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PIPE ENAMEL

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The present invention relates to an asphalt base protective coating composition which is applicable and serviceable over a wide temperature range as an inside or outside coating for pipes to protect them from corrosive elements which exist in the atmosphere, the soil, or from the attack of corrosive liquids which might be carried by the pipe.

More specifically the present invention is directed to an improved asphalt base pipe enamel, prepared from crude oil, for application to the surfaces of pipelines to protect them both internally and externally, whether buried in the soil or laid on the surface thereof.

With few exceptions, pipe enamels used in the United States for protecting pipe lines are derived from coal tar bases, due to the fact that petroleum asphalt base pipe enamels heretofore employed have not possessed the critical ranges in properties necessary to result in the uniformly high field performance required for an asphalt pipe enamel. In order for a pipe enamel to be satisfactory under field conditions, it must comply with a wide variety of requirements in order not to show erratic behavior under widely varying conditions. In the past, petroleum derived pipe enamels have been prepared with some of the required properties, but attempts to produce an enamel from a crude oil base stock having all of the required properties of a good protective coating have failed. This is primarily due to the fact that the properties are more or less interrelated and improvements in one required property very often has caused deterioration of others. In addition to a lack of understanding of the controls necessary, the critical ranges in requirements necessary also have not been appreciated.

In view of the above desiderata, the only petroleum base asphaltic pipe enamels heretofore employed with any degree of success have comprised an asphalt mastic, consisting of selected asphalts and aggregates applied as thick coatings; and a two coat system requiring a soft asphalt undercoat and a relatively hard asphalt outercoat to resist soil stress. The drawbacks inherent in the use of such coatings are apparent.

Perhaps the main reason accounting for the lack of a successful petroleum base asphaltic pipe enamel is that knowledge of hydrocarbon compounds in petroleum fractions has not progressed to include compounds more complex than those within the gasoline boiling range, in spite of the fact that asphalts have been used for many centuries. The study of asphalts is complicated by its complex structure and the fact that individual asphalts vary widely in their physical and chemical make-up. With higher boiling points and increase in molecular weight, a staggering number of isomers can occur, and it is impossible to do more than break these down into groups. The asphalts comprise one such broad group in fractionating asphalt base petroleum stocks. The asphalts in turn may be broken down into asphaltenes, resins, oils and wax fractions. While the presence of the latter fractions may be readily determined, such knowledge is

insufficient to provide insight and understanding of the physical behavior of the asphaltic material.

Research on the composition of asphalts has demonstrated that its nature is variably colloidal. The asphaltene fraction, having the highest molecular weight, is the disperse phase, and the resins are considered the dispersing medium, with the oils and content of wax which they can dissolve being the continuous phase. If excess wax is present beyond the solubility limit in the continuous phase, this can often be noted as a bloom or dull lustre on the surface of the asphalt.

Both from the colloidal and solubility aspects, it immediately is apparent that, in addition to the importance of the quantity of each fraction in determining the degree of dispersion and behavior of the asphalt, the character of each fraction is very important. Also the fact that the interrelationships of the components change with temperature must be taken into consideration in selecting base stock for the preparation of a good pipe enamel.

While the desirability of having a knowledge of the above factors in producing protective asphaltic coatings is well recognized, asphalt technology has not progressed to an extent permitting the exact determination of these fatcors, and the very best that can be done in defining the properties to be possessed by the asphalt base stock is by empirical physical properties such as softening point, penetration, viscosities, ductility and the like, and by considering such properties as an entity, an idea can be obtained of the likely service behavior of the finished product. It should be emphasized, however, that crude asphalts vary widely in individual properties, depending on crude oil source, and such variance has even been detected from material derived from adjacent wells. Hence, the necessity of considering empirical properties as a group in predicting possible behavior of the material under service conditions. While the empirical properties previously recited can be determined for a given base stock, such information is of little aid in connection with other base stocks as it has been found that the empirical properties of different base stocks may be different and still be satisfactorily employed in the practice of the present invention due to the difference in the chemical and physical make-up of different asphalts.

In accordance with the present invention we have discovered that a highly superior asphaltic base protective pipe enamel may be produced from crude oils, with or without the addition of modifiers such as native asphalts, oils and resinous materials, by reducing with or without vacuum, a low salt content selected crude oil base stock. The reduced material is air oxidized and treated with a mineral filler of a critical degree of fineness to render an improved product.

