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PROTECTIVE COATING ON A METALLIC SURFACE

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6 Claims

ABSTRACT OF THE DISCLOSURE

A protective coating for metallic surfaces consisting of a primer coating containing from 60 to 40% by weight of a liquid hydrocarbon solvent and from 40 to 60% by weight of a non-air blown, solvent extracted asphalt having a penetration at 77° F. of 1 to 25 and a softening point of 140–220° F., and a bituminous finish coating compatible with said primer coating.

This application is a continuation-in-part of copending application Ser. No. 444,019, filed Mar. 30, 1965, which copending application was a continuation-in-part of application Ser. No. 64,258, filed Oct. 24, 1960, now abandoned.

This invention relates to an improved coating structure and is particularly concerned with an improved asphaltic prime coating for metallic surfaces coated with a finish bituminous protective coating subjected to cathodic protection.

Billions of dollars have been spent in recent years on the construction and modernization of oil and gas pipelines. Since such oil and gas pipelines are underground, deterioration from corrosion is a problem. It has become customary to coat such pipelines with bituminous coatings such as tars and asphalts. Proper selection of coating compositions has become a real factor in determining maintenance cost of such lines. In fact, the performance level of a pipe coating is one of the major factors in determining maintenance cost of such lines. In fact, the performance level of a pipe coating is one of the major factors in determining the maintenance and operating budget of a pipeline company. Tremendous advances have been achieved recently in asphalt technology. Asphalts are now tailored to achieve a desired result in a particular service.

It has become common practice to complement pipe coatings by the application of cathodic protection voltages to the pipe system. Cathodic protection is well described in the art and comprises the use of an impressed current to prevent or reduce the rate of corrosion of a metal in an electrolyte by making the metal the cathode for an impressed DC current. While cathodic protection tends to minimize corrosion, it also tends to cause disbonding of the coating compositions.

In order to improve bonding of finish coating compositions to metallic surfaces, it is customary to use a compatible primer between the finish coating and the metallic surfaces. The primer must not only be adhesive to the metallic surface but the primer must also be compatible with the finish coating. Since the use of cathodic protection is widely used as a complementary measure for corrosion mitigation, it is necessary that the primer be highly resistant to disbonding from the metal surface under cathodic protection.

Therefore, it is a primary object of this invention to provide an asphaltic primer composition which, when used

with a bituminous finish coating, is resistant to cathodic disbonding and which is easily applied to the pipe surfaces. It is a further object of this invention to provide a primer composition derived from a solvent extracted asphalt having particular physical and performance characteristics. Another object of this invention is to provide a metallic surface coated with a primer coating and with a finish coating, said primer coating being between said metallic surface and said finish coating.

In accordance with the present invention, there is provided an improved protective coating for metallic surfaces such as underground pipes comprising a primer coating layer tightly adhered to said metallic surface; said primer coating layer consisting essentially of from 40 to 60% by weight of a non-air blown, solvent extracted asphalt having a penetration at 77° F. of 1 to 25 and a softening point of 140–220° F. and from 60% to 40% by weight of a liquid hydrocarbon solvent and a bituminous finish coating layer compatible with said primer coating layer adhered to the outer surface of said primer coating. The useful non-air blown, solvent extracted asphalts often have a sulfur content of at least 3% by weight and may contain up to 6 or 7% by weight of sulfur. Preferably, the non-air blown, solvent extracted asphalt has a penetration at 77° F. of 3 to 12 and a softening point of 160 to 185° F.

