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COATING COMPOSITION OF CUTBACK ASPHALT AND AN IRON SOAP

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This invention relates to hard film rust preventives prepared by the addition of a minor amount of an iron soap of an oxidized petrolatum to a cutback asphalt made by blending a petroleum solvent with an asphalt prepared by straight reduction or straight reduction followed by oxidation.

This application is a continuation-in-part of Serial No. 559,787, filed on January 18, 1956, now abandoned.

Hard film solvent cutback rust preventives are used to protect metallic surfaces for long periods of time under severe exposure conditions. Metal parts which are protected with this type of rust preventive composition may be exposed to rain, sun, snow or corrosive fumes for periods of time up to several years without serious corrosion. These solvent cutback rust preventive compositions are fluid materials and may be applied by dipping, brushing or spraying. They are similar to paints in that they leave a hard film upon the protective surfaces but unlike paints, they do not contain any drying oils. The film is formed by solvent evaporation. Unlike paints again, this film is easily removed by a petroleum solvent by spraying, brushing, or swabbing.

The hard film rust preventive compositions in general are often based on a cutback asphalt. The term "cutback" refers to a blend of an asphaltic material with a solvent, usually a petroleum solvent.

The improved hard film rust preventive compositions of this invention comprise cutback asphalts which contain therein a minor amount of an iron soap of an oxidized petrolatum.

THE CUTBACK ASPHALT

The major component of this invention, the cutback asphalt, is prepared by blending a petroleum solvent with an asphalt prepared by straight reduction or reduction followed by oxidation. In the strict sense, a straight reduced asphalt is produced as a residue by the simple removal of the lighter fractions from a crude. In this concentration process, the more oil that is removed from the crude, the higher will be the consistency of the asphalt recovered as a residual. There are four general methods by which reduced asphalts may be manufactured. These commonly used methods are by steam distillation, vacuum flashing in pipe stills, solvent separation, and by blending techniques. With the exception of the latter method, the common factor is the removal of lighter fractions leaving a heavier residue.

With the usual distillation methods, there is a practical limit to which the reduction of an asphalt crude can be carried without seriously degrading the asphalt by cracking. Furthermore, very high softening point asphalt produced by distillation or by solvent separation is inherently hard and brittle. It has been found in the past that the distillation of an asphalt while in contact with oxidizing chemicals resulted in a product of improved tenacity and decreased brittleness at high softening point. It has also been found in the past that blowing air through asphalt or asphalt fluxes which are maintained at an

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elevated temperature gives the same improvement. This technique is utilized in the production of most oxidized asphalts by the industry today. By a selection of the consistency of the asphalt oxidizing base and by adjusting the temperature and rate of air blowing, it has been found possible to alter the susceptibility of the product to temperature change, the toughness and pliability of the oxidized asphalt at low temperatures, and the resistance of the product to shock. These advantages may also be obtained by reduction of an asphalt flux followed by oxidation to higher softening point.

A cutback asphalt is a simple mixture of an asphalt with a suitable solvent. The rate of drying and the hardness of the asphalt film remaining are controlled by the proper selection of the base asphalt and the volatility of the solvent vehicle. If a naphtha solvent is used, the resulting product is of the rapid-drying type while if a kerosene fraction is used as the solvent vehicle, medium or slow-drying products result.

The blending operation which results in the cutback asphalt is preferably carried out by pumping metered quantities of the asphalt and the solvent in the desired proportion through an orifice or other mixing device so that uniform solution of the asphalt develops before the cutback is stored.

The relative hardness of an asphalt at a given temperature is determined normally by the ASTM D5-25 method. This standard method utilizes a penetrometer and the hardness or penetration value is defined as the distance that a standard needle vertically penetrates the sample under specified conditions of load time and temperature. The units are expressed in hundredths of a centimeter, and the penetration value varies inversely with the consistency of an asphalt.