While the steps of reduction, air oxidation and treatment with mineral filler are known to the asphalt art, we have found that if these steps are carried out on selected crude oils to a degree and extent as to provide the resulting asphaltic material with a specific range of properties, a highly superior protective coating composition is obtained. Due to the variation in the chemistry of asphalts derived from different sources, we have found it necessary to determined the extent of reduction and oxidation of each asphalt by adjusting these steps until the properties of the resulting material fall within the ranges to be hereinafter prescribed for our composition.

It is accordingly a principal object of the present invention to produce an improved asphaltic protective coating composition derived from petroleum oils possessing all of the properties required of such materials under the widely varying conditions likely to be encountered in service, and to establish criteria by which the material may be judged prior to use.

A further object is to produce a one-coat protective

pipe enamel which possesses physical properties rendering it resistant to soil stress and at the same time providing a desirable and tight bond to the pipe and a high resistance to aging.

A still further object is to produce a protective pipe coating composition which will prevent corrosion or damage to the surfaces of the pipe whether buried in the soil, or subjected to the corrosive action of the atmosphere.

A still further object is to produce a protective coating which is flexible and tough and which will permit handling of the coated pipe under normal construction conditions, but which will retain the required resistance to flow and flexibility under the heat of summer as well as the extremes of winter whether buried in the soil or on the surface of the ground, and which readily adheres to the primed pipe, and which can be easily applied without coating holidays.

A still further object is to provide a pipe enamel which does not produce fumes irritating to the workmen during application, and which has a high flash point in order that application may be safe and easy and without danger of breakdown or decomposition of the material under conditions of application.

A further object is to provide a coating composition relatively low in weight compared to prior art compositions of this nature to render savings in freight and handling costs for a given film thickness.

A further object is to render as asphaltic base protective coating composition which is characterized by high durability, and which does not crack upon being deformed.

Further objects and advantages of the present invention will be apparent from the description which follows.

According to our invention, we produce from crude oils an asphaltic pipe enamel having the combination of properties and critical ranges which have been determined by field tests to be essential to such protective coatings. Prior to the present invention such a combination of properties in a single coat enamel derived from crude oil had not been achieved and had not been recognized as necessary for a good single coat enamel.

The asphaltic protective coating compositions of this invention have incorporated therein from 17% to 25% by weight of an inert mineral filler of a fineness permitting 90% of the filler to pass through a 325 mesh screen, and are characterized by a maximum viscosity of 1,000 seconds (Saybolt Furol) at 375° F., a flash point of at least 125° F. above the temperature at which the coating composition has a viscosity of 1,000 second (Saybolt Furol), a maximum penetration at 150° F. (50 g., 5 secs.) of 45, a maximum settlement ratio at 450° F. of 1.3, a water absorption of less than 1.0% after 35 weeks' immersion of a 90–100 mil film, a stain index of less than 15, a maximum sag of 1/16" at 160° F. after 24 hours, no cracking and disbonding at —20° F., no visible cracking under bend test at 77° F., no cracking under impact test at 32° F., a maximum of 9 mils penetration at 85° F. for 100 hours as determined by rod deformation test, an initial electrical resistivity of at least 1×10^{15} ohm-cm. and an electrical resistivity greater than 1×10^{12} ohm-cm. after 35 weeks' immersion of a film of said composition in water, all as determined in accordance with the tests hereinafter set forth.

Extensive service testing has conclusively demonstrated that enamels which meet these properties give superior durable service under widely varying conditions. This is in contradistinction to prior art enamels derived from crude oils, which vary in properties from batch to batch, depending on the source of crude oil and the extent of control rigidity employed in the manufacture of the material.

As has been previously indicated, asphalt technology has not progressed to the point where sufficient knowledge of the chemistry of asphalts is available to enable one to take any crude oil and produce a satisfactory pipe enamel therefrom. Even crude oils which yield excellent paving asphalts or roofing asphalts very often are unsuitable for use as a base stock for producing our improved coating composition as the requirements of a good pipe enamel are much more extensive. It is possible, however, to modify some base asphalts otherwise unacceptable by adding natural asphalts, resins or oils prior to, or following, oxidation to render an acceptable enamel.