The bituminous finish coating used in the protective coating of this invention may be any bituminous finish coating known to those skilled in the art but, preferably, the bituminous finish coating is the composition disclosed and claimed in application Ser. No. 427,154, filed Jan. 21, 1965, now abandoned. This preferred finish coating comprises an air-blown solvent extracted asphalt having a penetration at 77° F. (100 grams, 5 seconds) of 50 to 200 prior to air blowing, having incorporated therein from 17 to 25% by weight of an inert mineral filler of a fineness permitting at least 90% of the filler to pass through a 325-mesh screen, the protective coating composition being characterized by a maximum viscosity of 1000 seconds (Saybolt Furol) at 425° F., a flash point of at least 125° F. above the temperature at which the coating composition has a viscosity of 1000 seconds (Saybolt Furol), a maximum penetration at 150° F. (50 grams, 5 seconds) of 32, a maximum penetration at 77° F. (100 grams, 5 seconds) of 8, a maximum settlement ratio at 400° F. of 1.2, a water absorption of less than 1% after 35 weeks immersion of a 90–100 mil film, a maximum sag of 1/16 inch at 160° F. after 24 hours, no cracking and disbonding at 5° F., no cracking under impact test at 32° F., a maximum of 7 mils penetration at 85° F. for 100 hours as determined by rod deformation test, a maximum of 14 mils penetration at 115° F. for 6 hours as determined by rod deformation test, an initial electrical resistivity of at least 1×10^{15} ohm-cm., an electrical resistivity greater than 1×10^{12} ohm-cm. after 35 weeks immersion on a film of said composition in water, a salt content of less than 20 grams per barrel of coating, and a maximum cathodic disbonding of 1.25 square centimeters in a period of 7 days.

The primer coatings of this invention provide improved resistance to the deteriorative effects of cathodic protection and an improved coating-to-metal bond with the bituminous finish coating. In order to achieve the desired physical properties and performance characteristics of the protective coating of this invention, it is necessary to make the primer coating and the finish coating from a solvent extracted asphalt. Solvent extracted asphalts are asphalts prepared by solvent extraction of residual oil, which may include certain other oils such as residual oils from catalytic cracking, known as cycle oils, with low molecular weight paraffinic hydrocarbons, e.g., C_3 – C_5 compositions such as propane, butane, etc. As used in

this specification and claims, solvent extracted asphalt is that portion of the residual oil or crude asphalt which is not soluble in the solvent. Particularly useful solvent extracted asphalts are those prepared from a residuum of South Arkansas crude oil, although other crude oils may be used. Solvent deasphalting is essentially a liquid-liquid extraction process which is used to separate paraffinic materials from aromatic and asphaltic materials in the reduced crude oils. This process is especially well suited for crude oils which are difficult to reduce by steam and vacuum distillation. The solvent-to-charge ratios may vary considerably, but usually varies from a low of 2:1 to a high of 6:1. The minimum operable solvent-to-charge ratio is highest for high paraffinic base crude residues and lowest for low paraffinic base crude residues. Solvent extraction takes place in an extractor tower which serves as an intimate countercurrent flow contactor for the solvent and residual oil charge. The deasphalted oil-solvent mixture flows from the top of the extractor tower and the asphalt which is insoluble in the solvent is withdrawn from the bottom of the tower. Usually, the asphalt recovered from the bottom of the tower passes through an asphalt stripper which is a vertical column equipped with perforated baffle plates wherein steam is used for stripping the remaining solvent and oil from the asphalt.

The residual oil charge for solvent deasphalting comes from the flux oil fraction provided by the fractionation of crude oils. It has been discovered that best results have been achieved when the salt content of the asphalt is maintained at less than 20 grams per barrel of sodium chloride content.

The compositions of this invention are subjected to the following tests to determine that the compositions comply with the claimed physical qualifications. These tests are ASTM penetration test, ASTM softening point test, and cathodic disbonding test, as further described in U.S. 2,973,280 and U.S. 3,070,523.

The cathodic disbonding test is conducted in an apparatus consisting of a panel board which has metering available to drain sufficient current to each of several test specimens to maintain a negative potential from 0 to 6 DC volts. Power for the panel board is furnished by an 8 volt half-wave selenium rectifier which is connected through a constant voltage transformer to a 110 volt AC source. Equipment capable of measuring current flow up to 50 milliamperes is used. A high internal resistance voltmeter is used to measure specimen potential to a saturated calomel electrode.

The test specimens were prepared from 2 3/4" x 5 7/8" x .035" open hearth steel panels. The metal panels were cleaned, dipped in boiling naphtha and sandblasted on both sides. Thereafter, copper lead wires were soldered to the panels using rosin core solder. The panels were placed in an oven at 150° F. for 30 minutes and thereafter flushed with hot methanol. Thereafter, each panel was primed by brushing a thin layer of a primer composition onto the metal surfaces. The primed metal panels were allowed to dry overnight.

