either double wall corrugated or solid kraft fiber board. The coating material, as spread, will comprise a slurry wherein water is employed to carry in emulsion a binder material, such as an acrylic resin, and in suspension, small particles of solid materials as further explained hereinafter. The material may also comprise subsidiary chemicals for performing, for example, wetting, defoaming, thickening, coloring, and plasticizing functions.

A preferred formulation for a coating material for
3

single coat application to graft fiber board comprises the following in parts by weight:

<table>
<thead>
<tr>
<th>Component</th>
<th>Parts by weight</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>80</td>
<td>Base fluid carrier.</td>
</tr>
<tr>
<td>Polyphosphate (water dispersion)</td>
<td>4.0</td>
<td>Wetting agent.</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>3.0</td>
<td>Stiffener.</td>
</tr>
<tr>
<td>Carbon black (water dispersion)</td>
<td>4.0</td>
<td>Coloring and cleavage.</td>
</tr>
<tr>
<td>Green slate</td>
<td>50</td>
<td>Cleavage.</td>
</tr>
<tr>
<td>Talc (50 mesh)</td>
<td>20</td>
<td>Do.</td>
</tr>
<tr>
<td>Muscovite mica (1,000 mesh)</td>
<td>20</td>
<td>Do.</td>
</tr>
<tr>
<td>Acrylic resin (water dispersion)</td>
<td>7.8</td>
<td>Binder.</td>
</tr>
<tr>
<td></td>
<td>94.4</td>
<td>129.6</td>
</tr>
</tbody>
</table>

In the formula of Example I, the water acts as a carrier for the solids and the polyphosphate and calcium stearate disperse in the water, the resin in the water, and the carbon black, green slate, talc and mica comprise discrete solid particles in the slurry, suspended in the water. The amount of water is, of course, variable to provide a more dense or less dense slurry, with more or less flow, as required in the particular method of applying the slurry. This may be accomplished by preparing the slurry by a simple method, although sufficient water should be included to carry the solid particles in free suspension. The water dries from the finished coating, and in the slurry the water serves primarily as a medium for retaining the other materials in mechanically spreadable form or condition.

The amount of polyphosphate is governed primarily by the amounts and nature of the solid particles which must be wetted to provide a suspension. Accordingly, in Example I, sufficient polyphosphate is included to insure wetting of the carbon black, green slate, talc and mica particles. It should be understood that in the preparation of slurries in accord with this invention only a sufficient amount of wetting agent should be employed to decrease the surface tension of the water to the point at which substantially all of the solid particles become wetted.

The polyphosphate wetting agent actually employed in the formula of Example I was a mixture of hexametaphosphate and heptametaphosphate, but sodium hexametaphosphate, sodium salt of alkyl aryl sulfonate plus sulfate, polyhydroxyalcohols, and certain sulfates and phosphates of higher synthetic alcohols have been found entirely satisfactory when used alone, or in combination of two or more, in approximately equivalent quantities, that is, quantities that provide approximately the same reduction in surface tension of the solution. Since certain grades and sizes of the solids employed in the formula may be more or less difficult to wet, it is appropriate to increase or decrease the amount of wetting agent accordingly as is well known in the art. It will be understood that the wetting agents mentioned are typical, and that these or other wetting agents compatible with the other materials of the slurry may be employed as desired in the formula of Example I and in the slurries hereinafter specified.

The carbon black provides coloring which is particularly appropriate in the packaging of asphalt or other black or nearly black materials. It has been found also that carbon black assists the internal cleavage action of the coating, and if carbon black is omitted or, as, for example, when a black color is not desired, it may be found desirable slightly to increase the amount of one or more of the other cleavage solids, such as the green slate, talc or mica. Alternatively, if increased blackness of the coating is desired, the quantity of carbon black may be increased and the quantity of one or more of the other cleavage solids may be accordingly slightly decreased.

Economic considerations dictate that no more than the minimum amount of carbon black be employed to provide the necessary coloration, and economics may further require that some of the blackening function be performed by the graphite, preferably in the form of small flakes of the order of 325 mesh. Thus it has little effect on the action of the coating if graphite flakes are substituted for part or all of the carbon black, or even if up to a few parts of graphite are substituted for a minor portion of one or more of the cleavage solids. A specific formula comprising substantial amounts of graphite and bentonite clay, for example, is given hereinafter in Example II.

