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PROTECTIVE COATING COMPOSITIONS FOR USE IN AIRLESS SPRAY EQUIPMENT FOR COATING METALLIC UNDERBODIES OF AUTOMOTIVE VEHICLES

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This application is a continuation-in-part of co-pending application Ser. No. 390,756, filed Aug. 19, 1964, which, in turn, is a continuation-in-part of application Ser. No. 304,627, filed Aug. 26, 1963 and now both abandoned.

The present invention relates to sprayable compositions for protecting surfaces from corrosive and abrasive attack, and is especially concerned with sprayable, essentially non-fluid, thixotropic gel-like compositions which are capable of forming a firm, dry, corrosion-, abrasion- and impact-resistant coating on motor vehicle frames and underbodies.

It is a well known practice to coat the metallic under-surfaces of motor vehicles with materials possessing sound deadening as well as, and more importantly, corrosion preventative properties. To this end, both in point-of-manufacture and after-market applications, numerous materials have found utility, and while, in the main, they have been reasonably satisfactory from the standpoint of their sound deadening and corrosion inhibition properties, they nevertheless have various significant shortcomings.

Perhaps the most generally known and widely used conventional automotive undercoating materials are the "filled" asphalt type. It is well known that such materials are difficult to handle and create messy overspray cleanup problems. In addition, substantial quantities, of the order of four to six gallons, or more, of the material are used to undercoat the average passenger vehicle. Thus, while the ingredients of conventional "filled" asphalt undercoating materials are low in cost, any savings in this regard are substantially offset by the cleanup problems concomitant to their use, and the time and labor required in the application of the large quantities used to properly undercoat a vehicle. A still more significant shortcoming of these products in their use as automotive undercoating materials has resulted from the development of pneumatic-hydraulic equipment for the spray application of undercoating materials. Such equipment, unlike previously used spray application apparatus, does not employ air to attain material atomization, but instead accomplishes this result by the release of material at high pressure through a nozzle having extremely small orifices. These so-called "airless" spray units have a number of advantages over air-spray apparatus which have led to the widespread use thereof, especially in after-market channels. Conventional "filled" asphalt type undercoating materials have proven to be unsatisfactory for use with such airless spray units due to their tendency to clog the nozzle orifices through which the undercoating material is forced.

In an effort to overcome the problems encountered with the conventional "filled" asphalt type undercoating materials, especially in airless spray operations, the automotive undercoating industry has developed grease or wax-like materials which are chemically inert and resist the corrosive action of water and road chemicals to which vehicles are subjected in use. While these grease or wax-like undercoating materials have proven satisfactory for utilization in connection with airless spray equipment, they are nevertheless considered only temporary coatings when applied to automotive underbodies, and require fre-

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quent inspection to determine the adequacy of the protection being afforded the metallic surfaces coated therewith. The temporary character of such coating is due, in the main, to the fact that the grease or wax-like materials are non-drying and readily can be removed by abrasion, impact, or by subjection to elevated temperatures.

In accordance with the present invention, improved coating compositions, having special utility in the automotive underbody coating field, have been discovered which substantially overcome the disadvantages heretofore encountered with previously known undercoating materials. The improved compositions of the present invention, apart from producing a long-lasting, firm, dry, corrosion-, abrasion- and impact-resistant film, provide a film having vibration damping and sound deadening properties. In addition, the improved compositions of this invention have excellent adhesion properties and can be applied with no problem over other protective coating materials. A firm, dry film is formed at ambient or ordinary temperatures with the compositions in a matter of a few hours after application to a metal surface and only thin films are required to accomplish the desired results. The film formed by the compositions retains its toughness and resiliency, and does not "split" or crack, under wide extremes of high and low temperature conditions. The compositions are particularly suitable for airless spray application and, when utilized in connection with such equipment, enable a motor vehicle to be effectively undercoated in approximately half the time, with substantially less material, than is required with conventional undercoating materials. In their unapplied form the compositions are stable for prolonged periods over a wide temperature range.

The improved coating compositions of the present invention are characterized in that they are essentially non-fluid and gel-like in an unapplied state, but manifest thixotropic properties under flow and mechanical forces such as are used in airless spray undercoating equipment. More specifically, the improved coating compositions of this invention are characterized by being flowable at ambient or ordinary temperatures under pressure, and while in a flowable state can be mechanically broken-up, disrupted or atomized, and, thereafter, will rapidly reform into an essentially non-fluid, gel-like state without running or dripping. In their reformed applied state, the compositions, upon exposure to atmosphere, will provide a firm, dry, corrosion-, abrasion-, and impact-resistant film or coating. Generally speaking, the pressures at which the compositions of this invention will become flowable in airless spray equipment will range from about 1500 p.s.i. to about 4000 p.s.i., usually from about 2000 p.s.i. to about 2500 p.s.i. Under such pressure, the compositions can be mechanically disrupted at the nozzle of the airless spray equipment and will pass through orifices in the nozzle of a size ranging from 0.010 to 0.060, usually about 0.015 to about 0.025 inch in diameter. The compositions will reform on a surface to which they are applied in from 1 second to 4 seconds, usually in 2 to 3 seconds, without running or dripping off the surface, to provide thereon a continuous film or coating of the character described.

