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ORGANIC COMPOSITIONS

Harry J. Andress, Jr., Pitman, and Paul Y. C. Gee, Woodbury, N.J., assignors to Mobil Oil Corporation, a corporation of New York

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This invention relates to improved organic compositions and, in one of its aspects, relates more particularly to improved organic compositions in the form of liquid and solid hydrocarbons that are normally susceptible to deterioration by corrosion or oxidation. Still more particularly, in this aspect, the invention relates to improved organic compositions in the form of petroleum distillate hydrocarbon fuels, lubricating oils and greases which, in their uninhibited state, tend to react with and corrode metal surfaces with which they may come into contact in performing their intended functions.

It is well-known that certain types of organic compounds are normally susceptible to deterioration by oxidation or by corrosion when coming into contact with various metal surfaces. For example, it is known that liquid hydrocarbons in the form of fuels oils or lubricating oils tend to accumulate considerable quantities of water when maintained for long periods of time in storage vessels; and when subsequently brought into contact with metal surfaces in their functional environments, deterioration of equipment as a result of corrosion, occurs. In addition, where such lubricating oils or other corrosion-inducing materials are incorporated into solid lubricants as in the form of greases, similar deleterious results are encountered, thus clearly indicating the necessity for incorporating into such organic compositions an effective antioxidant and rust-inhibiting agent.

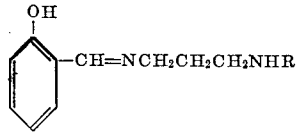
Accordingly, it is an object of this invention to provide organic compositions having improved antioxidant and anti-corrosion properties.

Another object of the invention is to provide improved organic compositions in the form of liquid and solid hydrocarbons containing an additive which is adapted to prevent corrosion and oxidative deterioration of metallic surfaces.

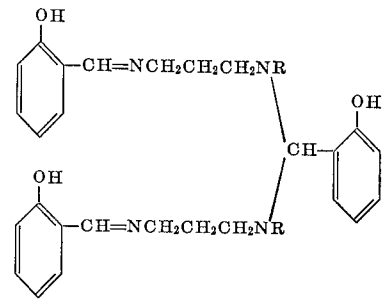
Still another object of the invention is to provide an effective antioxidant and corrosion inhibiting agent, and a method for its manufacture, for incorporation into the aforementioned organic compositions.

Other objects and advantages inherent in the invention will become apparent to those skilled in the art from the following more detailed description.

It has now been found that the aforementioned oxidative and corrosive properties of organic compositions, particularly in the form of fuels and lubricants, can be effectively overcome by incorporating therein, as an antioxidant and anti-corrosion agent, small amounts of a salicylaldimine of the group consisting of:



and



in which R is an alkyl group having from about 8 to about 18 carbon atoms.

In general, the present invention, in its preferred applications, contemplates organic compositions which are normally susceptible to oxidative and corrosive deterioration, containing a small amount of the aforementioned salicylaldimine, usually from about .001 to about 10 percent, by weight, of the total of such compositions. When this salicylaldimine is incorporated into liquid hydrocarbon compositions, such as jet fuels, turbine fuels, gasolines and the like, or in lubricating oils, it is preferably employed in an amount from about .001 to about .01 percent, by weight, of the total composition. When the salicylaldimine is incorporated into a hydrocarbon grease composition, it is preferably employed in an amount from about 0.1 to about 5 percent, by weight, of the total grease.

The organic compounds improved in accordance with the present invention may comprise any materials that are normally susceptible to deterioration by oxidation or corrosion, in the manner previously described. A field of specific applicability is the improvement of liquid hydrocarbons in accordance with the present invention, boiling from about 75° F. to about 750° F. Of particular significance is the treatment of petroleum distillate fuel oils having an initial boiling point from about 75° F. to about 135° F. and an end boiling point from about 250° F. to about 750° F. It should be noted, in this respect, that the term "distillate fuel oils" is not intended to be restricted to straight-run distillate fractions. These distillate fuel oils can be straight-run distillate fuel oils, caalytically or thermally cracked (including hydrocracked) distillate fuel oils, or mixtures of straight-run distillate fuel oils, naphthas and the like, with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well-known commercial methods, such as acid or caustic treatment, hydrogenation, solvent-refining, clay treatment, and the like.