The internal cleavage function is obtained primarily because of the inclusion of the coating of what are herein referred to as cleavage solids, and these solids in the above formula comprise green slate, mica and talc, although, as explained, the cleavage function is further aided by the carbon black and would be aided by any added or substituted flake graphite.

While the use of talc in release coatings has been previously suggested, the function of the talc in the present invention differs from that in previous proposals. Mica has been used as a protective coating to a painted surface in certain wax coating formulations to increase the viscosity of the wax and to bridge over pores in the wax film. The primary functions of the muscovite mica (as distinguished from phlogopite mica, for example, which has a different chemical structure and crystalline shape) in the present release coating, however, are to provide heat insulation and aid in internal cleavage or film splitting characteristics. Unexpectedly superior results have been obtained with coatings comprising a high proportion of clean green slate, which it has been found functions to assist the cleavage characteristics and the heat insulating characteristics of the mica and talc, while permitting a substantial reduction of the amounts of relatively costly talc and mica.

The inclusion of green slate in the coating formulations herein described makes unnecessary the inclusion of the relatively much more expensive clay heretofore employed in many release coatings in relatively large proportions to give body and spreadability to the coating slurry. It has been found important that the amount of sand, even in finely ground state, be maintained at a minimum in the coating, since even a very small percentage results in rapid settling out of the particles suspended in the slurry, thereby seriously reducing the internal cleavage of the resulting coating, and since small quantities of sand further result in severe erosion of equipment. Sand-free clay is, of course, much more costly than the usual commercial grades. It is possible to formulate excellent release coatings, however, which contain sand-free clay to replace a few parts of any one of the three primary cleavage solids of the formula of the above table.

The theory of many prior release coatings has been to provide a coating to which the packaged material, such as resin, asphalt, or latex, will not adhere. The coatings of the present invention, however, are designed to adhere to the packaged material, at the upper face of the coating film, and to adhere strongly to the container wall at the wet surface of the film. Release action is obtained by cleavage within the film itself.

Unlike previous release coatings, the binder employed in this invention is both bendable and tacky after drying and after completion of any polymerization. The tack characteristics of the coating of Example I are imparted by the acrylic resin, and a result should be exhibited high tackiness at temperatures above about 150°F. to 170°F. but which has little tackiness below such temperature. A coating having the mentioned tackiness characteristics can be applied to the fiber board and dried thereon and the board may then be rolled without appreciable resulting sticking together of the turns of the roll, but when the container is formed and is introduced into the container, the coating is raised in temperature by the asphalt above the temperature at which the
coating exhibits sufficient tackiness to adhere to the asphalt. To prepare a coating composition in accord with the formula given above, the wetting agent or agents are first added to the proper amount of water, with slow agitation, and then the carbon black is next added. With the addition of the green slate, mica and talc, the speed of the agitator is increased to between about 600 to 1000 r.p.m. for a commercial agitator, thereby to provide thorough mixing and smooth consistency. Finally the binder material is added with continued high speed agitation. A certain amount of foam is normally to be expected and this foam is preferably reduced or eliminated by spraying with anti-foaming agents, such as a sulfonated oil or a naphtha. The amount of anti-foaming agent required will be negligible, has been found not to affect the final coating in any noticeable way, and its use is advisable only for making the handling of the slurry more convenient and to eliminate the waste and extra handling which would otherwise result from mechanical removal of the foam.

Costing material prepared in the specified manner in accord with the formula of Example I was spread by flowing on the upper surface of a length of corrugated kraft fiber board, the board being fed under a wiper roll to limit the coating thickness. The costing material thickness was such as to contain substantially 8–10 pounds dry weight of material per one thousand square feet of coated surface. After drying for approximately two minutes at 300° F. and conditioning at 72° F. at 50% relative humidity for two hours, the coating solids were measured, the coated fiber board was formed into containers and the containers were filled with dead-level asphalt at about 400° F. The filled containers were then held for two hours at 250° F. and thereafter permitted to cool. At atmospheric temperatures thereafter the containers were torn away from the solid asphalt blocks which had formed inside. The fiber board came away readily and completely from the asphalt and the inner surface of the container walls was found to be still covered by a film of the coating. Even at corners of the container, no fibers of the kraft paper board had become adhered to the asphalt. The surfaces of the asphalt block were a dull very dark gray, almost black, indicating that a portion of the coating had become bonded to and remained on the asphalt.

