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# CORROSION PROOFING COMPOSITION AND METHOD

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## ABSTRACT OF THE DISCLOSURE

The application discloses protective compositions adapted for application by various modes, including especially spraying. The safety and smoothness of application, high corrosion resistance and durability of these corrosion-proofing systems in automotive undercoating and other applications are attributed to the interaction of the negative oliensis petroleum asphalt, characteristically platy particulate mineral filler, water insoluble waxy oxidate soap with acid number of about 20 to 50 and organophilic modified clay which they contain. Modified systems are also disclosed in which the mineral filler includes asbestos "floats."

## RELATED APPLICATION

This application discloses and claims subject matter which it bears in common with prior copending application Ser. No. 533,224, filed Mar. 10, 1966, now abandoned.

## BACKGROUND OF THE INVENTION

This invention relates to coating compositions and methods for protecting various types of objects, including especially the metallic underparts of vehicles, from corrosion.

Experience has shown that a corrosion-proofing coating material for vehicular underbodies, commonly known as "undercoating", must possess and/or satisfy a number of critical properties and/or requirements which are essential for its successful utilization. Of particular importance, for example, is the property of "sprayability," ease of uniform application from a spray-gun. A readily sprayable composition, one having sprayability, is a composition which will discharge from a spray-gun in an even pattern with a minimum of over-spray and without the use of higher pressures than are available from the air-compressing equipment possessed by the wide majority of filling stations, automobile dealers and other shops which do undercoating application work. Such a composition should discharge smoothly, rather than in a stringy fashion. It should be capable of drying to the touch relatively quickly but should not contain solvents that are so volatile as to create a fire hazard. It should be adaptable to application at adequate levels of thickness without excessive dripping and sagging, and yet be sufficiently fluid to penetrate and coat crevices and close-fitting joints in the object being coated. It should discharge smoothly from an air-less spray gun. It should discharge smoothly over a wide temperature range. It should not dribble from the spray-gun tip when spraying operations are interrupted for short periods. It should not give off odors that would be offensive to personnel applying the material. In view of the close proximity between the spray and personnel applying it, the material should not contain components which may tend to endanger the health of personnel.

The dried undercoating which remains on the vehicular underbody or other object after the volatile solvent has evaporated should be resistant to the action of brine, in



view of the common use of salts on the highways for melting snow and ice. The coating should have considerable impact and abrasion resistance so that it is not easily punctured by stones and other objects thrown up against the vehicle underbody by the wheels. It should be resistant to weathering, impervious to water and, above all, free of any tendency to absorb or "wick" moisture, in order to prevent corrosion-inducing moisture and oxygen from initiating rust beneath its surface. There should be no substantial tendency for the coating to soften and "run" in warm weather or to become brittle and lose its impact resistance in cold weather. The coating should possess good sound deadening properties. In addition, it is desirable that the dried coating have a stippled or relatively dull pebbly finish. Interestingly, it has been found that unless an undercoating possesses such a finish, which finish or appearance was characteristic of some of the earlier undercoating compositions to which members of the public have long been accustomed, the saleability of the undercoating is adversely affected to a substantial extent.

From the foregoing discussion, it should be apparent that mere corrosion resistance and ease of application, as important as these properties are, are not alone sufficient to qualify a coating material for undercoating purposes. Thus, a deficiency in any of the previously described critical properties renders a coating material unsuitable for undercoating purposes.

Heretofore, corrosion-proofing compositions based on cut-back coal tar and filled with talc and amine-treated clay have been suggested for corrosion proofing purposes. Such coatings have been said to possess a consistency suitable for easy and effective application to surfaces and to be stable against settling. Although evidence has been presented which indicates that such coatings possess corrosion resistance, they nevertheless suffer from certain disadvantages and fail to possess all of the critical properties set forth hereinabove.

For instance, coal tar pitch is substantially more expensive than pitch derived from petroleum. Secondly, coal tar pitch has a characteristic strong odor which can be irritating and offensive to personnel. Thirdly, coal tar has been reported to cause dermatitis and skin cancer when in contact with the skin for long periods. Thus it is apparent that compositions and methods for protecting vehicular underbodies and other objects against corrosion through the use of coal tar products suffer from certain disadvantages.

Corrosion-proofing compositions based upon petroleum asphalt have been suggested in the past. Such compositions had a tendency to spray in an unacceptably stringy fashion during the early development of the art. Later, the stringiness of such coatings was reduced by incorporating therein relatively large amounts of filler, e.g., 20% by weight of asbestos or natural clay in the undercoating composition. It was also believed that the length of the asbestos fibers, coupled with their tendency to mat and entangle with one another contributed considerable additional mechanical strength to those coating compositions which contained them. Unfortunately, although the asbestos and clay largely cured the stringiness problem, they introduced still another problem. It has been found that the presence of relatively large amounts of filler such as asbestos and/or clay in an automobile undercoating actually causes a transfer of moisture from the outer surface of the coating to the metal/coating interface, where the moisture causes corrosion of the metal. The experience gained with such coatings suggests that that a high degree of corrosion resistance is not attainable with compositions which are based upon petroleum asphalt and which contain enough filler material to have


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satisfactory sprayability. Thus, it appears that prior art undercoating compositions and methods which employed petroleum asphalt binders suffered from certain disadvantages and that there is a need for improvements in compositions and methods for protecting vehicular underbodies and other objects against corrosion.

