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LUBRICATING OIL ADDITIVES COMPRISING MIXTURES OF POLYVALENT METAL DITHIOCARBAMATES

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This invention relates to the preparation and use of oil additives and is particularly concerned with the preparation and use of mixtures of polyvalent metal dithiocarbamates as oil additives.

Deterioration of the moving parts of bearings appears to result from the formation of undesirable products in the oils which are used to lubricate the bearings. These undesirable products are caused primarily by dilution and oxidation which tend to change the viscosity of the lubricants and provide reactive chemicals which pit the surfaces of the bearings. This problem is particularly acute when the bearings are made from sensitive metal alloys which may contain mixtures comprised in part of copper, lead, cadmium, nickel, silver and tin. Bearing failure is particularly noticeable in heavy-duty service, e.g,. the operation of trucks, buses, ships, planes and stationary power plants.

Many attempts have been made to overcome the problem of deterioration of metal bearings, but these efforts have not proved to be completely successful. Most such attempts have been in the nature of adding various chemical compositions to the oils which are used to lubricate the bearings. For example, alkaline acid inhibitors have been added to lubricating oils in order to prevent the oil from becoming acid, and various soap-like materials have been added to oils in order to help remove deposited sludge. In addition, various anti-oxidants have been added in order to inhibit oxidation of the oils and the subsequent formation of undesirable chemicals within the lubricating oil.

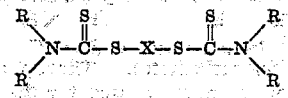
Also, individual polyvalent metal dithiocarbamates are known to be useful oil additives because they serve the dual function of sequestering undesirable metal components of the oil and because they function as antioxidants. The practice has developed of adding individual polyvalent metal dithiocarbamates to lubricating oils in the form of compatible oil concentrates. These compatible oil concentrates are much easier and more convenient to add to the lubricating oils than the pure powdered dithiocarbamates because the latter must be processed into the oil by means of heating, stirring and filtering. It is, therefore, economically imperative that the concentration of polyvalent metal dithiocarbamates in the compatible oils be as high as possible but low enough to prevent crystallization of the dithiocarbamates during shipment.

Because the polyvalent metal ions in the dithiocarbamates are the effective components of the additives, it is desirable that the concentrate contain a maximum concentration of polyvalent metal dithiocarbamates which are comprised of the lowest possible effective molecular weights.

It is a general object of this invention to prepare improved polyvalent metal dithiocarbamate oil additives. It is another object of this invention to prepare mixtures comprised of at least two polyvalent metal dithiocarbamates. It is a further object of this invention to prepare mixtures comprised of at least two polyvalent metal

dithiocarbamates which have improved solubilities in oils. It is another object of this invention to prepare concentrates comprised of a mixture of at least two polyvalent metal dithiocarbamates in petroleum base hydrocarbon oils.

It has been discovered that the concentration of polyvalent metal dithiocarbamates in compatible oils can be increased without the danger of crystallization when the dithiocarbamates are mixtures comprised of at least two polyvalent metal dithiocarbamates. These mixtures can be described as a mixture of at least two dithiocarbamates of the general formula



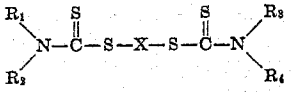
wherein X is a polyvalent metal and wherein the R's are selected from the group consisting of aliphatic radicals, cycloaliphatic radicals, aralkyl radicals, cycloaliphatic rings formed by the joining together of the pair of R's on a nitrogen atom and heterocyclic rings formed by the joining together of the pair of R's on a nitrogen atom.

The polyvalent metals which are useful in the practice of this invention are generally selected from the group consisting of zinc, ferric iron, barium, magnesium, calcium, strontium and radium. The mixed zinc dithiocarbamates constitute a preferred class of additives.