We produce our improved enamel from selected asphaltic base crude oils with the crude asphalt residuum obtained therefrom having less than about 20 grams/barrel sodium chloride content, either naturally or by removal of excess salt above this limit. The asphaltic base crude is reduced by steam and/or vacuum reduction if necessary, to prevent decomposition of the heavier fractions, and the residual asphaltic fraction air oxidized for a period of from about five to fifteen hours depending upon the crude source, type still and temperature at which carried out. Normally we prefer to air oxidize at from about 460° F. to 525° F. Due to the fact that this is an exothermic reaction it is necessary to cool the asphalt commencing at about 500° F. to prevent the temperature rising much above 525° F.

Upon completion of this step, an inert mineral filler such as slate flour is added. We have discovered that the mineral filler must be of a fineness so that at least 90% passes through a 325 mesh screen, and added not in excess of about 25% by weight or less than about 17%. An ash determination on the finished product determines whether the proper addition of filler has been made. For best results, we prefer to have the slate flour of a fineness permitting 95% to pass through a 425 mesh screen, although the coarser material has been given satisfactory results. The asphalt so treated is then subjected to the following tests to ascertain whether the material meets the criteria which we have established for our improved enamel and to determine whether the crude base stock is in fact suitable for making our improved enamel.

TEST PROCEDURES AND LIMITS

Flash point by means of open cup—

Procedure: Determined by American Society of Testing Materials Specification D92–52.

Limit: At least 125° F. above the temperature at which the coating composition has a viscosity of 1,000 seconds (Saybolt Furol).

Penetration values—

Procedure: Determined in accordance with American Society of Testing Materials Specification D5–52.

Limit: 150° F., 50 g., 5 sec. max. 45 mm./10; preferred 40 mm./10.

These values are a measure of consistency and one indication of field behavior which can be expected under different conditions.

At 150° F., the penetration value has been found to correlate with the deformation which can be expected when the coated pipe is handled above ground in the summer time or when resting on skids prior to being utilized.

Viscosity—

Procedure: Determined in accordance with American Society of Testing Materials Specification D–88–44, excepting an ASTM low distillation thermometer 30° to 580° F., is used to measure temperature.

Limit: The maximum viscosity, Saybolt Furol at 375° F. is 1,000 seconds.

This upper range is considered a measure of the practical limit in consistency for application purposes; and, of course, the value must also be considered in conjunction with the flash point of the enamel. Thus, if the material possessed a flash point of 525° F., application in the winter months could lead to material temperatures

appreciably above this value if the viscosity were greater than 1,000 seconds at 375° F.

The viscosity is related to the composition of the enamel, such as the characteristics of the base asphalt and the mineral filler.

Determination of settlement ratio—

Procedure: In accordance with American Association of State Highway Officials Procedure No. T109–42, excepting the test is made at 450° F. ±5° F.

Limit: The settlement ratio should be 1.3 maximum, with a rato of less than 1.2 preferred.

In application of the enamel, heating is carried out in a kettle which is usually provided with an agitator. Even so, settlement of the mineral filler occurs unless the fineness can be controlled. A proper mineral filler on dry sieve analysis usually has not less than 90% passing through a 325 mesh sieve, but this does not always result in the settlement ratio being low, and actual test is required on the enamel to determine that the values do not exceed those given.

Test for water absorption—

Procedure: Test panels are prepared by pouring the molten enamel down the inclined face, at approximately 30° from the horizontal, of the polished aluminum test panels, each 2¾" x 5⅞" of 20 guage metal. By balancing the inclination of the panel and the temperature of the coating against the viscosity of the test material, test films of 90 to 100 mils thickness can be obtained on both sides of the panel. After cooling, the edges of the coating are trimmed at an angle of 45° and the edges then coated uniformly by hand dipping in the enamel. The panels are weighed initially and again after 35 weeks' immersion in water, the water absorption being reported as percentage by weight of initial weight of film.

Limit: Less than 1.0% absorption in 35 weeks' immersion of a 90–100 mil film.

Water absorption is primarily a surface function, the penetration proceeding inwardly by diffusion. Excessive water absorption will soften the surface of the enamel and result in blistering and finally cracking and pulling loose from the metal.

