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ADDITION AGENT FOR OIL COMPOSITIONS
AND THE LIKE

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No Drawing. Application November 2, 1953,
Serial No. 389,862

8 Claims. (Cl. 252—34)

The present invention relates to the improvement of non-gaseous organic materials such as essentially hydrocarbon products, animal and vegetable fats and oils, and other natural and synthetic, non-gaseous substances by the incorporation therein of a class of additives which impart improved properties to such compositions. The invention is particularly concerned with a new class of compounds having utility as oxidation inhibitors, corrosion inhibitors, etc., when employed in relatively small concentrations in oleaginous materials such as lubricating oils and related substances.

In accordance with the present invention a new class of compounds has been discovered which when added to oils such as refined oils and the like in small proportions substantially reduces the tendency of such oils to corrode metal surfaces. They are likewise effective in inhibiting oxidation of petroleum hydrocarbon products, synthetic oils, and animal and vegetable oils that are susceptible to oxidation. The products of the present invention also have utility as rusting inhibitors. Since the products contain no metal, they are particularly useful as ashless additives in service where ash-forming constituents lead to harmful effects in engines operating under severe conditions.

The compounds of the present invention may be broadly described as nitrogen base salts of alkylene bis-amino aliphatic carboxylic acids. In these compounds the alkylene groups may have in the range of from 2 to 6 carbon atoms or even higher, and the carboxylic acid is preferably a lower acid such as acetic, propionic, butyric, and the C₅ and C₆ aliphatic acids. Although the partial salts in which only 1, 2 or 3 of the 4 carboxylic acid groups have been converted to salts by the nitrogen base are useful, the tetra-substituted nitrogen base salt compounds are preferred. The nitrogen base radicals of the compounds preferably contain oil solubilizing groups, such as hydrocarbon radicals, that will render the compounds soluble in useful proportions in the material in which it is used. Amine salts of the amino carboxylic acids are particularly preferred, especially those contributing a total of at least 10 carbon atoms to the molecule.

Although the compounds impart a number of useful properties to materials of the type described above, they have been found to be particularly useful in inhibiting oxidation, especially in preventing color-degradation of oily materials during processing, transportation or storage. Although it is not desired to be bound by theoretical considerations, it is believed that the effectiveness of these compounds as anti-oxidants depends upon a buffer action which reduces the acidity of the material or an accumulation of acidic compounds in the material, and also upon the formation of complexes with metals when the oily material contacts metal parts that have a catalytic action in causing oxidation.

The preparation and testing of compounds of the present invention are illustrated by the examples to be described in detail below, but such examples are not to be construed as limiting the scope of the invention in any manner.

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EXAMPLE 1.—PREPARATION OF PRODUCT

Product A.—Piperidine salts of ethylene diamine tetraacetic acid

5 A mixture of 200 ml. of isopropyl alcohol and 29.2 gms. (0.1 mol) of ethylene diamine tetra-acetic acid was prepared. 34 g. (0.4 mol) of piperidine was added to this mixture, and the mixture was heated with stirring to its boiling point. The alcohol was then evaporated by
10 passing a stream of nitrogen through the mixture to leave a pale, yellow viscous liquid termed product A. This product had the following analysis: 55.5 weight percent carbon, 11.2 weight percent hydrogen, and 11.7 weight percent nitrogen. From this analysis the product was
15 indicated to consist of a mixture of various piperidine salts of the tetra-acetic acid.

Product B.—Dioctadecyl amine salt of ethylene diamine tetra-acetic acid

20 This product was prepared by substantially the identical procedure used in preparing product A, with the exception that 4.2 g. (0.015 mol) of ethylene diamine tetra-acetic acid was reacted with 30 g. (0.06 mol) of dioctadecyl amine. The resulting dioctadecyl amine salt of
25 ethylene diamine tetra-acetic acid had the following analysis: 75.0 weight percent carbon, 13.8 weight percent hydrogen and 2.24 weight percent nitrogen. This product appeared to consist chiefly of a mixture of various substituted amine salts of the acid.

30 EXAMPLE 2.—EFFECT OF PRODUCTS AS ANTI-
OXIDANT ADDITIVES

The products described in Example 1 were tested as mineral lubricating oil anti-oxidants by the following
35 procedure. A blend of the product dissolved in a mineral oil base stock, to be described specifically below, was exposed to cyclic conditions of heating and cooling. To do this, 300 g. of the oil blend were introduced into a
40 600 cc. Pyrex glass beaker, and a sand-blasted steel panel was supported in the beaker so that three-fourths of the panel was covered by the oil. The oil blends were heated at 150° F. for about 100 hours, then cooled to room
45 temperature, examined, and then heated again for another period of 100 hours. This heating and cooling was continued until the samples had been exposed to the elevated temperature of 150° F. for at least 500 hours. In each
50 case, the Tag-Robinson color of the oil blend was determined before subjecting to the heating test and after each 100 hours' period of heating. The steel panels
55 were also examined for evidences of rust.