It is believed, from the results of tests, from microscopic examinations and from theoretical analysis of the facts developed from the studies of the present and other coatings, that the muscovite mica which is included in the mud is primarily responsible for the excellent internal cleavage characteristics of the coating film. It is also clear that the acrylic resin binds the coating securely to the fiber board surface and tends to strengthen the surface by impregnation of the fibers, and that it causes adherence of the film surface to the asphalt or other packaged material. Muscovite mica comprising very small plate-like particles so reduces the internal strength of the coating film that the film may be cleft between its inner and outer surfaces. This cleavage action is aided appreciably by the inclusion of green slate as one of the solid components, although it would be expected that green slate, like sand, would greatly reduce the cleavage or release characteristics. It has been found that the amount of green slate may not greatly exceed approximately the combined amount of mica and talc without some reduction of desired cleavage characteristics. Green slate may be introduced up to approximately 70% of the total solids weight if the percentage of muscovite mica is maintained at least 14% to produce a useful coating with good cleavage action. The introduction of green slate up to about 40% of the total weight of the total solids in suspension permits some reduction in the amounts of much more costly talc required, thereby providing a substantial reduction in overall costs over a coating with a high percentage of talc. Reduction in the proportion of talc may also be accomplished by the substitution of certain types of sand-free clay, and it has been found that the use of a kaolinite type of clay comprising particles in the form of flat plate crystals, such as that mined near McIntyre, Georgia, and sold by Edgar Brothers Company of McIntyre, Georgia, as type ASP 900, having a particle size of about 2 microns, which is used to replace part or all of the green slate, permits a reduction in the amount of talc and a slight reduction in the amount of mica below the proportions given in Example I, as is more particularly exemplified hereafter in specific formulas.

The talc, green slate and mica all contribute to the heat insulating properties of the film, which resulted in the avoidance of any damage to the fiber board in the herein above described experiment from 400° F. asphalt, for example. The green slate and talc seem to become oriented between plates of mica in a manner such that the heat insulation obtainable is comparable to that of a coating of equal thickness, and of the same total solids content, but in which mica was substituted for the talc and green slate.

Example II

As a second example of a single release or cleavage coating material, a slurry may be prepared as outlined above having the following formula:

| Water | 80 |
| Water | 1.0 |
| Ammonium | 0.1 |
| Zern dispersion | 0.8 |
| Clay (ASP 900) | 80.0 |
| Mica | 10.0 |
| Ardent | 2.0 |
| Acrylonitrile and methacrylate copolymer resin binder | 50.0 |
| Polyacrylate | 1.0 |
| 20% Zein | 5.0 |
| 40% solids | 40.0 |

tions executed in this invention is as follows:

Example III

It will be seen that the two formulas last set forth include somewhat less mica than the first formula, and that in each later instance a different binder resin is specified. Thoroughly satisfactory results are obtained with the slurries of Examples II and III spread and dried as described above at a rate to form a coating of between 6 to about 12 or 14 pounds dry weight of solids per 1000 square feet of coated container wall surface. It will be seen, accordingly, that the minimum weight of mica per 1000 square feet in a coating comprising between 7 and 8% of mica would be approximately 0.45 or 0.50 pound. More economic and higher quality coatings comprise from about 12% mica to 20% mica, giving about one pound of mica per 1000 square feet of surface. As herein explained, the percentage of mica which can be employed with good results reaches a maximum practical limit of approximately 40% and a coating of 12 or 13 pounds per 1000 square feet might, accordingly, comprise about 5 pounds of mica per 1000 square feet.
While coatings thicker than 12 pounds per 1000 square feet would be operative, economics dictates that the coating thickness should be no more than at this rate but should be as thin as experience may prove acceptable for economic reasons. Since from about 60% to 92% of the total solids weight may be cleavage, filler or release solids other than mica, the total weight per 1000 square feet for these materials may range from about 3.5 pounds to about 12 pounds.