As a practical control on water absorptivity, the salt content of the asphalt base is determined by the method described hereinafter and should not exceed about 20 grams/bbl. A low amount of inorganic salts dispersed throughout the asphalt decreases the diffusion and hence the driving force which causes the inward diffusion of water vapor.

In addition, the characteristics of the mineral filler determine the water absorption of the final enamel product and for this reason the water absorption is measured on the final product as a check of any given system. Service testing has shown that if water absorption in 35 weeks' immersion does not exceed 1%, and if the hardness of the enamel is within the ranges specified, no difficulty can be expected from softening or blistering of the enamel in the field.

Stain test—

Procedure: In accordance with American Society of Testing Materials Tentative Method of Test for Asphalts, (modified pressure method), ASTM Designation: D1328–54T.

Limits: Stain Index at 210° F., 50 p.s.i., 18 hours, to be not greater than 15.

The durability of an asphalt in underground service is affected by its rate of oxidation and by the hardening occasioned by the loss of oils, which due to the colloidal nature of asphalt, slowly exude from the continuous medium which is primarily an oil fraction. If the amount of exudation is excessive, undue hardening of the asphalt enamel can be expected, both because of loss of plasticizer and because diffusion of oxygen inward is increased to cause a polymerization hardening.

The stain thus is a direct measure of durability and is highly important to consider in selecting the raw materials for our improved pipe enamel.

High temperature sag test—

Procedure: In accordance with Asphalt Institute Construction Specification No. 96, "Asphalt Protective Coatings for Pipe Lines" (May 1954), paragraphs 1, 2 and 3, pages 17 and 18, excepting coating to be 3/32" ±1/64" thick, and in accordance with Method A.

Limit: Maximum sag of 1/16" at 160° F. after 24 hours.

Preferred: No sag.

This test is empirical to determine amount of deformation which can be expected at high summer temperatures, as with the coating exposed to direct sunshine, where film temperatures can reach as high as 160° F.

Cracking or disbonding test at −20° F.—

Procedure: In accordance with Asphalt Institute Specification No. 96, "Asphalt Protective Coatings for Pipe Lines" (May 1954), pages 17 and 18, paragraphs 1, 2 and 4, except coating be 3/32" ±1/64" thick and in accordance with Method A.

Limit: No cracking or disbonding of the coating from the panel at −20° F.

Pipe which has been shop-coated and is stored outdoors must withstand a wide temperature variation without showing cracking or disbonding of the coating. This test is an empirical measure of ability to withstand such conditions.

Bend test—

Procedure: Three 1 x 6 inch strips of 28 gauge galvanized metal are primed, and after air-drying the primer a minimum of 3 hours at room temperature, are coated by "pouring" to have a film of enamel 3/32"±1/64" in thickness. After cooling to room temperature the test pieces are placed in a water bath and held at 77° F.±1° F. for at least 1 hour. Each test piece is removed from the bath and bent 180° around a 1 inch mandril at 77° F. in 2 seconds. The presence of cracking or disbonding of the enamel coating is noted after the test, and again after storage of the bent specimens under room conditions for 24 hours.

Limit: No cracking or disbonding.

The bend test is a direct measure of the enamel to withstand deformation at ordinary temperatures without showing cracking or disbonding, and indirectly is a measure of the balance between tensile strength and flowability of the coating. Products which have a high content of paraffin wax or which are too brittle usually are found to show failure in this simple but effective test.

Impact test at 32° F.—

Procedure: A steel ball of 2.5–2.7 inch diameter, and weighing 772–870 g. is dropped a height of one foot on a sample of enamel on a steel plate, the assembly being chilled at 32° F. for two hours prior to test. The enamel is held enclosed by a retaining ring ¼" in height, 4" in diameter, tack welded on a steel plate ¼" in thickness and 8" in diameter.

Limit: No cracks visible in the enamel after dropping the ball.

The coating must be able to resist handling at low temperatures and also sudden blows as in backfilling of the pipeline in the winter time. The impact test is a simulated test to measure the ability of the coating to absorb shock without cracking or shattering.