The distillate fuel oils are characterized by their relatively low viscosity, pour point and the like. The principal property which characterizes these contemplated hydrocarbons, however, is their distillation range. As hereinbefore indicated, this range will lie between about 75° F. and about 750° F. Obviously, the distillation range of each individual fuel oil will cover a narrower boiling range, falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially, continuously, throughout its distillation range.

Particularly contemplated among the fuel oils are Nos. 1, 2 and 3 fuel oils, used in heating and as diesel fuel oils, gasoline and the jet combustion fuels, as previously

indicated. The domestic fuel oils generally conform to the specifications set forth in ASTM Specification D396–48T. Specifications for diesel fuels are defined in ASTM Specification D975–48T. Typical jet fuels are defined in Military Specification MIL–F–5624B. In addition, as previously indicated, hydrocarbon lubricating oils of varying viscosity and pour points, falling both within and outside the indicated ranges for the aforementioned fuel oils, may also be effectively treated through the use of the aforementioned salicylaldimines, as antioxidation and anti-corrosion agents.

As previously indicated, the aforementioned salicylaldimines may also be incorporated, as an anti-corrosion agent, in grease compositions. Such greases, may comprise a combination of a wide variety of lubricating vehicles and thickening or gelling agents. Thus, greases in which the aforementioned salicylaldimines are particularly effective, may comprise any of the conventional hydrocarbon oils of lubricating viscosity, as the oil vehicle, and may include mineral or synthetic lubricating oils, aliphatic phosphates, esters and di-esters, silicates, siloxanes and oxalkyl ethers and esters. Mineral lubricating oils, employed as the lubricating vehicle, may be of any suitable lubricating viscosity range from about 45 SSU at 100° F. to about 6,000 SSU at 100° F., and, preferably, from about 50 to about 250 SSU at 210° F. These oils may have viscosity indexes varying from below 0 to about 100 or higher. Viscosity indexes from about 70 to about 95 are preferred. The average molecular weights of these oils may range from about 250 to about 800. The lubricating oil is employed in the grease composition in an amount sufficient to constitute the balance of the total grease composition, after accounting for the desired quantity of the thickening agent, and other additive components to be included in the grease formulation.

As previously indicated, the oil vehicles employed in the novel grease formulations of the present invention, in which the aforementioned salicylaldimines are incorporated as an antioxidative or anti-corrosion agent, may comprise mineral or synthetic oils of lubricating viscosity. When high temperature stability is not a requirement of the finished grease, mineral oils having a viscosity of at least 40 SSU at 100° F., and particularly those falling within the range from about 60 SSU to about 6,000 SSU at 100° F. may be employed. In instances, where synthetic vehicles are employed rather than mineral oils, or in combination therewith, as the lubricating vehicle, various compounds of this type may be successfully utilized. Typical synthetic vehicles include: polypropylene, polypropylene glycol, trimethylol propane esters, neopentyl and pentaerythritol esters, di-(2-ethyl hexyl) sebacate, di-(2-ethyl hexyl) adipate, di-butyl phthalate, fluorocarbons, silicate esters, silanes, esters of phosphorus-containing acids, liquid ureas, ferrocene derivatives, hydrogenated mineral oils, chain-type polyphenyls, siloxanes and silicones (poly-siloxanes), alkyl-substituted diphenyl ethers typified by a butyl-substituted bis (p-phenoxy phenyl) ether, phenoxy phenyl ethers, etc.