For hot dead level asphalt the coating is generally somewhat thicker than for mopping asphalt and depending largely on the maximum temperatures involved. Thus, while a coating of only 3 or 4 pounds per 1000 square feet might suffice if the coating contains at least about 14% mica for materials poured into the container at 175° F. and 200° F. dead level asphalt introduced at 375° F., for example, would require a minimum of about 8 or 10 pounds per 1000 square feet and the formula for the coating should comprise somewhat more than 8% of mica and should further comprise a resin which is not destroyed when heated to the region of 375° F. to 400° F. Double coats as herein are generally preferred to single coats in high temperature dead level asphalt packaging. While approximately 10 parts of resin emulsion is specified in each of Examples I, II and III, the parts of resin may be substantially increased, for example, to about 20 parts, without thereby reducing the effectiveness of the coating. Increasing the parts of resin binder above about 10 parts may be found necessary or desirable to reduce any flaking of the coating which may be encountered.

The “Mineralite” mica of the muscovite type as employed in the coating compositions of this invention should be of very fine mesh. Specifically, excellent heat insulation and cleavage characteristics of the coating and good spreading characteristics of the slurry are obtained with 1000 mesh mica, but appreciably less readily spread and less stable slurries and less effective coatings result from the use of mica having particle sizes greater than sizes corresponding to 325 mesh and particles as large as 250 mesh are not suitable, best results being obtained with particles of about 1000 mesh or smaller, such as 3000 mesh.

The “Mineralite” mica of the muscovite type is characterized by the fact that its individual particles are of a scale-like crystalline shape. It is believed that this physical characteristic is closely tied in with the excellent cleavage characteristics exhibited by the coatings under discussion. The chemical analysis of these mica flakes is approximately as follows:

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>56.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>29.6</td>
</tr>
<tr>
<td>K₂O</td>
<td>6.9</td>
</tr>
<tr>
<td>CaO</td>
<td>1.1</td>
</tr>
<tr>
<td>MgO</td>
<td>0.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.15</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.5</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.05</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>2.5</td>
</tr>
</tbody>
</table>

A specific mica which has proved highly satisfactory is mineralite mica manufactured by Mineralite Sales Corp., 90 Pine Street, New York 5, N.Y., as Mineralite 5X (1,000 mesh), Mineralite 3X (250 mesh) and Mineralite 4X (1,000 mesh). Such mica is within the chemical requirements given above.

The clay provided in Examples II and III is of the flat platened crystal type such as is found at and near McIntyre, Georgia, and which is commercially available as Edgar Brothers Company, McHenry, Ill., type ASP-900 (2 micron size particles) and type ASP-400 (3 micron size particles). Example II shows the use of 80 parts of clay and only 9 parts of mica. It has been found, as will be understood from a comparison of this example with others given herein, that this clay is superior to talc or other cleavage or filler materials in making the mica effective as an anti-caking and heat insulating properties, and, while clay alone, without mica, does not provide the desired results, the amount of mica may be substantially reduced with use of substantial amounts of flat plate crystal clay and flake graphite without thereby appreciably affecting the coating or the properties of the coating. In Example II, mica comprises only about 8% of the total solids. Because of economic considerations it is found to be impractical to decrease the amount of mica to this minimum percentage, and better results are obtained and a less costly coating can be prepared if mica is included at not less than 10% or 12% of the total solids.

Green slate, sometimes called mineral stabilizer, useful in this invention comprises that mica mined near Fairmount, Georgia, of 325 mesh and sold by F. J. Funkhouser & Company, 138 W. Washington St., Hagerstown, Md.

Suitable tales are those of 325 mesh mined near Chatsworth, Georgia, and sold by Whittaker, Clark and Daniels, 260 Broadway, New York, 13, N.Y., as No. 1648 and No. 1767, and those mined near Alpine, Alabama, and sold by Whittaker, Clark and Daniels, as "Chatal" Tale No. 2952 and Tale No. 2953, the last mentioned, however, being of 200 mesh and somewhat less desirable in this invention.

Graphite No. 1132 sold by Jos. Dixon Crucible Co., Wayne & Monmouth Streets, Jersey City 3, N.J., is a commercially available 325 mesh graphite, and graphite No. 6580 is a 425 mesh graphite obtainable from the same source, each of which is adapted for use in this invention.

A black or graphite, or a combination thereof. In accord with this invention, a base coat so constituted, as more particularly described herein, is generally preferred to one containing graphite or some other material which is not compatible with the binder materials.
The preparation of this emulsion slurry is as described in connection with Example I, and an anti-foaming agent, as before, may be used in the course of mixing.