Resistance of coating to flow under soil stress (rod deformation—

Procedure: In accordance with Asphalt Institute Specification No. 96. "Asphalt Protective Coatings for Pipe Lines" (May 1954), paragraphs 1, 2, 3, 4 and 5, Method II–3, pages 21 and 22.

Limit: Not more than 9 mils penetration at 85° F., 100 hours.

The coating buried underground is subjected to stress transmitted from the soil, especially if the soil has a high content of colloidal material and becomes alternately wetted and dried. The flow is measured in this test under standardized conditions. By empirical correlations with observed performance, if the values obtained do not exceed the above values, the deformation in service will not be excessive.

Salt content, grams salt/bbl. of base asphalt stock.—

Procedure: Twenty-five to one hundred grams of base stock to be tested (depending on hardness, solubility in benzol, etc.) is weighed into a 500 ml. Erlenmeyer flask. In case of hard, rather insoluble materials, heat is applied to reduce the material to a fluid state and it is then distributed around sides of flask to obtain easier solution. 200 ml. of benzol is then added and the material swirled until it is in solution. The solution is then poured into a 500 cc. separatory funnel and a few drops of a 5% benzol solution of X–21 "Tret-O-Lite" (trade name of Tret-O-Lite Company, St. Louis, Missouri), solution added. The flask is rinsed with 200 ml. of distilled water, brought to boiling and this is also added to the separatory funnel. The funnel is agitated for 5 minutes and the material allowed to settle. (In some cases an electric charge may need to be applied to the solution to break the emulsion.) 100 ml. of water layer is drawn off through a soft filter paper and cooled to room temperature. The water layer is titrated with silver nitrate solution using 10 drops of a 5% solution of potassium chromate as indicator. A blank should be run on each new batch of distilled water, using a 100 ml. sample. Factor for 0.05 N silver nitrate per 10 g. sample=9.3. Factor for 0.01 N silver nitrate per 100 g. sample=1.86.

Grams salt/bbl. as sodium chloride per 100 g. is calculated as follows: Factor X (ml. silver nitrate used minus ml. for blank). 0.01 Normal silver nitrate is employed when salt content is expected to be low, and 0.05 Normal solution when salt content is expected to be high.

Limit: To be not greater than 20 grams/bbl., based on determination on asphalt base before air oxidation or addition of filler.

The salt content can be correlated with the tendency of asphalts to absorb water providing the inorganic salts are present as chlorides. This is usually the case with petroleum asphalts, and this test has been found to be a convenient indicator of the suitability of the base asphalt before processing. The final combination after air-blowing and addition of mineral filler is checked to determine the water absorption in 35 weeks.

Resistivity—

Procedure: Primed polished steel rods, ¾" x 6", with one end turned to a spherical shape, are primed and dip-coated with the enamel. The resistance of the coating is determined with a Beckman Ultrohmeter and the reading converted to a specific-resistance in ohm-cm. by measuring the film thickness and area.

Limit: The resistivity of the asphalt initially shall be not less than 1×10^{15} ohm-cm. and after 35 weeks' water immersion shall be greater than 1×10^{12} ohm-cm.

Bituminous coatings on pipe lines are used nearly altogether in conjunction with cathodic protection, either with buried anodes or an electrical rectifier system. In either case, if the current demand is large, the expense in maintaining the line is great. As a practical aspect, the resistivity of an asphalt coating shall remain sufficiently high that the conductance shall be negligible through the coating. The current demand then is related to the completeness of the coating on the pipe and the durability and ability of the enamel to remain in place. The electrical resistivity does not seem to be related to water absorption of the coating although there possibly would be correlation with enamels which show a very high water absorption. As a practical check, resistivity after 35 weeks is determined, and on the basis of this measure and the water absorption and the initial resistivity, prediction can be made that the selected base and filler are suitable to prepare an enamel to give long time protection.

The following examples and tables will serve to illustrate more clearly the manner and mode of practicing the present invention. Obviously, modifications and variations will occur to those skilled in the art. Such variations can, of course, be made without departing from the spirit and scope of our invention.

