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# UNITED STATES PATENT OFFICE

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## OIL COMPOSITIONS RESISTANT TO OXIDATION

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3 Claims. (Cl. 252—47)

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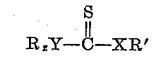
The present invention relates to the stabilization of oils against oxidative deterioration. More particularly, the invention has to do with the preparation of an oleaginous composition comprising a major amount of a normally oxidizable oil and a minor amount each of a thiocarbonic acid derivative and an aromatic amine, each being selected from specific classes of compounds. In accordance with the invention, it has been found that the combination of the aforesaid thiocarbonic acid derivative and aromatic amine has a synergistic antioxidant effect.

Among the adverse effects caused by oxidation may be mentioned the formation of corrosive acidic products, sludges, varnishes, resins and other oil-insoluble products, as, for example, with mineral oils. Other oils, such as certain synthetic hydrocarbons, tend to further polymerize on oxidation, thus becoming undesirably viscous, while other synthetic oils, for example the polyalkylene glycol type, tend to depolymerize giving off volatile products. Other oils thicken and become rancid, for example the animal and vegetable fatty oils.

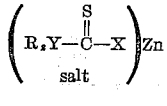
Now I have found that I can substantially increase the resistance to oxidation of these oils and others, whereby their quality and nature are maintained over a long period of time either during use or in storage, by the incorporation in the oil of a small amount of a non-acidic thiocarbonic acid derivative selected from the class consisting of esters, amides, salts, acyl disulfides and thioanhydrides of thiocarbonic acids.

More specifically, the non-acidic thiocarbonic acid derivative is one which is soluble in the oil to the extent of at least about 0.05%, preferably about 0.1%, by weight of the finished oil, and which has a molecular weight of at least about 150.

In general, the aforesaid thiocarbonic acid derivative may be represented by the following formulas:

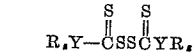


ester

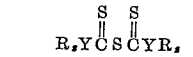


salt

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acyl disulfide



thioanhydride

In the above formulas, like letters have the same significance. Thus, R and R' represent like or different organic groups, such as alkyl groups; Y, oxygen, sulfur or nitrogen; X, oxygen or sulfur; *z*, the integer 1 when Y is oxygen or sulfur, and 2, when Y is nitrogen; C, carbon; S, sulfur; and Zn, zinc.

As above indicated, R and R' are substituted or unsubstituted alkyl or aryl groups. The substituent groups can be amino, hydroxyl, mercapto, alkoxy, aryloxy, thio, alkyl, aryl, alkaryl or arylalkyl radicals.

Specific examples of thiocarbonic acid derivatives contemplated by the invention are zinc di-n-butyldithiocarbamate, zinc i-propylxanthate, zinc sec.-amyl trithiocarbonate, zinc phenyl-n-butyl dithiocarbamate, butyl di-n-butyl dithiocarbamate, tolyl di-n-butyl dithiocarbamate, dibenzyl trithiocarbonate, di-i-butylxanthate, zinc salt of dithiocarbonic acid morpholide, tetramethyl thiouram disulfide, di-i-propyl xanthogen, and sec.-butyl xanthic thioanhydride.

In general, the amount of thiocarbonic acid derivative employed for the substantial inhibition of the base oil against oxidation ranges from about 0.03% to about 10% by weight of the finished oil. In most cases a satisfactory amount resides within about the range of 1.0% to 1.0%, with an optimum of about 0.2%, by weight of the finished oil.

The aromatic amine compound contemplated by the invention is one that has a minimum aromaticity of at least two aromatic rings. That is, the aromatic rings may be uncondensed, as in, for example, diphenylamine, or fused or condensed, as in, for example, the polynuclear aromatic amine $\beta$-naphthylamine.