It is a principal object of this invention to fulfill the aforementioned need. It is a further object to provide compositions and methods for protecting metal surfaces from the action of moisture and brine. Still another object is to provide compositions and methods for covering metal with a protective coating that possesses unusually good resistance to impact and abrasion over a wide temperature range without sacrificing corrosion protection. A further object is to provide compositions and methods for covering vehicular underbodies with a thick protective and sound-deadening coating without danger of stringiness during application, without danger of dripping and sagging during or after application, and without sacrificing the corrosion protection characteristics of the coating. A further object is to provide compositions and methods for protecting vehicular underbodies, which compositions and methods are based upon petroleum-derived bituminous material and are free of coal tar and coal tar products. Another object is to provide undercoating compositions and methods which possess and/or satisfy all of the above described critical properties and/or requirements. These and other objects of the invention will be readily apparent to those skilled in the art upon consideration of the description of the invention and of certain preferred embodiments thereof which are set forth hereinafter.

## BRIEF DESCRIPTION OF THE INVENTION

It has been found unexpectedly that the employment of certain ingredients in certain particular and critical quantities leads to coatings of excellent application, protection and strength characteristics. Specifically, it has been found that vehicular underbodies and other objects may be protected from corrosion by applying thereto a thixotropic composition consisting essentially of the following ingredients: about 26% to about 42% by weight of oxidized asphalt having a Saybolt Furol Viscosity of about 30 to about 100, a negative Oliensis, a melting point in the range of about 180° F. to about 230° F., and a penetration of about 20 to about 40; about 27% to about 42% by weight of mineral filler consisting essentially of hydrated magnesium silicate and characterized by fibrous, nodular and platy particles, at least about 50% by weight of which are finer than 10 microns by particle sedimentation and no more than about 3% of which are coarser than 325 mesh; about 16% to about 29% of a water insoluble metal soap of a waxy hydrocarbon oxidate characterized by an acid number in the range of about 20 to about 50; about 3% to about 7% of an organophilic modified clay; the basis of the foregoing weight percentages being the total weight of said asphalt, filler, soap and clay in said composition; and sufficient volatile hydrocarbon solvent to render said composition sprayable.

## DESCRIPTION OF A PREFERRED EMBODIMENT

In a preferred embodiment of the invention, the foregoing ingredients are present in the following percentages, employing the aforesaid basis: asphalt, about 26 to about 30%; mineral filler, about 35 to about 40%; soap, about 24 to about 29%; and organophilic modified clay, about 5% to about 7%; the composition being substantially free of all natural clay and asbestos in anything other than inconsequential amounts (e.g. not more than 5% of either) and containing in addition to the foregoing about 0.5 to about 2.5% of corrosion inhibitor of the type to be disclosed hereinafter.

It has been found that compositions of the foregoing type: spray on smoothly, with minimum overspray dribbling and stringiness at very reasonable operating pressures over a wide temperature range; dry quickly; build up into coatings of adequate thickness without excessive dripping and sagging; are sufficiently fluid to penetrate crevices; and are non-irritating and non-toxic to personnel. The dried undercoating of such compositions exhibit all of the desired physical properties set forth above. These compositions have been tested extensively in both the laboratory and under conditions of actual use and have been found to give superior corrosion resistance even when applied in rather thin coats. This, of course, is a definite advantage, since the cost of materials involved in obtaining a given degree of corrosion protection is thereby reduced. It has been found that applications to a wet thickness level on the order of about 10 to 20 mils give very good corrosion protection and physical properties. However, it has also been found that when the material is applied at wet thickness levels far above that required for commercially acceptable coatings, e.g. about 100 mils or more, sagging and dripping may occur. In ordinary practice, this difficulty is not encountered, but the ability to build up a sag-free, drip-free coating to a wet thickness of about 125 mils or more has been incorporated in some military specifications. See for instance, Federal Specification TTC 520*a*. Accordingly, it was desired to prepare a modification of the preferred composition which would meet such a specification.



## BACKGROUND AND BRIEF DESCRIPTION OF A MODIFIED FORM OF THE INVENTION

Upon studying the undesirable effects of incorporating relatively large amounts of asbestos fibers into undercoating compositions, it was noted that the longest grades of fibers, which offered the potential of greater reinforcement, appeared to have a more drastic effect on corrosion resistance than asbestos "shorts." The latter, however, while being somewhat less deleterious in respect to corrosion resistance, nevertheless were unsatisfactory in the composition of the invention in that they tended to plug the nozzles of "airless spray" application equipment. After further study and experimentation, an asbestos product known as "floats" (to be described in greater detail hereinafter) was found to be suitable for use in modifying the compositions of the present invention. It was found that substantially sag-free, drip-free coatings of a wet thickness on the order of about 125 mils or more could be built up, and that dried coatings of various thickness approaching the corrosion resistance of an equivalent amount of the above-described preferred formulation could be obtained, using the following formulation, all percentages being by weight and having the weight basis used with the preferred formulation ("dry" basis): the aforesaid asphalt, about 26% to about 42%; the aforesaid soap, about 16% to about 29%; the aforesaid organophilic modified clay, about 3% to about 7%; about 27% to about 36% total mineral filler consisting essentially of the aforesaid magnesium silicate filler which is characterized by containing platy particles and asbestos floats, said asbestos floats constituting at least 10% by weight of the total dry solids and no more than about half the total mineral filler.

