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PHENOXYALKYL DITHIOCARBAMATES

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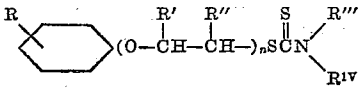
The present invention relates to a new class of compounds having a variety of uses and to methods for making the compounds. It relates particularly to phenoxyalkyl dithiocarbamates useful as additives for mineral lubricating oil compositions and the like.

This application is a continuation-in-part of Serial No. 197,647 filed November 25, 1950, now Patent No. 2,637,696.

In the development of petroleum lubricating oils the trend has been to use more and more efficient refining methods in order to reduce the tendency of the oils to form carbon and deposits of solid matter or sludge. While such highly refined oils possess many advantages, their resistance to oxidation, particularly under conditions of severe service, is generally decreased and they are more prone to form soluble acidic oxidation products which are corrosive. They are generally less effective than the untreated oils in protecting the metal surfaces which they contact against rusting and corrosion due to oxygen and moisture. Although generally superior to lightly refined oils they may deposit films of "varnish" on hot metal surfaces, such as the pistons of internal combustion engines, under very severe engine operating conditions.

In accordance with the present invention a new class of compounds has been discovered which when added to petroleum hydrocarbon oils, and especially to mineral lubricating oil fractions, substantially reduces the tendency of such oils to corrode metal surfaces, and which are particularly effective in inhibiting the corrosion of copper-lead and cadmium-silver bearings. These substances are also effective in dispersing sludge and in maintaining a clean engine condition when the oil is employed as a crankcase lubricant.

The new class of compounds which have been found to improve the properties of hydrocarbon oils in the manner described above may be considered as phenoxyalkyl dithiocarbamates, where the term "phenoxyalkyl" is intended to cover compounds where the molecule contains one or a chain of two of more oxyalkyl groups. These compounds are conveniently prepared by reacting a phenoxyalkyl chloride with an alkali metal dithiocarbamate, with the formation of an alkali metal chloride as a by-product. The new additives of the present invention may be defined more exactly as compounds having the formula



where R represents at least one alipatic hydrocarbon side chain, which may be a straight or branched chain and may be saturated or unsaturated, the total number of carbon atoms in all of such side chains being from 1 to 18; where R′ and R″ each represent hydrogen or alkyl groups, the total number of carbon atoms in both R′ and R″ being not greater than 4; where R‴ and R^{IV} represent hydrogen or an aliphatic or cycloaliphatic hydrocarbon group, saturated or unsaturated, containing 1 to 18 carbon atoms;

where the total number of carbon atoms in all of the R, R‴ and R^{IV} groups combined is not less than 4; and where n is an integer from 1 to 20, preferably 1 to 6. The function of the groups R, R‴, and R^{IV} is primarily to provide oil solubility.

Typical examples of compounds of the above described class, useful in accordance with the present invention, are the following:

p-n-Butylphenoxyethyl dithiocarbamate
o-Ethylphenoxyethyl dithiocarbamate
p-Isopropylphenoxyethyl n-butyl dithiocarbamate
p-2-ethylhexylphenoxyethyl n-butyl dithiocarbamate
p-tert.-Octylphenoxyethoxyethyl n-butyl dithiocarbamate
p-tert.-Amylphenoxyethoxyethyl n-butyl dithiocarbamate
2,4-di-tert.-amylphenoxyethoxyethyl n-butyl dithiocarbamate
Butenylphenoxyethoxyethyl n-butyl dithiocarbamate
p-tert.-Octylphenoxy-1,2-dimethylethoxy - 1,2 - dimethylethyl n-butyl dithiocarbamate
p-tert.-Octylphenoxy(diethoxy)ethyl n-butyl dithiocarbamate
p-tert.-Octylphenoxy(triethoxy)ethyl 2-ethylhexyl dithiocarbamate
p-tert.-Octylphenoxy(pentaethoxy)ethyl lauryl dithiocarbamate
p-tert.-Octylphenoxyethoxyethyl n-hexadecyl dithiocarbamate
p-tert.-Octylphenoxyethoxyethyl oleyl dithiocarbamate
p-tert.-Octylphenoxy(octaethoxy)ethyl cyclohexyl dithiocarbamate
p-tert.-Octylphenoxy(octadecylethoxy)ethyl di-n-butyl dithiocarbamate

The sodium or other alkali metal dithiocarbamate, which may be employed in preparing the compounds of the present invention, may be prepared by known means, for example, by slowly adding carbon disulfide to a mixture of an alkali metal hydroxide and a primary or secondary amine in the presence of a suitable inert medium such as methylethyl ketone. The solution of the dithiocarbamate thus formed may be used directly in the reaction with the phenoxyethoxyethyl chloride, in accordance with the present invention.

