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METAL PROTECTING COMPOSITIONS

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The present invention relates to compositions of matter containing petroleum products and, more particularly, to lubricants and other predominantly petroleum products adapted to the protection of metals from various causes of corrosion.

The application of an unctuous coating for the protection of metal surfaces, both external and internal, is an established practice. Compositions composed solely of hydrocarbon compounds have been used for slushing metallic surfaces, but they are not wholly effective because the films produced therefrom are not impervious to moisture, particularly under high humidity conditions where moisture is condensing on the film. In order to overcome this difficulty and to increase the effectiveness of the coating film, it has been suggested that materials in the nature of metal soaps be included in the hydrocarbon composition. Even though these metal soaps materially increase the effectiveness of hydrocarbon coating compositions, the resultant slushing compound is objectionable for certain types of uses. The objection arises through the fact that these soaps are ash-forming materials. If the protective coating containing metal soaps is employed on metal parts which are to be subsequently subjected to relatively high temperatures accompanied by considerable wear, such as, for instance, the pistons and cylinder walls of an internal combustion engine or the barrel, firing mechanism and breech of fire arms, then it is necessary or desirable to completely remove the protective coating before placing the protected article in service, otherwise the protective coating will be burned off, leaving an abrasive ash which will cause more rapid wear, necessitating more frequent overhauling and replacement.

An object of the present invention is the formation of a non-drying composition of matter for arresting, preventing and inhibiting the corrosion of metals, particularly ferrous metals, which composition will not form a combustion ash on being burned. This and other objects will be apparent to those skilled in the art upon reading the following description.

Corrosion inhibitors are known in the art. Typical examples of patent literature are the patents to Sloan, Patent No. 2,333,206 and to Wasson et al., Patent No. 2,401,993. In the prior art there is disclosed that long chain aliphatic amines may be used to protect metals against corrosion. There is also taught that a rust preventative may be formed by reacting a primary straight chain aliphatic amine having from 8 to 14 carbon

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atoms with an organic acid having a carboxyl group attached to a cyclic nucleus.

It has now been found that the reaction products of certain basic nitrogen compounds and sulfonic acids provide, in conjunction with petroleum hydrocarbons, a very effective means for protecting metals against the ravages of corrosion. The nitrogen bases employed in making the sulfonates of the present invention are selected from the primary amines such as methyl amine, ethyl amine, propyl amine, lauryl amine or octadecenyl amine; secondary amines, such as dimethyl amine, diethyl amine, dipropyl amine, dilauryl amine, etc.; tertiary amines, such as tri-
lauryl amine; polyamines, like ethylene diamine and lauryl diamine; heterocyclic nitrogen bases such as pyridine, quinoline and hydrocarbon-substituted imidazolines or oxazolines, and quaternary ammonium bases of the type of dimethyl
octyl benzyl ammonium hydroxide and tetramethyl ammonium hydroxide. In general, alkyl or alkenyl substituted nitrogen bases are preferred because of their improved solubility over aromatic naphthenic and alkylol derivatives, and of these, it is preferred to use the alkyl compounds wherein the alkyl groups contain from 1-5 carbon atoms, the methyl amine being especially preferred.

The sulfonic acids can be preferentially water-soluble petroleum sulfonic acids also known as "green acids" and preferably the preferentially oil-soluble petroleum oil sulfonic acids also designated as "mahogany acids." The sulfonic acids having a molecular weight of from 350 to 600 are operable and those having a molecular weight of from 400 to 500 are preferred.

The sulfonic acids are produced by the action of fuming sulfuric acid on petroleum oil. The following example describing the action of fuming sulfuric acid on a mineral oil distillate will sufficiently illustrate one method of obtaining sulfonic acids. A petroleum oil distillate, preferably one which will produce a white oil having a viscosity of from 150-500 S. S. U. at 100° F., after complete sulfonation, is treated with from about 7-10 pounds of fuming sulfuric acid per gallon of oil, depending upon the degree of sulfonation desired, in successive 1-2 pound increments or dumps per gallon of oil. The temperature during the acid treatment is maintained at or below about 100° F. After each increment of fuming sulfuric acid has been added to the oil and agitated to furnish contact between the acid and the oil, the acid is permitted to settle as an acid sludge which is removed