A base coat formulation yielding comparable excellent results is as follows:

### Example V

<table>
<thead>
<tr>
<th>Component</th>
<th>Parts by weight</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>90</td>
<td>Carrier</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>6</td>
<td>Glue</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>2.5</td>
<td>Stabilizer</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>1</td>
<td>Stabilizer</td>
</tr>
<tr>
<td>Carbon black</td>
<td>0.5</td>
<td>Coloring and cleavage</td>
</tr>
<tr>
<td>Muscovite mica</td>
<td>1</td>
<td>Cleavage and filler</td>
</tr>
<tr>
<td>Acrylic resin</td>
<td>1</td>
<td>Binder</td>
</tr>
<tr>
<td>Green slurry (600 mesh)</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Acrylic resin</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

In the above Example V, in place of the 35 parts of mica and 80 parts of green slate, one may use 25 parts of mica, 25 parts of talc (425 mesh) and 67 parts of green slate, or one may use 35 parts of mica and 65 parts of talc.

As a further alternative the base coat formulation may comprise the parts of water, wetting agents, calcium stearate and resin binder specified in Example IV and Example V, but with 22 parts of carbon black dispersion (11 parts of carbon black in 11 parts of water) and 55 parts of mineralite mica (10 mesh). Since carbon black and muscovite mica are more expensive than talc or clay, and much more expensive than green slate, it will usually be found desirable to include at least 60 parts of green slate, and, in order to insure maintenance of the excellent cleavage characteristics, to include a minimum of approximately 12% of mica.

Excellent cleavage characteristics of coating 8 are maintained with increased parts of muscovite mica in the formulas of Examples IV and V, with reduction of the parts of other solid constituents, but a noticeable and undesirable tendency of the mica to thicken the slurry to a dough-like consistency occurs when the proportion thereof is increased to more than approximately 40 parts, or to more than approximately 40% of the total solids.

In Example VI, the butadiene-styrene copolymer should be of the type having lower styrene percentages, that is, a styrene-butadiene ratio of 6-4 or 5.5-4.5. In the example given, the resin emulsion which is added forms a finished resin after setting and drying weighing 48% of the emulsion. As in the other examples given herein, the materials are listed in the preferred order of addition to the mixing vat, water being first placed in the vat and the remaining materials being thereafter introduced and mixed in the order indicated, although the order may be varied as desired. The wetting agents of Example VI will comprise, preferably, as added, a few parts of water, as may several other ingredients, whereby the final slurry may comprise some 90 or 100 parts of water. The amount of water may vary in different applications to produce a slurry of the desired flow characteristics for coating the specific composition material with a coating of the desired thickness using the specific coating machine available. The amount of water specified is sufficient to suspend, dissolve and emulsify the specified quantities of the materials, however, and is appropriate to provide a slurry of substantially the correct spreadability for application to Kraft paper board by means of a wiper roll spreading machine.
Example VII

<table>
<thead>
<tr>
<th>Parts by weight</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>80</td>
</tr>
<tr>
<td>Polyphosphate</td>
<td>0.1</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>0.3</td>
</tr>
<tr>
<td>Clay (ASP-900)</td>
<td>70</td>
</tr>
<tr>
<td>Graphite</td>
<td>24</td>
</tr>
<tr>
<td>Muscovite mica</td>
<td>34</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>70</td>
</tr>
<tr>
<td>Acrylic resin emulsion (60%) (Rohm &amp; Haas WN-80)</td>
<td>10</td>
</tr>
</tbody>
</table>

1 Solid weight.

Example VIII

<table>
<thead>
<tr>
<th>Parts by weight</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>80</td>
</tr>
<tr>
<td>Polyphosphate</td>
<td>0.1</td>
</tr>
<tr>
<td>Polyvinyl acetate</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbon black</td>
<td>4</td>
</tr>
<tr>
<td>Green color</td>
<td>24</td>
</tr>
<tr>
<td>Muscovite mica</td>
<td>34</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>70</td>
</tr>
<tr>
<td>Acrylic resin emulsion (60%) (Rohm &amp; Haas WN-80)</td>
<td>10</td>
</tr>
</tbody>
</table>

Several types of plastic or latex compositions have been found to be useful in base coat formulations for a double coat process and, in general, these types are useful in preparing a slurry for single coat application.