The characteristics desired in the improved coating compositions of the present invention are met by compositions, hereafter described in detail, which are based on either asphaltic materials or resinous materials, and/or mixtures thereof. The term "asphaltic material" is used herein in a generic sense and is intended to include normally solid native or natural asphalts, such as Trinidad, Bermudea, Cuban, gilsonite, grahamite, and glance pitch, bituminous substances such as steam- or vacuum-reduced asphalts and petroleum residues, cracking resi-

dues, oxidized or blown asphalts, crude oil-containing asphalts, coal tars, and pitches, and mixtures of such natural asphalts and bituminous substances, in addition to petrolatums and bituminous resins. The term "resinous material" as used herein refers to both natural and synthetic resins, and mixtures thereof, and includes such naturally-occurring resins as oleoresins, balsams, copal esters, shellac, rosin, and the like, and such synthetic resins as phenol-aldehydes, urea-aldehydes, alkyds, hydrocarbon resins, cumarone-indenes, hydrocarbon-aldehydes, ketonics, epoxies, amine-aldehydes, polyvinyls, polyacrylics, and the like. The present invention contemplates the modification of the foregoing base materials by the incorporation therein of agents capable of effecting changes, either physical or chemical, or both, in the materials to place them in a form suitable for the preparation of the coating compositions of this invention. Wherever the terms "base material" or "resinous coating material" appear herein they are used in a generic sense to encompass asphaltic materials and resin materials, or mixtures thereof, unless specifically stated to be otherwise.

Generally speaking, the base material, whether it be of the asphaltic or resinous type, or a mixture thereof, advantageously is utilized in the form of a suspension or solution in an organic solvent in the preparation of the thixotropic gel-like compositions of the present invention. Where the base material is provided, in commercial form, as a cut-back product, as in the case of certain asphaltic materials, it may so be utilized or it may be diluted further with mineral spirits or other compatible organic solvents. Where the base material is provided in solid form, that is, not in solution or not admixed with an organic solvent, the base material will be diluted with or dissolved in an organic solvent or solvents illustrative examples of which are petroleum solvents such as mineral spirits, coal oil, gasoline, kerosene, turpentine, coal tar solvents such as naphtha, benzene, toluene and xylene, chlorinated hydrocarbons such as carbon tetrachloride, dichloroethylene, trichloroethylene, ketones such as acetone, methylisobutylketone, and methylethylketone; methyl-Cellosolve, and the like. The diluent employed need not be a complete solvent for the base material but may serve merely as a softening agent therefor. In utilizing a flammable-type diluent, it is advantageous from a safe-handling standpoint to select a diluent such that the compositions in their ready-to-use form will have a minimum flash point of about 100° F.

The objectives of the present invention are particularly satisfactorily met by compositions which are based upon asphaltic material derived from crude petroleum residues of either the air-blown or air-unblown type. The properties of asphalts having utility for the purposes of the present invention are variable, excellent results, for example, being attainable with asphalts having a needle penetration of from about 5 to about 110, usually from about 16 to about 85, at 77° F. and a softening point ranging from about 130° to 235° F. Exemplary of asphalts of the character described are those available commercially under the trade designations "Korite #3," "Korite 0" and "Korite K502" (Standard Oil) and "Petrofina S-1083" (American). The "Korite K502" and "Petrofina S-1083" are sold in cut-back form, comprising, in the case of "Korite K502," a 50-50 solution of asphalt and mineral spirits, and, in the case of "Petrofina S-1083," a 60-40 solution of asphalt and mineral spirits, respectively.

The thixotropic gel-like compositions of the present invention should have two rather inconsistent properties, namely, relatively low viscosity in the airless spray equipment, but rigidity, or at least relatively high viscosity, immediately after striking the surface being covered. The compositions should, furthermore, be fairly readily disrupted by mechanical force at the nozzle of the airless spray equipment but should quickly reform on the sur-

face to which applied to avoid running or dripping when this force is removed. Thus, the compositions when at rest will act as solids, and, when flowing under pressure in an airless spray unit, will act as fluids of modest viscosity. This combination of characteristics of the compositions of this invention is attained by the intimate admixing of a suitable gelling agent with the diluted or solvent-containing base material. The term "gelling agent" as employed herein includes those substances which are compatible with the base materials per se, or as admixed with solid particulate components or fillers as described in detail hereafter, and which in combination with such materials are capable of forming a stable, homogeneous, even-textured, strongly adherent, sprayable thixotropic gel-like composition having low internal cohesive strength which, after application to a surface, forms a firm, dry, water- and road chemical-proof film or coating, the film or coating being resistant to corrosion, abrasion and impact, in addition to having good sound-deadening properties and retaining its toughness and resiliency over a wide temperature range.

Various gelling agents can be employed in the preparation of the compositions of this invention. Of especial utility are the alkali and alkaline earth metal salts of higher molecular weight monocarboxylic acids, particularly fatty acids, exemplary thereof being the sodium, potassium, lithium, calcium, barium and strontium salts of such fatty acids, as caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, lauroleic, myristoleic, palmitoleic, oleic, gadoleic, ricinoleic, linoleic, linolenic, elostearic, arachidonic, and clupanodonic, especially desirable being the C₁₆-C₁₈ fatty acids, notably oleic and stearic acid. Other metal fatty acid soaps which can be used include those of aluminum, lead, zinc, cobalt, manganese, and the like. Metal salts of mahogany and petroleum sulfonates as well as alkane sulfonates and alkyl-arylsulfonates also have utility for this purpose. In addition, ammonium salts and short chain and long chain amine salts of the aforementioned higher molecular weight monocarboxylic acids such as those derived from isopropylamine, butyl amine, amyl amine, dodecyl amine, tetradecyl amine, cetyl amine, oleyl amine and the like, can be used.

Illustrative examples of other gelling agents which can be employed are colloidal silicas such as silica aerogels, illustrative examples of which are those available commercially under the trademarks "Cab-O-Sil" (Godfrey Cabot) and "Santocel" (Monsanto Chemical Company); synthetic colloidal magnesium and aluminum silicates; clay reaction products such as those formed by combining bentonite, for instance, with long chain amines, imidazolines, and quaternary ammonium compounds, a number of which reaction products are sold under the trademark "Bentone" (National Lead Company), or those formed by reacting a heterocyclic tertiary amine sold under the tradename "Amine 0" (Geigy Chemical Co.) with an attapulgite derivative sold under the tradename "Atta Gel 20" (Minerals and Chemicals Philipp Corp.); and quaternary ammonium compounds such as higher alkyl (C₁₂ to C₁₈) trimethyl ammonium halides, particularly cetyl trimethyl ammonium chloride, cetyl trimethyl ammonium bromide, oleyl trimethyl ammonium chloride, octadecyl trimethyl ammonium chloride, nonyl benzyl trimethyl ammonium chloride, and the like.