The finish coatings were then applied to the primed test samples at a temperature of 450 to 474° F. to a thickness of about 60 mils. After both sides were so coated, the edges were dipped in the hot finish coating to insure complete coverage. Thereafter, the prepared samples were cooled by dipping in ice water.

The test specimens were tested in a solution of synthetic sea water conforming to specification MIL-L-21260 which was prepared in the following manner. The following ingredients were mixed together and added to sufficient fresh water to make one liter of synthetic sea water:

Ingredients:	Gram/liter
Magnesium chloride hexahydrate	11.0
Anhydrous calcium chloride	1.2
Anhydrous sodium sulfate	4.0
Sodium chloride	25.0

The pH of the solution was adjusted to a value of 8.0 to 8.2 by the addition of a 5% solution of sodium carbonate.

The test procedure consisted of inflicting intentional damage to the test side of the coating and immersing the specimen in the prepared electrolyte. The damage was inflicted by gouging the coating with a 1/16 inch drill bit which has been blunted. Sufficient current was drained to the specimens to maintain the desired -1.50 volt saturated calomel potential. At the end of 7 days, the specimens were removed and examined for disbonding beyond the initial damaged area.

In the examples reported in Table I, the primer compositions were prepared by dissolving the indicated asphalts in the indicated amounts of petroleum naphtha having a boiling range of 300-360° F. A thin coating of the primer coating was applied to the steel surface and thereafter coated with the finish coating.

The air oxidized solvent extracted asphalt finish coating used in Examples 1-3, 5 and 6 reported in Table I was prepared from a light Arkansas crude oil having a softening point of 115° F. (ASTM test D 36-26), a specific gravity at 77° F. of 1.028 (ASTM test D 70-52), a penetration of 90 at 77° F. (ASTM test D 5-52) and a solubility of 99.95% in carbon tetrachloride (ASTM test D 165-42). This asphalt was further processed by air blowing to a softening point of 235° F. (ASTM test D 36-26) and a penetration of 5 at 77° F. (ASTM test D 5-52). The blown asphalt was mixed with slate flour of a fineness permitting 98% to pass through at 325-mesh U.S. standard screen in an amount of about 20% by weight, based on the total weight of the asphalt composition. This gave a finish composition having the following properties:

Flash, C.O.C., ° F. (ASTM D 92)	650.
Pounds per gallon at 60° F. (ASTM D 71)	9.9.
Softening point (R&B), ° F. (ASTM D 36)	239.
Penetration at 77° F., 100 g., 5 sec., mm./10	
ASTM D 5)	5.
Penetration at 32° F., 200 g., 60 sec., mm./10	
(ASTM D 5)	3.
Penetration at 115° F., 50 g., 5 sec., mm./10	
(ASTM D 5)	9.
Penetration at 150° F., 50 g., 5 sec., mm./10	
(ASTM D 5)	24.
Viscosity, Saybolt Furol at 425° F. (ASTM E 102)	200.
Ash, percent by weight (ASTM D 271)	18.6.
Water absorption, 35 weeks, percent	0.7.
Sag test at 160° F., 24 hrs., inch (A.I.)	No sag.
Low temperature test, room to 0° F. (A.I.)	Pass.
Bend test at 85° F., immediate and 24 hrs.	Pass.
Impact test at 32° F. (So. Cal. Gas)	Pass.
Rod deformation at 85° F., mils (A.I.)	5.
Rod deformation at 115° F., mils (A.I.)	10.
Settlement ratio, 400° F., 2 hrs. (AASHO)	1.08.
Loss on heating, 24 hrs., at 400° F., percent	
(ASTM D 6)	0.09.
Voltage breakdown, volts/mil, above	1000.
Resistivity, ohm-cm., above	10 ¹⁵ .
Resistivity, ohm-cm., after 35 weeks immersion in distilled water, above	10 ¹³ .

The air oxidized vacuum and steam reduced asphalt finish coating used in Examples 4 and 7-9 reported in Table I comprised 19.2% by weight of a slate flour inert mineral filler having a fineness permitting 90% of the filler to pass through a 325-mesh screen and 80.8% by weight of the non-catalytically air-blown asphalt. This finish composition having the following properties:

Viscosity, Saybolt Furol at 425° F., sec.	215.
Flash point, C.O.C., ° F. above	575.
Penetration at 150° F., 50 g., 5 sec., mm./10	30.