## VARIOUS CONSIDERATIONS PERTAINING TO THE MATERIALS USED IN THE INVENTION, THEIR PROPORTIONS AND THE MIXING THEREOF

Oxidized asphalt is a well-known asphaltic material which is referred to in the art by such terms as, for example, blown asphalt, oxygenized asphalt, condensed asphalt, and oxygenated asphalt. The techniques of preparing oxidized asphalt are well known to those skilled in the art, for which reason it is believed unnecessary to describe them in detail herein. Generally, the oxidation process is effected by blowing a stream of oxygen-bearing gas, usually air, through the material to be oxidized,


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usually at an elevated temperature. By suitable selection of the source and consistency of the material(s) to be oxidized, the temperature, the oxidizing agent, the length of time the material(s) is subjected to oxidation, one can alter in an advantageous and controlled manner the viscosity, softening point, ductility, shock resistance, and temperature sensitivity of the product, as well as its toughness and pliability at lower temperatures.

Oxidized asphalt suitable for the compositions of the present invention may be obtained by oxidation of one or more material(s) derived from petroleum. The base material may be a non-asphaltic, semi-asphaltic or asphaltic petroleum or mixtures thereof. Semi-asphaltic and/or asphaltic petroleums are most suitable, preferably as phaltic petroleums. Among the materials which may be oxidized to obtain an oxidized asphalt suitable for the compositions of the present invention are sludge oil, residual oil, cylinder stock, straight run or vacuum reduced asphalt obtained by vacuum distilling a reduced crude petroleum, residual oil or comparable material, asphaltic crude oils, and so forth. Various combinations of these materials may be used in preparing the oxidized asphalt for the compositions of the present invention.

The Oliensis of an asphaltic material, which may be either positive or negative, is determinable by a test called the "Oliensis Asphalt Spot Test." This test is fully described in the American Association of State Highway Official's Bulletin entitled "Highway Material," page 113 et seq. 1942. Asphaltic material which does not have negative Oliensis, e.g. does not respond negatively to the Oliensis Asphalt Spot Test, is useless in the composition of the present invention.

The oxidized asphalt component may be one oxidized asphalt obtained from a single source material and having a softening point and penetration point within the desired range, or it may be an oxidized asphalt obtained by the oxidation of a mixture of base materials, or it may be a mixture of separately oxidized asphalts in which the properties of each oxidized asphalt more or less balance off the properties of the other oxidized asphalt(s) in the mixture. The preferred oxidized asphalt for the present invention is a straight-reduced asphalt which has been oxidized to a softening point within the range of about 200° F. to about 220° F. (ring and ball), to a needle penetration (77° F., 5 seconds, standard needle) of about 25 to about 35, and to a Saybolt Furol Viscosity of about 35 to about 65. If desired the oxidized asphalt may be a cut-back, e.g. one which has, before cooling, been mixed with at least part of the solvent constituting the fifth component of the compositions of this invention.

The hydrated magnesium silicate constituting the second component or mineral filler of the compositions of the present invention is readily available commercially. This material is mined near Gouverneur in St. Lawrence County of New York State, and has been employed heretofore in house-paints. A unique feature of the filler employed in the invention is that three different species or particles are readily discernible when the material is examined under the microscope. There are nodular particles, fibrous particles and platy particles, the presence of all three species of particles in appreciable amounts being a critical feature of the filler, which distinguishes its particle analysis from that of fillers which are not so characterized, e.g. conventional talcs.

It appears that the presence of the platy and nodular species of particles is the factor in the compositions of the present invention which prevents wicking. As previously mentioned, certain prior art undercoatings containing petroleum asphalt and fillers such as fibrous asbestos particles were subject to failure resulting from a wicking action which caused moisture to travel through such coatings, apparently along sinuous voids in the asphalt coating base created by the randomly oriented asbestos fibers. Surprisingly, although asbestos, like the mineral filler used in the present invention, is a form of magnesium silicate, no wicking action has been detected in the testing of those compositions of the invention which are substantially free of asbestos fibers longer than floats. Without an intention to be bound by any theory, it is believed that the presence of platy and nodular particles in appreciable amounts in the coating base results in a substantial reduction in the number and continuity of any sinuous voids which might otherwise occur in the coatings of the present invention.