A number of base coats, such as Example IV and V, and the binder material may comprise acrylic resins, such as polymerized acrylic acid, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, or mixtures thereof, or other polymerized acrylic resins of similar characteristics. The lower alkyl polyacrylates are generally softer than is desired, and polyvinylmethacrylates are preferred. Binders having the desired characteristics for use in bottom or base coat formulations and for use in single coat formulations, may be prepared by the combining of an acrylate or methacrylate resin with sufficient lower alkyl polyacrylates to provide a coating which exhibits tackiness at temperatures above about 170 degrees F., but which, at lower temperatures, possesses the characteristic hardness of acrylic resins. As later explained acrylic-methacrylate copolymers form sufficiently hard films to be useful as top coats in a double coat application.

Single coats and base coats, in Examples I, II, III, IV and V may comprise an acrylic resin combined with any of several other types of resins. Specifically, 1 part of a lower alkyl polyacrylate with 10 parts of acrylonitrile-methacrylate copolymer is suggested in Example II, and vinylidene chloride-acrylonitrile copolymer is useful with plasticizers selected to reduce the film hardness. Care should be taken, however, that the plasticizer does not cause the material to be destroyed by the tempera-tures of the material to be packaged. On the other hand, 4 parts of vinylidene chloride to 1 part of acrylonitrile copolymer with little or no added plasticizer provides an excellent hard top coat.

Examples of acrylic resin copolymer and polyvinyl acetate copolymer emulsions which are commercially available and are suitable for bottom coats or single coats are ACS-66, WN-77 and WN-80 manufactured by Rohm & Haas, Washington Square, Philadelphia 5, Pa. These emulsions may be employed with plasticizers to provide sufficient softness and tack for bottom or single coats, but the AC-33 is sufficiently soft and tacky without any added plasticizer, while the nonionic acrylic resin emulsion WN-80 and polyvinyl acetate emulsion WN-77 may be used as the top coating material. Walpol-9301 supplied by Reichold Chemical Co., Inc., 525 N. Broadway, 3,085,731 White Plains, N.Y., is a polyvinyl-acetate homopolymer which provides a satisfactory base or single coat. This material should be combined, however, with a plasticizer to reduce brittleness and impart tackiness, for temperatures of about 170°F, and above, such as dibutylphthalate or other compatible tacky alkyd resins.

It is important to control and limit the amounts of alkaline salts in the slurry when using acrylate, methacrylate and some other acrylic resins, since it has been found that swelling of the resin may occur, and that a gel may be formed in the slurry, and further, that very soft film may result. Thus the mica, talc, clay, slate and other ingredients should be selected to comprise a minimum of alkaline salts.

Example III indicates that butadiene styrene copolymers are useful in single coats, and it has been found that they are also useful in base or bottom coats and in top coats. Top coats require materials of the higher styrene percentages, i.e. more than 60% styrene, but materials of lower styrene percentages, such as Plu 101A, Plu 102 and Plu 160, which are approximately 40% to 45% butadiene—60% to 55% styrene emulsions supplied by Goodyear Tire and Rubber Co., 224 W. Third Street, Akron 16, Ohio, are well adapted for use in bottom or single coats. 40% butadiene—60% styrene emulsions, as exemplified by 512-K and 512-R of Dow Chemical Co., Midland, Mich., are satisfactory as bottom or single coats, as are the Chemigum 236 and Chemigum 246 butadiene-acrylonitrile emulsions of Goodyear Tire and Rubber Co.

Top coats 9 exhibiting desired characteristics include, in general, the resins previously mentioned. More specifically, suitable top coat resins are vinyl chloride, such as Pluovic 300 supplied by Goodyear Tire and Rubber Co., vinyl acetates, and vinyl chlorides, which polymerize to form suitably hard, non-tacky top coat films. If the films formed of any of these resins are too brittle in the specific application, appropriate plasticizers may be added. In the case of the specific exemplary commercial product Pluovic 300, the vinyl chloride should be polymerized in the presence of a catalyst to form a latex or resin prior to emulsification, and a highly effective top coat material comprises a high proportion, i.e. 60%—65%, of vinyl chloride, with a relatively low proportion (40%—35%) of vinylidene chloride, plasticized with a modified polyacrylate. Excellent films are obtained with X-2102 emulsion supplied by Dow Chemical Co., an emulsion of from about 50% to 35% vinylidene chloride, with 50% to 65% vinyl chloride. Polyvinyl acetate-vinylidene chloride copolymers are also suitable for top coats. Vinylidene chlorides provide medium hard films, and are most satisfactory as a top coat when mixed with a harder material, such as, for example, a vinyl material. Copolymers of polyvinyl acetate-acrylonitriles and of vinylidene chloride-methacrylates form suitably hard film top coats, while acrylonitrile alone, which polymerizes naturally, may be employed, as may polyvinyl acetates of low molecular weights. A commercial example of a suitable polyvinyl acetate is Rohm & Haas WN-77 emulsion, which it is believed, comprises, with the acetate, an acrylate copolymer.