Also suitable are the foregoing aromatic amines containing substituent groups on the ring portion of the molecule, with preferably the ortho or para position in respect to the nitrogen in at least

one ring being free. Also suitable are aromatic amine compounds having one remaining amino hydrogen, the other hydrogen having been replaced by substituent groups or radicals. The substituent groups on either the ring or nitrogen portion of the molecule can be amino, hydroxyl, mercapto, alkoxy, aryloxy, thio, alkyl, aryl, alkaryl, and arylalkyl radicals. Substituent groups containing oxygen which are acidic or acid strengthening in nature and which are not further oxidizable, such as the nitro, carboxyl and sulfonic acid radicals, are less desirable and for practical purposes are avoided. Moreover, the aromatic amine compound is one that is soluble in the base oil to the extent of at least 0.03% and preferably at least 0.2% by weight of the base oil.

Specific examples of aromatic amine compounds falling within the purview of the invention are phenyl-α-naphthylamine, α-naphthylamine, diphenylamine, p-hydroxy-diphenylamine, carbazole, di-β-naphthyl p-phenylene diamine, phenothiazine, p-i-propoxy diphenylamine, p,p'-didodecyl-diphenylamine, carbazole, benzidine, 1-amino-2-hydroxynaphthalene, N,N'-diphenyl p-phenylenediamine, and 1-amino-4-t-butylnaphthalene.

In general, the amount of aromatic amine inhibiting compound employed in accordance with the invention resides within about the range of 0.05% to 5.0% by weight of the finished oil, and preferably 0.05% to 2.0%, by weight of the finished oil.

Examples of commercially available base oils which may be benefited by the practice of the present invention are highly refined mineral hydrocarbon lubricating oils, which because of the exhaustive refining thereof contain substantially no aliphatic sulfur materials, for example, white oil. Other base oils are synthetic hydrocarbon oils or olefin polymer oils, for example the polybutenes and others derived from the lower olefins, such as ethylene, the propylenes, pentenes, etc., and from the Fischer-Tropsch process. Additional examples of base oils are the poly-alkylene glycols of lubricating oil viscosity derived most advantageously from 1,2-propylene oxide, these oils preferably having the terminal hydroxyl groups esterified and/or etherified. Also advantageously treated in accordance with the invention are the diester oils, that is, those derived from the esterification of certain dicarboxylic acids, for example adipic and sebacic, with alcohols, for example butyl, hexyl and octyl alcohols. Another important class of synthetic base oils are those containing silicon, for example the orthosilicates, and preferably those in which the alkyl groups attached to oxygen bound to silicon contain at least three carbon atoms in branched chain structure, for example bis(2-butyl)bis(2-ethyl-1-butyl) silicate, and isopropyltris(2-pentyl)silicate; and the polysiloxanes such as hexa(2-ethyl-1-butoxy)disiloxane.

A convenient method of measuring the resistance to oxidation possessed by the compositions prepared in accordance with the invention is the use of the apparatus and procedure described in Industrial and Engineering Chemistry, vol. 28, p. 26 (1936), wherein the rate of oxygen absorption at constant pressure by a definite weight of oil is regarded as a measure of the oxidative stability of the oil. According to this procedure, the oil sample is placed in an absorption cell, provided in the bottom with a fine-fritted glass filter to disperse the oxygen stream, circulating through the system at a constant rate, into fine bubbles. In obtaining the data hereinbelow appearing, the following modified apparatus and procedure were employed:

The oxidation or absorption cell is constructed of a large glass tube with the head portion having a connection for introducing oxygen, an annular space surrounding the upper end of the tube and a fitting for a removable high speed glass stirrer. The annular space contains potassium hydroxide pellets for the removal of water, carbon dioxide, volatile aldehydes, etc. The lower portion of the cell which contains the sample to be tested is immersed in an oil bath at a temperature of about 340° F. During the test, the oil sample is rapidly agitated by means of a high speed stirrer and is kept under a pressure of about 1 atmosphere of pure oxygen, the volume of oxygen added being automatically recorded. The time in hours required for 100 grams of oil to absorb 1200 cc. of oxygen is called the "Induction Period" (I. P.), and represents the point at which the sample begins to absorb oxygen or oxidize.