The asbestos floats used in the modified form of the invention set forth above are a by-product of the manufacture of the longer grades of asbestos fibers used in shingles, spinning and paper and the so-called "shorts" used in floor tiles, friction materials and so forth. At the asbestos mill the asbestos ore is reduced to pieces of about 1 inch in size which are fed to hammer mills in which the fiber is released from the rock. The fibers are then picked up by air blasts from classifying screens and collected in cyclone collectors. The longer fibers and shorts separate from the air stream in the cyclones, but the "floats" because of their lower density and shorter length are retained by the cyclones and are thereafter captured in a separate collection system, cleaned, graded and, to the extent necessary, further treated to control their bulk density. Such "floats" are readily available commercially, and will substantially completely pass through a 10 mesh screen. The preferred floats for use with the invention are characterized by containing 90% by weight of fibers which will pass a 65 mesh screen and be retained on a 100 mesh screen. The following is a typical analysis of the preferred floats material

| | |
|---|---|
| Ro-Tap (100 gms., 30 min.) screen test: | |
| 14 mesh, percent retained | trace |
| 28 mesh, percent retained | 1.0 |
| 35 mesh, percent retained | 5.0 |
| 100 mesh, percent retained | 80.0 |
| 200 mesh, percent retained | 8.5 |
| Pan, percent retained | 5.5 |
| Bauer McNett screen test: | |
| 80 mesh, percent retained | 0.4 |
| 325 mesh, percent retained | 9.0 |
| Pan, percent retained | 90.6 |
| Wet volume 2000/50/4 hrs. (Q.A.M.A.) | 500 |
| Air permeability: sec. | 260 |
| Wet volume (10/500) (c.c.m.) | 110 |
| Grit (20 gms.) | trace |
| Dry bulk lbs./cu. fg. LFP–LFJ, percent retained | 12.5 |

In general, the water insoluble soap constituting the third component of the compositions of the present invention is derived by oxidizing a waxy hydrocarbon material to produce an acidic product referred to as a waxy hydrocarbon oxidate. The acidic oxidate is then neutralized to produce the desired soap.

Any waxy hydrocarbon or hydrocarbons of a substantially non-crystalline nature may be employed. The waxy hydrocarbons may be obtained from petroleum fractions, such as petroleum distillates or residues; or the waxy hydrocarbons may be synthesized, as by polymerization of olefins or dehydration of long chain aliphatic alcohols. Waxy hydrocarbons from petroleum sources are especially suitable, because of their ready availability and relatively low cost. The desired waxes are smooth, unctious, long-fibered materials. The property of "fiber" is recognized in the grease art and may be observed in a wax by squeezing some wax between two fingers and then spreading them apart. As the fingers spread, elongated "fibers" or "strings" of wax stretch out between the fingers and eventually part. Such waxes may be obtained from any suitable petroleum fractions or crudes, such as Pennsylvania crude, East Texas (Ellenburg) crude, Corning crude and the like, according to method which are already known to persons skilled in the art. Slop, slack, paraffin, plate, malcrystalline and needle waxes are not suitable, however, and should not be used. The presence of oil in the wax, however, is not deleterious. In fact, the waxy hydrocarbon employed in

the preparation of the desired oxidate may beneficially contain substantial amounts, e.g. 30–40%, of oil.

The preferred waxy hydrocarbon is petrolatum. Petrolatum may be partially oxidized to produce a waxy hydrocarbon oxidate. There are various well-known oxidation procedures, such as those involving blowing with air or oxygen at elevated temperatures with or without catalysts. Such procedures are disclosed in a variety of U.S. patents, including: 1,863,004; 2,043,923; 2,156,226; 2,186,910 and 2,216,222. These procedures are of course only illustrative of a wide variety of procedures that might be employed.

The product obtained by such partial oxidization is of indefinite and complex composition, but it is known that the product is characterized by the presence of some neutral paraffins, neutralizable acid groups, and hydroxy, keto and ester groups, thus clearly differentiating the product from fatty acids on the one hand and the waxy hydrocarbon starting material on the other. One characterizing feature of waxy oxidates is their acid number, which is indicative of their extent of oxidation. Persons skilled in the art are acquainted with procedures for controlling the acid number of the waxy oxidates and, in accordance with the present invention, the waxy hydrocarbon oxidate should possess an acid number of about 20 to about 50, an acid number of about 20 to about 35 being preferred. An acid number of about 28 appears best. Acid numbers higher than about 50, though not definitely excluded, should be employed with caution, because they can lead to soaps which are grainy and less compatible with certain hydrocarbon solvents than those in the 20–50 acid number range.

In order to obtain the soap from the waxy hydrocarbon oxidate, the oxidate is substantially completely neutralized by reacting it with the hydroxide(s), oxide(s), carbonate(s) or other basic compound(s) of any selected metals(s). The resultant material is a water insoluble salt which has been referred to in the art as "wax soap." Among the many basic compounds which may be used to neutralize the acidic waxy hydrocarbon oxidate are the oxides and/or hydroxides of polyvalent metals having water-insoluble hydroxides, such as calcium, barium, magnesium, zinc, iron and lead. Lime is a particularly preferred neutralizing agent.

The recommended procedure for effecting neutralization includes heating the oxidate to a fluid condition. While the heated material is under agitation, the basic compound is added thereto in dry form, e.g. as a fine powder. After allowing sufficient time for the basic compound to be thoroughly mixed into the waxy hydrocarbon oxidate and then react therewith, the mixture may be allowed to cool. If desired, the soap may be mixed prior to cooling with added waxy hydrocarbon material which has not been oxidized, provided the resultant mixture has an acid number of at least 20 and less than 50. Also, in order to facilitate subsequent handling of the soap, whether mixed with additional non-oxidized waxy material or not, the soap may be cut-back, e.g. by adding thereto with agitation at least a portion of the solvent constituting the fifth-mentioned component of the compositions of the present invention.