In the reaction of the phenoxyalkoxyalkyl chloride with the alkali metal dithiocarbamate, the reactants are merely heated together, preferably at temperatures of 50° to 150° C. The reaction may be caused to take place either with or without the presence of a solvent, but it is generally preferred to employ a solvent, such as ethyl alcohol, isopropyl alcohol, acetone, methylethyl ketone, dioxane, or the like. The heating is conveniently carried out under refluxing conditions, and the reaction is generally completed within a period of two hours or less. It is preferable to employ an amount of the alkali metal dithiocarbamate which is approximately a stoichiometrical equivalent of the phenoxyalkoxyalkyl chloride. If a solvent is employed, one should be selected in which the alkali metal chloride is insoluble, in order that the by-product will be precipitated out of solution and be readily removed by decantation or filtration.

When the products of the present invention are added to mineral oils for the purpose of inhibiting oxidation, for dispersing sludge, or for reducing the pour point of the oil, they are preferably added in proportions of 0.01 to about 5%, preferably 0.1 to 2%, by weight. The proportions giving the best results in given cases will vary somewhat according to the nature of the additive and of the base oil and in accordance with the specific purpose the oil is to serve in a given case. For commercial purposes, when an additive is to be employed in mineral lubricating oils, it is convenient to prepare concentrated lubricating oil solutions in which the amount of the additive in the

composition ranges from 25% to 50% by weight, and to transport and store them in such form. In preparing a lubricating oil composition for use, as in the crankcase of an internal combustion engine, the additive concentrate is merely blended with the base oil in the required amount.

Below are given detailed descriptions of the preparation and testing of an example of a mineral oil additive prepared in accordance with the present invention. It is to be understood that this example is given by way of illustration only and is not to be construed as limiting the scope of the present invention in any way.

Example 1

(*a*) 12.75 g. (0.32 mol) of sodium hydroxide flakes and 160 cc. of methylethyl ketone were placed in a 1-liter reaction flask. Then 23.3 cc. (0.24 mol) of n-butylamine was added and the solution cooled in a water-ice bath. While stirring this mixture a solution of 26.7 cc. (0.42 mol) of carbon disulfide dissolved in 50 cc. of methylethyl ketone was added dropwise. Stirring was continued for two hours at room temperature.

(*b*) To the sodium butyl dithiocarbamate solution prepared as in (*a*) was added 100 g. (0.32 mol) of p-tert.-octylphenoxyethoxyethyl chloride and the mixture stirred and heated for two hours at the refluxing temperature of the methylethyl ketone. The product was then filtered through a filter aid ("Hyflo") to remove the precipitated sodium chloride and blown with nitrogen on the steam bath to remove the solvents. The product gave the following analysis:

	Per cent
Chlorine	1.43
Nitrogen	2.21
Sulfur	12.46

Example 2.—Lauson engine test

The product prepared as described in Example 1 was tested in a Lauson engine, using a blend of 1.0% by weight of the additive in a solvent extracted Coastal naphthenic oil of 60 seconds viscosity (Saybolt) at 210° F. For comparison, a sample of the unblended base oil was likewise tested. The test was conducted for a period of 25 hours, the Lauson engine being operated at 1800 R. P. M. with a 1.5 indicated kilowatt load, 300° F. oil temperature and 295° F. water jacket temperature. The oils were rated on a demerit system wherein a perfectly clean surface is given a rating of 0, while a rating of 10 is given the worst condition which can be expected on that surface. Observations were also made on the loss in weight of the copper-lead bearings during the test. The results are shown in the following table—