The following tabulated data were obtained from a number of experiments performed in accordance with the test above described.

In Table I, the white oil employed was a medicinal white oil having a viscosity of about 350 SSU at 100° F. It was prepared from a suitable distillate fraction of a California naphthenic type crude by phenol treatment followed by exhaustive treatment with fuming sulfuric acid and finished by percolating through fuller's earth.

TABLE I

*Effect of aromatic amine and thiocarbonic acid derivatives on white oil*

| Thiocarbonic Acid Deriv. | Percent Thiocarbonic Acid Deriv. | Percent Phenyl-α-naphthylamine | Induction Period (Hrs. at 340° F.) | | |
|---|---|---|---|---|---|
| | | | With Thiocarbonic Acid Derivative and Phenyl-α-naphthylamine | Without Thiocarbonic Acid Derivative but with Phenyl-α-naphthylamine | With Thiocarbonic Acid Derivative but without Phenyl-α-naphthylamine |
| 1. Zinc di-n-butyl dithiocarbamate | 0.1 | 0.1 | 67 | 2.0 | 7.1 |
| 2. Zinc isopropylxanthate | 0.1 | 0.1 | 38 | 2.0 | 1.3 |
| 3. Tetramethyl thiouram disulfide | 0.1 | 0.1 | 56 | 2.0 | 0.9 |
| 4. Di-sec.-butyl xanthogen | 0.1 | 0.1 | 42 | 2.0 | 0.7 |
| 5. Butyl di-n-butyldithiocarbamate | 0.1 | 0.1 | 48 | 2.0 | 0.2 |
| 6. Di-i-propylxanthic thioanhydride | 0.1 | 0.1 | 32 | 2.0 | 0.9 |
| 7. Zinc t-butyltrithiocarbonate | 0.1 | 0.1 | 61 | 2.0 | 2.1 |

In Table II, the polypropylene glycol was an ethyl hexanol-initiated propene oxide polymer having a molecular weight of about 900.

TABLE II

*Anti-oxidant effect of aromatic amine and thiocarbonic acid derivatives on polypropylene glycol oil*

| Thiocarbonic Acid Deriv. | Percent Thiocarbonic Acid Deriv. | Percent Phenyl-α-naphthylamine | Induction Period (Hrs. at 340° F.) | | |
|---|---|---|---|---|---|
| | | | With Thiocarbonic Acid Derivative and Phenyl-α-naphthylamine | Without Thiocarbonic Acid Derivative but with Phenyl-α-naphthylamine | With Thiocarbonic Acid Derivative but without Phenyl-α-naphthylamine |
| 8. Di-i-propylxanthogen | 2.1 | 0.25 | 5.0 | 0.2 | 0.0 |
| 9. Tetramethyl thiouram disulfide | 1.7 | 0.25 | 4.0 | 0.2 | 0.0 |
| 10. Di-n-butyl dithiocarbamate-initiated propene oxide polymer (mol. wt. about 500) | 10.0 | 0.25 | 6.0 | 0.2 | 0.0 |
| 11. Butylxanthate-initiated propene oxide polymer (mol. wt. about 500) | 10.0 | 0.25 | 4.0 | 0.2 | 0.0 |

In Table III, the synergistic anti-oxidant effect of a representative number of aromatic amines and the thiocarbonic acid derivative tetramethyl thiouram disulfide is illustrated.