The organophilic modified clays comprising the fourth component of the compositions of the present invention are well known. They differ from the usual natural and synthetic clays in that they have been modified with organic cations which make them organophilic, which alter the natural tendency of such clays to absorb water and which, in fact, render said clays capable of swelling in organic media.

The clays which may be modified in the above-described manner are those which exhibit cationic exchange properties. Preferably, the clays should have comparatively high exchange properties and should have cations which are capable of relatively easy replacement. Among the suitable clays or cation-exchangeable inorganic colloids are: natural clays, including the bentonites, such as Wyoming bentonite; montmorillonites, such as hectorite, beidellite, saponite, nontronite, sepiolite, biotite, attapulgite, vermiculite; zeolites, for example Edingtonite, chabazite, natrolite and mordenites; synthetic clays, such as magnesia-silica-sodium oxide; lime-silica-potassium oxide, baria-silica-lithium oxide; and synthetic zeoltes, such as the complex aluminum silicates with exchangeable cation is hydrogen, sodium, potassium, barium, magnesium or ammonium.

In the preparation of the organophilic modified clays, the exchangeable inorganic cation of the natural or synthetic clay is replaced by one or more substituted organic onium bases. This reaction is well known to persons skilled in the art and constitutes no part of the present invention. Generally speaking however, it is preferred that the noium compounds be titratable with mineral acids. Among the reactive onium base compounds are many alkaloids, and cyclic, aliphatic and heterocyclic amines. The onium compounds are preferably aliphatic amines, their salts and quaternary ammonium salts. Examples of such amines and salts are: decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, hexadecyl ammonium acetate, octadecyl ammonium acetate, dimethyldidodecyl ammonium acetate, dimethylhexdecyloctadecyl ammonium acetate, dimethyldicetyl ammonium acetate, dimethyldioctyl ammonium acetate, dimethyldioctadecyl ammonium acetate, and the corresponding chlorides and quaternary ammonium chlorides. The organic bases employed should be such as to impart substantial organophilic properties to the resulting compounds. The preferred bentonite compounds are prepared from quarternary ammonium compounds in which the N-substituents are aliphatic groups containing at least one alkyl group having a total of at least 10 to 12 carbon atoms. When aliphatic amines are used they preferably contain an alkyl group with a total of at least 10 to 12 carbon atoms.

The amount of modified clay in the compositions of the present invention is capable of considerable variation. The most advantageous amount is readily determinable by one of ordinary skill in the art. Generally, if the coating composition has a high solids content, it is possible to use a very small amount of the modified clay. A lower total "solids" (meaning asphalt, soap and filler) content usually calls for more of the modified clay to aid in imparting "body" to the composition and thereby minimize tripping during application. The preferred range of clay content is about 3% to about 5% by weight, based on the total weight of asphalt, filler, soap and clay in the composition.

The fifth component of the compositions of the present invention is a volatile organic solvent or mixture of solvents which has the ability to dissolve the oxidized asphalt and soap components at ambient temperatures. By "volatile" solvent it is meant one having a sufficiently high vapor pressure at ambient temperatures to evaporate from the composition after application to leave a thin, firm film. Generally speaking, any light liquid hydrocarbon boiling below the lubricating oil range may be employed. Among the hydrocarbons falling in this range are toluene, xylene, kerosene, gasoline, naphtha, and chlorinated hydrocarbon solvents such as chlorobenzene, trichloroethylene, ethylene dichloride and carbon tetrachloride. The rate of drying of compositions can be controlled by proper selection of the volatility of the solvent vehicle. For example, if a naphtha solvent is used, the resulting product is of the rapid-drying type, while if a kerosene fraction is used as the solvent vehicle, medium or slow-drying products result. A rapid-drying solvent is preferred. The particularly preferred solvent is petroleum distillate boiling in the range of about 330° F. to about 352° F. Predominantly aliphatic solvents are recommended because their odor is less objectionable than those which are predominantly aromatic.


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The amount of solvent in the compositions of the present invention depends upon such factors as the nature of the base material from which the oxidized asphalt is prepared, the "capacity" of the solvent, and the consistency of the composition desired. The particular proportion of solvent to solids is easily determinable by one of ordinary skill in the art in the light of the application desired and the requirements of the equipment available. Usually the solvent should be present in at least sufficient amount to produce a sprayable composition. Preferably, the amount of solvent should be such as to provide a viscosity in the range of about $6\times10^4$ to about $1.2\times10^5$, or more preferably about $7\times10^4$ to about $1.0\times10^5$ cps., as measured at 77° F. with a Brookfield RVT viscosimeter, number 7 spindle, operating at 5 r.p.m.

As optional added component(s) the compositions of the invention may include one or more of the known additives for organic-base rust-proofing compounds. For example, it is preferred to incorporate in the compositions of the invention a small amount, e.g. about 1% to about 5% by weight on the entire composition, of an organic corrosion inhibitor, many examples of which are known to persons skilled in the art. The presently preferred corrosion inhibitor is sodium sulfonate, which is prepared by sulfonating any of various petroleum hydrocarbon oil fractions, ruch as gas oil, kerosene, light oil, turbine oil, lube oil, or heavy oil, with a sulfonating agent such as sulfuric acid, oleum, chlorosulfonic acid, sulfur trioxide and their mixtures. The resultant sulfonated hydrocarbon material is neutralized to form the sodium salt, e.g. by mixing with caustic, and is then recovered from the remainder of the hydrocarbon fraction, e.g. by extraction with aqueous alcohol. The extracted material is referred to as "sodium sulfonate." In like manner, a wide variety of oil-soluble, water insoluble metallo petroleum sulfonate salts can be obtained, which, as a class, are effective as rust inhibitors when present in amounts of about 1% and higher. The preferred salts are those of the alkali, alkaline earth and heavy metals.