With respect to the use of vinyl chloride-vinylidene chloride chlorides in coatings in accord with this invention, it has been found that 20% to 70% vinyl chloride to 50% to 30% of vinylidene chloride is an acceptable range for top coatings. The vinyl chloride tends to impart toughness or hardness and tensile strength to the film, while more vinylidene chloride tends to increase the ease of spreading at lower temperatures and increases the water resistance and tack of the final coating. A top coat of not more than 40% vinylidene chloride suitably plasticized with chemical and polymeric plasticizers such as tri-ethylene glycol di-2 ethylhexylate, or with lower styrene butadiene-styrene copolymer emul-
sions, or with water-soluble plasticizers with high evapo-
ration tendencies. In the last mentioned case, the heat of
drying of the film facilitates evaporation and sub-
sequent fusion of the copolymer. Examples of such sol-
uble plasticizers are alcohols, such as glycerol or ethylene
glycol, or their derivatives such as diethylene glycol
monooethyl ether acetate. Approximately 10 to 35 parts
of the 100% plasticizer to 90 to 65 parts of the vinyl
chloride-vinylidene chloride copolymer is generally ap-
propriate. In certain cases, it may be found desirable to
harden the film and reduce its tackiness by the addition of a urea
formaldehyde type of resin. Such addition might be de-
sired, for example, with vinyl chloride-vinylidene chloride
copolymers wherein the vinyl chloride is in the range of
about 50%.

Vinyl chloride-vinylidene chloride may form a suitable
base coat or single coat if plasticizer, for example, with
synthetic latex.

An acrylic resin material useful as a top coat is sold by
Rohm & Haas as WN-77, and such material is ex-
emplary of polyvinyl acetate-acrylate copolymers which
form good top coats and which, with suitable plastici-
cizers, be used in a single coat or base coat formulation.

The high styrene butadiene-styrene copolymers, such as
Pilolite 170 furnished by Goodyear Tire and Rubber
Co., which comprises approximately 30% butadiene and
70% styrene, are useful either alone, or with other resins,
as top coat materials.

Polyethylenes of molecular weights between about 1500
and 6000 may be emulsified for use in top coats, al-
though polyethylenes of higher molecular weights are
not readily emulsifiable. Obtainable from Semet Solvay
Petroleum Division, Allied Chemical and Dye Corpo-
rated, 40 Rector Street, New York 6, N.Y., are solid
polyethylene AC-6 (molecular weight 2,000), AC-7;
AC-617 (molecular weight 1,500) AC-615 (molecular
weight 5,000) which may be emulsified and which are
useful as top coats.

Vinylidene chloride, 4 parts, to 1 part acrylonitrile
copolymer, acryloxy-methylmethacrylate copolymers, vinyl-
idene, chloroethylene-methylmethacrylate copolymers, and
acrylonitrile are also useful as top coats.

While each of Examples VI, VII and VIII provide
when applied an operable single coat on the container
wall, a superior coating for the wall results from the ap-
lication of a top coat to cover such single coat. A top
coat emulsion for spreading purposes is preferably prepared from
the slurry of any one of Examples I through VIII, but
which is particularly applicable to the base coating
formed by the slurry of Example VI, comprises, as Ex-
ample VI(a), 250 parts water, 6 parts starch, 1.5 parts
sodium alginate, and 100 parts 50% emulsion of
vinylidene chloride-acrylonitrile copolymer. In this
top coat mixture, the starch and the sodium alginate func-
tion only to thicken the mixture for more effective spread-
ing, and neither of these materials perform any useful
function in the finished coat. Upon filling a container so
coated with hot dead-level asphalt it seems probable that the
two thickening agents are destroyed, but whether or
not destroyed, the top coat bonds satisfactorily to the
asphalt and the base coat ceases in the desired manner.