In achieving the desired thixotropic gel-like structure of the compositions of this invention, it is important that intimate contact of the asphaltic and/or resinous material base be made with the gelling agent to obtain substantially uniform distribution of the agent throughout the mass. This result can be attained in a variety of ways depending on the nature of the gelling agent employed. When utilizing a salt of a higher molecular weight fatty acid, for instance, as the gelling agent, an excellent gel structure can be produced by introducing the fatty acid and an aqueous solution of sodium hydroxide, for ex-

ample, into the organic solvent solution of the base material and allowing the sodium salt of the fatty acid to form in situ under agitation. On the other hand, when utilizing a gelling agent such as a lightweight, porous silica aerogel, for example Cab-O-Sil effective results are attainable by adding the aerogel to the organic solvent solution of the base material and mechanically working the mass until the gel structure develops. A colloid mill or paint mill conveniently may be used for this purpose.

In the particularly preferred embodiments of the present invention, as indicated above, the gelling agent is formed in situ and this is especially desirably accomplished by adding to the organic solvent solution of the base material a strong aqueous solution of a metal hydroxide, for instance, and a higher molecular weight fatty acid, particularly oleic or stearic acid, or acid source materials high in such acids, the hydroxide advantageously being used in excess of the stoichiometric proportions necessary to form the corresponding metal salt of the aforesaid fatty acids. In utilizing an alkali metal hydroxide, such as, for example, sodium hydroxide, in forming the thixotropic gel-like structure of the compositions of this invention, an excess of the order of two to six times, and more advantageously two to three times, the stoichiometric proportion required to form the sodium salt of the fatty acid is employed. In forming the gel-like structure with an alkaline earth metal hydroxide, for example, calcium hydroxide, good results have been attained with excesses of the order of 50 to 100%, usually 75 to 85%, over the stoichiometric proportions required. It has been found that such excesses of the hydroxides are especially desirable in producing a thixotropic, gel-like structure in the final coating compositions which is not only stable over a reasonable temperature range but which has little internal cohesive strength, thus adapting it particularly satisfactorily to airless spraying. The rate of addition of the fatty acid, and the extent of the agitation or mixing, in the production of the compositions play a role in the exact character of the thixotropic gel-like structure obtained in the final composition. In general, an excellent gel-like structure results from the aforesaid in situ formation thereof and wherein, in the final coating composition, the water and free alkali or alkaline earth metal hydroxide, for example, constitute from 1 or 2 to 10%, by weight, or somewhat higher.

The formation and character of the thixotropic gel-like structure of the compositions of this invention, as well as the properties of the film or coating formed by the compositions, from the standpoint of its adhesion, abrasion resistance, corrosion resistance and sound deadening characteristics, can be enhanced, augmented and fortified by incorporating in the asphaltic and/or resinous material base of the compositions a solid inorganic particulate material or filler. As in our co-pending application Serial No. 390,756, filed August 19, 1964, the term "filler-less" has applicability in describing the compositions of the present invention and, as used herein, the term is intended to indicate that the physical character of the compositions is such that, to the extent that they contain solid particulate material, the particles of such material will be of a size and will be dispersed in the compositions in a manner to enable the compositions of this invention successfully to be utilized in airless spray equipment.

The particulate material or filler utilized may be selected from a wide group and may range in size from sub-microscopic to macroscopic. However, due to the particular suitability of the thixotropic gel-like compositions for use in airless spray equipment, which, as indicated hereinabove, usually includes a hard-steel nozzle having extremely small orifices, the particulate material or filler, in order to prolong nozzle life, desirably is of the "soft" type, that is, one that has little or no abrasive qualities. Also, due to the small size of the nozzle orifices, the particulate material or filler employed should have a particle size sufficiently small to pass freely through the orifices of the

nozzle to prevent clogging. Depending upon the extent to which the particulate material or filler is dispersed in the compositions to eliminate substantially agglomeration of the particles thereof, compositions of this invention containing a particulate material or filler of size ranging from 0.05 to 2 microns to a mesh size of from about 60 to 70 can be utilized satisfactorily in airless spray equipment employing pressures of about 2000 to 2500 p.s.i. or higher, and using a nozzle having an orifice size of from about 0.015 to about 0.025 inch in diameter. Generally speaking, in order to reduce processing costs, particulate materials or fillers having mesh sizes of 100, usually 300 to 400, or smaller, are preferred. Exemplary of particulate materials or fillers having utility in the present invention are Portland cement, graphite, aluminum powder, slate flour, fly ash, calcium silicate, asbestos, calcium carbonate, spent fuller's earth, talc, mica, clay and the like. Especially desirable results can be attained with a precipitated calcium carbonate sold under the trademark "Kalite" (Diamond Alkali Company). This product has a particle size in the range of 0.1 to 1 micron, and the particles are provided with a 1% fatty acid (stearic acid) coating which aids in the formation of the gel-like structure of the compositions. As indicated, it has been found that, in many of the compositions of this invention, the particulate materials or fillers actively partake and perform an important function in the formation of the gel-like structure of the compositions. It is noteworthy that these effects are attained in accordance with the practice of this invention with solid particulate materials or fillers having particle sizes in both the sub-microscopic and the macroscopic ranges. In addition to this action of the particulate materials or fillers, which permits the substitution or replacement of a portion of the usually relatively more costly gelling agent by the less costly particulate material or filler, their use in the preparation of the compositions has important economic advantages.