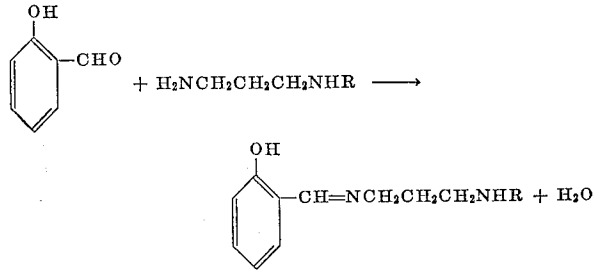
The lubricating vehicles of the aforementioned improved greases of the present invention containing the above-described salicylaldimines as additives, are combined with a grease-forming quantity of a thickening agent. For this purpose, a wide variety of materials may be employed. These thickening or gelling agents may include any of the conventional metal salts or soaps, which are dispersed in the lubricating vehicle in grease-forming quantities, in such degree as to impart to the resulting grease composition, the desired consistency. Other thickening agents that may be employed in the grease formation may comprise the non-soap thickeners, such as surface-modified clays and silicas, aryl ureas, calcium complexes and similar materials. In general, grease thickeners may be employed which do not melt and dissolve when used at the required temperature within a particular environment; however, in all other respects, any material which is normally employed for thickening or gelling hydrocarbon fluids for forming greases, can be used in preparing the aforementioned improved greases in accordance with the present invention.

The salicylaldimines of the present invention may be prepared, in general, by condensing a salicylaldehyde and a diamine having the structural formula

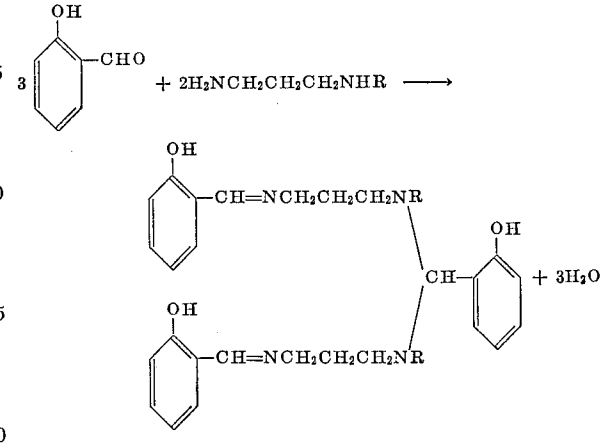
$$H_2NCH_2CH_2CH_2NHR$$

in which R is an alkyl group having from about 8 to about 18 carbon atoms. The diamines employed for this purpose are commercially available under the trade name "Duomeens," and are manufactured by Armour Industrial Chemical Company. Duomeen C has an average molecular weight of about 320, and Duomeen T and Duomeen S, each have an average molecular weight of about 400. As the aforementioned structural formula indicates, the Duomeens contain both a primary and a secondary amine group.

More specifically, the novel salicylaldimines of the present invention are prepared by condensing either one mole of salicylaldehyde with one mole of the diamine, or by condensing three moles of salicylaldehyde with two moles of the diamine. The condensation reaction of one mole of salicylaldehyde with one mole of the diamine is represented as follows:



The condensation reaction of three moles of salicylaldehyde with two moles of the diamine is represented as follows.



In each of the above condensation reactions, R represents an alkyl group having from about 8 to about 18 carbon atoms.

The following examples will serve to illustrate the preparation of the aforementioned novel salicylaldimines of the present invention and to demonstrate the effectiveness thereof in organic compositions which are normally susceptible to deterioration by oxidation and corrosion, and particularly with respect to their use in hydrocarbon fuels, lubricating oils and greases. It will be understood, of course, that it is not intended the invention be limited to the particular compositions shown or to the operations or manipulations involved. Various modifications thereof, as previously described, can be employed and will be readily apparent to those skilled in the art.

EXAMPLE 1

A mixture of 300 grams (0.75 mole) of Duomeen T, 91.5 grams (0.75 mole) of salicylaldehyde and 150 cc. of xylene was refluxed at 150° C. for 2 hours. This mixture was then gradually heated to 200° C. and was maintained at that temperature until water stopped coming over. The final product was clear and fluid at room temperature.

EXAMPLE 2

A mixture of 300 grams (0.75 mole) of Duomeen S, 91.5 grams (0.75 mole) of salicylaldehyde and 150 cc. of xylene was refluxed at 150° C. for 5 hours. This mixture was then gradually heated to 250° C. and was maintained at that temperature until water stopped coming over. The final product was clear and fluid at room temperature.