Several different crude oils are set forth as satisfactory for the practice of the present invention. Other crude oils can be employed, if by our tests, asphalts derived therefrom meet the required specifications. Due to the state of asphalt technology, we are unfortunately usable to predetermine with any degree of accuracy which crude oils may be employed in the practice of our invention beyond the requirement that it must be an asphaltic base crude and must have a low salt content. Beyond these criteria, each asphalt must be processed and tested in the manner described to determine whether its chemical and physical make-up permits its use in accordance with the present invention.

Example I

From Arkansas crudes.—Crude asphalt of 60–70 penetration at 77° F. and with 15 grams/bbl. of salt obtained by steam and vacuum reduction from desalted crude oil from the Smackover Field of Arkansas was air-blown for 5 hours at a temperature of 475°–525° F. to a softening point of 228°–234° F. Addition of 19%–21% by weight of green slate flour from Fairmount, Georgia, of which at least 95% passed through a 325 mesh sieve, was made to the air-blown base in the blowing still, with the air on at a low rate to provide mixing. An ash determination was made on the product to determine that the correct filler content had been added, and the product checked for the following properties, to be in the ranges given:

Softening point (R. & B.), ° F.	234°–240° F.
Penetration at 77° F., 100 g., 5 sec., mm./10	7–9.
Penetration at 32° F., 200 g., 60 sec., mm./10	4 mm. min.
Penetration at 150° F., 50 g., 5 sec., mm./10	36 mm. max.
Saybolt Furol viscosity at 375° F.	900 sec. max.
Ash, percent by weight	18.5–20.5.
High temperature sag test, 160° F., 24 hrs., inches	1/16" max.
Low temperature sag test, —20° F.	No cracking or disbonding.
Peel test, 60°–160° F.	No peeling.
Impact test at 32° F.	Pass.
Pounds/gallon at 60° F.	9.95.
Flash point, C.O.C., ° F.	600 min.

Bend test at 77° F.	Pass.
Settlement ratio	1.2.
Water absorption, 35 weeks	0.9%.
Stain index	11.
Resistance of coating to flow under soil stress:	
At 85° F.	8.
At 115° F.	16.
Electrical resistivity	1×10^{16} ohm-cm.

Where the base is otherwise suitable for the practice of the present invention, the penetration requirements can be met, however, by addition of Gilsonite, as a hardening agent, and this product air-blown to the required range.

The example which follows demonstrates the manner of adjusting the hardness of a base stock lacking in this requirement only.

Example II

To asphalt of 150–200 penetration, containing less than 20 g./bbl. salt content, obtained by the steam or vacuum reduction of Shuler crude oil or from Smackover crude oil of South Arkansas, is added 10% by weight of Gilsonite selects. The penetration at 77° F. of the base blend is thereby reduced to 55–65. This base blend is then oxidized as before and to the same range in softening point, and mineral filler added as in Example I. The final product was found to meet our required ranges and to perform satisfactorily as a pipe enamel.

Example III

Wyoming crudes. — Vacuum reduced asphalt from Oregon Basin crude of 150–175 penetration at 77° F. and a salt content of 2.0 g./bbl. was air-blown at 475°–500° F. to a softening point of 225° F., and thereafter addition made of 20% by weight of 425 mesh slate flour. The blended product tested as follows:

Flash point, C.O.C., ° F	530.
Softening point (R. & B.), ° F	229.
Penetration at 77° F	8.
Penetration at 32° F	4.
Penetration at 150° F	42.
Viscosity, S. Furol at 375° F	940 sec.
Ash, percent by weight	20.0.
Impact at 32° F	Pass.
Deformation, 6 hrs. at 115° F	17.
Deformation, 100 hrs. at 85° F	8.
Stain index	12.
High temperature sag test	No sag.
Settlement ratio	1.2.
Water absorption, 35 weeks	0.4%.
Cracking or disbonding at —20° F	None.
Peel test	Pass.
Bend test	Pass.
Resistivity, initial	5×10^{15} ohm.-cm.
Resistivity, 35 weeks	1×10^{12} ohm.-cm.
Weight, lbs./gal. at 60° F	9.9.

Subsequent field observations showed this product to perform satisfactorily in application and service.

Example IV

Canadian crude.—A crude from the Leduc Field in Saskatchewan, Canada, was reduced by vacuum distillation to a penetration of 180–200 at 77° F. The salt content of the crude asphalt was 6.0 g./bbl. On air-blowing at 480–500° F. a base 229° F. in softening point (R. & B.) and 8 in penetration at 77° F. was obtained.