One blend tested in this manner consisted of 0.67 weight percent of product A in oil 1, which was an acid-treated Venezuelan distillate having an S. U. S. viscosity at 210° F. of about 55. Another blend consisted of 0.3
60 weight percent product B in oil 2, an acid-treated Coastal distillate having an S. U. S. viscosity at 210° F. of 70. Runs were also carried out on both oils 1 and 2 containing no additive for comparative purposes. The results of
65 these tests are shown in Table I below:

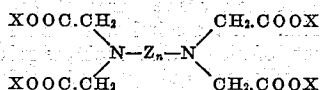
TABLE I

Oil used	Product in Oil, Weight percent	Tag-Robinson Color of Oil	
		Before Heating	After 500 Hrs. at 150° F.
1	None	9½	2¼
1	0.67 Wt. percent Product A	9½	8
2	None	11	4
2	0.3 Wt. percent Product B	10¼	10¼

It is seen that each of the oil base stocks per se dis-

colored to an appreciable extent during the heating period, losing about 7 Tag-Robinson color units during the 500 hours. On the other hand, the oils containing either products A or B lost very little or no color during this time. Whereas the oil panels immersed in the uninhibited oils rusted appreciably during the heating period, those contained in the inhibited oils showed no or hardly any evidence of rust.

The nitrogen base salts of the present invention are preferably those represented by the following formula:



wherein Z is an alkylene group, n is an integer, and X is selected from the group consisting of hydrogen and nitrogen base radicals, at least one of the X groups being a nitrogen base radical.

These salts are conveniently prepared by merely reacting an alkylene bis-amino aliphatic tetra-carboxylic acid with the desired nitrogen base employing a suitable molar ratio of the two reactants, such as from 1 to 4 mols of nitrogen base per mol of acid, to obtain the desired degree of substitution of the acid. The reaction is facilitated by heat, and may for example be carried out at an elevated temperature such as in the range of 50° to 150° C. The reaction may be carried out in the presence of a suitable solvent for the reactants, such as the lower aliphatic alcohols, ketones, ethers, etc., the mixture being heated at refluxing temperature to complete the reaction. The solvent may then be removed by distilling, evaporating or by other means. The time of reaction is not particularly critical and will depend on the extent of salt formation desired, reaction temperature, etc.

The polycarboxylic acids useful in preparing the amine salts may vary in molecular weight, those in which the integer n in the symbol Z_n of the above formula is in the range of 1 to 4 being preferred. Specific acids include ethylene diamine N,N' -tetraacetic acid; propylene 1,2-diamine N,N' -tetraacetic acid; butylene 1,2-diamine N,N' -tetraacetic acid; etc. Such acids are well known to the art.

The nitrogen bases employed in the reaction with the acids of the above type include any of those that have sufficiently high basicity to react with the acids. Nitrogen bases having oil-solubilizing hydrocarbon radicals, such as those containing in the range of 3 to 30 carbon atoms, especially 5 to 24 carbon atoms are preferred. The total number of carbon atoms in these radicals will vary depending on the ultimate use of the compound. For example, the X radicals may supply no or only very few carbon atoms when the compound is used as a dispersion or solution in low concentrations in light hydrocarbons. A total of at least 10-15 carbon atoms in the X radicals is preferred, however, if the compound is to be used as a lubricating oil additive.

The nitrogen base compounds which may be employed include ammonia and the organic nitrogen bases such as amines and amine derivatives, guanidines and their derivatives, morpholine, piperidine, quinoline, decahydroquinoline, and like substances. Primary, secondary and tertiary amines may be used, but secondary amines are preferred because of their high basicity and ease of preparation. Useful hydrocarbon substituent groups on these amines and guanidine-type compounds include alkyl, cycloalkyl, alkenyl and the like aliphatic groups as well as aromatic groups such as aralkyl, alkaryl and the like radicals. Heterocyclic amines, particularly the highly basic saturated members such as piperidine and related compounds are useful.

Specific amines include methylamine, isopropylamine, diisopropylamine, dibutyl amine, hexylamines, didodecylamine, dioctadecyl amine and the higher amines derived from animal fats and oils, wax amines, such as C_{20} - C_{26}

wax amines, dibenzylethylamine, dicyclohexylamine, and the like. Guanidine-type compounds include guanidine, alphamethylguanidine, trimethylguanidine, alphaphenylethylguanidine, alphanohexylguanidine, triethylguanidine, tribenzylguanidine, etc.