EXAMPLE 3

A mixture of 213 grams (⅔ mole) of Duomeen C, 122 grams (1 mole) of salicylaldehyde and 100 cc. of benzene was refluxed at 125° C. for 3 hours. This mixture was then gradually heated to 150° C. and was maintained at that temperature until water stopped coming over. The final product was clear and fluid at room temperature.

EXAMPLE 4

A mixture of 200 grams (0.5 mole) of Duomeen T, 91.5 grams (0.75 mole) of salicylaldehyde and 100 cc. of benzene was refluxed at 125° C. for 3 hours. This mixture was then gradually heated to 150° C. and was maintained at that temperature until water stopped coming over. The final product was clear and fluid at room temperature.

EXAMPLE 5

A mixture of 200 grams (0.5 mole) of Duomeen S, 91.5 grams (0.75 mole) of salicylaldehyde and 100 cc. of benzene was refluxed at 125° C. for 3 hours. This mixture was then gradually heated to 150° C. and was maintained at that temperature until water stopped coming over. The final product was clear and fluid at room temperature.

The anti-screen clogging characteristics of fuel oils, having incorporated therein the novel salicylaldimines of the present invention, were determined from a standard screen clogging test. This test is conducted using a Sundstrand V3 or S1 home fuel oil burner pump with a self-contained 100-mesh Monel metal screen. About 0.05 percent, by weight, of naturally-formed fuel oil sediment, composed of fuel oil, water, dirt, rust, and organic sludge is mixed with 10 liters of the fuel oil. This mixture is circulated by the pump through the screen for 6 hours. Then, the sludge deposit on the screen is washed off with normal pentane and filtered through a tarred Gooch crucible. After drying, the material in the Gooch crucible is washed with a 50:50 (volume) acetone-methanol mixture. The total organic sediment is obtained by evaporating the pentane and the acetone-methanol filtrates. Drying and weighing the Gooch crucible yields the amount of inorganic sediment. The sum of the organic and inorganic deposits on the screen can be reported in milligrams recovered or converted into percent screen clogging.

EXAMPLE 6

The salicylaldimines prepared in accordance with the foregoing Examples 1 through 5 were individually blended in test fuel oils comprising a blend of 60 percent distillate stock obtained from continuous catalytic cracking and 40 percent straight-run distillate stock, having a boiling range of between about 320° F. to about 640° F., and typical of No. 2 fuel oils. Each blend was subjected to the above-described screen clogging test. The test results obtained, are set forth in the following Table I:

TABLE I.—SCREEN CLOGGING TESTS

Inhibitors	Concn., Lb./1,000 Bbls.	Screen Clogging, Percent
Uninhibited fuel blend	0	100
Uninhibited fuel blend plus Ex. 1	50	5
Uninhibited fuel blend plus Ex. 2	100	4
Uninhibited fuel blend plus Ex. 3	20	50
Uninhibited fuel blend plus Ex. 4	30	47
Uninhibited fuel blend plus Ex. 5	30	42

In order to determine the sedimentation characteristics of fuel oils in which the novel salicylaldimines of the present invention are incorporated, the 100° F. Fuel Oil Storage Test was employed. In this test a 500-milliliter sample of the fuel oil under test is placed in a convected oven maintained at 100° F. for a period of 12 weeks. Thereafter, the sample is removed from the oven and cooled. The cooled sample is filtered through a tared asbestos filter (Gooch crucible) to remove insoluble matter. The weight of such matter in milligrams is reported as the amount of sediment. A sample of the blank uninhibited oil is run along with a fuel oil blend under test. The effectiveness of a fuel oil containing an inhibitor is determined by comparing the weight of sediment formed in the inhibited oil with that formed in the uninhibited oil.

EXAMPLE 7

The salicylaldimines prepared in accordance with the foregoing Examples 1 through 5, were individually blended in test fuel oil similar to the aforementioned test fuel oils employed in the aforementioned screen clogging tests. The test results comparing the blended fuels, containing the novel salicylaldimines of the present invention, and uninhibited fuels are set forth in Table II below:

TABLE II.—FUEL OIL STORAGE TESTS

[Twelve weeks storage at 110° F.]