During the preparation of the compositions of the invention, certain additives are used to assist in the gellation of the organophilic modified clay(s). For instance, we employ small amounts, e.g. about 1% to about 4% by weight on the whole composition, of a lower alkanol having 1 to 6 carbon atoms. Small amounts of butyl Cellosolve may also be employed. Also, the addition of water, e.g. up to about 10% by weight on the whole composition, has been found to be of assistance in gelling the clay. If the composition is heated during the blending process, as is often the case, the measurable content of the water and other additives in the composition may be reduced to a very low level by evaporation. For instance the water content may then be reduced to about 0.02%.

When the components of the invention have been mixed thoroughly, it is beneficial to pass the resultant mixture through a colloid mill. The homogeneity and stability of the compound are substantially improved thereby. A preferred type of colloid mill has a conical rotor and a closely-fitting hollow stator which surrounds the rotor. A setting of about 0.004" clearance (measured normal to the rotor and stator surfaces) is recommended. Following homogenization, the composition is strained through a filter having abut 0.005" openings, so that the composition is substantially free of particles which will be retained on such a filter.

The composition of the invention may be used alone, or may be blended with other coating materials or coating material components, provided such blending does not destroy or seriously reduce sprayability. For instance, the composition may be blended with, for example, 15% of its own weight of finely divided pigment-grade metal particles, viz: aluminum, with a consequent masking of the black color of the asphalt. Colorants may also be added, if desired.

In the following examples, in which all parts are by weight, certain preferred compositions and procedures for mixing the components are set forth. It is recommended that these procedures be followed carefully.

Example 1

A highly paraffinic petrolatum from a Pennsylvania crude having about 35 to about 70 carbon atoms per molecule is oxidized to an acid number of about 28.5. 14.1 parts of the resultant waxy oxidate are heated to about 350° F. and are agitated while 0.7 part of lime are incorporated. The resultant mixture is held under agitation at 350° F. for about an hour. Then, as the mixture is cooled, approximately 13.7 parts of an essentially aliphatic solvent boiling in the range of 310° F. to 365° F. are run into the mixture. The resultant cut-back soap has a needle penetration of about 40–45 (77° F., 5 seconds, standard needle). Cylinder stock from an Illinois crude is blown for 36 hours at a temperature of 500° F. at an air rate of .03 cubic feet of air per gallon of oil per minute, resulting in the production of an oxidized asphalt having a negative Oliensis, a Saybolt Furol Viscosity of about 45, a softening point of 210° F., and a needle penetration of about 30. Shortly after the asphalt has cooled to a temperature below the boiling point of the solvent, it is cut-back with the above-described preferred solvent in a ratio of 42 parts solvent per 58 parts oxidized asphalt. 28.5 parts of the cut-back soap are blended with 1.5 parts of sodium sulfonate, 36 parts of the cut-back asphalt just described and 2 parts of butyl Cellosolve. The resultant mixture is agitated thoroughly. As agitation continues, 3 parts of Baragel 24, dimethyldioctadecyl onium bentonite, and 22 parts of Nytal 200, hydrated magnesium silicate fillter, are gradually incorporated. The filler has a specific gravity of about 2.85, a pH (ASTM D–1208–52T4a) of about 9.5, a Hegman Fineness (ASTM D–605–53T) of 0, a Consistency KU of 72, a maximum of about 2% by weight of particles that will not pass a 325 mesh sieve, an oil absorption (ASTM D–1483–60, Gardner-Coleman) of about 36 and a particle size analysis in accordance with the values set forth in the following table:

| Particle size by sedimentation: | Weight percent |
|---|---|
| Finer than 20 microns | 88 |
| Finer than 10 microns | 67 |
| Finer than 7 microns | 55 |
| Finer than 5 microns | 45 |
| Finer than 3 microns | 34 |
| Finer than 2 microns | 28 |
| Finer than 1 micron | -- |

The amounts of platy and nodular particles in the filler vary somewhat; however, the platy and nodular particles therein must constitute at least one-third of the total weight of the filler and preferably constitute at least about half the weight thereof. In the material employed in the present example, the platy and nodular particles are present in about equal weights and together constitute a predominant proportion, e.g. about 60% of the total weight of the filler. Mixing is continued as the temperature of the mixture is raised to about 160° F. and all the filler solids are wetted by the asphalt. Then, 2 parts of methyl alcohol are added as mixing continues. 5 parts of water are then sprayed onto the surface of the agitated mixture so that it is rapidly incorporated, whereupon the mixture gels. The gelled mixture is then processed through a Charlotte colloid mill with a 0.004" clearance and a sieve with 0.005" openings. The resultant material is found to have a viscosity, as measured by a Brookfield RVT Viscosimeter at 77° F. with a No. 7 spindle of 400,000 at 0.5 r.p.m., 80,000 at 5 r.p.m. and 20,000 at 50 r.p.m.