before the next increment of fuming sulfuric acid is added to the oil. After all of the fuming sulfuric acid has been added to the oil and the oil freed of acid sludge, the acid-treated oil containing the preferentially oil-soluble sulfonic acids dissolved therein is in condition for further treatment designed to remove the oil-soluble sulfonic acids. The oil-soluble sulfonic acids can be recovered from the acid oil either by solvent extraction or neutralization followed by solvent extraction. If solvent extraction is employed, the acid oil is agitated with an alcohol such as ethyl alcohol or isopropyl alcohol or with phenol or other appropriate solvent, which dissolves out the oil-soluble sulfonic acids, forming, on standing a lower liquid phase of solvent and sulfonic acid removable from the upper oil phase by decantation. The solvent can then be recovered by distillation or the sulfonic acids may be neutralized with the organic base before recovery of the solvent by distillation. The more common procedure is to neutralize the acid-treated oil with aqueous sodium hydroxide or other alkali, thus forming an oil-soluble sulfonate soap in the oil. The neutralized oil is then treated with a solvent for the soap, such as aqueous alcohol of about 60% strength. An alcohol layer containing dissolved sulfonates is then separated from the oil and subsequently distilled to recover the alcohol and remove water. Instead of aqueous alkali, the acid-treated oil can be neutralized with basic nitrogen compounds to form the sulfonates of the present invention directly, and these sulfonates can then be recovered from the neutralized oil by solvent extraction with a solvent such as alcohol or phenol.

Other methods of making the amine sulfonates of the present invention include the direct neutralization of sulfonic acids as such and a double decomposition reaction with metal sulfonates such as sodium or calcium sulfonate. Where direct neutralization is employed, the reaction proceeds quite rapidly at atmospheric temperatures. In the case where metal sulfonates are used as the source of the sulfonate ion, the metal salt can be decomposed with a mineral acid such as hydrochloric or sulfuric acid and then neutralized with a basic nitrogen compound; or the metal sulfonate may be reacted with an amine salt as, for instance, methyl amine hydrochloride. A ready means of preparing an amine sulfonate is illustrated below.

Example 1

1500 grams of a 30% solution of sodium sulfonate (450 mol. wt.) in oil was blended with one mol equivalent of lauryl amine (186 g.) and the solution comingled with one mol equivalent of hydrochloric acid (37 g.) as a 10% aqueous solution. The resultant emulsion was then heated to 300° F. to evaporate the water employing one drop of a silicone polymer to control foaming, and the mixture filtered through a filter aid to remove the sodium chloride which results from the neutralizing reaction. Analysis of the product showed a sodium content of 0.06%, indicating about 96% conversion of the sodium sulfonate to the amine derivative.

The improved metal protecting compositions of the present invention contain in addition to the above-described nitrogen base sulfonates, the usual constituents of a protective base material, which generally include a non-siccative oleaginous material such as a mineral oil product which may be either a light mineral oil distillate,

a mineral oil of about lubricating consistency or a more resistant non-drying coating material such as petrolatum or any of the various petroleum waxes. Also waxes and oils of animal origin, such as degreas or lanolin, or of vegetable origin, such as carnauba wax, may be used in the base material if desired. Heavy viscous rust preventive compositions such as those containing petrolatum or other waxes, may be diluted with a volatile solvent if necessary to facilitate application. In many instances it may be desirable to include auxiliary agents in the rust preventive composition. Among such auxiliary agents there may be mentioned carboxylate soaps, phosphorus compounds, metal sulfonates such as calcium soaps of mahogany sulfonic acids; metal phenates, metal phenol sulfides, natural fats and oils such as wool fat, etc. For special purposes, such as to enable the composition to dislodge water from metal surfaces, polar compounds such as alkylol amines, alcohols, esters, ethers, ether alcohols and the like may be incorporated in the composition. In still other instances thickeners such as polyisobutene, acrylic acid ester polymers, copolymers of styrene and olefins or diolefins; ester polymers, metal deactivators, dyes, oiliness agents, extreme pressure additives, bearing corrosion inhibitors, anti-oxidants and grease-forming soaps may be desirable.

