(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 332 247**
A1

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 89200481.3

(22) Date of filing: 27.02.89

(51) Int. Cl.4: C10M 167/00 , //(C10M167/00, 129:10,129:68,129:93,129:95, 133:12,133:56,135:10,135:18, 135:30,137:10,139:00,143:04, 143:06,143:12,145:14,159:18, 159:20,159:22,159:24)

(30) Priority: 02.03.88 IT 1960988

(43) Date of publication of application:
13.09.89 Bulletin 89/37

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR LI LU NL SE

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(54) **Lubricating compositions containing complexes endowed with anti-oxidant activity.**

(57) The present invention relates to lubricating compositions containing Cu-(I) as an oil-soluble complex constituted by a copper salt containing a monovalent anion and a phosphorus-based ligand.

These complexes inhibit the oxidation of the lubricant during the use of the same lubricant, with simultaneously showing an anti-wear activity.

EP 0 332 247 A1

LUBRICATING COMPOSITIONS CONTAINING COMPLEXES ENDOWED WITH ANTI-OXIDANT ACTIVITY

The present invention relates to lubricating compositions containing oil-soluble complexes constituted by salts of Cu-(I) with monovalent anions, and organic ligands based on phosphorus.

The addition of such compounds to the lubricant blend causes a considerable increase in oxidation resistance and in antiwear activity, which result in a longer useful life of the lubricant, without showing any interferences with other types of additives.

The present invention relates as well to concentrated blends, in oil, of commonly used additives for lubricant oils, additionally containing complexes formed by salts of Cu-(I) with monovalent anions, and organic ligands containing phosphorus. Such concentrated blends, which are incorporated into the mass of the lubricant, are used in order to supply said lubricant with the necessary additives.

Compounds endowed with antioxidant activity, suitable for use in lubricating composition, have been long known. For example, sterically hindered phenols (Wasson, Smith, Industrial and Engineering Chemistry 45 N. 1, pages 197-200, January 1953; Ingold, Journal of Physical Chemistry, 64, N. 11, pages 1636-1642, November 1960), sulphurized phenols, aryl amines (GilkS J.H., Journal of Institute of Petroleum, 50, N. 491, pages 309-318, November 1964); nitrogen-containing heterocyclic compounds (Murphy, Ravner, Smith, Industrial and Engineering Chemistry, 42, N. 12, pages 2479-2489, December 1950), sulphur-phosphorus containing antioxidants (Lason, Scientific Lubrication, vol. 10, pages 12-19, August 1958), with these latter being mainly used as antiwear agents. The need for using large amounts of them, and the possibility of the arising of problems of interference with other types of additives contained in the lubricating composition caused a very limited use of such compounds.

Furthermore, also particular copper compounds have already being described as antioxidants. In U.S. patents N. 2,343,756 and 2,356,662, copper-based compounds are generally mentioned in addition to sulphur-containing compounds; and im U.S. patent N. 2,552,580, the use of cuprous thiophosphates is claimed. Also such additives have anyway to be used in large amounts.

As a consequence, during the use of the lubricant the formation occurs of non-negligible amounts of undesired sulphur-containing residues. In U.S. patents N. 3,346,493; N. 3,652,616; and 4,122,033, the use is disclosed of componds containing polymeric amines, and, in general, "metals".

Patent application EP-A-24,146 discloses lubricating compositions containing oil-soluble copper compounds, typically oil-soluble salts.

As one can deduce from the specification, the best performances are achieved when organic salts of Cu-(II), such as, e.g., rameic oleate and naphthenate, are used.

The concentrations claimed for copper are of at least 5 ppm, but one can clearly see from the examples that, in order to attain acceptable results, the threshold value of 120 ppm results to be already critical.

The poor results obtained at low concentrations could be attributed to the fact that, as described in the relevant technical literature, too low concentrations of Cu operate by advantaging the action thereof as an oxidation catalyst, as compared to its action as an antioxidant (see S. Del Ross "I Lubrificanti [The Lubricants]", page 262-267, 1977).

The present Applicant has surprisingly found now that when in the lubricating composition and in the concentrates particular complexes are used which are formed by salts of Cu-(I) in which the anion is monovalent and the ligand is an organic, phosphorus-containing ligand, the antioxidant activity which is obtained persists even at extremely low values of concentration, values at which the compounds according to the prior art are no longer active.

This behaviour is attributed to the fact that the complexes, to the contrary of the salts, do not show any longer the typical reactions of the metal, which is hence inactivates as regards an undesired behaviour as a catalyst of oxidative reactions, with the antioxidant activity being simultaneously retained.