In order to determine the protective and physical properties possessed by the compositions of the present invention, a number of steel test panels are each uniformly coated with 10 mil layers of the composition of


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the foregoing example. After the panels dry firm at ambient temperature (16 hours at about 77° F.), the panels are subjected to each of the following tests:

Impact flexibility.—A low temperature impact flexibility test is conducted. All of the panels are cooled to −10° F. in a refrigerator and are removed therefrom one by one and immediately tested on the G. E. Impact Flexibility Tester before any significant increase in panel temperature occurs.

In accordance with the G.E. Impact Flexibility Test, a solid metal cylinder is dropped through a guide track from a height of approximately four feet. This impacter strikes the reverse side of the coated test panel made of canstock tinplate, which is supported by a rubber pad so that the circular imprint of the impacter is barely definable in the panel metal. Each end of the impacter is studded with a group of protruding spherical knobs arranged in a circle. When the impacter strikes the panel, these knobs form their imprints under the film. The film is distended beyond its original plane according to the curvature of the spherical segment forming a given knob. The spherical segments are calibrated in terms of percent flexibility, based on the elongation or draw that they can produce in the metal panel. A reading is quickly made by observing the last indentation in ascending order to show no cracking of the undercoating film under test. It can be demonstrated mathematically that the actual elongation of the films is a function solely of the central angle defining the spherical segment, and is not dependent upon the thickness of the metal panel or other dimensions. The average elongation at failure was 60%, and the panels all withstood 40% elongation.

Bending flexibility test.—In this test, test panels are subjected to a 180° bend at varying temperatures to determine the temperature range over which the panels will withstand such treatment without the development of cracks in the coating. The panels tested were found to have withstood such treatment at temperatures ranging down to about 0° F.

Salt fog test.—In this test, the test panels are continuously exposed at a constant temperature of 95° F. in a spray of atomized aqueous mist or fog having a salt (NaCl) concentration of 20% in accordance with Federal Test Method Standard 791A-Protection-Salt Spray (fog) Method 4001.1. The panels satisfactorily withstood 1200 hours of treatment.

Spraying characteristics.—Spraying tests are conducted at ambient temperature (about 82° F.) to determine the spraying characteristics of compositions in accordance with the invention. A batch of the composition of the example is sprayed from an air-less spray-gun at a tank pressure of about 80–85 p.s.i.g. and a tip pressure of about 4000 p.s.i. through a gun with tips having openings of about .019" and .021" in diameter. An excellent, uniform spray pattern free of misting with a coating of medium thickness, e.g. 4 to 6 mils, is obtained in a single pass.

Example 2

This example discloses the formulation which is presently considered best, in that it is believed to constitute the best blend of features of corrosion protection, physical properties, application characteristics and economy. This formulation is prepared in accordance with the procedure set forth in Example 1, except that the amounts of ingredients are adjusted to provide the following analysis:

| Component | Weight percent "wet" basis | Weight percent "dry" basis |
|---|---|---|
| Asphalt | 16.5 | 27.6 |
| Soap | 16.2 | 27.0 |
| Clay | 3.5 | 5.9 |
| Sodium sulfonate | 1.6 | 2.7 |
| Nytal (or equivalent) | 22.0 | 36.8 |
| Methanol | 1.0 | |
| Water | 5.5 | |
| Butyl Cellosolve | 2.0 | |
| Solvent | 31.7 | |
| Total | 100.0 | 100.0 |



This material compares favorably with the material set forth in Example 1.

Example 3

This example pertains to the modification of the invention which includes asbestos floats. The procedure of Example 1 is repeated, except that the amounts of certain of the ingredients are altered to conform to the analysis set forth below, and all of the asbestos "floats" (the preferred asbestos floats disclosed in detail hereinabove) are mixed with the soap and the portion of the solvent used to cut-back the soap, and the resultant mixture is agitated for a period of about ½ hours at ambient temperature. The analysis of the material is as follows:

| Component | Weight percent "wet" basis | Weight percent "dry" basis |
|---|---|---|
| Asphalt | 17.0 | 30.9 |
| Soap | 16.2 | 29.2 |
| Clay | 2.5 | 4.5 |
| Sodium sulfonate | 1.6 | 2.9 |
| Nytal (or equivalent) | 10.0 | 18.0 |
| Asbestos floats | 8.0 | 14.5 |
| Methanol | 1.2 | |
| Water | 5.0 | |
| Butyl Cellosolve | | |
| Solvent | 38.5 | |
| Total | 100.0 | 100.0 |

This material exhibits less corrosion protection than the material of Example 1, when applied in coatings of equivalent thickness and especially where the coating traverses a sharp edge on the substrate. Some deterioration of the coating is noted in the locality of such sharp edges upon extended subjection to corrosive testing. Therefore, in order to obtain with this material a level of corrosion protection similar to that realized with the material of Example 1, it is necessary to use thicker coatings and exercise particular care in fully coating sharp edges and bends. However, the formulation of this example is quite well adapted to the building up of thick coatings with a minimum of sagging and dripping so the necessary extra coating thickness can be readily provided without difficulty. It has also been found that this material can be successfully applied over a rather wide range of viscosity levels. This degree of operating flexibility contributes substantially to the usefulness of this material. Therefore, despite its lesser corrosion-proofing capabilities as compared to the material of Example 1, it is nevertheless a desirable material to employ in corrosion-proof coatings applications.