Various means, both mechanical and chemical, can be employed for providing adequate dispersion of solid particulate material or filler in the compositions. Generally speaking, conventional stirring equipment will provide the results desired. A standard paint mill, if available, gives excellent dispersion and is especially effective in substantially eliminating agglomeration of larger mesh size particles. A wide variety of chemical dispersants can be incorporated to facilitate distribution of particles in the compositions. Good results have been obtained, for example, with a small amount of the sodium salt of a polymerized alkyl aryl sulfonic acid available commercially under the trade designation "Darvan No. 1" (R. T. Vanderbilt Co.).

The adhesion properties of the compositions of this invention can be enhanced by the addition of materials such as elastomers. Neoprene is particularly suitable for this purpose and is desirably added in dissolved form. An illustrative example of such a solution is one consisting of 15% neoprene AC and 85% xylene. While neoprene is preferred, it may be completely or partially substituted by solutions of natural and reclaimed rubbers, or solutions of synthetic rubbers such as butadiene-acrylonitrile copolymers, butadiene-styrene copolymers, butyl rubber, isobutylene polymers, polyester rubbers, and the like. Neoprene rubbers are particularly desirable additions in amounts of the order of 0.5 to 1%, by weight of the final composition. The neoprene or similar materials should, generally speaking, not be used in proportions beyond their range of solubility in the organic solvent employed in the coating compositions and, ordinarily, of the order of 0.2 to 15% or even somewhat more, but due to economic considerations, usually 0.6 to 2%, by weight of the composition as a whole, commonly will be utilized.

The consistency of the thixotropic gel-like compositions of the present invention in their unapplied state is suggestive of that of petroleum jelly, but they do not have the

grease-like character or feel of such a product. They are, generally speaking, in the main, smooth, even-textured and non-tacky, and are in a non-fluid state at ordinary temperatures. On standing, the viscosity increases so that the resulting gel-like compositions, before application, generally have a cone penetration of about 150 to about 400 as measured on a conventional cone penetrometer using a cone weight of 150 grams.

The following examples are illustrative of particularly preferred coating, especially automotive underbody coating, compositions of the present invention. It will be understood that other coating compositions can readily be made in the light of the guiding principles and teachings provided herein by changes in the selection of the base material, organic solvent diluent, and gelling agent, and the relative proportions thereof, without departing from the spirit of the present invention.

Example 1

Ingredients:	Weight percent
Vacuum reduced asphalt ("Petrofina S-1083") cut back further with mineral spirits to provide 50% solution of asphalt in mineral spirits	78.9
Sodium hydroxide (50% aqueous)	9.4
Oleic acid	7.9
Neoprene (15% neoprene AC-85% xylene)	3.8

In the production of an approximately 4000 pound batch, the asphalt-mineral spirits solution is charged into a mixing tank. The sodium hydroxide is then added over a period of 30 minutes. The oleic acid is then added over a period of 45 minutes. Lastly, the neoprene-xylene solution is added over a 20 minute period. The mixture is then brought to a temperature of 140° F. Generally speaking, the mixing of the ingredients under high-speed shear agitation favors gel formation, even at low temperatures such as room temperature. At low-speed agitation, somewhat elevated temperatures should be used to promote gel formation. The composition is black in color, is a non-fluid gel, and has a smooth feel.

Example 2

Ingredients:	Weight percent
Asphalt (blown)	42.8
Mineral spirits	46.4
Sodium hydroxide (50% aqueous)	5
Oleic acid	5.8

The asphalt and the mineral spirits are first admixed and the aqueous sodium hydroxide is then dispersed therein, with agitation, until the mixture is essentially homogeneous. The oleic acid is added and the mixture is stirred for 30 minutes at 180° F. until completely uniform. The composition is black in color, is a non-fluid gel, and is smooth and homogeneous in character.

Example 3

Ingredients:	Weight percent
Vacuum reduced asphalt ("Petrofina S-1083") cut back further with mineral spirits to provide 50% solution of asphalt in mineral spirits	78.9
Butadiene-acrylonitrile rubber (15% Hycar 1022-85% toluene)	4
Sodium hydroxide (50% aqueous)	9.3
Tall oil fatty acids	7.8

The procedure used in Example 1 is followed. The product is a smooth non-fluid gel.

Example 4

Ingredients:	Weight percent
Asphalt (blown)	45
Gilsonite	5.5
Benzene	40
Silica aerogel (Cab-O-Sil)	9.5

The asphalt, gilsonite and benzene are admixed until homogeneous. The silica aerogel is then added and the entire mixture is introduced into a colloid mill and worked for 45 minutes at a temperature of 130° F. The composition is black in color, is a non-fluid gel, and has a smooth, non-tacky feel.

Example 5

Ingredients:	Weight percent
Asphalt (blown)	44.8
Mineral spirits	46.5
Neoprene	1
Sodium hydroxide (50% aqueous)	5.2
Stearic acid	2.5

The asphalt, neoprene (first dissolved in xylene) and mineral spirits are first admixed. Thereafter the procedure set forth in Example 1 is followed. The product is a black non-fluid gel.

Example 6

Ingredients:	Weight percent
Asphalt (Korite 0)	48.2
Mineral spirits	48.4
Red oil (oleic acid)	2.4
Hydrated lime	0.5
Water	0.5
Darvan No. 1 (dispersant)	Trace

The asphalt and the mineral spirits are first admixed. The red oil is then added to the mixture. The hydrated lime, water and Darvan No. 1 are slurried together and then slowly added to the asphalt mixture. The mixture is stirred for 30 minutes at a temperature of 180° F. until uniform. The composition is black in color, is a non-fluid gel, and is smooth and homogeneous in character.

Example 7

Ingredients:	Weight percent
Asphalt (Korite No. 3) cut back with mineral spirits to provide 50% solution of asphalt in mineral spirits	75
Sodium hydroxide (50% aqueous)	1.4
Stearic acid	3.6
Calcium carbonate (Kalite)	20

The calcium carbonate is added to the cutback asphalt. The stearic acid is melted and poured slowly into the asphalt-calcium carbonate mixture with agitation. The sodium hydroxide is then added slowly while stirring the mixture. The composition is stirred for 45 minutes at a temperature of 125° F. The resulting composition is black in color, is a non-fluid gel, and has a smooth, non-tacky feel.