Since an asphalt is not crystalline, it does not have a sharp melting point but gradually softens as the temperature increases. This softening property is usually determined by ASTM Method D-36. In this method the softening point is defined as the temperature in ° F. of the bath when a 3/8" solid steel ball drops through a 5/8" diameter by 1/4" thick mold of asphalt held in a standard metal ring.

The cutback asphalt of this invention is preferably obtained from an asphaltic crude such as Lagunillas or Bachequero, although other asphaltic crudes may be used. The crude is reduced to the desired consistency by any of the methods described above, usually by steam distillation, to a flux of a 21-30 penetration. However, the basic starting material may also be of a softer consistency such as 61-70 penetration. This flux is then preferably oxidized to a softening point within the range of from 160-170° F. This asphaltic base is preferably "cutback" or diluted with a volatile solvent such as petroleum naphtha having a boiling range of about 200 to 600° F. Especially preferred are those solvents having a boiling range of about 275 to 420° F. The proportions of the materials will depend upon the thickness of the film desired on the metal parts to be protected. It is ordinarily desired to have a film thickness of about 0.002 inches. With a reduced and oxidized asphalt having a softening point within the range of from 160-170° F. and a petroleum naphtha boiling within the range of from 275 to 425° F., it has been found that proportions of 64 to 45 wt. percent asphalt to from 36 to 55 wt. percent solvent will give the desired film thickness. A particularly preferred cutback contains 51% of the asphalt described above with 49.0% of a petroleum naphtha.

THE IRON SOAP

The rust preventive compositions of this invention contain from about 1.0 to about 5.0% by weight based on

the weight of the total formulation of an iron soap of a partially oxidized petrolatum.

Generally speaking, the iron soap is prepared by the double decomposition of a corresponding sodium soap with a compound of iron such as ferric chloride.

The petrolatum which forms the base for the soap molecule is prepared by the solvent dewaxing of a paraffinic crude. The preparation of this material is known to the art and forms no part of this invention. Operable petrolatums will have viscosities at 210° F. within the range of from about 65 to about 73 SUS and penetrations according to the ASTM D-937 method of from about 175 to about 215 mm./10.

The petrolatum is oxidized to convert to paraffinic acids by blowing with air or oxygen at elevated temperatures with or without a catalyst. The oxidation is normally continued until a saponification number of from 60 to 110 and an acid number of from 20 to 50 are attained. The sodium soap of the oxidized product is then prepared and converted into the iron soap as described.

An example of the preparation of the iron soap is as follows:

The sodium soap of the partially oxidized petrolatum is dissolved in a petroleum solvent having a boiling range of about 300 to 410° F. This solution is thoroughly admixed with a saturated solution of ferric chloride in water. A minor amount of a C₁ to C₄ alcohol may be added as a catalyst. The mixture is heated for 1 to 3 hours at temperatures between 160 and 200° F. to convert the sodium soap to the iron soap. The mixture is allowed to stand and the water layer, containing sodium chloride, is drawn off and discarded. The iron soap in the solvent may then be washed with water which is also separated and discarded. The product is then heated under vacuum to remove the solvent and any entrained water, leaving the dried iron soap.

In accordance with the concept of the instant invention, several hard film cutback rust preventive compositions were prepared and subjected to the following test procedures. The tests are described briefly as follows:

(1) *Drying time*.—A steel panel 2" x 4" x 1/16" polished with a 280 grit emery cloth is immersed in the test compound at room temperature for one minute. It is then withdrawn at the rate of 4" per minute, hung vertically, and allowed to remain hanging for 4 hours at room temperature. If any transfer of compound from the panel or any film tackiness is observed when handled with normal finger pressure, the rating is "fail." In the absence of tackiness or film transfer, the material has successfully passed the drying test.

(2) *Low temperature adhesion*.—The polished steel panels described above are immersed in the testing compound at room temperature for one minute and withdrawn at the rate of 4" per minute. The panels are hung 24 hours in the laboratory to dry. They are then cooled to 0° F. and held at that temperature for 1 hour. The cooled panels are then scratched with a standard tool holding four razor blades 1/8" apart and rated as to flaking tendencies on a scale from 0 to 6. If no flaking occurs on scratching with a standard tool, the rating is "0," while "6" represents maximum or 1/8" flaking. A value of 2.0 or lower must be attained for satisfactory results.