Lubricant	Piston Varnish Demerit	Cu-Pb Bearing Weight Loss (Gm./Bearing)
Unblended base oil	4.25	0.108
Base oil+1% product of Example 1	3.25	0.039

Example 3.—Laboratory bearing corrosion test

A blend was prepared containing 0.25% by weight of the additive prepared as described in Example 1, using as the base oil a solvent extracted paraffinic type mineral lubricating oil of SAE-20 viscosity grade. A sample of this blend and a sample of the unblended base oil were submitted to a laboratory test known as the S. O. D. corrosion test, designed to measure the effectiveness of the additive in inhibiting the corrosiveness of a typical mineral lubricating oil towards the surfaces of copper-lead bearings. The test was conducted as follows:

500 cc. of the oil was placed in a glass oxidation tube (13 inches long and 2⅝ inches in diameter) fitted at the bottom with a ¼ inch air inlet tube perforated to facilitate air distribution. The oxidation tube was then immersed in a heating bath so that the oil temperature was maintained at 325° F. during the test. Two quarter sections of automotive bearings of copper-lead alloy of known weight having a total area of 25 sq. cm. were attached to opposite sides of a stainless steel rod which was then immersed in the test oil and rotated in 600 R. P. M., thus providing sufficient agitation of the sample during the test. Air was then blown through the oil at the rate of 2 cu. ft. per hour. At the end of each four-hour period the bearings were removed, washed with naphtha and weighed to determine the amount of loss by corrosion. The bearings were then repolished (to increase the severity of the test), reweighed, and then subjected to the test for additional four-hour periods in like manner. The results are given in the following table as "corrosion life," which indicates the number of hours required for the bearings to lose 100 mg. in weight, determined by interpolation of the data obtained in the various periods.

Oil	Bearing Corrosion Life (Hrs.)
Unblended base oil	10
Base oil+0.25% product of Example 1	25

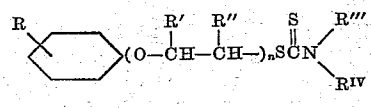
The products of the present invention may be employed not only in ordinary hydrocarbon lubricating oils but also in the "heavy duty" type of lubricating oils which have been compounded with such detergent type additives as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, phosphites, thiophosphates, and thiophosphites, metal xanthates and thioxanthates, metal thiocarbamates, and the like. Other types of additives, such as phenols and phenol sulfides, may also be present.

In addition to being employed in lubricants, the compounds of the present invention may also be used in other mineral oil products such as motor fuels, heating oils, hydraulic fluids, torque converter fluids, cutting oils, flushing oils, turbine oils, transformer oils, industrial oils, process oils, and the like, and generally as antioxidants in mineral oil products. They may also be used in gear lubricants, greases and other products containing mineral oils as ingredients.

The specific compound selected for use in accordance with the above teachings will depend to some extent on the medium to which it is added and the particular improvement to be obtained. Compounds having 1 to 6, preferably 1 to 3, oxyalkyl groups are generally more potent antioxidants than those having a greater number of such groups, other substituent groups in the compounds being the same. Compounds containing a large number of oxyalkyl groups are usually preferred as detergents and the like.

What is claimed is:

1. As a new composition of matter a compound of the formula



where R represents at least one aliphatic hydrocarbon side chain, the total number of carbon atoms in all of such side chains being 1 to 18; where R′ and R″ each represent a member of the group consisting of hydrogen and alkyl groups, the total number of carbon atoms in both of such groups being not greater than 4; where R‴ and R^{IV} represent members of the group consisting of hydrogen and aliphatic and cycloaliphatic hydrocarbon groups containing 1 to 18 carbon atoms; where the total number of carbon atoms in all of the R, R‴, and R^{IV} groups is not less than 4; and where *n* is an integer from 1 to 20.

2. A composition according to claim 1, in which *n* is from 1 to 6.

3. A composition according to claim 2 in which R′ and R″ each represent hydrogen.

4. A composition according to claim 3 in which R and R‴ each represent a single alkyl group and R^{IV} is hydrogen.

5. A composition according to claim 4 in which R represents an octyl radical and R‴ represents an n-butyl radical.

6. As a new composition of matter p-tert.-octylphenoxyethoyethyl n-butyl dithiocarbamate.

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