TABLE III

*Anti-oxidant effect of various aromatic amines and a thiocarbonic acid derivative on white oil*

| Aromatic Amine | Percent aromatic amine | Percent Tetra methyl thiouram disulfide | Induction Period, Hrs. at 340° F. | | |
|---|---|---|---|---|---|
| | | | With tetramethyl thiouram disulfide and aromatic amine | Without tetramethyl-thiouram disulfide but with aromatic amine | Without aromatic amine but with tetramethyl thiouram disulfide |
| 1. Phenyl-α-naphthylamine | 0.10 | 0.1 | 56 | 2.0 | 0.9 |
| 2. α-naphthylamine | 0.068 | 0.1 | 12 | 0.6 | 0.9 |
| 3. Diphenylamine | 0.079 | 0.1 | 21 | 0.6 | 0.9 |
| 4. p-hydroxy diphenylamine | 0.086 | 0.1 | 42 | 4.7 | 0.9 |
| 5. Carbazole | 0.078 | 0.1 | 6.0 | 0.3 | 0.9 |
| 6. Di-β-naphthyl-p-phenylene diamine | 0.084 | 0.1 | 23 | 0.3 | 0.9 |
| 7. Phenothiazine | 0.093 | 0.1 | 61 | 21.5 | 0.9 |

The data accumulated in Table IV illustrates the anti-oxidant effect of aromatic amines and thiocarbonic acid derivatives of the types defined on a representative number of base oils.

TABLE IV

*Anti-oxidant effect of aromatic amine and thio-carbonic acid derivative on various base oils*

| Base Oil | Induction Period, Hrs. at 340° F. | | |
|---|---|---|---|
| | Except as indicated, with 0.1% Phenyl-α-naphthylamine and 0.1% Di-sec.-butyl xanthogen | Except as indicated, only 0.1% Phenyl-α-naphthylamine | Except as indicated, only 0.1% Di-sec.-butyl xanthogen |
| Polybutene polymer (M. W., about 400) | 4.4 (0.2% phenyl-α-naphthylamine, 0.2% di-sec.-butyl xanthogen). | 0.0 (0.2% phenyl-α-naphthylamine). | 0.0 (0.2% di-sec.-butyl xanthogen). |
| Bis (2-ethylhexyl) sebacate | 83 | 12.0 | 1.2. |
| Tetra-(2-ethylbutyl) silicate | 16.0 | 1.6 | 0.0. |
| Tricresyl phosphate | 26 | 3.1 | 1.4. |
| Polypropylene glycol[1] | 5.2 (0.25% phenyl-α-naphthylamine; 1.7% di-sec.-butyl xanthogen). | 0.2 (0.25% phenyl-α-naphthylamine). | 0.0 (1.7% di-sec.-butyl xanthogen). |
| Polypropylene glycol +50%, by volume, mineral white oil[2] | 6.6 | 0.3 | 0.0. |
| Hexa-sec.-butyl disiloxane | 8.4 | 0.9 | 0.3. |

[1] Ethylhexanol-initiated propene oxide polymer, mol. wt. about 900.
[2] "Polypropylene glycol"=isooctanol-initiated propene oxide polymer acetate, mol. wt. about 600.
"Mineral white oil"=stock prepared as previously described (column 4), but with a viscosity of about 72 SSU at 100° F.

It will be observed from the tabulated data that in each case the combined inhibiting effect of thiocarbonic acid derivative and aromatic amine is far greater than the sum of the effects of the individual additives used separately.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. An oil composition having improved stability toward oxidation, which composition is made up of a normally oxidizable oil together with from about 0.03 to 10 per cent by weight of at least one compound selected from the group consisting of tetramethyl thiouram disulfide and di-sec.-butyl xanthogen and from about 0.05 to 5 per cent by weight of phenyl-α-naphthylamine.

2. An oil composition having improved stability toward oxidation, which composition is made up of a normally oxidizable oil together with from about 0.03 to 10 per cent by weight of tetramethyl thiouram disulfide and from about 0.05 to 5 per cent by weight of phenyl-α-naphthylamine.

3. An oil composition having improved stability toward oxidation, which composition is made up of a normally oxidizable oil together with from about 0.03 to 10 per cent by weight of di-sec.-butyl xanthogen and from about 0.05 to 5 per cent by weight of phenyl-α-naphthylamine.



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