(3) *Salt spray test*.—A polished steel panel as described above is immersed for one minute in the test compound at room temperature, withdrawn at the rate of 4" per minute, and allowed to dry for 24 hours. The coated panel is then placed in a standard salt spray cabinet (Method 400.1 of VV-L-791c) and subjected to the test conditions prescribed for 14 days. At the end of the test period, the coating is removed and the panel is examined for rusting. Any rusting of the panel excepting 1/4" of the margin of the panel is scored as a failure.

(4) *Gelling resistance*.—A standard steel panel as described above is weighed and then immersed in the test compound at room temperature for one minute, withdrawn at the rate of 4" per minute, and then allowed to dry for 24 hours in the laboratory. The panel is then weighed and the film weight recorded. The compound is then stored for 30 days and a second standard polished steel panel is coated as described above and dried for 24 hours at room temperature. The weight of this film is also determined. Any increase in the weight of the film formed by the stored compound is recorded. An increase up to 5% is rated as good, an increase of 5-15% is rated as fair and any increase in excess of 15% is rated poor.

The hard film cutback rust preventive compositions tested by the procedures above were prepared from blends of 1 to 3 wt. percent of the iron soap of an oxidized petrolatum having a saponification number of about 93 and an acid number of about 28. The cutback asphalt was prepared by blending 40% of a petroleum naphtha having a 287 to 395° F. boiling range with 60% of two different asphalts. Asphalt A had a softening point of 161 to 170° F. and was prepared by oxidizing by air blowing at 400-440° F. a flux having a 21-30 penetration. Asphalt B had a softening point of 161-170° F. and was prepared by oxidizing a flux having a 61-70 penetration.

Included in the data reported in Table I below on the tests described above are blends of asphalt B containing from 1 to 3% of dibutyl phthalate and 1% of diisooctyl phthalate. These diesters have attained wide acceptance in the plasticizer art. Included is the data on blends of asphalt B containing 2 wt. percent of a copolymer of isobutylene and isoprene made by a low temperature copolymerization process and commercially available as GRI synthetic rubber and 2% of a copolymer of butadiene and styrene, commercially available as GRS synthetic rubber. None of these plasticizers gives a product meeting all of the stringent requirements for a hard film solvent cutback rust preventive.

Table I.—Rust preventives

	Drying Time	Low Temperature Adhesion	14 Day Salt Spray Test	Resistance to Gelling
Asphalt A.....	Pass....	6.0	Pass....	Good.
+3% Iron Soap ¹	do....	1.5	do....	Do.
+3% Calcium Soap ¹	do....	5.5	do....	Do.
Asphalt B.....	do....	6.0	Pass....	Good.
+3% Iron Soap ¹	do....	1.5	do....	Fair.
+1% Iron Soap ¹	do....	2.0	do....	Good.
+1% Dibutyl Phthalate.....	do....	3.5	do....	Do.
+2% Dibutyl Phthalate.....	do....	2.5	do....	Do.
+3% Dibutyl Phthalate.....	Border-line.	1.0	Fail....	Do.
+1% Diisooctyl Phthalate.....	Pass....	5.0	do....	Do.
+2% Copolymer A ²	do....	4.0	Pass....	Poor.
+2% Copolymer B ³	do....	5.5	Border-line.	Do.

¹ Soap of partially oxidized petrolatum.

² Copolymer of isobutylene and isoprene.

³ Copolymer of butadiene and styrene.

It will be seen that the inclusion of from 1 to 3 wt. percent of the iron soap enables rust preventive compositions of this invention to successfully pass the stringent low temperature adhesion test of MIL-C-16173A without adversely affecting the drying time, salt spray protection, or gelling tendencies of the asphaltic material.