Example 8

Ingredients:	Weight percent
Asphalt (Korite K502 cut back-50% Korite #3 asphalt and 50% mineral spirits)	79
Sodium hydroxide (50% aqueous)	2
Stearic acid	4
Spent fuller's earth	15

The spent fuller's earth is added to the asphalt cutback and thoroughly dispersed therein with a mechanical stirrer. The stearic acid and sodium hydroxide are then added as in Example 7. The composition is stirred for 1 hour at a temperature of 160° F. until uniform. The resulting composition is black in color, is a non-fluid gel, and is smooth and homogeneous in texture.

Example 9

Ingredients:	Weight percent
Asphalt (Korite No. 3) cut back with gasoline to provide a 60% solution of asphalt in gasoline	80.5
Sodium hydroxide (50% aqueous)	4
Oleic acid	4.5
Mica	11

The asphalt and gasoline are first admixed and the mica is then dispersed therein. The aqueous sodium is added,

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with agitation, until the mixture appears uniform. The oleic acid is then added and the mixture stirred for 40 minutes at 175° F. The composition is black, is a non-fluid gel, and is smooth textured and homogeneous in character.

Example 10

Ingredients:	Weight percent
Asphalt (blown) -----	44
Gasoline -----	46
Stearic acid -----	4
Barium hydrate -----	2
Water -----	4
Darvan No. 1 (dispersant) -----	Trace

The asphalt and gasoline are first admixed. The stearic acid is melted and poured slowly into the asphalt mixture. The barium hydrate, water and Darvan No. 1 are slurried together and then slowly added to the asphalt mixture. The mixture is stirred for 30 minutes at a temperature of 180° F. until uniform. The composition is black in color, is a non-fluid gel, and is smooth and homogeneous in character.

Example 11

Ingredients:	Weight percent
Hydrocarbon Resin (Piccopale SF-100) -----	44
Mineral spirits -----	46
Red Oil (Oleic acid) -----	4
Hydrated lime -----	2
Water -----	4
Darvan No. 1 (dispersant) -----	Trace

The resin and mineral spirits are first dissolved. The red oil is then added to the mixture. The hydrated lime, water and Darvan No. 1 are slurried together and then slowly added to the resin solution. The composite is stirred for 30 minutes at a temperature of 180° F. until uniform. The composite is brown in color, is a non-fluid gel, and is smooth and homogeneous in character.

Example 12

Ingredients:	Weight percent
Vinyl toluene copolymer (Keltrol 1074) -----	25
Vacuum reduced asphalt cut back to 50% solids with VM & P naphtha -----	30
Toluene -----	5
Stearic acid -----	3
Calcium carbonate (Kalite) -----	36
Sodium hydroxide (50% aqueous) -----	1

The resin, asphalt cutback and solvent are first admixed. The calcium carbonate is then added. The stearic acid is melted and poured slowly into the asphalt-resin mixture. The aqueous hydroxide is then added slowly with stirring until uniform. The resulting composition is black in color, is a semi-fluid gel, and has a smooth, non-tacky feel.

Example 13

Ingredients:	Weight percent
Petroleum sulfonate (Alox 600) -----	.5
Naphthenic acid -----	2.0
Litharge -----	.5
Hydrated lime -----	.5
Asphalt (Korite #3) cut back 50% with mineral spirits -----	66.5
Asbestos (grade 7TF1) -----	24.0
Calcium carbonate -----	6.0

The petroleum sulfonate and naphthenic acid are admixed and brought to 300° F. temperature. The litharge and hydrated lime are then added slowly with mixing and stirred for 60 minutes. The asphalt cutback is then added until uniform. The asbestos is added followed with the calcium carbonate and mixed until homogeneous. The resulting composition is black in color, is a semi-fluid gel, and has a textured, non-tacky feel.

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Example 14

Ingredients:	Weight percent
Asphalt (blown) -----	38
Mineral spirits -----	38
Attapulgite clay (Attagel 20) -----	20
Heterocyclic tertiary amine (Nalcomine 39GM) -----	4

The asphalt and the mineral spirits are first admixed and the Attagel 20 is dispersed therein, with agitation, until the mixture is uniform. The amine is then added and the mixture stirred until it is homogeneous. The composition is black in color, is a non-fluid gel, and is smooth and homogeneous in character.

Example 15

Ingredients:	Weight percent
Coal tar (needle penetration of 70-80 at 77° F.) cut back to 50% solids with toluene -----	74
Sodium hydroxide (50% aqueous) -----	2
Red oil (Oleic acid) -----	4
Calcium carbonate (Kalite) -----	20

The calcium carbonate is added to the coal tar cutback. The red oil is then added to the mixture. The sodium hydroxide is then added slowly while stirring the mixture. The composition is stirred for 45 minutes at a temperature of 125° F. The resulting composition is black in color, is a non-fluid gel, and has a smooth, non-tacky feel.

Example 16

Ingredients:	Weight percent
Petrolatum (Gulf No. 5) cut back to 50% solids with mineral spirits -----	77
Red oil (Oleic acid) -----	2
Sodium hydroxide (50% aqueous) -----	1
Calcium carbonate -----	20

The calcium carbonate is added to the petrolatum cutback. The red oil is then added to the mixture. The sodium hydroxide is then added slowly while stirring the mixture. The composition is stirred for 30 minutes at a temperature of 130° F. The resulting composition is brown in color, is a non-fluid gel, and has a smooth, non-tacky feel.

Example 17

Ingredients:	Weight percent
Terpene-phenolic resin (Durez No. 12603) -----	38
Oil (200 viscosity) -----	15
Mineral spirits -----	38
Oleic acid -----	4.5
Sodium hydroxide (50%) -----	4.5

The resin, oil and mineral spirits are mixed and then heated until the mixture is fluid. The mixture is cooled to 130° F. and the oleic acid is added with stirring. The sodium hydroxide is slowly added over a period of 20 minutes. The initial viscosity of the mixture is similar to that of a heavy syrup. Upon setting and cooling, the mixture forms a very heavy gel. An additional 25%, by weight, of mineral spirits is added and the heavy gel converts to a smooth, thixotropic gel.

