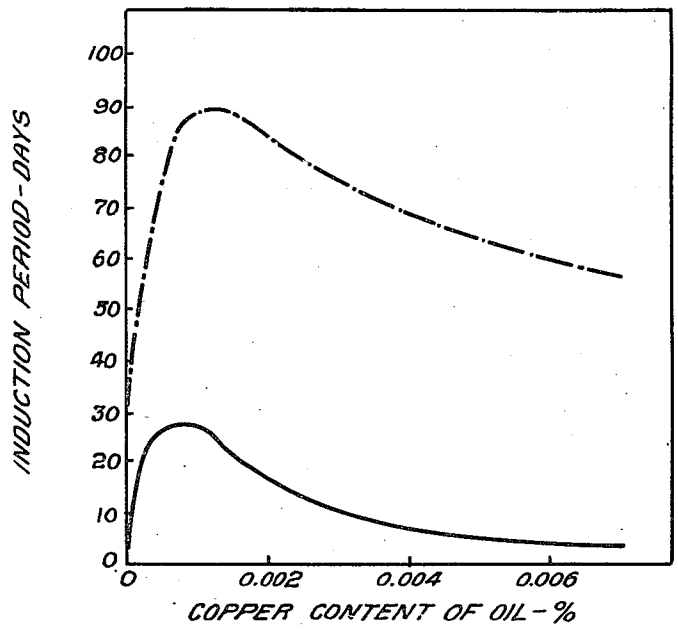
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HYDROCARBON OILS HAVING IMPROVED OXIDATION RESISTANCE

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HYDROCARBON OILS HAVING IMPROVED OXIDATION RESISTANCE

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The present invention relates to new and useful hydrocarbon oils and to a method for improving the oxidation-resistant characteristics of hydrocarbon oils, including mineral oils, etc.

Oxidation of hydrocarbon oils in service adversely affects their physical and chemical properties. Excessive oxidation in hydrocarbon oils (1) increases the viscosity which interferes with oil circulation and/or filtering systems in installations, (2) increases the acidity of the oil which accelerates the wear and corrosion of parts in contact therewith, (3) produces an obnoxious odor, and (4) produces sludges and varnishes which clog oil circulatory channels and produce undesirable deposits. In addition, it is well known that oils used in electrical installations, for example, transformers, are used for conducting away from the transformer the heat resulting from power-loss as well as for their special electrical insulating and dielectric properties. Excessive oxidation interferes with the desired function of these oils (1) by decreasing the rate of convection circulation due to higher viscosity and increasing the thermal insulation of transformer parts by covering them with carbonaceous deposits and (2) also by altering the dielectric properties in such a manner as to deleteriously influence the power factor performance.

It has been found that when hydrocarbon oils are placed in service where they are in contact with oxygen or with other oxygen-containing atmospheres such as air, oxidation will take place and the viscosity of the oils will increase markedly with consequent deleterious effects on the properties of said oils. The art has recognized that metals such as copper, cobalt, iron, etc., when present, either in the form of the metal or in the form of soluble compounds, in hydrocarbon oils will promote oxidation thereof. These metals, e. g., copper, cobalt, iron, etc., and/or the aforementioned compounds thereof are known as "pro-oxidants." In the past, efforts have been made to exclude pro-oxidant materials, especially copper, from the oil. However, although attempts were made to improve the oxidation resistance of hydrocarbon oils and to overcome the foregoing difficulties and other disadvantages, none, as far as we are aware, was entirely successful when carried into practice.

It has now been discovered that the oxidation-resisting properties of hydrocarbon oils, especially at elevated temperatures, can be improved by the addition of special combinations of specific additives.

It is an object of the present invention to provide hydrocarbon oils having improved oxidation resistance.

Still another object of the invention is to provide a method of improving the oxidation-resisting properties of hydrocarbon oils.

It is a further object of the invention to provide hydrocarbon oils characterized by extended life without appreciable increase in viscosity, acidity and/or sludge formation.

The invention also contemplates a method for improving the oxidation-resisting properties of oils suitable for use as lubricating oils, transformer oils, cooling oils, etc.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing which is a graph showing the effects upon the viscosity induction period of a hydrocarbon oil treated with varying amounts of particular combinations of additive constituents contemplated by the present invention.