While the compositions of the invention included in Table I represent excellent rust preventive compositions, they may be further diluted with additional solvent in order to better adapt them for application by spraying. As an example of such a more dilute rust preventive a rust preventive was prepared which consisted of 3.2 wt. percent of the iron soap used in the previous examples, 49.0 wt. percent of asphalt B, 36.9 wt. percent of a petroleum naphtha having a boiling range of 287 to

395° F. and 10.9 wt. percent of a second petroleum naphtha having a boiling range of 315 to 350° F. This composition passed all requirements of MIL-C-16173-A, including the sprayability test described therein.

To summarize briefly, the instant invention relates to an improved hard film rust preventive composition which in its preferred embodiment comprises a solvent cutback asphalt containing combined therein from 1 to 5, e.g. 2 to 4 wt. percent of the iron soap of an oxidized petrolatum. The asphalt base material is either reduced or reduced and oxidized and has a softening point within the range of from 160-170° F. This asphaltic base is cut back with a petroleum naphtha having a boiling range within 275 to 425° F. The proportions of the asphalt material used vary from 64 to 45% asphalt and from 36% to 55% solvent. Especially preferred is a cutback prepared from 51% of the asphalt and 49% of the solvent. The iron soap utilized in proportions ranging from 1 to 5% by weight is the iron soap of an oxidized petrolatum having a saponification number of from 60 to 110 and an acid number of from 20 to 50, which has been prepared by oxidizing a petrolatum of a melting point within a range of from 120 to 130° F., and a viscosity at 210° F. of about 65 to 73 SUS.

It is to be understood that other additive materials may be blended with the rust preventive compositions of this invention without departing from the spirit thereof. We claim:

1. A hard film rust preventive composition which consists essentially of 99% to 95% by weight of a solvent cutback asphalt and 1% to 5% of the iron soap of an oxidized petrolatum, said solvent cutback asphalt consisting essentially of from 64.0 to 45.0 wt. percent of an asphalt having a softening point of from 160 to 170° F. selected from the group of reduced and reduced and oxidized asphalts with from 36.0 to 55.0 wt. percent of a petroleum naphtha having a boiling range of from 275° to 425° F.

2. A hard film rust preventive composition according to claim 1 wherein said iron soap is the iron soap of an oxidized petrolatum having a saponification number of from 60 to 110 and an acid number of from 20 to 50,

which has been prepared by oxidizing a petrolatum of a melting point of from 120 to 130° F. and a viscosity at 210° F. of about 65 to 73 SUS.

3. A rust preventive composition according to claim 2 which contains from 2 to 4% of said iron soap.

4. A rust preventive composition according to claim 1 wherein said asphalt is a reduced and oxidized asphalt prepared by oxidizing, by air blowing at 400 to 440° F., a flux having a 21-30 penetration.

5. A rust preventive composition according to claim 1 wherein said asphalt is a reduced and oxidized asphalt prepared by air blowing, at 400 to 440° F., a flux having a 61-70 penetration.

6. A hard film rust preventive composition which consists essentially of about 96 to 98% by weight of a solvent cutback asphalt and about 2 to 4% by weight of an iron soap of an oxidized petrolatum having a saponification number of about 93 and an acid number of about 28, said solvent cutback asphalt consisting essentially of about 51% of a reduced and oxidized asphalt prepared by air blowing a flux having a 61-70 penetration at 400 to 440° F. to a composition having a softening point of 161° to 170° F. and about 49% by weight of a petroleum naphtha having a boiling range of from 287 to 395° F.

7. A method of protecting metal surfaces from corrosion and rust which comprises coating said surfaces with a composition consisting essentially of 99% to 95% by weight of a solvent cutback asphalt and 1% to 5% of the iron soap of an oxidized petrolatum, said solvent cutback asphalt consisting essentially of from 64.0 to 45.0 wt. percent of an asphalt having a softening point of from 160 to 170° F. selected from the group of reduced, and reduced and oxidized asphalts with from 36.0 to 55.0 wt. of percent of a petroleum naphtha having a boiling range of from 275° to 425° F., and allowing said coating to harden to form a hard film.

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