The proportions of the various ingredients utilized in the preparation of the unique coating compositions of the present invention are somewhat variable. The base material together with the organic solvent diluent constitute by far the greatest proportion of the compositions, usually from about 50% to 97%, by weight, thereof, with the base material comprising, anywhere from about 20% to 50%, usually about 40% to about 45%, of the total weight of the compositions. When the base material is partially substituted by a solid particulate material or filled, the latter desirably will comprise from about 10 to 50%, usually 20 to 40%, by weight of the composition. The amount of gelling agent utilized is dependent on the gelling properties of the particular agent employed. Generally speaking, the gelling agent will constitute from 1% to 25%, by weight, of the compositions. In those instances where in situ gel development

techniques are used, the gelling agent will advantageously comprise from about 5% to about 15%, usually about 6 to 10%, of the total weight of the compositions, while in those cases where a gel structure is obtained by mechanical means, that is, for example, by milling the base material with a silica suspension, the gelling agent will comprise from about 1% to about 15%, usually from about 3% to 10%, by weight, of the composition depending upon the particular silica composition and milling procedure utilized.

The thickness of the coating applied to a metallic surface, for instance, will vary within appreciable limits depending, among other things, upon the environment in which the coated metal is used. In automotive underbody coating applications, outstanding corrosion-, abrasion- and impact-resistance, as well as vibration damping and sound deadening results can be attained with a coating having a thickness of from 5 to 15 mils, usually 8 to 10 mils. A coating of approximately 10 mils on the metallic undersurfaces of an average automobile can be obtained with about one gallon of the compositions of the present invention. A film of such a thickness on a metal panel was subjected to salt spray tests and found to be capable of resisting attack on the metal surface by a 5% salt solution spray over a period of 2000 hours at a temperature of from 95 to 100° F. A film of this thickness on a metal panel, in addition, demonstrated 100% retention at -10° F. and no sag or drip at temperatures up to 325° F.

In order to demonstrate the outstanding characteristics of the coating compositions of the present invention, an asphaltic material based composition prepared in accordance with the teachings hereof was compared from various aspects with commercially available undercoating compositions of the grease-base type, the conventional "filled" asphalt type, and the emulsion type. The results of these comparative tests are set forth in the following table.

TABLE

	Gelled compositions	Grease-base type	Conventional asphalt type	Emulsion type
Rust Protection (5% salt spray), hrs.	2,000	250	400	400
Sound Deadening (Decibels Decay 70° F.)	5	1-1½	6	4
Gallons Required Per Auto.	1	2-2½	6	6
Sag Temperature (° F.)	325	180	325	325
Added Weight Per Car (Lbs.)	8	20	60	48
Abrasion Test—S.A.E.	Passed	Failed	Passed	Failed

It will be understood that various changes can be made in the compositions with respect to the ingredients and the amounts thereof utilized; and changes can be made in the methods employed for achieving the desired gel structure without departing from the spirit of the invention.

What is claimed is:

1. A protective coating composition for use in airless spray equipment for coating metallic underbodies of automotive vehicles comprising a normally non-fluid, sprayable, thixotropic gel-like mixture containing as essential ingredients from 50% to 97%, by weight, of a solution of a substantially water-insoluble resinous coating material and an organic solvent which is a solvent for said material at ambient temperatures (said material constituting from 20% to 50%, by weight, of the thixotropic gel-like mixture), and from 1% to 25%, by weight, of said gel-like mixture of a gelling agent, said gelling agent being selected from a member of the group consisting of: (a) an in situ formed metal salt of a higher molecular weight fatty acid; (b) an in situ formed ammonium salt of a higher molecular weight carboxylic acid; (c) an in situ formed amine salt of a higher molecular weight carboxylic acid; and mixtures thereof, said normally non-fluid, sprayable, thixotropic gel-like mixture when sprayed

on the underbody of a motor vehicle forming a firm, dry, impact-, corrosion- and abrasion-resistant coating having sound deadening properties.

2. A protective coating composition for use in airless spray equipment for coating metallic underbodies of automotive vehicles comprising a normally non-fluid, sprayable, thixotropic gel-like mixture containing as essential ingredients from 50% to 97%, by weight, of a solution of an asphaltic material and an organic solvent which is a solvent for said material at ambient temperatures (said material constituting from 20% to 50%, by weight, of the thixotropic gel-like mixture), and from 1% to 25%, by weight, of said gel-like mixture of a gelling agent, said gelling agent being selected from a member of the group consisting of: (a) an in situ formed metal salt of a higher molecular weight fatty acid; (b) an in situ formed ammonium salt of a higher molecular weight carboxylic acid; (c) an in situ formed amine salt of a higher molecular weight carboxylic acid; (d) a gel-forming silica aerogel; (e) a synthetic colloidal metal silicate; (f) an in situ formed clay-amine reaction product; and mixtures thereof; said gelling agent being characterized in that it is compatible with said material and is capable of forming therewith a stable, homogeneous, strongly adherent, normally non-fluid, sprayable, thixotropic gel-like structure which when at rest will act as a solid and when flowing at ambient temperatures under pressure in airless spray equipment will act as a fluid, said mixture being characterized in that it is flowable at ambient temperatures under pressures of from about 1500 to about 4000 p.s.i. in airless spray equipment and is capable under such flow pressures of being mechanically disrupted to a state to enable the mixture to pass through openings of a size of from about 0.01 to about 0.06 inch in diameter in the nozzle of airless spray equipment without any essential clogging thereof and is capable after mechanical disruption of reforming in from 1 to 4 seconds into a substantially continuous coating which is strongly adherent and forms a firm, dry

film which is impact-, corrosion- and abrasion-resistant and has sound deadening properties.