Generally speaking, the present invention contemplates new and ipmroved hydrocarbon oils having superior oxidation-resisting properties comprising a hydrocarbon oil, e. g., mineral oil, having incorporated therein at least one thermally stable, oil-soluble, iron-group metal derivative of alkyl di-thio acids in small but effective amounts up to about 5% and a small but effective amount up to about 0.01% of copper to impart improved oxidation-resisting properties to said oil; and the present invention also contemplates a method for providing said new and improved hydrocarbon oils.

The iron-group metal derivative of alkyl di-thio acids suitable for use in the present invention must be thermally stable in the service temperature range contemplated and must also be soluble in the hydrocarbon oil at least to the extent of 0.05% by weight. When it is stated that the metal acid derivative is soluble in oil, it is meant to include colloidal and other fine dispersions as well as true solubility. The iron-group metal derivatives of alkyl di-thio acids are iron-group derivatives of alkyldithiocarbamates, alkyldithiophosphates and alkylxanthates; and include such compounds as di-n-hexyldithiocarbamates, di-2-ethylhexyldithiocarbamates, di-2 - ethylhexyldithiophosphates, di-isopropyldithiophosphates, and 2-ethylhexylxanthates of nickel, cobalt and iron, i. e., a metal of the iron group. It is usually desirable to add at least 0.02%, e. g., 0.05%, of the iron-group metal derivative of an alkyl di-thio acid to the oil.

When a small but effective amount of copper, preferably in the form of an oil-soluble copper-containing compound, e. g., an organic copper-containing compound such as copper naphthenate, copper stearate, copper di-n-hexyldithiocarbamate, etc., is added to a lubricating oil in combination with one of the aforementioned derivatives of alkyl di-thio acids, the oxidation-resistance properties of the lubricating oil, as evidenced by the viscosity induction period, are very materially improved.

The addition to oil of very small amounts of copper in accordance with the invention, e. g., only about 0.00035% copper in the form of copper naphthenate, was found to very materially improve the oxidation-resistance properties of the oil in the co-presence of at least one of the aforementioned iron-group metal derivatives of alkyl di-thio acids as contemplated by the invention. Increasing the amount of the copper increases the oxidation-resistant properties of the oil in an unusual and critical manner as illustrated in the drawing. However, it is not contemplated that the new and improved oil would contain more than about 0.01% of copper.

In carrying the invention into practice it is preferred to prepare the new and improved oil by incorporating into hydrocarbon oil between about 0.00035% and about 0.003% of copper (usually in the form of an oil-soluble copper-containing compound) and between about 0.02% and about 2% of the aforementioned iron-group metal derivative of an alkyl di-thio acid. The nickel derivatives of alkyl, di-thio acids are preferred.

In the drawing the general effect obtained by adding a copper-containing compound to one portion of a hydrocarbon oil containing 0.1% nickel di-n-hexyldithiocarbamate and to another portion of the same hydrocarbon

oil containing 0.3% nickel di-n-hexyldithiocarbamate is shown. It will be noted that the greatest improvement in the antioxidant properties of the hydrocarbon oils in accordance with the invention are usually obtained with the addition of between about 0.00035% to about 0.003% by weight of copper (equivalent to about 0.005% to about 0.04% of copper naphthenate) to the new and improved oil, for example, through the addition of about 0.005% to about 0.04% of a copper naphthenate containing about 7.2% copper. The drawing also illustrates another very important aspect of the present invention. When amounts of copper greater than that preferred in accordance with the invention are incorporated in the hydrocarbon oil, the oxidation-resistance properties, although not quite as good as when the preferred amounts of copper are incorporated in the oil, are still improved over the oxidation-resistance properties of the oil without the copper.

The action of the copper on lubricating oils containing at least one of the alkyl di-thio acid derivative constituents contemplated by this invention, is entirely different from the action of copper on lubricating oils containing other organic antioxidant additives in place of the alkyl di-thio acid derivatives. Thus, an oil containing phenyl-alpha-naphthylamine, a common organic antioxidant, had an induction period of between 16 and 17 days. When 0.001% of copper (in the form of copper naphthenate) was added to another sample of the oil containing 0.1% of phenyl-alpha-napthylamine, the induction period was lowered to 2 days or less.