Settlement ratio, 400° F., 2 hrs. -----	1.041.
Water absorption, 35 weeks, percent -----	0.8.
Sag test at 160° F., 24 hrs., inches -----	No sag.
Cracking and disbonding at 0° F. -----	None.
Bend test at 85° F. -----	No cracking.
Rod deformation at 85° F., penetration in mils -----	7.
Rod deformation at 115° F., penetration in mils -----	16.
Electrical resistivity, initial, ohm-cm. -----	1.8×10^{18} .
Electrical resistivity, after 35 weeks im- mersion -----	8.5×10^{15} .

ing the properties of the finish coating of Example 1 were thereafter applied to the pipeline. The line was buried to a depth of about 8 feet and thereafter placed under cathodic protection with a potential of at least -1.0 volt DC at any point on the line. The temperature at which the coating composition was applied was about 475-495° F. The primer composition brushed on easily and smoothly to form a very thin coating. A subsequent test wherein the pipe with the coating was struck with a hammer indicated that the primers of this invention provide superior adhesion properties.

The physical properties which will provide the im-

TABLE I.—CATHODIC DISBONDING TEST RESULTS

Example No.	Method of manufacture of primer base asphalt	Physical properties of base asphalts			Composition of primer, percent by weight		Primer viscosity, Saybolt Furol sec. at 77° F.	Hot applied finish coat	Cathodically disbanded area, cm. ²
		Penetration at —		Softening point, ° F.	Base asphalt	Naphtha			
		77° F.	115° F.						
1-----	Solvent extraction (no air oxidation).	3	15	183	50	50	28	Air oxidized solvent extracted asphalt.	0.50
2-----	do-----	6	22	175	48.1	51.9	25	do-----	0.32
3-----	do-----	8	52	160	49.5	50.5	21	do-----	0.50
4-----	do-----	8	52	160	49.5	50.5	21	Air oxidized vacuum and steam reduced asphalt.	0.75
5-----	do-----	11	69	154	49.5	50.5	20	Air oxidized solvent extracted asphalt.	0.50
6-----	do-----	20	120	142	49.5	50.5	19	do-----	0.72
7-----	Vacuum and steam reduction plus air oxidation.	11	28	195	45	55	31	Air oxidized vacuum and steam reduced asphalt.	2.89
8-----	do-----	21	40	195	45	55	46	do-----	4.52
9-----	do-----	26	46	196	45	55	50	do-----	7.25

The several examples reported in Table I illustrate the significant improvement in resistance to cathodic disbonding afforded by the protective coating composition of this invention. It should be noted that the primer compositions of Examples 1-6 are made from a base asphalt which has been only solvent extracted, i.e., no air oxidation. The use of primer compositions made from a solvent extracted base asphalt which has been air blown does not give the good results of the primer compositions of the present invention. The primer compositions of Examples 7-9 are made from base asphalts manufactured by conventional vacuum and steam reduction methods, plus air oxidation. It is obvious from this table that the non-air oxidized solvent extracted asphalts of this invention provide new and unexpectedly superior primer compositions. It should further be noted that the primer composition of Example 4, which is a typical non-air blown, solvent extracted asphalt primer composition of this invention, shows only 26% as much disbanded area as the conventional primer composition of Example 7. The improvement is even greater when Example 4 is compared with Examples 8 and 9. The table further illustrates the fact that the excellent and unexpected resistance to cathodic disbonding which results from the use of the non-air blown, solvent extracted asphalt primer compositions of this invention are inherent in solvent extracted asphalts having a rather wide range of physical properties.

Additional samples were prepared and tested wherein the solvent content was varied from 60 to 40% by weight, based on total weight of primer.

The invention is further illustrated by examples wherein benzene, toluene, kerosene and isopropyl benzene are substituted for the petroleum naphtha.

The efficacy of the invention is further shown by tests in actual use. A 10-inch pipeline was coated in the following manner. Nine gallons of a primer composition comprised of a solvent extracted asphalt dissolved in a solvent in a proportion of 48% by weight of asphalt to 52% by weight of naphtha was applied to 1300 feet of pipeline. About 1¼ tons of asphalt finish coating composition hav-

proved primer composition of this invention are shown in Table II.