Those compositions of the present invention in which the base material is of lubricating oil consistency will be found to be useful not only as metal protective compositions but also as crankcase lubricating oils, thus allowing the same composition to be employed as a preservative during periods of non-use of the engine as is used as the lubricant during periods when the engine is in use. Such a lubricant has many apparent advantages, particularly for engines operating in moist climates where corrosion of parts may occur during even short shut-down periods.

The efficiency of the metal protective composition is evaluated by certain standard tests of which the humidifier test is one of the more important:

Test procedure

Sand blasted panels of hot rolled steel are dipped into slushing compound samples, then maintained vertically in a box for 16 hours under ordinary room conditions to allow the rust preventive film to reach an equilibrium condition. Compounds containing petrolatum or waxes are applied at temperatures above their melting point and fluid products are applied at room temperatures. The coated panels are then placed and spaced apart in an upright position in a humidifier chamber wherein at 100° F. they are subjected to continuous moisture condensation. The time, in hours, for a panel subjected to these conditions to develop initial evidence of rusting is observed and recorded as the resistance life of the coating composition.

The following data illustrate the rust preventive effectiveness of the present invention:

Blend	Hours to Corrosion
45 Vis. at 210° F. Extracted Coastal distillate.....	1
45+3% Octadecenyl amine petroleum sulfonate.....	200+
45+3% Methyl amine petroleum sulfonate.....	200+
120 Vis. at 210° F. Aviation engine oil.....	1
120+3% di-2-ethyl hexyl amine petroleum sulfonate.....	200+
120+3% Lauryl amine petroleum sulfonate.....	200+

The foregoing data clearly demonstrate the effectiveness of compositions made in accordance with the present invention in preventing metal corrosion even under the most adverse conditions.

In order to show, in a comparative manner the outstanding corrosion resistance of the compounds of this invention, a test was run using a base oil containing respectively 5% of lauryl amine, 5% of lauryl amine petroleum sulfonate, 5% of lauryl amine salicylate and 5% of methyl amine petroleum sulfonate. Test data are reported below:

Test Material	Hours to Corrosion
Base Oil ¹	1.
Base Oil+5% lauryl amine.....	3-147 (erratic performance indicates borderline quality).
Base Oil+5% lauryl amine sulfonate ² ...	3-27.
Base Oil+5% lauryl amine salicylate....	<3.
Base Oil+5% methyl amine sulfonate ² ...	411+.

¹ Base Oil=Extracted Coastal distillate of SAE 30 grade.

² From a petroleum sulfonic acid having a molecular weight of 430

An examination of the data reported above shows that the material of this invention is outstandingly superior to either the long chain amine or the long chain amine salicylate.

The organic nitrogen base sulfonates of the present invention are also effective in preventing corrosion to metals resulting from the use of chlorine containing lubricants or solvents; they are useful as ash-free engine oil detergents; serve to stabilize leaded gasolines against lead precipitation and to prevent corrosion of fuel containers resulting from water contamination. The organic nitrogen base sulfonates of the present invention will also be found to be useful as steam cylinder oil emulsifiers and detergents, soluble oil emulsifiers, asphalt wetting agents, wax modifiers, rubber plasticizers and grease modifiers.

The organic nitrogen base sulfonates of the present invention may be used in amounts ranging from about 1% to about 10% by weight based on the oil base, but preferably in the amount of about 3%.

This application is a continuation-in-part of Serial Number 636,500, which is now abandoned, filed on December 21, 1945, by the same inventors.

What is claimed is:

1. A non-corrosive metal protective composition consisting essentially of from 90% to 99% by weight of a mineral base lubricating oil and from 1% to 10% by weight of methyl amine petroleum sulfonate wherein the molecular weight of the uncombined petroleum sulfonic acid is between 350 and 500.

2. A composition according to claim 1 wherein the methyl amine petroleum sulfonate is derived from a petroleum sulfonic acid having a molecular weight of about 450.

3. A rust preventative composition which consists essentially of about 97% by weight of a mineral base lubricating oil and containing combined therein about 3% by weight of a methyl amine petroleum sulfonate made by combining a methyl amine with a salt of a petroleum sulfonic acid having a molecular weight of about 450.

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REFERENCES CITED

The following references are of record in the file of this patent:

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