Hence the small amount of starch present does not in
any way alter the cleavage function.

A top coat formulation specifically appropriate for ap-
lication over a base coat formed from Example VII,
but useful with the other base coats, if desired, com-
priases, as Example VII(a), 250 parts water, 1.5 parts
sodium alginate and 100 parts polyvinyl acetate emulsion
(Rohm & Haas WN-77).

A top coat mixture generally useful but specifically
adapted for application to a base coat formed from Ex-
ample VIII is as follows, 250 parts water, 6 parts starch,
1.5 parts sodium alginate, and 100 parts acrylic resin emulsion (40%) (Rohm & Haas

WN-80). As in Examples VI(a) and VII(a), the starch and sodium alginate have no function in the fin-
ished coating.
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a sand-free cleavable coating consisting essentially of muscovite mica particles of between about 300 and 3000 mesh dispersed in an acrylic resin having sufficient lower alkyl polyacrylate and higher alkyl acrylate copolymers incorporated therein to provide a tacky surface at temperatures above about 170° F. and a substantially non-tacky surface below about 170° F., and further comprising dispersed solid particles of between 200 and 3000 mesh of a material selected from the group consisting of clay substantially only of the kaolinite type, fuller's earth, lamp black, flake graphite, green slate, carbon black, and talc and mixtures thereof, the solids content of said resin being present in proportions by weight between about 3–7.5% of the total solids content of the named substances and said mica being present in proportions by weight between substantially 7–40% of the total solids content of the named substances.

4. A fiber board container for dead-level asphalt or the like having a wall the inner surface of which is protected by a substantially sand-free cleavable base coat consisting essentially of a polymerized organic resin which is tacky at normal atmospheric temperatures and solid particle cleavage constituents comprising between substantially 7–40% by weight of plate-like shaped mica particles of particle size between substantially 300 and 3000 mesh, said resin being selected from the group consisting of polymerized acrylic acid, polymerized ethyl acrylate, polymerized methyl acrylate, polymerized methacrylate, polymerized ethyl methacrylate and copolymerized mixtures thereof, and acrylonitrile-methacrylate copolymer, butadiene-styrene copolymer, vinylidene chloride-acrylonitrile copolymer, vinylidene chloride-vinylidene chloride copolymer and polyvinyl acetate, and mixtures thereof, the solids content of said resin being present in proportions by weight between about 3–7.5% of the total solids content of said resin and cleavage constituents combined and said wall being further protected by a top coat overlying said base coat and comprising a polymerized organic resin which is tacky at elevated temperatures of about 400° F. and above and which is substantially hard and non-tacky at temperatures below substantially 150° F.

5. A double coated fiber board container for asphalt or the like wherein the base coat on the inner surface of said fiber board consists essentially of a heat resistant substantially sand-free internally cleavable coating containing muscovite mica particles, a particulate material selected from the group consisting of flake graphite, carbon black, lamp black, clay substantially only of the kaolinite type, fuller's earth, green slate, and talc, and mixtures thereof and a tacky binder selected from the group consisting of polymerized acrylic acid, polymerized ethyl acrylate, polymerized methyl acrylate, polymerized methyl methacrylate, polymerized ethyl methacrylate and copolymerized mixtures thereof, and acrylonitrile-methacrylate copolymer, butadiene-styrene copolymer, vinylidene chloride-acrylonitrile copolymer, vinylidene chloride-vinylidene chloride copolymer and polyvinyl acetate, and mixtures thereof, said mica being present in the form of particles of a size between 300 and 3000 mesh, the solids content of said tacky binder being present in proportions by weight between about 3–7.5% of the total solids content of the named substances and said mica being present in proportions by weight between substantially 7–40% of the total solids content of the named substances, and wherein the top coat is disposed over said base coat and consists essentially of an asphalt-adherent coat selected from the group consisting of polymerized acrylic acid, polymerized ethyl acrylate, polymerized methyl acrylate, polymerized ethyl methacrylate, polymerized methyl methacrylate, polymerized vinyl chloride, polymerized vinyl acetate, polymerized vinyl alcohol, vinylidene chloride, acrylonitrile, polyethylene and polyvinyl acetate and copolymers thereof.

6. The container of claim 5 in which said top coat presents a tacky surface at temperatures above substantially 400° F. and presents a substantially hard and non-tacky surface at temperatures below substantially 150° F.

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