Addition of 20% of a 425 mesh slate flour from Slate Hill, Pennsylvania, resulted in a product with the following properties:

Flash point, C.O.C., ° F	510° F.
Softening point (R. & B.)	235° F.
Penetration at 77° F	6.

Penetration at 32° F	4.
Penetration at 150° F	45.
Viscosity, S. Furol at 375° F	700 sec.
Ash, percent by weight	19.0.
Impact at 32° F	Pass.
Deformation, 6 hrs. at 115° F	17.
Deformation, 100 hrs. at 85° F	8.
Stain index	13.
High temperature sag test	Pass.
Settlement ratio	1.3
Water absorption, 35 weeks	0.6%.
Cracking or disbonding at —20° F	None.
Peel test	Pass.
Bend test	Pass.
Resistivity, initial	2×10^{15} ohm.-cm.
Resistivity, 35 weeks	1×10^{13} ohm.-cm.
Weight, lbs./gal. at 60° F	9.95.

Example V

Texas crudes (a) Gulf Coastal.—A vacuum stock asphalt from a Gulf Coastal crude was oxidized to obtain a softening point of 238° F. and a penetration of 8. On addition of 20% by weight of a blue-black slate filler from Slate Hill, Pennsylvania, a product with the following properties was obtained:

Softening point (R. & B.)	242° F.
Penetration at 77° F	6.5.
Penetration at 32° F	4.5.
Penetration at 150° F	34.
Bend test at 77° F	Fail after 24 hours.
Stain index	9.
Impact at 32° F	Pass.
Salt content, g./bbl	30.

This enamel was unsuitable because of higher salt content, which would lead to excessive water absorption and softening of the enamel, and because of a poor tensile strength-viscosity relation leading to a failure in the bend test, fine cracks being shown on the deformed area after standing. A change in composition which might be brought about by blending would be necessary before a serviceable product could be produced from this crude source.

Example VI

Again representing an attempt to manufacture our improved enamel from Gulf Coast crude, a propane precipitated asphalt was blended with a Gulf Coastal residual to obtain a base stock which oxidized to a softening point of 238° F. and a penetration at 77° F. of 9. On addition of 20% by weight of 425 mesh blue-black slate flour a product with properties as follows was obtained:

Softening point (R. & B.)	246° F.
Penetration at 77° F	8.
Penetration at 32° F	5.
Penetration at 150° F	29.
Viscosity, S. Furol at 375° F	689 sec.
Impact at 32° F	Pass.
Flash, C.O.C	595° F.
Bend test at 77° F	Fail, initially.
Deformation, 6 hrs. at 115° F	14 mils.
Deformation, 100 hrs. at 85° F	4 mils.
Salt content, g./bbl	7.5.
Stain index	19.

The salt content was greatly reduced, but the product again was not suitable because of the high stain index shown and the decisive failure in bend test. The higher than normal content of paraffin wax is evidenced also by the lower than normal viscosity and the dull lustre shown on the enamel after standing at room conditions for several days.

Example VII

A still further asphaltic composition was prepared possessing the following properties:

Flash point, C.O.C., ° F.	575
Saybolt Furol viscosity at 375° F., seconds	525
Penetration at 150° F., 50 g., 5 sec., mm./10	47
Mineral filler (ash) percent by weight	9.0
Flow, 1/16" coating at 160° F. for 24 hrs., in.	0
Bend test at 77° F., 180° over 1" mandril, 2 sec.	O.K.
Cracking and disbonding at —20° F.	O.K.

The high penetration value indicated that the asphaltic composition would not perform satsfactorily under the temperature conditions encountered during summer months. This was found to be the case. In hot weather the material became so pliable that it could be molded by hand. The finished coat had a sticky feeling. After coating, and prior to drying, the composition had a tendency to run to the bottom of the joint. This caused a lump on one side of the pipe and decreased the protective coating elsewhere o the joint.