The novel and improved oils provided by the present invention may be prepared, for example, by admixing together a normally liquid hydrocarbon oil, copper, e. g., copper naphthenate, copper stearate, etc., and an iron-group metal derative of an alkyl di-thio acid, e. g., nickel di-n-hexyldithiocarbamate. However, it is not essential that the iron-group metal derivative of the alkyl di-thio acid be added as such; it may be added in an equivalent form, e. g., the iron-group metal may be added as a compound such as nickel naphthenate and the remainder of the required alkyl di-thio acid derivative may be added as an oil-soluble compound other than an iron-group metal compound provided that the respective proportions of the additive constituents are within the ranges specified hereinbefore. Thus, an improved oil of the present invention may be prepared by admixing with the hydrocarbon oil copper-di-n-hexyldithiocarbamate and an oil-soluble nickel salt, e. g., nickel napthenate, nickel stearate, etc. Likewise, a hydrocarbon oil composition to which has been added about 0.1% nickel naphthenate, about 0.1% di-n-hexyldithiocarbamic acid, and about 0.01% copper naphthenate is within the scope of the invention and had an induction period of ten days whereas a similar oil composition containing only 0.1% nickel naphthenate and 0.1% di-n-hexyldithiocarbamic acid had an induction period of only three days.

For the purpose of giving those skilled in the art a better appreciation of the advantages of the invention, the following illustrative examples are given. In the examples a heavy white mineral oil was treated by passing oxygen therethrough at a constant rate of 9 liters per hour per 100 milliliters of oil while this oil was maintained at a temperature between 134° C. and 136° C. This oil by itself had a very short induction period of less than one day (the induction period being taken as the time which elapsed before the oil showed a perceptible increase in viscosity).

Example I

The aforedescribed mineral oil was tested with the addition of the iron-group metal derivatives and copper naphthenate in the amounts shown in the following table. The results also shown in the following table indicate some of the new and improved results achieved in accordance with the present invention.

Derivative of Alkyl Di-thio Acid	Copper Naphthenate, percent	Induction Period (Days)
0.1% Ni di-(n-H)DTC	none	Between 1 and 2.
0.1% Ni di-(n-H)DTC	0.01	18.
0.1% Co di-(n-H)DTC	none	Less than 1.
0.1% Co di-(n-H)DTC	0.01	Greater than 2.
0.1% Fe di-(n-H)DTC	none	Less than 1.
0.1% Fe di-(n-H)DTC	0.01	Greater than 2.

(n-H)DTC=(n-hexyl)dithiocarbamate.

Example II

Other portions of the aforementioned oil were tested with the addition of additives within the scope of the present invention as shown in the following table. The data in the following table include the results obtained by using various operative iron-group metal derivatives of alkyl di-thio acids in accordance with the present invention.

Derivative of Alkyl Di-thio Acid	Copper Naphthenate, percent	Induction Period (Days)
0.1% Ni di-(2-EH)DTP	none	Less than 1.
0.1% Ni di-(2-EH)DTP	0.01	Between 18 and 19.
0.1% Ni di-(2-EH)DTP	0.1	Between 11 and 14.
0.4% Ni di-(2-EH)DTP	none	22.
0.4% Ni di-(2-EH)DTP	0.01	Between 34 and 35.
0.1% Ni 2-EHxanthate [1]	none	Between 22 and 23.
0.1% Ni 2-EHxanthate [1]	0.01	69.
0.1% Ni di-(IP)DTP	none	Between 3 and 6.
0.1% Ni di-(IP)DTP	0.01	Between 11 and 13.
0.1% Ni di-(2-EH)DTC	none	Between 1 and 3.
0.1% Ni di-(2-EH)DTC	0.01	Between 7 and 9.

(2-EH)DTP=(2-ethylhexyl)dithiophosphate.
EHxanthate=ethylhexylxanthate.
(IP)DTP=(isopropyl)dithiophosphate.
(2-EH)DTC=(2-ethylhexyl)dithiocarbamate.
[1] Tested at 100° C. instead of the usual 135° C.

Example III

Still other portions of the aforementioned oil were tested with the addition of 0.1% nickel di-n-hexyldithiocarbamate and varying amounts of the copper as copper naphthenate as shown in the following table. These results are the basis for the solid line curve in the drawing.