3. A protective coating composition for use in airless spray equipment for coating metallic underbodies of automotive vehicles comprising a normally non-fluid, sprayable, thixotropic gel-like mixture containing as essential ingredients from 50% to 97%, by weight, of a solution of a substantially water-insoluble resinous coating material and an organic solvent which is a solvent for said material at ambient temperatures (said material constituting from 20% to 50%, by weight, of the thixotropic gel-like mixture), and from 1% to 25%, by weight, of said gel-like mixture of a gelling agent, said gelling agent being selected from a member of the group consisting of: (a) a gel-forming silica aerogel; (b) a synthetic colloidal metal silicate; (c) an in situ formed clay-amine reaction product; and mixtures thereof, said normally non-fluid, sprayable, thixotropic gel-like mixture when sprayed on the underbody of a motor vehicle forming a firm, dry, impact-, corrosion- and abrasion-resistant coating having sound deadening properties.

4. A composition as claimed in claim 2 wherein from about 10% to about 50% of the asphaltic material is substituted by a substantially non-abrasive solid inorganic particulate material.

5. A protective coating composition for use in airless spray equipment for coating metallic underbodies of automotive vehicles comprising a normally non-fluid, sprayable, thixotropic gel-like mixture containing as essential ingredients from 50% to 97%, by weight, of a solution of a substantially water-insoluble resinous coating material and an organic solvent which is a solvent for said material at ambient temperatures (said material constituting from 20% to 50%, by weight, of the thixotropic gel-like mixture), and from 3% to 15%, by weight, of said gel-like mixture of a gelling agent, said gelling agent being selected from a member of the group consisting of: (a) an in situ formed metal salt of a higher molecular weight fatty acid; (b) an in situ formed ammonium salt of a higher molecular weight carboxylic acid; (c) an in situ formed amine salt of a higher molecular weight carboxylic acid; (d) a gel-forming silica aerogel; (e) a synthetic colloidal metal silicate; (f) an in situ formed clay-amine reaction product; and mixtures thereof, said normally non-fluid, sprayable, thixotropic gel-like material when sprayed on the underbody of a motor vehicle forming a firm, dry, impact-, corrosion- and abrasion-resistant coating having sound deadening properties.

6. A corrosion- and abrasion-resistant automotive undercoating composition comprising a normally non-fluid, sprayable, thixotropic gel-like mixture containing as essential ingredients from 50% to 97%, by weight, of a solution of an asphaltic material and an organic solvent which is a solvent for said material at ambient temperatures (said material constituting from 20% to 50%, by weight, of the thixotropic gel-like mixture), and from about 3% to about 15%, by weight, of the gel-like mixture of the in situ formed reaction product of a 50% aqueous sodium hydroxide solution with stearic acid, the hydroxide being used in excess of the stoichiometric amount necessary to form the corresponding sodium salt of stearic acid.

7. A composition as claimed in claim 5 wherein from about 20% to about 40% of the resinous coating material is substituted by a substantially non-abrasive solid inorganic particulate material having a particle size of from about 0.05 micron to 400 mesh.

8. A non-fluid thixotropic gel-like composition for use in airless spray automotive undercoating equipment consisting essentially of a substantially homogeneous mixture of from 50% to 97%, by weight, of an organic solvent solution of an asphaltic material and from about 3% to about 15%, by weight, of a gelling agent in the form of an in situ formed metal salt of a higher molecular weight fatty acid.

9. A non-fluid thixotropic gel-like composition for use in airless spray automotive undercoating equipment consisting essentially of a substantially homogeneous mixture of from 50% to 97%, by weight, of an organic solvent solution of an asphaltic material and from about 3% to about 15%, by weight, of a gelling agent in the form of an in situ formed salt of a metal selected from the group consisting of alkali and alkaline earth metals and a fatty acid having 16 to 18 carbon atoms.

10. A sprayable, non-fluid automotive undercoating composition consisting essentially of an intimate, homogeneous thixotropic gel of from 50% to 97%, by weight, of an organic solvent solution of an asphaltic material and from about 3% to about 15%, by weight, of the in situ formed reaction product of a fatty acid having 16 to 18 carbon atoms with an excess of a hydroxide selected from the group consisting of alkali and alkaline earth metal hydroxides.

11. A protective coating material for metal surfaces consisting essentially of a sprayable non-fluid thixotropic gel comprising, by weight, about 70% of an organic solvent solution of an asphaltic material in which the asphaltic material constitutes about 35%, by weight, of the gel, about 10% of an in situ formed sodium stearate,

and about 20% calcium carbonate having a particle size of about 0.1 to 1 micron.

12. A protective coating material for metal surfaces consisting essentially of a sprayable non-fluid thixotropic gel comprising, by weight, 90 to 97% of an organic solvent solution of an asphaltic material in which the asphaltic material constitutes 40% to 45%, by weight, of the gel, and from about 10% to 3% of an in situ formed calcium salt of a higher molecular weight fatty acid.

13. A coating material as claimed in claim 12 wherein the calcium salt is one selected from the group consisting of calcium oleate and calcium stearate.

14. A protective coating composition in the form of a normally non-fluid, sprayable, thixotropic gel for use in airless spray automotive undercoating equipment containing as essential ingredients basis weight about 90% of an organic solvent solution of a hydrocarbon resin in which the resin constitutes 40% to 45%, by weight, of the composition, and about 10% of the in situ formed alkaline earth metal salt of a fatty acid having from 16 to 18 carbon atoms.

15. A protective coating composition in the form of a normally non-fluid, sprayable, thixotropic gel for use in airless spray automotive undercoating equipment containing as essential ingredients basis weight about 77% of an organic solvent solution of petrolatum in which the petrolatum constitutes about 40% to 50%, by weight, of the composition, about 3% of the in situ formed alkali metal salt of a fatty acid having from 16 to 18 carbon atoms, and about 20% of calcium carbonate.