Furthermore, and antiwear activity is evidenced, which is not observed in the antioxidants already known from the prior art.

Complexes of Cu-(I) which can be advantageously used in the lubricating compositions according to the present invention are those oil-soluble complexes of salts of Cu-(I) with monovalent anions, in which the ligands are organic, phosphorus-containing ligands.

As regards the nature of the organic ligands, they can be phosphites and phosphines, in particular aryl and alkyl-aryl phosphites and phosphines, which are capable of endowing the complex with the salt of Cu-(I) with characteristics of oil-solubility. For example, as the ligands: triphenylphosphite, trinonylphenylphosphite, tridodecylphenylphosphite, tri(2,4-ditert.-butylphenyl)phosphite, triphenylphosphines and alkylated triphenylphosphines can be used.

Counter-ions of the cuprous salt which can be advantageously used are, e.g.: Cl, Br, I, SCN, CN, BF_4, BH_4, NO_2 and NO_3.

These complexes are obtained according to conventional techniques, by reacting a cuprous salt and a suitable phosphite or phosphine in at least equimolecular amounts.

This reaction can be carried out in the presence of the same lubricant oil, or in a suitable organic solvent.

In the first case, the reaction is typically carried out under an inert atmosphere, at a temperature comprised within the range of from room temperature to 80 °C, for a time comprised within the range of from 30 minutes to 5 hours.

At the end of the reaction, filtering off any traces of possibly undissolved residues may be necessary.

In the second case, the reaction is carried out in an inert, apolar solvent, e.g., benzene, under anhydrous conditions, at a temperature comprised within the range of from room temperature to the refluxing temperature, for about half an hour.

The product is then recovered by evaporating the solvent (Wulfman, J.C.S. Dalton, 1975, pages 522-529; Nishizawa, Bull. Chem. Soc. Japan 1961, 34, 1170). The so obtained complexes are oil-soluble and active as antioxidant/antiwear agents for lubricant oils even at very low concentrations, down to 30 ppm. They are thus advantageously used in lubricating blends having the following general composition:

1) a lubricant oil;

2) from 3 to 6% of an ash-less dispersant;

3) from 5 to 10% of a viscosity index-improver dispersant;

4) from 2 to 5% of a detergent;

5) from 0.8 to 1.5% of a dialkyldithiocarbamate;

6) from 30 to 100 ppm of Cu-(I) as an oil-soluble complex of a salt of Cu-(I) and a phosphorus-based ligand, as hereinabove disclosed.

The lubricant oil can either be a mineral oil, or a synthesis oil (carboxy esters, polyolefins, carbonic acid esters, and so forth), as well as a mixture of both of them.

To it an ash-less dispersant is added, with the purpose of keeping dispersed any matter foreign to the oil, whether coming from the external environment, or deriving from thermal or oxidative alterations of the same oil.

The commonly used dispersants are in general nitrogen-containing derivatives, esters, anhydrides and salts of mono- and bi-carboxy acids bearing a long hydrocarbon chain of from 50 to 400 carbon atoms.

In particular anhydrides of succinic acids with high-molecular weight aliphatic substituents, or esters of these acids with mono- and poly-alcohols, phenols, naphthols, or, still, amides or imides of these acids with polyethyleneamines are preferred. As regards the possible high-molecular-weight aliphatic substituents, alkenyl chains, such as, e.g, in case of isobutenyl-succinic acids, are preferred.

A viscosity-index improver is then necessary, the purpose of which is of keeping the viscosity changes with temperature comprised within a narrower range than as obtained with the oil to which such an additive is not added. Compounds displaying such an activity are oil-soluble polymers, among which the most representative are: ethylene-propylene copolymer, poly-iso-butenes, styrene-diene copolymers, poly-acrylates and poly-methacrylates.

Then, in order that the lubricating composition may endow the engine with antiwear capabilities, in the mixture also a Zn dihydrocarbyldithiophosphate is contained, in which the substituents can be alkyl groups, alkenyl groups, aryl groups, alkylaryl groups, cycloalkyl groups, with such grops being either equal to, or different from, each other. Furthermore, the presence of a detergent preventing impurities and residues from depositing on the metal surfaces, can be necessary.

The most commonly used detergents are neutral calcium or magnesium sulphonate; the super-basic calcium or magnesium sulphonate; calcium, magnesium and barium phenolates and sulpho-phenolates; calcium and magnesium alkyl-salicylates and naphthenates.

The activity of the oil-soluble complexes constituted by salts of Cu-(I) and phosphorus-based organic ligands was compared to that of additives already known in the art, by means of a set of tests capable of evaluating the antioxidant and antiwear capabilities of them. The antioxidant properties were evaluated on the lubricant, after that this latter was submitted to the IP 48-MOT oxidation test; with the changes being measured, which occurred in three typical parameters, viz.: viscosity, neutralization number and absorbance of the oxidation band meaured on the I.R. spectrophotometer at 1,700 cm^{-1}.

The oxidation test consists in submitting a sample of lubricant oil to an air stream flowing at the rate of 0.3 litres/hour per sample gram at 165 °C over 72 hours, in the presence of a homogeneous iron catalyst (50 ppm, as the metal).

In the following table, the results relevant to the activity of trinonylphenylphosphite.Cucl, as compared to the activity displayed by antioxidants already known from the prior art, not containing copper, are reported.

The cuprous complex was prepared by reacting 160 g of trinonylphenylphosphite (0.24 mol) with 24 g of CuCl (0.24 mol) in 185 g of SN 450 oil under a blanketing nitrogen atmosphere.

The reaction mixture is kept with stirring at room temperature for 4 hours.

A filtration coadjuvant is then added, and the mixture is stirred for a further 30 minutes. The reaction mixture is filtered through a Funda filter, thus removing any traces of possibly undisslved residues (elemental analysis: P = 1.9%; Cu = 3.3%; Cl = 1.9%).

The lubricating composition used in this example is formed by SN 450 oil admixed with

- 4.4% of boron-treated polyisobutenylsuccinimide
- 1.8% of super-basic calcium sulphonate
- 1.3% of zinc diamyldithiophosphate

	Antioxidant	%	ΔV%40 °C	A/cm	N.N., mg of KOH
E_7D_{47}	---	---	1,119	111.4	10.7
E_7D_{47}	3,5-3′,5′-tert.-butyl-4,4′-hydroxydiphenylmethane	0.3	954	109.0	5.4
E_7D_{47}	diphenyloctylamine	0.3	880	102.0	0.1
E_7D_{47}	trinonylphenylphosphite.CuCl	0.1	65	57.6	4.2

ΔV% 40 = viscosity change measured at 40 °C with a capillary-viscometer of Cannon Fenske type.
A = absorbance at 1,700 cm^{-1}.
N.N. = mg of KOH necessary in order to neutralize 1 g of product.

From the above data, it clearly appears that the lubricant to which the cuprous complex is added supplies a much better performance, as regards the oxidation, than already known additives. Such better properties are retained also when the comparison is made with additives known from the prior art, in their turn containing copper.

In the following table, the results are compared, which are obtained by submitting to the oxidation test the SN 450 lubricant oil to which copper oleate or copper naphthenate is added, and the same oil to which the two complexes: trinonylphenylphosphite.Cucl and tri(2,4-ditert.-butylphenyl)phosphite.Cucl are added.

Trinonylphenylphosphite.Cucl was prepared as hereinabove seen, and tri(2,4-ditert.-butylphenyl)-phosphite.Cucl was obtained according to the same route, by reacting 154 g of tri(2,4-ditert.-butylphenyl)-phosphite (0.24 mol) with 24 g of CuCl (0.24 mol) in 178 g of SN 450 oil.

	Cu ppm	ΔV%40 °C	A/cm	N.N.
Sn 450	--	>6000	n.d.	11.7
trinonylphenylphosphite.CuCl	60	68	48.7	5.8
	30	400	78.0	9.1
tri(2,4-ditert.-butylphenyl)phosphite.CuCl	60	70	53.2	5.9
	30	450	85.5	10.0
copper-(II) oleate	60	68	51.4	6.0
	45	5300	n.d.	13.5
copper-(II) naphthenate	60	70	57.9	5.9
	45	5600	n.d.	13.1

n.d. = the value was not measured, because the oil turned into a solid.

The behaviour of these cuprous complexes as regards oxidation are further enhanced when to the lubricant oil also a dialkyldithiocarbamate is added, which shows a synergistic effect on the additive. For an SN 450 oil, the data as collected in the following Table were observed:

	Add. %	ΔV%40 °C	A/cm	N.N.
SN 450	0	>6000	n.d.	11.7
SN 450 + dithiocarbamate	1.3	>6000	n.d.	14.8
SN 450 + trinonylphenylphosphite.CuCl	0.1	66	53.7	5.0
SN 450 + trinonylphenylphosphite.CuCl	0.1	7	3	1.0
+ Zn diamyldithiocarbamate	1.3			

Even when the operating conditions are particularly hostile, the cuprous complexes perform a very good antioxidant protection.

If, for example, a "fail" oil, to which an amount of 0.1% of trinonylphenylphosphite. CuCl is added, is submitted to the ASTM IIID test, a change in viscosity of only 60% is obtained.

By a "fail" oil, an oil is understood which, when is submitted to the ASTM IIID test, showed a change in viscosity greater than 375%.

The ASTM IIID test, developed by General Motors, uses a 1977 version of the 5.7-litre Oldsmobile V-8 engine, running at a high speed (3,000 rpm) at the temperature of 160 °C, for 64 hours, under a constant load of 100 BHP.

As regards the antiwear activities, an E_7D_{47} composition was submitted to the "4-ball-wear" ASTM D4172 test, before and after undergoing the oxidation process. In this test, on three balls blocked on a same plane, with each one of said balls being into contact with both of the other two balls, a fourth ball is placed and made revolve under load, sliding on only three points of contact with the underlying balls.

According to the performance of the lubricant, behaviours can be observed, which range from the limit case of welding of the balls, to the opposite limit case of deformation, due to the friction heat, of the upper ball, with softening of the material, which is forced to flow downwards into the free room remaining between the stationary balls.

A mixture containing 0.1% of tri(2,4-ditert.-butylphenyl)phosphite.CuCl underwent an analogous treatment. The data, expressed as the diameter, as mm, of the wear print (Ø) is collected in the following Table:

	Antioxidant additive	Ø before oxidation	Ø after oxidation
E_7D_{47}	----	0.40	0.92
E_7D_{47}	0.1%	0.36	0.54

This data demonstrates that the complex of Cu-(I) contributes to decrease the wear rate both before and after the oxidation. This contribution is performed to a larger extent on the mixture which underwent the oxidation: this demonstrated an action of protection of Zn dialkyldithiophosphate by the Cu-based complex during the oxidative process.

Claims

1. Lubricant composition composed by:

a) a lubricant oil;
b) from 3 to 6% of an ash-less dispersant; or
c) from 5 to 10% of a viscosity index-improver dispersant;

or

d) a mixture of (b) and (c);
e) from 2 to 5% of a detergent such as to supply from 500 to 5,000 ppm of calcim and/or magnesium;
f) from 0.8 to 1.5% of a Zn dihydrocarbyldithiophosphate;
g) from 30 to 100 ppm of Cu-(I) as an oil-soluble complex of a salt of Cu-(I) with a monovalent anion and a phosphorus-based ligand.

2. Concentrate of an oil-based lubricant composition containing:

a) from 10 to 55% of an ash-less dispersant;

or

b) from 2.5 to 30% of a viscosity index-improver dispersant;

or

c) a mixture of (a) and (b);

d) from 2.5 to 25% of a detergent such as to supply from 1.10^4 to 1.10^5 ppm of calcim and/or magnesium;

e) from 2 to 30 % of a Zn dihydrocarbyldithiophosphate;

f) from 0.05 to 2% of Cu-(I) as an oil-soluble complex of a salt of Cu-(I) containing a monovalent ion and a phosphorus-based ligand.

3. Lubricating composition according to claim 1 or 2, wherein the phosphorus-based ligands are alkyl or alkylaryl phosphites and phosphines, which are capable of endowing the complex with the salt of Cu-(I) with characteristics of oil-solubility.

4. Lubricating composition according to claim 3, wherein the ligand contained in the oil-soluble complex of Cu-(I) is selected from the group consisting of: trinonylphenylphosphite, tridodecylphenylphosphite, tri-(2,4-ditert.-butylphenyl)phosphite, triphenylphosphite, triphenylphosphine and alkylated triphenylphosphines.

5. Lubricating composition according to claim 1 or 2, wherein the monovalent ion in the cuprous complex is selected from the group consisting of: Cl, Br, I, CN, NO_3, NO_2, BH_4 and BF_4, .

6. Composition according to claim 5, wherein the monovalent ion in the cuprous complex is selected from the group consisting of: Cl, Br, I.

7. Lubricating composition according to claim 1 or 2, wherein the ash-less dispersant is selected from nitrogen-containing derivatives, esters, anhydrides and salts of mono- and bi-carboxy acids bearing a long hydrocarbon chain of from 50 to 400 carbon atoms, in particular anhydrides of succinic acids bearing high-molecular weight hydrocarbyl substituents, or esters of said acids with mono- and poly-alcohols, phenols and naphthols, or amides and imides of said acids with polyethyleneamines.