Derivative of Alkyl Di-thio Acid	Copper Napthenate, percent	Induction Period (Days)
0.1% Ni di-(n-H)DTC	none	2.
0.1% Ni di-(n-H)DTC	0.005	Between 24 and 25.
0.1% Ni di-(n-H)DTC	0.01	Between 26 and 27.
0.1% Ni di-(n-H)DTC	0.02	Between 64 and 68.
0.1% Ni di-(n-H)DTC	0.03	Between 11 and 12.
0.1% Ni di-(n-H)DTC	0.05	9.

(n-H)DTC=(n-hexyl)dithiocarbamate.

Example IV

The aforementioned oil was also tested with the addition of 0.3% nickel di-n-hexyldithiocarbamate and varying amounts of the copper-containing constituent of the additive as shown in the following table. These results are the basis for the broken line curve in the drawing.

Derivative of Alkyl Di-thio Acid	Copper Naphthenate, percent	Induction Period (Days)
0.3% Ni di-(n-H)DTC	none	Between 30 and 31.
0.3% Ni di-(n-H)DTC	0.005	Between 66 and 67.
0.3% Ni di-(n-H)DTC	0.01	87.
0.3% Ni di-(n-H)DTC	0.02	Between 80 and 81.
0.3% Ni di-(n-H)DTC	0.03	84.
0.3% Ni di-(n-H)DTC	0.05	Between 94 and 97.
0.3% Ni di-(n-H)DTC	0.1	57.

(n-H)DTC=(n-hexyl)dithiocarbamate.

Example V

A similar oil was also tested with the addition of 0.1% nickel di-n-hexyldithiocarbamate and varying amounts of copper stearate as shown in the following table:

Derivative of Alkyl Di-thio Acid	Copper Stearate, percent	Induction Period (Days)
0.1% Ni di-(n-H)DTC	none	2
0.1% Ni di-(n-H)DTC	0.01	18
0.1% Ni di-(n-H)DTC	0.025	17
0.1% Ni di-(n-H)DTC	0.05	9
0.1% Ni di-(n-H)DTC	0.10	8
0.1% Ni di-(n-H)DTC	0.15	7

(n-H)DTC=(n-hexyl)dithiocarbamate.

It is to be observed that the present invention provides a novel improved hydrocarbon oil and a method for improving the oxidation-resistant properties of hydrocarbon oils in applications where improved oxidation resistance of said oils is of utility, e. g., lubricating oils, transformer oils, cooling oils, quenching oils, oils used in hydraulic devices, etc.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A hydrocarbon mineral oil containing at least one thermally stable, oil-soluble, iron-group metal derivative of an alkyl acid from the group consisting of dithiocarbamic, dithiophosphoric and xanthic acid in small but effective amounts up to about 5% and a small but effective amount up to about 0.01% of copper as an oil-soluble copper salt of an acid selected from the group consisting of a fatty acid and naphthenic acid sufficient, together with said alkyl acid derivative, to impart improved oxidation-resistant properties to said hydrocarbon mineral oil.

2. A hydrocarbon mineral oil composition as defined in claim 1 containing about 0.00035% to about 0.01% of copper added as copper stearate.

3. A hydrocarbon mineral oil composition as defined in claim 1 containing about 0.00035% to about 0.01% of copper added as copper naphthenate.

4. A hydrocarbon mineral oil composition as defined in claim 1 wherein the iron-group metal derivative is the nickel derivative.

5. A method for improving the oxidation-resistance properties of a hydrocarbon mineral oil which comprises incorporating in a hydrocarbon mineral oil at least one thermally stable, oil-soluble, iron-group metal derivative of an alkyl acid from the group consisting of dithiocarbamic, dithiophosphoric and xanthic acids in small but effective amounts up to about 5% and a small but effective amount up to about 0.01% of copper as an oil-soluble copper salt of an acid selected from the group consisting of a fatty acid and naphthenic acid sufficient, together with said alkyl acid derivative, to improve the oxidation-resistance properties of said hydrocarbon mineral oil.

6. A method according to claim 5 wherein about 0.00035% to about 0.01% of copper is incorporated in said hydrocarbon mineral oil as copper stearate.

7. A method according to claim 5 wherein about 0.00035% to about 0.01% of copper is incorporated in said hydrocarbon mineral oil as copper naphthenate.

8. A method according to claim 5 wherein the iron-group metal derivative is the nickel derivative.

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