In choosing the salt to be used in the practice of the present invention, due consideration should be given to the type of base stock to which it is added and the specific property to be improved. Obviously, solubility factors will limit to some extent the specific type of salt to be employed, the lower molecular weight substituted salts having relatively few oil solubilizing groups being less satisfactory than corresponding high molecular weight members when the salts are to be used in relatively high concentrations in mineral lubricating oils and the like. In general, in the range of about 0.01 to 5.0% by weight of the nitrogen base salt, based on the total composition, will be satisfactory for inhibiting oxidation, corrosion, or rusting of metal parts. Generally in the range of 0.3 to 2.0 weight percent will be most effective for anti-oxidant properties. Amounts in the range up to 15% or even higher may sometimes be desired for imparting these and other characteristics to lubricating oils and the like. For convenience in transporting and storing the nitrogen base salts, it is frequently desirable to prepare concentrates containing in the range of about 20 to 50% by weight of the salt in a mineral oil base stock such as a lubricating oil, and then adding the required amount of the concentrate to the base stock to be improved in preparing the final blend. In general, compositions prepared in accordance with the present invention will include a major proportion of the oil base stock and minor proportions of the nitrogen base salts. The oil compositions may, of course, include minor amounts of other additive materials as will be described below.

The products of the present invention may be employed not only in ordinary lubricating oils but also in the "heavy duty" type of lubricating oils which have been compounded with such detergent type additives as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, thiophosphates, phosphites and thiophosphites, metal salicylates, metal xanthates and thioxanthates, metal thiocarbamates, amines and amine derivatives, reaction products of metal phenates and sulfur, reaction products of metal phenates and phosphorus sulfides, metal phenol sulfonates, and the like. Thus, the additives of the present invention may be used in lubricating oils containing such other addition agents as barium tert-octylphenol sulfide, calcium tert-amyphenol sulfide, nickel oleate, barium stearate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum naphthenate, calcium cetyl phosphate, barium di-tert-amyphenol sulfide, calcium petroleum sulfonate, zinc methyl cyclohexyl thiophosphate, calcium dichlorostearate, etc. Other types of additives such as phenols and phenol sulfides may be employed.

The base stocks used in the preferred compositions of this invention include animal, vegetable, mineral and synthetic oils. Preferably, they are essentially hydrocarbon oils such as straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichlorodiethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins; e. g., high molecular weight polyisobutylenes, or by the

reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances, cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special application, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed alone or in admixture with mineral oils. Synthetic oils of the ester, polyester, polyether and related types may also be used. These include di-2-ethyl hexyl sebacate, dibasic acid esters, polyalkylene oxides, etc.

For the best results the base stock chosen should normally be that oil which without the new additive present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must, of course, be observed. The oils must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. Lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of diesel engine and some gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the material to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed.

Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having eight or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol ($C_8H_{17}OH$), lauryl alcohol ($C_{12}H_{25}OH$), cetyl alcohol ($C_{16}H_{33}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol, ($C_{18}H_{37}OH$), heptadecyl alcohol ($C_{17}H_{35}OH$), and the like, the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes, the wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g., paraffin wax, petrolatum, etc.

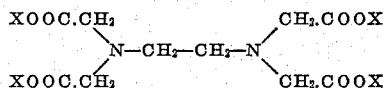
In addition to being employed in crankcase lubricants, the additives of the present invention may also be used in extreme pressure lubricants, engine flushing oils, industrial oils, general machinery oils process oils, rust preventative compositions and greases.

The additives of the present invention may be employed as antioxidant or stabilizing agents not only in lubricants of the types described above but also in other organic materials, including petroleum hydrocarbon products generally, where improved resistance to oxidation or other improved properties are desired. Thus, the products may be added to motor oils, diesel fuels, kerosene, waxes, hydrocarbon polymers, etc., and other mineral oils. The products may also be added to natural and synthetic rubbers, asphalts, plastics and other solid and liquid organic materials.

The present invention is not to be considered as limited by any of the examples described herein, which are given by way of illustration only, but is to be limited solely by the terms of the appended claims.

What is claimed is:

1. A liquid oily composition of matter comprising a major portion of an essentially hydrocarbon oil and in the range of about 0.01 to 20% by weight, based on the total composition, of an oil-soluble material having the formula



wherein X is selected from the group consisting of hydrogen, monobasic amine radicals of piperidine and monobasic amine radicals of alkyl secondary amines containing between 5 to 24 carbon atoms, at least one of the X groups being a monobasic amine radical.

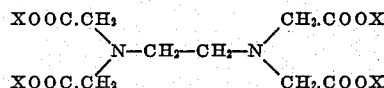
2. A composition as in claim 1 wherein said amine radical is piperidine.

3. A composition as in claim 1 wherein said amine radical is dioctadecyl amine.

4. A lubricating oil composition comprising a mineral lubricating oil and in the range of 0.1 to 5% by weight of a piperidine salt of ethylene diamine tetra acetic acid.

5. A lubricating oil composition comprising a mineral lubricating oil and in the range of 0.1 to 5% by weight of a dioctadecyl amine salt of ethylene diamine tetra acetic acid.

6. As a new compound, an oil-soluble material having the formula



wherein X is selected from the group consisting of hydrogen, monobasic amine radicals of piperidine and monobasic amine radicals of alkyl secondary amines containing between 5 to 24 carbon atoms, at least one of the X groups being a monobasic amine radical.

7. As a new compound, a piperidine salt of ethylene diamine tetra acetic, acid.

8. As a new compound, a dioctadecyl amine salt of ethylene diamine tetra acetic acid.

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