16. A method of preparing a protective coating composition in the form of a non-fluid, thixotropic gel for use in airless spray equipment to coat the metallic underbodies of automotive vehicles, said composition being characterized by being flowable at ambient temperatures in airless spray equipment under pressures of from about 1500 to 4000 p.s.i. and capable under said pressures of mechanical disruption to a state to enable the composition to pass through openings of a size of from about 0.01 to 0.06 inch in diameter in the nozzle of airless spray equipment without any essential clogging thereof and further being capable after mechanical disruption under said pressures of reforming on a surface to which it is applied in from 1 to 4 seconds into a substantially continuous coating which, upon exposure to air at ambient temperatures, forms a firm, dry, impact-, corrosion- and abrasion-resistant film having sound deadening properties, the steps comprising providing a thixotropic gel-like mixture containing as essential ingredients from 50% to 97%, by weight, of a solution of a substantially water-insoluble resinous coating material and an organic solvent which is a solvent for said material at ambient temperatures (said material constituting from 20% to 50%, by weight, of the thixotropic gel-like mixture), and from 1% to 25%, by weight, of said gel-like mixture of a gelling agent, said gelling agent being selected from a member of the group consisting of: (a) an in situ formed metal salt of a higher molecular weight fatty acid; (b) an in situ formed ammonium salt of a higher molecular weight carboxylic acid; (c) an in situ formed amine salt of a higher molecular weight carboxylic acid; (d) a gel-forming silica aerogel; (e) a synthetic colloidal metal silicate; (f) an in situ formed clay-amine reaction product; and mixtures thereof; said gelling agent being characterized in that it is compatible with said coating material and is capable of forming therewith a stable, homogeneous, strongly adherent, normally non-fluid, sprayable, thixotropic gel-like structure which when at rest will act as a solid and when flowing at ambient temperatures under pressure in airless spray equipment will act as a fluid.

17. A method as claimed in claim 16 wherein the gelling agent is the in situ formed reaction product of a metal hydroxide and a higher molecular weight fatty acid.

18. A method as claimed in claim 16 wherein a solid inorganic particulate material is admixed with the solvent

solution and the gelling agent to promote formation of the thixotropic gel.

19. A method of preparing a non-fluid, sprayable automotive undercoating composition comprising providing a solution consisting essentially of from 50% to 97%, by weight, of an asphaltic material and an organic solvent which is a solvent for said material at ambient temperatures, and converting the solution to a non-fluid, sprayable thixotropic gel by forming in situ a salt of a metal selected from the group consisting of alkali and alkaline earth metals and a fatty acid having 16 to 18 carbon atoms, said salt comprising from about 3% to about 15%, by weight, of the thixotropic gel, the gelled solution when applied to the underbody of a motor vehicle forming a firm, dry, impact-, corrosion- and abrasion-resistant coating.

20. A method of preparing a non-fluid, sprayable metal coating composition comprising providing a mixture of an organic solvent solution of an asphaltic material, said asphaltic material being present in an amount to constitute about 20% to 50%, by weight, of said composition, and a substantially non-abrasive solid inorganic particulate material having a particle size of from about 0.05 micron to 400 mesh, said particulate material being added in amount such that it will constitute from about 20 to 40%, by weight, of the coating composition, converting said mixture to a non-fluid sprayable thixotropic gel by admixing therewith a higher molecular weight fatty acid and a strong aqueous solution of a metal hydroxide, the hydroxide being in excess of the stoichiometric amount required for the production of the metal salt of the fatty acid, said metal salt of the acid being present in proportions of about 5 to 10%, by weight, of said composition.

21. The method of claim 20, wherein the particulate material is calcium carbonate and the metal hydroxide is selected from the group consisting of alkali and alkaline earth metal hydroxides.

22. A method of coating the metallic underbodies of automotive vehicles with a firm, dry, impact-, corrosion-, and abrasion-resistant coating having sound deadening properties comprising providing a thixotropic gel-like mixture containing as essential ingredients from 50% to 97%, by weight, of a solution of a substantially water-insoluble resinous coating material and an organic solvent which is a solvent for said material at ambient temperatures (said material constituting from 20% to 50%, by weight, of the thixotropic gel-like mixture), and from 1% to 25%, by weight, of said gel-like mixture of a gelling agent, said gelling agent being selected from a member of the group consisting of: (a) an in situ formed metal salt of a higher molecular weight fatty acid; (b) an in situ formed ammonium salt of a higher molecular weight carboxylic

acid; (c) an in situ formed amine salt of a higher molecular weight carboxylic acid; (d) a gel-forming silica aerogel; (e) a synthetic colloidal metal silicate; (f) an in situ formed clay-amine reaction product; and mixtures thereof; said gelling agent being characterized in that it is compatible with said coating material and is capable of forming therewith a stable, homogeneous, strongly adherent, normally non-fluid, sprayable, thixotropic gel-like structure which when at rest will act as a solid and when flowing at ambient temperatures under pressure in airless spray equipment will act as a fluid, said mixture being characterized in that it is flowable at ambient temperatures under pressures of from about 1500 to about 4000 p.s.i. and is capable under such flow pressures of mechanical disruption to a state to enable it to pass through openings of a size of from about 0.01 to 0.06 inch in diameter without any essential clogging thereof and is capable after mechanical disruption of reforming in from 1 to 4 seconds into a substantially continuous coating, applying pressure of from 1500 to 4000 p.s.i. to said mixture to cause it to flow, applying a disrupting force to the flowing mixture to atomize it, passing the atomized mixture through an opening of a size of from about 0.01 to 0.06 inch in diameter to form a spray of the mixture, directing the spray at a surface to be coated, allowing the atomized mixture to reform on the coated surface, and exposing the coated surface to atmosphere at ambient temperatures to form a firm, dry, impact-, corrosion- and abrasion-resistant coating having sound deadening properties.

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