The dithiocarbamates which are used in the practice of this invention are mixtures of two or more different dithiocarbamates wherein all of the radicals attached to the terminal nitrogens of each individual component of the mixture are the same or different. These radicals may be aliphatic radicals, cycloaliphatic radicals, aralkyl radicals, cycloaliphatic rings formed by joining together pairs of radicals on a nitrogen atom, or heterocyclic rings formed by joining together pairs of radicals on a nitrogen atom. Because it is desired to keep the molecular weights as low as possible, the preferred radicals are alkyl radicals having from 1 to 9 carbons, particularly ethyl, propyl, isopropyl, butyl and amyl radicals. The preferred composition is a mixture of coprecipitated zinc dithiocarbamates prepared from an aqueous solution which contains 1.0 to 1.5 moles of sodium di-n-butyl dithiocarbamate, 0.1 to 0.5 mole of sodium diethyl dithiocarbamate, 0.1 to 0.5 mole of sodium diamyl dithiocarbamate and 0.05 to 0.2 mole of sodium diisopropyl dithiocarbamate which is precipitated by the addition of one half the number of moles of a soluble zinc salt as there are total moles of the sodium salts. However, the percentages of the mixtures may vary considerably, the only requirement being that a mixture be comprised of at least two polyvalent metal dithiocarbamates which are present in substantial proportions, the proportions being sufficient to increase the solubility of the mixture in oil over the solubilities of the individual components of the mixture. Normally each component will be present in a proportion of at least 5% by weight, based on the weight of the mixture.

The concentrations of mixtures of polyvalent metal dithiocarbamates in the compatible oils will vary considerably. However, the concentration will normally range from about 15% by weight of polyvalent metal dithiocarbamates, based on the weight of the oil-dithiocarbamates solution, to 50% by weight and will vary depending upon the composition of the mixture of dithiocarbamates. When the mixture is comprised of mixtures of zinc dithiocarbamates in compatible oils, the concentration of effective zinc in the oil carrier will be at least 13% by weight of zinc based on the weight of the mixture of zinc dithiocarbamates. In this form, the oil concentrates can be added to customary lubricating oils in the most effective proportions.

The mixtures of dithiocarbamates may also be described as mixtures of at least two dithiocarbamates having the following formula



wherein R_1, R_2, R_3 and R_4 are selected from the group consisting of aliphatic radicals, cycloaliphatic radicals, aralkyl radicals, cycloaliphatic rings formed by the joining together of the pair of R's on a nitrogen atom and heterocyclic rings formed by the joining together of the pair of R's on a nitrogen atom.

The products of this invention may be made by preparing an aqueous solution of monovalent metal dithiocarbamates and thereafter reacting the solution of monovalent metal dithiocarbamates with a soluble polyvalent metal salt and thereby precipitating the mixture of polyvalent metal dithiocarbamates. The soluble sulfates, nitrates and chlorides may be used for the purpose, although other soluble salts are satisfactory. Mixtures of polyvalent metal dithiocarbamates may also be obtained by combination of two or more individually prepared polyvalent metal dithiocarbamates.

These mixtures may also be prepared by mixing the amines before reacting with a strong monovalent metal alkali (such as sodium hydroxide) and carbon disulfide in an aqueous solution. Reaction with one or more polyvalent metal salts produces the mixture of polyvalent metal dithiocarbamates.

The mixtures of dithiocarbamates are thereafter added to an oil, which is compatible with the customary lubricating oils, in the highest possible concentration. This concentration will customarily range from about 15% by weight to about 50% by weight based on the weight of the compatible oil-dithiocarbamates solution.

Tests have been made to illustrate that mixtures of polyvalent metal dithiocarbamates are more soluble in organic liquids, such as oils, than are the pure components. A hydrocarbon solvent was prepared by mixing together equal volumes of benzene and n-hexane. The solubilities of various zinc dithiocarbamates and mixtures of zinc dithiocarbamates are shown in Table I. The test solutions were prepared by saturating the solutions with the indicated components at 40° C. and thereafter allowing the solutions to reach equilibrium by allowing them to cool to routine temperature.

TABLE I

Salt	Solubility in 100 Grams of Solvent, grams
1. Zinc diethyl dithiocarbamate	0.85
2. Zinc diisopropyl dithiocarbamate	0.49
3. Zinc di-n-butyl dithiocarbamate	42.7
4. Mixture of salts 1 and 3	108.3
5. Mixture of salts 2 and 3	98.4
6. Mixture of salts 1, 2 and 3	150.0

Thus, it is quite apparent that mixtures are considerably more soluble in organic solvents than are the pure compounds and that the more complex the mixture the greater the solubility.