8. Lubricating composition according to claim 7, wherein the ash-less dispersant is selected from the group consisting of the amides of alkenylsuccinic acids as such, or after a treatment with a boron-based compound, anhydrides or esters of said acids with mono-and poly-alcohols, phenols and naphthols.

9. Lubricating composition according to claim 1, wherein the viscosity-index improver is an oil-soluble polymer selected from the group consisting of: ethylene-propylene copolymer, poly-isobutenes, styrene-diene copolymers, poly-acrylates and poly-methacrylates.

10. Lubricating composition according to claim 1 or 2, wherein the substituents of Zn dihydrocarbyl-dithiophosphate can be alkyl groups, alkenyl groups, aryl groups, alkylaryl groups, cycloalkyl groups

11. Lubricating composition according to claim 1 or 2, wherein the detergent is selected from among neutral calcium sulphonate, neutral magnesium sulphonate, superbasic calcium sulphonate, super-basic magnesium sulphonate, calcium phenolates and sulpho-phenolates, magnesium phenolates and sulpho-phenolates, barium phenolates and sulpho-phenolates, calcium alkyl-salicylates and naphthenates and magnesium alkyl-salicylates and naphthenates.

12. Lubricating composition according to claim 1 or 2, wherein the ash-less dispersant is boron-treated polyisobutenyl succinimide, the detergent is superbasic Ca sulphonate, the alkyl substituents of Zn dithiophosphate are amyl radicals.

13. Lubricating composition according to claim 12, wherein Cu-(I) is present as tri(2,4-ditert.-butyl-phenyl)phosphite.Cucl or as trinonylphenylphosphite.CuCl.

14. Lubricating composition according to claim 1 also containing from 0.5 to 1.5% of a Zn dialkyl-dithiocarbamate.

15. Lubricating composition according to claim 1 containing less than 0.5% of other antioxidants selected from the group consisting of sterically hindered phenols, aromatic amines, esters and sulphurized alkyl-phenols.

16. Concentrate of a lubricating composition according to claim 2, also containing from 2 to 3% of a Zn dialkyldithiocarbamate.

17. Concentrate of a lubricating composition according to claim 2 containing from i to 2% of other antioxidants selected from the group consisting of sterically hindered phenols, aromatic amines, esters and sulphurized alkyl-phenols.

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EUROPEAN SEARCH REPORT

Application Number

EP 89 20 0481

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	EP-A-0 024 146 (EXXON RESEARCH AND ENGINEERING CO.) * Page 3, line 16 - page 4, line 4; page 4, line 19 - page 5, line 5; page 9, lines 10-23; page 10, line 5 - page 11, line 11; page 11, line 20 - page 12, line 15; page 17, line 17 - page 18, line 18; page 22, lines 12-24; page 31, example 1; page 33, table 1; page 34, example 3 * ---	1,2,7-12,15,17	C 10 M 167/00 // (C 10 M 167/00 C 10 M 129:10 C 10 M 129:68 C 10 M 129:93 C 10 M 129:95 C 10 M 133:12 C 10 M 133:56 C 10 M 135:10 C 10 M 135:18 C 10 M 135:30 C 10 M 137:10 C 10 M 139:00 C 10 M 143:04 C 10 M 143:06 C 10 M 143:12 C 10 M 145:14 -/-
A	US-A-2 645 613 (D.E. ADELSON et al.) * Column 1, line 28 - column 3, line 5; column 3, examples 1,3; column 4, examples 6,7; column 6, line 35; column 9, line 48 - column 10, line 73 * ---	1-6,9-11,13,15	
A	US-A-2 199 944 (A.J. VAN PESKI et al.) * Column 1, line 25 - column 2, line 34; column 2, lines 45-55; claims 1,7,11 * ---	1-6,13	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	US-A-3 933 878 (W.E. TYLER et al.) * Column 2, line 53 - column 3, line 28; column 4, examples I,II * ---	1-6,13	C 10 M C 07 F
A	GB-A- 476 329 (N.V. DE BATAAFSCHE PETROLEUM MIJ.) * Page 1, lines 11-48; page 2, lines 23-40; examples I,III; page 3, example 4 * -----	1-4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	05-06-1989	HILGENGA K.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
			C 10 M 159:18 C 10 M 159:20 C 10 M 159:22 C 10 M 159:24) C 10 N 10:02 C 10 N 10:04 C 10 N 30:06 C 10 N 30:10
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)

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THE HAGUE	05-06-1989	HILGENGA K.J.

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