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(21) International Application Number: PCT/US95/13840 (22) International Filing Date: 25 October 1995 (25.10.95) (30) Priority Data: 08/328,209 25 October 1994 (25.10.94) US (71) Applicant: EXXON RESEARCH AND ENGINEERING COMPANY [US/US]; P.O. Box 390, 180 Park Avenue, Florham Park, NJ 07932-0390 (US). (72) Inventors: HOLT, David, G., L.; 1973 Remo Drive, Brights Grove, Ontario N0N 1C0 (CA). FRANCISCO, Manuel, A.; 9 Pohatcong Terrace, Washington, NJ 07882 (US). (74) Agents: SCUORZO, Linda, M. et al.; Exxon Research and Engineering Company, P.O. Box 390, Florham Park, NJ 07932-0390 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: NOVEL COBALT CONTAINING DEPOSIT CONTROL ADDITIVES		
(57) Abstract The present invention provides for lubricating oil compositions that comprise a base oil of lubricating viscosity, a copper containing antioxidant, such as copper naphthenates, oleates and polyisobutylene succinic anhydrides and a cobalt containing antioxidant such as cobalt naphthenates, oleates, stearates and polyisobutylene succinic anhydrides and for the methods of making them. The invention provides enhanced deposit control by virtue of the synergistic effect of the cobalt and copper compounds, and has utility in lube applications.		

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NOVEL COBALT CONTAINING DEPOSIT CONTROL ADDITIVES

Field of the Invention

The present invention relates to novel lube oil base stock compositions containing deposit control additives.

Background of the Invention

Copper is a common lube oil antioxidant additive. However, it forms deposits at higher temperatures. As a result additives and methods for increasing the lifetime of copper antioxidants and for retarding their degradation and resulting deposit formation would be desirable. The present invention addresses these needs.

Summary of the Invention

The present invention provides for formulated lubricating oil compositions, comprising a base stock of lubricating viscosity, a copper containing antioxidant and a deposit control enhancing amount of an oil soluble or oil dispersible cobalt containing compound.

The present invention also provides for a method of controlling deposit formation in an engine lubricating system, comprising adding a deposit control enhancing amount of an oil soluble or oil dispersible cobalt containing compound to a base oil of lubricating viscosity formulated with a copper containing antioxidant.

The present invention may suitably comprise, consist or consist essentially of the elements disclosed herein and may be practiced in the absence of any element not disclosed herein as required.

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Detailed Description of the Invention

The present invention provides for a method of controlling deposits, i.e. retarding deposit formation and buildup, in internal combustion engines by enhancing the performance of a certain base stocks containing copper containing antioxidants, with the addition of cobalt containing compounds. The invention also provides for novel formulated oil and additive compositions related thereto. As a benefit the life of the copper containing antioxidant and the formulated oil can be extended.

The starting materials disclosed herein may be made by methods known in the art or obtained from commercial sources.

Generally copper containing compounds and the cobalt containing compounds are individually present in a minor amount by weight percent of the compound to a major amount of the oil. The term "minor amount" as used herein is intended to mean that amount is less than 50% by weight of the composition. The term "major amount" is intended to mean that amount is more than 50% by weight of the composition.

The copper antioxidant should be present in a hydrocarbon, preferably oil soluble or dispersible form. These antioxidants are of the type and are present in amounts typically used as lube additives for internal combustion engines as these represent an economical and readily available source of the materials. Suitable examples include copper naphthenates, oleates and polyisobutylene succinic anhydride ("PIBSA") compounds. Thus, these amounts may vary with the particular formulation without affecting the present invention.

The cobalt containing compounds that produce the synergistic effect of enhancing deposit control in formulated oils having copper containing antioxidants therein should be present in a hydrocarbon, preferably oil soluble or dispersible form. Thus, any source of cobalt is acceptable provided that it is oil soluble or dispersible.

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Examples include oil soluble cobalt salts such as cobalt naphthenates, or cobalt stearates and inorganic cobalt salts in combination with suitable dispersants or surfactants, for example cobalt PIBSA or cobalt acetylacetonate ("acac"). It is desirable that the cobalt containing compound be compatible with the copper containing compound as well as the base stock or formulated oil to which it is added in order to achieve the synergistic effect of retarding deposit formation and extending the life of the copper antioxidant and formulated oil. The cobalt is present in an amount sufficient to enhance deposit control performance, i.e., to retard deposit formation and, thus, extend the life of the lube oil containing the copper antioxidant. This amount, for lube applications, typically is a minor amount of cobalt metal, preferably from about 10-1000 ppm, more preferably about 50-500 ppm, most preferably about 75-200 ppm, as determined on the basis of the amount of the metal present in the formulated compositions.

The foregoing may be added to the base and formulated oils by means well known in the art.

As used herein the term hydrocarbon or oil "soluble" and "dispersible" means that the material is soluble or stably dispersible in hydrocarbons, preferably oils of lubricating viscosity, that are liquid at temperatures found in the environments at which the formulated oils are typically used. The term "stably dispersible" means that the material is capable of being dispersed in the hydrocarbon or oil to an extent that allows it to function in its intended manner. Thus, for example in lube oil formulations, a copper antioxidant or the cobalt antioxidant is hydrocarbon or oil soluble or dispersible if it is capable of being dissolved, dispersed or otherwise suspended in the oil in a manner sufficient to allow the oil to function as a lubricant. Detergents such as neutral and/or overbased blends of calcium sulfonated detergents and dispersants such as borated PIBSA-PAM may be used to achieve oil solubility or dispersibility.

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The base oils employed in the lubricant compositions according to the invention may be any base oil suitable for the intended use of the lubricant. Thus, the base oil may be, for example, a conventionally refined mineral oil, an oil derived from coal tar or shale, a vegetable oil, an animal oil, a hydrocracked oil, or a synthetic oil, or a mixture of two or more of these types of oils. Examples of synthetic oils include hydroisomerised paraffins, polyalpha-olefins, polybutenes, alkylbenzenes, polyglycols, esters such as polyol esters or dibasic carboxylic acid esters, alkylene oxide polymers, and silicone oils. The viscosity of the base oil depends upon the intended use, but generally is in the range of from 3 to 20cSt at 100°C.

The present invention also permits the use of other additives in the oil compositions. These other additives include such conventional additive types as viscosity modifiers, extreme pressure agents, corrosion-inhibiting agents, pour point depressants, color stabilizing agents, anti-foam agents, and other such additive materials known generally to those skilled in the art of formulating lubricants.

It is expected that the benefits described herein can be achieved over the range of amounts and types of copper containing antioxidants generally used as lube oil additives.

It is expected that similar benefits could be obtained in fuels.

The present invention may be exemplified by reference to the following examples:

Example 1 -- Inclined Panel Deposit Test

The effect of the presence of cobalt containing compounds in a lube oil formulated with a copper containing antioxidant was evaluated using the Inclined Panel Deposit Test (IPDT). The

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beneficial and synergistic effect on engine deposit formation of adding cobalt containing compounds to base oils formulated with copper containing antioxidants can be determined by measuring the buildup of deposits during the course of the test. The beneficial effect of cobalt addition is evidenced by smaller amounts of deposit formation.

The IPDT is a bench test that simulates piston deposit formation during engine operation. 35 ml of oil was heated to 150°C and run down a metal panel heated to 308°C at a 2 degree angle. The oil was then pumped through a sump back onto the panel. The oil was exposed to a synthetic blow-by gas throughout the 2 hour duration of the test. The panel was cooled and washed with heptane. The rating figure (demerit) value indicates the amount of deposition on the plate. A higher number (greater demerit) indicates greater deposit formation, with 10 being the highest and zero the lowest.

Table 1 shows the results of the IPDT using a commercially available mineral oil base stock formulated with commercially available additive package containing copper PIBSA and a monofunctional olefin copolymer VI improver, borated PIBSA pour point depressant, calcium sulfonate overbased detergent, neutral calcium sulfonate detergent, nonyl phenyl sulfide antioxidant, ZDDP antiwear, molybdenum dithiocarbonate antiwear additive alone (Run 1) and in the presence of cobalt additive (Run 2) demonstrating the synergistic effect of adding cobalt in copper antioxidant systems. A comparative example demonstrating the deterioration of results upon addition of cobalt to a commercially available diphenyl amine and hindered phenolic antioxidant additive package is shown in Table 2.

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TABLE 1INCLINED PANEL DEPOSIT TEST

<u>FORMULATED OIL</u>	<u>RESULT (DEMERITS)</u>
(1) Lube base stock formulated with copper antioxidant*	6.4
(2) Lube base stock formulated with copper antioxidant* + 100 ppm cobalt antioxidant**	3.4

* 0.3 wt% copper PIBSA antioxidant

** 0.17 wt% cobalt naphthenate

TABLE 2INCLINED PANEL DEPOSIT TEST (COMPARATIVE DATA)

<u>FORMULATED OIL</u>	<u>RESULT (DEMERITS)</u>
(1) Lube base stock formulated with diphenyl amine and hindered phenolic antioxidant	2.4
(2) Lube base stock formulated with diphenyl amine and hindered phenolic antioxidant + 100 ppm cobalt	4.0

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CLAIMS:

1. A formulated internal combustion engine lubricating oil composition, comprising: a synergistic combination of a base engine oil of lubricating viscosity, a copper containing antioxidant and a deposit control enhancing amount of from 10 to 1000 ppm of an oil soluble or oil dispersible cobalt containing compound.

2. The composition of claim 1 wherein the cobalt containing compound is selected from the group consisting of cobalt naphthenates, cobalt stearates, cobalt polyisobutylene succinic anhydrides and cobalt acetylacetonates.

3. The composition of claim 1 wherein the copper containing antioxidant is selected from the group consisting of copper naphthenates, oleates, stearates and polyisobutylene succinic anhydrides.

4. The composition of claim 1, further comprising at least one agent selected from the group consisting of a dispersant and a detergent.

5. The composition of claim 1, further comprising at least one additive selected from the group consisting of antiwear agents, viscosity modifiers, extreme pressure agents, antifoam agents, pour point depressants, and color stabilizing agents.

6. A method of controlling deposit formation in an internal combustion engine lubricating system, comprising: combining a synergistic deposit control enhancing amount of from 10 to 1000 ppm of an oil soluble or oil dispersible cobalt containing compound with a base engine oil of lubricating viscosity formulated with a copper containing antioxidant to enhance deposit control in the oil.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 95/13840

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C10M129/00 C10M129/40 C10M129/58 C10M129/93
 //(C10M129/00,129:24,129:40,129:58,129:93),C10N10:02,C10N10:16,
 C10N30:10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 372 222 (EXXON RESEARCH AND ENGINEERING COMPANY) 23 June 1978 see page 14, line 30 - line 37 see page 16, line 16 - line 21 see page 33; example 16 see claim 5	1-3
A	--- EP,A,0 444 830 (ETHYL PETROLEUM ADDITIVE) 4 September 1991 see page 2, line 31 - page 3, line 2	1,3,5,6
A	--- US,A,3 360 467 (K.L.MC HUGH) 26 December 1967 see column 7, line 18 - line 20 see column 8, line 23 - line 41; claim 4 --- -/--	1,2

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 412 028 (A.W. GODFREY) 19 November 1968 see column 1, line 65 - column 2, line 4 see column 3, line 30 - line 41; claim 1 ---	1-6
A	GB,A,772 029 (SHELL RESEARCH LIMITED) 10 April 1957 see page 4; examples II,III -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/13840

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