The preparation of mixed polyvalent metal dithiocarbamates is illustrated by the following examples which are not intended as limitations on the scope of the invention.

Example 1

A solution containing 60 milliliters of a 1 molar sodium di-n-butyl dithiocarbamate solution, 20 milliliters of a 1 molar sodium diisopropyl dithiocarbamate solution and 20 milliliters of a 1 molar sodium diethyl dithiocarbamate solution was prepared. This solution was then slowly added to a solution of 14.4 grams of $ZnSO_4.7H_2O$ in 200 milliliters of water. The resultant precipitate was filtered, washed with water and dried. It was ground to a fine white powder which weighed 20.0 grams.

Example 2

A solution containing 15.1 milliliters of a 1 molar sodium (mixed)-di-amyl dithiocarbamate solution, 54.0 milliliters of a 1 molar sodium di-n-butyl dithiocarbamate solution, 4.8 milliliters of a 1 molar sodium diisopropyl dithiocarbamate solution and 16.9 milliliters of a 1 molar sodium diethyl dithiocarbamate solution was prepared. This solution was then slowly added to a solution of 13.1 grams of $ZnSO_4.7H_2O$ in 200 milliliters of water. The resultant precipitate was filtered, washed with water and dried. It was ground to a fine white powder which weighed 19.5 grams.

Various solutions of polyvalent metal dithiocarbamates in oils were prepared. The oils were petroleum hydrocarbon oils as shown in Table II.

TABLE II

Oil	Flash Point Cleveland Open Cup, ° F.	Viscosity at 100° F. Saybolt Universal, sec.
A	340	497
B	385	107

The following oil concentrates were prepared:

TABLE III

Component	Solution 1	2	3	4	5
	G.	G.	G.	G.	G.
Oil A	30.20	30.20	30.20	15.10	15.10
Oil B	2.18	2.18	2.18	1.09	1.09
Zinc di-n-butyl dithiocarbamate	17.62	14.98	13.22	-------	-------
Zinc diethyl dithiocarbamate	-------	2.64	2.20	-------	-------
Zinc diisopropyl dithiocarbamate	-------	-------	2.20	-------	-------
Product of Example 1	-------	-------	-------	8.81	-------
Product of Example 2	-------	-------	-------	-------	8.81

These oil concentrates were set aside for a period of four weeks after which they were tested for opaqueness, to wit, whether or not crystallization had occurred. These results are listed in Table IV.

TABLE IV

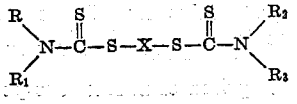
Solutions	1	2	3	4	5
Appearance	opaque almost solid.	translucent.	translucent.	translucent.	translucent.

Thus, it is shown that mixtures do not tend to crystallize out of organic solvents, such as oils, as readily as pure compounds.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it wil be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

We claim:

1. A lubricating oil additive composition consisting of a petroleum hydrocarbon lubricating oil solution of a mixture of at least two different dithiocarbamates of the general formula:



wherein X is a polyvalent metal selected from the group consisting of zinc, ferric iron, barium, magnesium, calcium, strontium and radium and R, R_1, R_2 and R_3 are aliphatic radicals having from 1 to 5 carbon atoms, and wherein the average number of carbon atoms in

$$R+R_1+R_2+R_3$$

for all the different dithiocarbamates in said mixture is less than 15, the concentration of divalent metal dithiocarbamates in solution in the petroleum hydrocarbon lubricating oil being between 15 and 50% by weight of said oil additive composition.

2. A lubricating oil additive composition consisting essentially of a petroleum hydrocarbon lubricating oil solution of a mixture of coprecipitated zinc dithiocarbamates prepared from an aqueous solution which contains 1.0 to 1.5 moles of sodium di-n-butyl dithiocarbamate, 0.1 to 0.5 mole of sodium diethyl dithiocarbamate, 0.1 to 0.5 mole of sodium diamyl dithiocarbamate and 0.05 to 0.2 mole of sodium diisopropyl dithiocarbamate which is precipitated by the addition of one half the number of moles of a soluble zinc salt as there are total moles of the sodium salts.

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