We claim:

1. A thixotropic protective composition suitable for application to substrates by spraying and characterized by the properties of discharging from a spray gun in a smooth, uniform pattern substantially free from stringiness and over-spray, freedom from dripping and sagging when applied to substrates in a thickness sufficient to provide material corrosion protection, sufficient fluidity at ambient temperatures to penetrate crevices and close-fitting joints, having the ability to dry to a highly corrosion-resistant, tightly adherent coating of substantial impact and abrasion resistance over a wide temperature range to withstand abrasion, cracking and puncture, and being substantially completely free from a tendency to "wick" moisture from the outer surface of the coating to the coating substrate interface, said composition consisting essentially of the following constituents in the weight percentages indicated: about 26% to about 42% of oxidized asphalt having a Saybolt Furol Viscosity of about 30 to about 100, negative Oliensis, a softening or melting point (ring and ball) in the range of about 180° F., to about 230° F., and a penetration (77° F., 5 seconds Standard needle) of about 20 to about 40; about 27% to about 42% of mineral filler consisting essentially of hydrated magnesium silicate and characterized by fibrous, nodular and platy particles, at least 50% of which are finer than 10 microns by particle sedimentation and no


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more than about 3% of which are coarser than 325 mesh, said platy and nodular particles together constituting at least about one-third by weight of said hydrated magnesium silicate filler; about 16% to about 29% of a water-insoluble metal soap of a waxy hydrocarbon oxidate characterized by an acid number in the range of about 20 to about 50; about 3% to about 7% of an organophilic onium base clay; the basis of the weight percentages of the asphalt, the total quantity of magnesium silicate filler, the soap and the modified clay being the total combined weight of said asphalt magnesium silicate filler, soap and modified clay; and sufficient volatile hydrocarbon solvent to render said composition sprayable.

**2.** A composition according to claim **1** wherein said asphalt has a viscosity of about 35 to about 65, a softening point of about 200° F. to about 220° F., and a penetration of about 25 to about 35; said nodular and platy particles are both present in appreciable proportions and together constitute at least about 50% by weight of said hydrated magnesium silicate filler; and said solvent is present in sufficient amount to provide the composition with a viscosity of about 70,000 cps. to about 100,000 cps., as measured by a Brookfield RVT Viscosimeter at 77° F. with a No. 7 spindle operating at 5 r.p.m.

**3.** A composition according to claim **1** wherein said composition contains about 1% to about 5% on the weight of the entire composition of an oil-soluble, water-insoluble metallo petroleum sulfonate salt.

**4.** A composition according to claim **1**, said composition being substantially free of solid particles which will not pass a screen with 0.005" openings.

**5.** A composition according to claim **2** wherein said soap is a salt of an oxidate of unctious, long-fibered petrolatum having an acid number in the range of about 20 to about 35 and a basic compound selected from the group consisting of oxides and hydroxides of polyvalent metals having water-insoluble hydroxides.

**6.** A composition according to claim **2** wherein said organophilic onium base clay is the reaction product of a bentonite clay and a sufficient quantity of onium compound(s) in which the N-substituent(s) thereof include(s) at least one alkyl group having a total of 10 to 12 carbon atoms so as to render said bentonite organophilic and capable of swelling in organic media.

**7.** A composition in accordance with claim **2** wherein said solvent is a predominantly aliphatic light liquid hydrocarbon distilled from petroleum and boiling in the range of about 330° F. to about 352° F.

**8.** A composition in accordance with claim **2** wherein said asphalt is an oxidized, straight-reduced asphalt.

**9.** A method of protecting an object comprising placing on the surface thereof in an average film thickness of at least about 4 mils, a tightly-adherent layer of the composition of claim **1**.

**10.** A method of protecting a vehicular underbody comprising metallic elements from the effects of corrosion, comprising spraying onto said underbody the composition of claim **2**, and drying said sprayed composition to a tightly adherent, continuous and void-free coating covering at least said metallic elements in an average film thickness of at least about 6 mils.

**11.** A composition in accordance with claim **1** wherein the total mineral filler content, including said hydrated magnesium silicate constitutes about 27% to about 36% of the composition, and the total mineral filler content is further characterized by the presence of at least 10% by weight on the total dry solids of asbestos floats, said asbestos floats constituting no more than about half the total mineral filler.

**12.** A composition in accordance with claim **11** wherein 90% by weight of the total weight of asbestos floats will pass a 65 mesh screen and be retained upon a 100 mesh screen.

**13.** A composition in accordance with claim **1** characterized by about 26 to about 30% of said asphalt, about 35 to about 40% of said mineral filler and about 24 to about 29% of said soap.

**14.** A composition in accordance with claim **13** wherein said organophilic onium base clay constitutes about 5% to about 7% of said composition.

**15.** A composition in accordance with claim **13** containing about 0.5 to about 2.5% of sodium sulfonate corrosion inhibitor.

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