Examples V, VI and VII are included for the purpose of demonstrating the necessity of selecting the crude base stock on the basis of test performance. These examples are not to be construed as demonstrating the unacceptability of all Gulf Coast crudes, but are presented to substantiate our findings relative to the variable nature of asphaltic base stocks. It will also be noted that crude asphalts from the Shuler and Smackover Fields of Arkansas having a penetration above 100 at 77° F. must be hardened by the addition of Gilsonite for the practice of our invention, while certain other crude asphalts from the Leduc Field in Canada, for example, can be air-blown to a satisfactory product without any hardening, even though they possess very high penetration values. This apparent anomaly appears to be traceable to the presence of fractional components, the nature of which are unknown with the present state of asphalt technology.

The foregoing examples serve to illustrate the broad principles involved in the manufacture of serviceable enamels in accordance with this invention, and are not to be construed as limiting the processing which might be involved in meeting the ranges set forth as necessary for adequate field performance. In this respect the product of this invention differs from ordinary asphaltic enamels, which might be serviceable under mild conditions, but which fail when the service demands increase and by their failure have resulted in the almost complete exclusion of asphaltic materials from this application.

Our improved enamel may be applied to pipe surfaces by several different known methods but usually is machine applied, with or without reinforcing with surface wrappings. While our improved pipe enamel functions satisfactorily for a one-coat application, various combinations may be employed, as coating without wrap, or coating with single wrap, or various multiple coats and multiple wraps, where such coatings, due to circumstances, are deemed advisable. For normal use, however, our enamel need be applied in one coat only which is sufficient to yield superior results.

As is customary with coatings of this nature, a primer is first applied to the surface to be coated, to insure thorough adhesion of the coating composition. A selected asphalt in solvent solution has been found to be an excellent primer for use with our improved enamel.

This application is a continuation-in-part of copending application Serial No. 483,439, filed January 21, 1955, now abandoned.

What is claimed is:

1. An improved asphaltic protective coating composition having incorporated therein from 17% to 25% by weight of an inert mineral filler of a fineness permitting 90% of the filler to pass through a 325 mesh screen characterized by a maximum viscosity of 1,000 seconds (Saybolt Furol) at 375° F., a flash point of at least 125° F. above the temperature at which the coating composition has a viscosity of 1,000 seconds (Saybolt Furol), a maximum penetration at 150° F. (50 g., 5 secs.) of 45, a maximum settlement ratio at 450° F. of 1.3, a water absorption of less than 1.0% after 35 weeks' immersions of a 90–100 mil film, a stain index of less than 15, a maximum sag of 1/16" at 160° F. after 24 hours, no cracking and disbonding at —20° F., no visible cracking under bend test at 77° F., no cracking under impact test at 32° F., a maximum of 9 mils penetration at 85° F. for 100 hours as determined by rod deformation test, an initial electrical resistivity of at least 1×10^{15} ohm-cm. and an electrical resistivity greater than 1×10^{12} ohm-cm. after 35 weeks' immersion on a film of said composition in water.

2. An improved asphaltic protective coating composition having incorporated therein from 17% to 25% by weight of an inert mineral filler of a fineness permitting 95% of the filter to pass through a 425 mesh screen, characterized by a maximum viscosity of 1,000 seconds (Saybolt Furol) at 375° F., a flash point of at least 125° F. above the temperature at which the coating composition has a viscosity of 1,000 seconds (Saybolt Furol), a maximum penetration at 150° F. (50 g., 5 secs.) of 45, a maximum settlement ratio at 450° F. of 1.3, a water absorption of less than 1.0% after 35 weeks' immersion of a 90–100 mil film, a stain index of less than 15, a maximum sag of 1/16" at 160° F. after 24 hours, no cracking and disbonding at —20° F., no visible cracking under bend test at 77° F., no cracking under impact test at 32° F., a maximum of 9 mils penetration at 85° F. for 100 hours as determined by rod deformation test, an initial electrical resistivity of at least 1×10^{15} ohm-cm. and an electrical resistivity greater than 1×10^{12} ohm-cm. after 35 weeks' immersion of a film of said composition in water.

3. A composition as described in claim 2 wherein the mineral filler is slate flour.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,973,280 February 28, 1961

Arnold J. Hoiberg et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 24, for "fatcors" read -- factors --; column 8, line 32, for "usable" read -- unable --; column 11, line 22, for "o" read on --; column 12, line 33, for "filter" read -- filler --.

Signed and sealed this 10th day of October 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC