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ASPHALT ADHESIVE COMPOSITION

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The present invention is concerned with an improved asphaltic adhesive composition. More particularly the invention is concerned with an adhesive composition particularly adapted for adhering sheet metal foil, such as aluminum, to roofing structures, metal tanks and the like.

The durability and heat reflecting value of metal foils, in particular aluminum, has been found to be of great value in roofing applications as well as in protecting oil and gas storage tanks. Practical problems, however, in adhering such foils to these structures in a permanent manner have not heretofore been overcome. Numerous attempts have been made prior to our invention to adhere metal foils, e.g. aluminum, to roof surfaces or to metal storage tanks with varying degrees of success. Such materials as asphalt roof coatings, asbestos roof coatings, cold process roofing cement, lap cement, asphalt emulsions and styrene pitch compounds derived from cotton seed meal, among others, have been utilized in an attempt to permanently adhere metal foils to metal and composition roof surfaces.

Most of the above enumerated compounds provide the necessary initial adhesive force required for the purpose. However, upon aging for prolonged periods at least a partial failure results. Either the adhered foil becomes loosened and detached by the wind, in the nature of sheets of paper, or else the foil develops splits, either laterally or longitudinally. Also wrinkles or buckles occur in the sheets of foil which results in the foil becoming loosened at the laps. Due to its appearance such loosening is referred to in the art as "fish-mouths."

A thorough study of the above enumerated difficulties indicates that the main causative factors are the limited tensile and beam strength of the 2–6 mil foil as commonly employed in such applications, and the differential movement between the foil and underlying adhesive and roofing or metal tank surface. In addition, the metal foil is exposed to cyclic daily temperature variations producing a fatigue phenomena which also enters into the foil destruction.

With the metal foil adhered to the roof deck or other surface, the temperature in the first part of the day is increased first of all in the foil layer. The foil, with its relatively high coefficient of expansion (in the neighborhood of 0.00003 inch per inch), tends to increase in length before there is any appreciable expansion of the underlying adhesive and roof structure. If the adhesive is not of the proper nature such as to permit expansion of the foil, a buckle forms and the laps become loosened. On cooling in the latter part of the day the foil again decreases in temperature first and since it has the highest rate of contraction, considerable stress is set up. With the foil tending to move faster than the substrata, these local stresses are often high enough to cause tearing of the foil. Since metal foil has only medium yield strength, which in the case of aluminum is in the neighborhood of 5000 p.s.i. for a 2 mil thickness, a pull of 10 pounds or more is sufficient to result in permanent deformation or stretch in a strip one inch wide and 0.002 inch thick.

Once the edges of the foil become loosened or tears occur weathering influences work inward, and if the adhesive is not of the proper character, exudation of oil from the adhesive at the interface with the foil can occur. The adhesive forces holding the foil to the roof then become weakened and the foil is at the mercy of high winds or other forces. Tests, under actual service conditions over long periods, have conclusively demonstrated that these conditions can and do occur with prior art adhesives used for this purpose.

In addition to maintaining a permanent bond between the metal foil and the underlying surface, such an adhesive must meet certain other criteria. The adhsive material must be non-toxic, have a relatively high flash point, and must show no flow on roofs of ordinary pitch or when applied to circular metal tanks, even under high summer temperature conditions.

If asphalt was a relatively simple chemical material, preparing an adhesive therefrom to meet the above criteria might be a rather straightforward procedure. Unfortunately, however, relatively little is known of the chemistry of asphalt due to the fact that this material comprises a mixture of asphaltenes, resins, waxes and oils which may each comprise a large number of isomers and chemical fractions. It is only by studying the service behavior of an asphaltic composition designed for a particular application that the required physical properties of the composition and the ingredients thereof can be determined. It is therefore necessary to charactrize the composition in terms of empirical properties.

It is the principal object of the present invention to provide an improved petroleum base asphaltic adhesive composition. A further object is to provide such a composition particularly adapted for adhering metal foil to roofing and tank surfaces in a permanent fashion. A still further object is to provide such a composition which is non-toxic, easy to apply and which has a sufficiently high flash point as to be safe for use in roofing applications. Other objects and advantages of the invention will be apparent from the examples and description which follow.

The objects of the present invention are broadly accomplished by providing an adhesive composition having certain empirical properties which we have found by extensive and prolonged testing to be essential for proper service behavior.

We have found that our adhesive composition fully meets the requirements for the permanent bonding of sheet metal foil such as aluminum, lead, zinc, etc. to roofing decks, petroleum storage tanks and the like. Furthermore, we have found that our composition overcomes the enumerated disadvantages of prior art materials in an exemplary fashion.

Example 1 which follows sets forth the preferred procedure for preparing our improved composition. It will be understood from the discussion following this example that variations in the procedure set forth is possible without departing from the spirit and scope of the invention.

EXAMPLE 1

Crude oil from the Shuler Field of south Arkansas was reduced by topping and then by steam and vacuum reduction to a residual having a float value at 122° F. (ASTM D139–49) within the range of 150–200 seconds. To the residual was added from 25% to 30% by weight of a high boiling petroleum fraction with an initial boiling point at between 400° and 500° F. and an end point of less than 750° F. (ASTM D158–54). To this cutback vehicle, which had a viscosity (Saybolt Furol at 122° F.) of 400–600 seconds, there was added from 7% to 12% of a short fibered asbestos such as is designated by the trade as 7M Grade. On mixing the mineral filler in the cutback, a product was obtained which had a vis-

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cosity of 150–300 seconds (Stormer, ASTM D562). Other empirical properties of the finished adhesive composition are tabulated below.

Flash, Cleveland Open Cup, ° F. (ASTM D92–52)	200
Solids (ASTM D6–39%), excepting that a 2 gm. sample was spread in the bottom of a round aluminum dish approximately 15 mm. deep and 60 mm. in diameter	80
Touch test	Pass
Cold test, bend at	Pass
Flow test, 4 hrs. at 150° F., 30° angle	Pass
Stain test	Pass

In the preceding example, and throughout the specification and claim, certain test procedures will be alluded to in connection with the asphalt base, the solvent and the adhesive composition per se. Most of these test procedures for the asphalt base, solvent, etc. have been developed by the American Society of Testing Materials, except where modifications are indicated, and where appropriate the ASTM number describing the test procedure has been indicated. Certain other very important tests have been developed by us to characterize the finished adhesive composition, and we have found that it is necessary for our improved composition to pass these tests in order to prove satisfactory after prolonged service. The tests developed by us and the procedure for conducting same are as follows.

1. *Touch test.*—A thin film of the adhesive composition ($\frac{1}{32}'' \pm \frac{1}{64}''$) is spread on a metal panel and dried for 48 hours at room temperature. After this period the film shall on light touch of the finger show a tacky soft condition.

2. *Cold test.*—Three strips of 28 gauge galvanized metal and three strips of 15 pound roofing felt, each 1" x 6", are coated with $\frac{1}{16}''$ wet thickness of adhesive composition. A 1" x 4" strip of 0.002 inch aluminum foil is then placed on the adhesive and pressed down lightly to obtain complete bonding. The six strips so assembled are then placed horizontally in an oven and subjected to a temperature of 145°–150° F. for a period of eight days.

After the above eight day heat treatment, the six strips are then placed in a cold chamber at −20° F. for two hours. After the two hour period the strips are each bent 180° over a 1" diameter mandril in two seconds without removing from the chamber. Splitting or tearing of the foil on any of the six specimens is considered as a failure.

3. *Flow test.*—A film, $\frac{3}{32}''$ thick of adhesive composition is spread over a centered rectangular area $1\frac{1}{2}''$ x $2\frac{1}{2}''$ on a 4" x 6" steel panel, the $2\frac{1}{2}''$ distance being parallel to the 6" side. A $1\frac{1}{2}''$ x $2\frac{1}{2}''$ piece of 0.004 inch aluminum foil is then placed on the adhesive and pressed down to reduce the adhesive thickness to approximately $\frac{1}{16}''$. The panel assembly is then placed in a rack at an angle of 30° from the horizontal and subjected to a temperature of 140°–145° F. for a period of 24 hours in an oven. After this heat treatment there shall be less than $\frac{1}{2}''$ flow of the coating or slippage of the adhered foil.

4. *Stain test.*—As previously indicated, excessive exudation of oils at the interface between the adhesive and foil surface is to be avoided. We have found that if an area greater than about 50% of the foil surface in contact with the adhesive shows oil stains, after stripping from the adhesive under the conditions of the above described flow test, eventual failure of the adhesive in this respect can be predicted.

Table 1 which follows, sets forth nine different adhesive formulations prepared to illustrate the necessity for making adjustments in the components of our composition in certain instances. With the exceptions of compositions G and H, failure of the adhesive compositions in one or more respects was noted due to the failure to make the requisite adjustments in preparing the finished composition.

While we have developed certain criteria and ranges of properties for the components of our improved composition to be hereinafter discussed, such values are not intended to be inflexible. For example, while we prescribe a certain preferred penetration and float value for the asphalt base, it will be apparent that harder or softer asphalt bases may be utilized, if the deviation from the preferred property value is compensated for by a preliminary treatment with oils, etc. or if taken into ac-

Table I

Blend	A	B	C	D	E	F	G	H	I
Asphalt Base:									
Float at 122° F., sec.	23	164	1,200	164	164	155	155	155	164
Penetration at 32° F., 100 g., 60 sec.	500+	48	12	48	48	55	55	55	48
Softening Point (R. & B.), ° F.	60	92	122	92	92	90	90	90	92
Crude Source	Smackover	Shuler	Smackover	Shuler	Shuler	Smackover	Smackover	Smackover	Shuler
Solvent:									
Type	Gas Oil	Gas Oil	Gas Oil	Gas Oil	Gas Oil	Kerosene	Gas Oil	Lube $1	Gas Oil
Initial Boiling Point, ° F.	470	470	470	304	470	335	470	(1)	470
50% Point, ° F.	570	570	570	327	570	410	570		570
End Point, ° F.	680	680	680	396	680	520	680		680
A.P.I. Gravity	32	32	32	51	32	45	32	21	32
Flash, fog open cup, ° F. ASTM D1310-54T	250	250	250	103	250	130	250	[2] 340	250
Asphalt—Solvent Blend: Viscosity, S. Furol @122 ° F., sec.	456	263	460	265	263	289	323	329	263
Adhesive Composition, Percent by Weight:									
Asphalt Base	86	63	63	72	68	70	68	55	59
Solvent	2	25	25	16	24	18	20	33	21
Asbestos Fiber	12	12	12	12	8	12	12	12	20
Total	100	100	100	100	100	100	100	100	100
Grade of Fiber	7M	7M	7M	7M	7M	7M	7M	7M	7M
Adhesive Composition Test Data:									
Viscosity, Stormer, S.P., 1,500 g., 50 rev. @ 77° F., sec.	500	250	525	100	35	225	242	328	330
Cold Test, Bend at −20° F. on cured film	Pass	Pass	Fail	Fail	Pass	Pass	Pass	Pass	Fail
Flow Test at 140° F., 24 hrs. at 15°, $\frac{1}{16}''$ film under foil	None	2"	None	None	Fail	None	None	None	None
Stain or Bleed Test under conditions of Flow Test	Fail	Pass	Pass	Pass		Pass	Pass	Fail	Pass
Touch Test	Pass	Pass	Pass	Fail	Pass	Pass	Pass	Pass	Pass

[1] S.U.S. at 100° F. of 150 seconds.
[2] Cleveland Open Cup.

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count in selecting the solvent for the vehicle. Similar deviations from the preferred, if otherwise compensated for, are permissible. Such devices will readily occur to the skilled asphalt technologist. As long as the finished composition possesses the requisite physical and chemical characteristics to enable the adhesive to successfully pass the stain test, flow test, cold test, and touch test, we have found that satisfactory service behavior may be expected.

In the table, the two crude sources are listed as "Smackover," and "Shuler," both being derived from oil fields in south Arkansas of the same name. These crudes have been chosen for convenience, and because these particular crudes are good asphalt base materials. Other asphalt base crudes may be similarly utilized.

In the foregoing Table I, only blends F and G successfully passed the required tests indicating their suitability for permanently bonding metal foils to roofing surfaces and the like. The data set forth in this table is not to be construed as indicating the unsuitability of any of the particular asphalt bases or solvents, etc. in the practice of our invention as indicated in the preceding discussion. Data has been presented to indicate the necessity for compensating for deviations from the preferred values for ingredients in preparing the composition.

In the practice of our invention, we prefer an asphalt base produced from a straight reduced asphalt, or an air-blown product from straight reduced asphalt with or without a catalyst. We prefer that the asphalt base material have a float value of 100–300 seconds at 122° F. It should be again emphasized, however, that the preferred values for the asphalt base, the solvent, the cutback vehicle, and the mineral filler are to be considered only as guides in preparing our improved adhesive, since the empirical properties of the adhesive composition per se, as determined by the tests which we have devised, are the determining factors. As an additional guide, the asphalt base should preferably have a minimum penetration of about 30 mm./10 at 32° F., 100 g., 60 seconds.

Referring to Table I, adhesive composition "A" was prepared with an asphalt base which had a float value at 122° F. of 23 seconds. This asphalt base required only 2% of solvent gas oil to reduce the viscosity to the preferred range for the cutback vehicle. Although this particular composition could be applied satisfactorily, passed the cold test, and showed no sag or flow at 140° F., this particular composition exhibited exessive stain and bleeding during the flow test and therefore was considered a failure in this respect.

Again referring to Table I, in composition "C," the asphalt base had a float value at 122° F. of 1200 seconds and a penetration at 32° F. of 12. This formulation failed on subjecting it to the cold test at —20° F. The unsuitability of this particular formulation as a permanent type adhesive was confirmed in a service test with adhered areas of foil 6′ x 12′ being used on a composition roof. Both fish mouths and splits in the foil became pronounced during prolonged exposure of the adhered foil sheets. In this instance in order for this asphalt base to be employed in preparing our improved composition, it would be necessary to add oil fractions to soften the hard asphalt base. As indicated, an asphalt base harder than about 300 seconds float should be softened, prior to cutting back with solvent, by treatment with an oil fraction.

The solvent is not critical in the sense that a particular solvent is required. For reasons of economy, petroleum solvents having an initial boiling point above 300° F., and an end point of less than 750° F. are preferred. Other materials, however, which are good solvents for asphalt and which are non-toxic may be employed. Kerosene, gas oil and naphtha, falling within the previously mentioned boiling range, are particularly preferred. The selection of the solvent should be balanced with the selection of the asphalt base in order to control the flow properties and the tendency of the adhesive composition to bleed during the flow test. For example, if an asphalt base having a low float value is selected, lighter solvents such as kerosene or naphtha should be employed. If a heavier asphalt base is selected, gas oil can be used as a solvent without undesirable results in the flow or stain tests.

As examples of the necessity for selecting the solvent having regard for the base, naphtha was employed as the solvent in composition "D" of Table I. The adhesive composition so produced failed the cold test, since during aging a considerable amount of the naphtha evaporated leaving a film lacking in the required flexibility. Composition "A" utilized a very light asphalt base containing a high content of lubricating oil fraction with gas oil as the solvent, and composition "H" contained an added fraction of lubricating oil. Both of these blends were found to fail the stain test. The solvent, therefore, must have enough volatility when mixed with a particular asphalt base so as to render the adhesive composition non-bleeding or staining, which is a function of the rate of the evaporation of the solvent.

The viscosity of the cutback vehicle is determined by the nature of the asphalt base and the amount and type solvent added. We prefer that the cutback vehicle have a viscosity (Saybolt Furol 122° F.) within the range 250–500 seconds. If the viscosity of the cutback vehicle falls much below 250 seconds the final adhesive composition will require too high a content of mineral filler to raise the adhesive consistency to the point where the composition will pass the flow test. An excessive amount of mineral filler in turn causes the adhesive composition to become brittle on aging due to an excessively high ratio of filler to asphalt. If the viscosity of the vehicle is much greater than about 500 seconds, the composition is difficult to apply, particularly in cold weather, due to the composition becoming excessively tacky.

We prefer a mineral filler comprising short asbestos fiber classified as 7M and 7T grade under the Canadian Crysolite asbestos classification. A mixture of 7M and 7T grade may be employed, or the asbestos may be comprised solely of one or the other grades. The above-mentioned grades of asbestos fiber are arrived at on a Quebec Standard Asbestos Testing Machine comprising a series of superimposed boxes having screens with varying meshes (see Canadian Department of Mines Bulletin #707, 1931), (U.S. Bureau of Mines Bulletin 403 on Asbestos, 1937). The amount of mineral filler required to render a composition having good adhesive properties and which passes the flow test will depend in some measure upon the cutback vehicle composition and its viscosity. In general we prefer less than 20% in order that the adhesive may have the required flexibility at —20° F. after long aging.

In addition to the aforementioned asbestos fiber, other mineral fillers such as limestone, slate dust, mica, or China glass may be used in lieu of a portion of the asbestos fiber with fair results. The latter materials are generally of low cost but due to the fact that such materials do not satisfy the principal criteria of the mineral filler, which are to give resistance to flow and increase in adhesive properties, to the extent as does asbestos fibers, their use to an appreciable extent as a substitute for asbestos is not preferred.

As previously indicated, the physical properties which we have found necessary in the finished adhesive composition must be described in terms of how the composition performs under certain test procedures heretofore outlined which we have developed.

The flash point of the finished adhesive composition should preferably not be below 100° F. in order to provide safety in storage and application. Also solvents having lower flash points are usually of the rapid setting type which are undesirable for use in formulating our composition. It should be pointed out, however, that certain

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poorly fractionated petroleum hydrocarbon solvents have flash points lower than 100° F. Such solvents have been employed successfully in preparing our improved adhesive.

The total solids content of the finished adhesive should not be below 75%, since high shrinkage is undesirable. The actual amount of total solids will depend on the asphalt base and the mineral filler together with the viscosity required of the vehicle.

In addition to the stain test, cold test and the like, the adhesive after eight days at 145°–150° F. should not have developed sufficient adherency to tear an adhered sheet of foil therefrom on peeling the foil from the adhesive.

Having described our invention and the preferred manner and mode of practicing same, we claim:

An improved petroleum base asphalt adhesive composition particularly adapted for bonding sheet metal foil to composition roofing comprising an asphalt base having a consistency of 100–300 seconds (Float) at 122° F., a penetration (32° F., 100 g.; 60 seconds) of about 30 mm./10, a softening point (R. & B.) of from 85–95° F., a solvent for said asphalt base, said solvent having an initial boiling point of not less than 300° F., and a maximum end point of 750° F., said solvent together with said asphalt base constituting a vehicle having a viscosity (Saybolt Furol) of 250–500 seconds at 122° F., a mineral filler in amount less than 20% by weight of said finished composition, said composition being characterized by a flash point (Cleveland open cup) of above 100° F., a total solids content of not less than 75%, by remaining soft and adhesive after 48 hours at 77° F. ($\frac{1}{32}'' \pm \frac{1}{64}''$ film on a metal panel), by passing the cold test, by a flow of less than ½" in 24 hours at 140° F. ($\frac{1}{16}''$ film on steel panel at 30° angle), and staining less than 50% of the undersurface of a sheet of metal foil adhered thereto under the condition of said flow test.

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