TABLE II

	Method of test	Requirements
Solvent extracted base asphalt:		
Softening point, ° F.	ASTM D 36-26	140/220
Penetration at 77° F.	ASTM D 5-52	1/25
Penetration at 115° F.	ASTM D 5-52	4/75
Primer composition:		
Flash point, Open Cup, above ° F.	ASTM D 1310-63	5
Viscosity, Saybolt Furol, sec. at 77° F.	ASTM D 88-53	25/300
Weight, lbs./gal. at 60° F.		6.50/8.50
Asphalt content, percent by weight.		40/60
Cathodic disbonding, cm. ² , max ¹		1.25

¹ When tested in accordance with the test described herein.

The solvents which may be used in preparing the primer compositions of this invention are the well known hydrocarbon solvents such as benzene, toluene, petroleum naphtha, coal tar naphtha, xylene, etc. The preferred hydrocarbon solvents generally boil in the range of 200° F. to 450° F. The proportion of solvent to solvent extracted asphalts is not critical and will range from very fluid compositions to rather viscous compositions. These compositions may contain from about 40% to about 60% by weight of a solvent extracted asphalt and about 60% to about 40% by weight of solvent. Preferably, the compositions may contain from about 45% to about 55% by weight of solvent extracted asphalts and from about 55% to about 45% by weight of solvent.

If desired, the protective coating structure of this invention may be wrapped with wrapping materials such as asbestos felt or paper in order to avoid marring the surface finish of the bituminous finish coating. In some instances, it is also desirable to apply a glass fiber inner-wrap material to the hot bituminous finish coating as it is placed on the primed metallic surface. This glass fiber innerwrap is normally imbedded in the bituminous finish coating so that the bituminous finish coating forms the outer surface of the protective coating.

Reasonable variations and modification of the invention as described are possible, the essence of which is that there have been provided (1) protective coating compositions for application to metallic surfaces, said coating compositions comprising a primer coating layer and a finish coating layer, said primer coating layer being tightly adhered to said metallic surface, (2) novel primer coating compositions, and (3) methods for reducing the cathodic disbonding of protective coatings from metallic surfaces.

What is claimed is:

1. An improved protective coating on a surface of a metallic underground pipe, said protective coating consisting essentially of a primer coating tightly adhered to said metallic surface, said primer coating consisting essentially of a non-airblown, solvent extracted asphalt having a penetration at 77° F. of 1 to 25 and a softening point of 140–220° F., and a bituminous finish coating compatible with said primer coating adhered to the outer surface of said primer coating, said bituminous finish coating consisting essentially of an air-blown solvent extracted asphalt having a penetration at 77° F. (100 grams, 5 seconds) of 50 to 200 prior to air blowing, having incorporated therein from 17 to 25% by weight of an inert mineral filler of a fineness permitting at least 90% of the filler to pass through a 325-mesh screen.

2. The coated metallic surface of claim 1 wherein the non-airblown, solvent extracted asphalt of the primer coating is the asphalt obtained by solvent extraction of a residual oil or crude asphalt with a C₃–C₅ paraffinic hydrocarbon solvent.

3. The coated metal surface of claim 1 wherein the non-airblown, solvent extracted asphalt has a penetration at 77° F. of 3 to 12 and a softening point of 160 to 185° F.

4. An improved primer coating composition which adheres tightly to metallic surfaces such as underground pipes which are to be coated with a bituminous finish coating and then subjected to cathodic protection, said composition being compatible with said protective coating, consisting essentially of from about 40% to about 60% by weight of a non-airblown, solvent extracted asphalt having a penetration at 77° F. of 1 to 25 and a softening point of 140–220° F. and from about 60% to about 40% by weight of a liquid hydrocarbon solvent.

5. The composition of claim 4 wherein the non-airblown, solvent extracted asphalt is the asphalt obtained by solvent extraction of a residual oil or crude asphalt with a C₃–C₅ paraffinic hydrocarbon solvent.

6. The composition of claim 5 wherein the liquid hydrocarbon solvent is petroleum naphtha.

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