Inhibitors	Concn., Lb./1,000 Bbls.	Sediment, mg./liter
Uninhibited fuel blend	0	36
Uninhibited fuel blend plus Ex. 1	100	3
Uninhibited fuel blend	0	107
Uninhibited fuel blend plus Ex. 2	100	61
Uninhibited fuel blend	0	131
Uninhibited fuel blend plus Ex. 3	30	34
Uninhibited fuel blend	0	131
Uninhibited fuel blend plus Ex. 4	30	28
Uninhibited fuel blend	0	131
Uninhibited fuel blend plus Ex. 5	30	29

A similar storage test was performed with respect to the salicylaldimines prepared in accordance with the foregoing Examples 3, 4 and 5, which were incorporated in a gasoline blend comprising 100 percent catalytically cracked component, and boiling within the range from approximately 100° F. to approximately 400° F., and containing 3 cc. of tetraethyl lead per gallon, as shown in Table III.

TABLE III

Inhibitors	Concn., Lb./1,000 Bbls.	ASTM Gum Increase (after 16 weeks at 110° F.), mg./100 ml.
Uninhibited gasoline plus 3 cc. TEL/gal	0	17.5
Uninhibited gasoline plus 3 cc. TEL/gal. plus Ex. 3	5	5.5
Uninhibited gasoline plus 3 cc. TEL/gal. plus Ex. 4	5	4.7
Uninhibited gasoline plus 3 cc. TEL/gal. plus Ex. 5	5	5.5

It will be seen from Table III, above, that a marked decrease in ASTM gum content is observed with respect to the aforementioned gasoline blend containing the specified salicylaldimines, as compared, in each instance, with the same gasoline blend, but not containing the salicylaldimine additive.

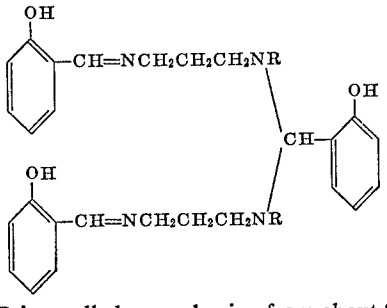
From the foregoing it will be apparent that the salicylaldimine additives of the present invention are markedly effective in inhibiting clogging and deterioration of hydro-

carbon compositions by corrosion and oxidation, and particularly with respect to the treatment of such hydrocarbons as petroleum distillate fuels.

Furthermore, although the present invention has been described with preferred embodiments, it will be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand.

We claim:

1. Lubricant and liquid hydrocarbon fuel compositions normally susceptible of causing deterioration of metal surfaces, containing a small amount, sufficient to inhibit said deterioration, of a salicylaldimine having the structure:



in which R is an alkyl group having from about 8 to about 18 carbon atoms.

2. A composition in accordance with claim 1 wherein said salicylaldimine is present in an amount from about .001 to about 10 percent, by weight, of the total of said composition.

3. A composition in accordance with claim 1 wherein said salicylaldimine is present in an amount from about .001 to about .01 percent, by weight, of the total of said composition.

4. A composition in accordance with claim 1 wherein said salicylaldimine is present in an amount from about 0.1 to about 5 percent, by weight, of the total of said composition.

5. A composition in accordance with claim 1 wherein said composition is a liquid hydrocarbon comprising a petroleum distillate fuel oil having an initial boiling point from about 75° F. to about 135° F. and an end boiling point from about 250° F. to about 750° F.

6. The composition of claim 5 wherein said liquid hydrocarbon comprises a gasoline.

7. The composition of claim 5 wherein said liquid hydrocarbon comprises a jet fuel.

8. The composition of claim 5 wherein said liquid hydrocarbon comprises a turbine fuel.

9. A composition in accordance with claim 1 wherein said composition comprises a grease.

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PATRICK P. GARVIN, *Primary Examiner.*

DANIEL E. WYMAN, *Assistant Examiner.*