PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C10M 159/20, 163/00, 129/10, 129/54, 135/10 // (C10M 163/00, 129:10, 133:12, 137:10, 159:20), C10N 30:04

A1

(11) International Publication Number: **WO 99/55808**

(43) International Publication Date: 4 November 1999 (04.11.99)

(21) International Application Number: PCT/EP99/02842

(22) International Filing Date: 23 April 1999 (23.04.99)

(30) Priority Data:
98303245.9 27 April 1998 (27.04.98) EP

(71) Applicant: INFINEUM HOLDINGS B.V. [NL/NL]; Carel van Bylandtlaan 30, NL–2596 HR 'S–Gravenhage (NL).

(72) Inventors: WILLARS, Malcolm; Shell Research and Technology Centre, P.O. Box 1, Thornton, Chester CH1 3SH (GB). SANT, Peter; Shell Research and Technology Centre, P.O. Box 1, Thornton, Chester CH1 3SH (GB).

(74) Agents: BAWDEN, Peter, Charles et al.; Infineum UK Ltd., Law Dept., Milton Hill, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).

(81) Designated States: CA, CN, JP, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: LUBRICATING OIL COMPOSITIONS

(57) Abstract

A lubricating oil composition comprising, as a detergent, metal salt of a long chain hydrocarbyl–substituted organic acid, at a concentration of not more than 15 mmol/kg oil.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

LUBRICATING OIL COMPOSITIONS

This invention relates to lubricating oil compositions suitable for use in the crankcase of internal combustion engines.

It is well known that the lubricating ability of lubricating oil compositions, (lubricants or simply oils) deteriorates with use in internal combustion engines. For example, in diesel (compression ignited) engines the viscosity of the oil may increase undesirably due to increasing soot levels. This increase may still occur despite the presence of ashless dispersants in the oil. A recognised measure of viscosity increase for diesel engines is the so-called Mack T8 test which forms part of the American Petroleum Institute (API) performance category CG-4. In order to attain acceptable levels of performance in tests such as the Mack T8, it is often necessary to increase the quantity of ashless dispersant present in the oil. However, this is often undesirable due to the poor seal compatibility properties of the dispersant and the increased likelihood of corrosion to bearings.

Lubricating oil compositions may also comprise neutral or overbased metal detergents as additives, or additive components. Chemically, they consist of metal salts of organic acids, such as hydrocarbyl-substituted sulphonic or aromatic carboxylic acids, or may be metal salts of hydrocarbyl-substituted phenols. Such metal salts are sometimes referred to as surfactants or as soaps. The hydrocarbyl substituents are of a sufficient length to confer oil-solubility to salts which would generally be insoluble in oils of lubricating viscosity. The metal is usually an alkaline earth metal, although other metals may also be used. Mixtures of metals may also be used.

The term "overbased" is intended to define additives which contain a metal content in excess of that required by the stoichiometry of the particular metal and the particular organic acid used. The excess metal exists in the form of particles of inorganic base, e.g. a hydroxide or carbonate, surrounded by a sheath of metal salt. The sheath serves to maintain the particles in dispersion in a liquid oleaginous vehicle. The amount of excess metal is commonly expressed as the ratio of total equivalents of excess metal to equivalents of organic acid and is typically 0.1 to 30.

CONFIRMATION COPY

The principal function of metal detergents in lubricating oil compositions is to neutralise acidic products within the oil, and/or to prevent the formation of deposits on the surfaces of an engine. Depending on the nature of the acid used, the detergent may have additional functions, for example, antioxidant properties. Typically, lubricating oil compositions contain metal detergents comprising either overbased detergents or mixtures of neutral and overbased detergents.

The present invention is based on the realisation that an improvement in the control of oil viscosity can be obtained, without increasing the levels of ashless dispersants, if low concentrations of surfactant in metal detergents are used in the lubricating oil composition. The metal detergents used are of long chain hydrocarbyl substituted organic acids.

Thus, a first aspect of the invention is a lubricating oil composition comprising, as a detergent, one or more metal salts of long chain hydrocarbyl-substituted organic acids such as selected from aromatic carboxylic acids, sulfonic acids or phenol derivatives, the total concentration of said metal salts being not more than 15 mmol/kg of the composition, provided that the composition is not an SAE 5W composition whose base stock comprises less than 5, such as less than 6 or 10, wt. % non-conventional lubricant. Preferably, the acids are selected from aromatic carboxylic acids or phenol derivatives.

The concentration of metal salt is that of the salt as such and does not include any overbasing material (or base) in the detergent. In particular, it has been found that concentrations of the metal salt as low as 8 mmol per kg oil or lower are sufficient to achieve a performance in diesel engine tests exceeding current specification requirements.

Therefore, the present invention allows the amount of ashless dispersant required to maintain the viscosity of a lubricating oil composition within acceptable limits to be reduced to economically-attractive levels, such as from 3 to 10 mass %, based on the mass of the composition. The present invention also allows the lubricating oil compositions to maintain a high level of performance in areas such as seals and bearings.

It is surprisingly found that the metal salts, in the form of salicylates when used at the above-stated concentrations, provide the lubricating oil composition with a

cleanliness performance that exceeds current specification requirements, as evidenced by performance in a range of standard US and European diesel engine tests, including:

- the Caterpillar 1K test, which forms part of the API performance category CF-4;
- the Mercedes Benz OM364A test, which forms part of the ACEA performance categories E1-E3 96.

A second aspect of the invention is a method of making a lubricating oil composition comprising admixing a major amount of an oil of lubricating viscosity and minor amounts of metal salt as defined in the first aspect of the invention.

A third aspect of the invention is a method of lubricating a diesel engine which comprises supplying to the engine a lubricating oil composition according to the first aspect of the invention or made according to the second aspect of the invention.

A fourth aspect of the invention is a method of alleviating viscosity in a lubricating oil composition due to the presence of increasing levels of soot when the composition is lubricating a diesel engine, which comprises using, in the composition, a detergent as defined in the first aspect of the invention.

In this specification:- "Major amount" means in excess of 50 mass % of the mass of the composition.

"Minor amount" means less than 50 mass % of the mass of the composition, both in respect of the stated additive and in respect of the total mass % of all of the additives present in the composition, reckoned as active ingredient of the additive or additives.

"Comprises", or cognate words, is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

"Non-conventional lubricants (NCL's)" are basestocks that do not fall within Groups 1 and 2 according to the classification of basestocks provided by the American Petroleum Institute (API) in its Publication 1509 dated January 1993 entitled "Engine Oil Licensing and Certification System" (EOLCS) in Appendix E, 1.2.

"SAE 5W" is a viscosity requirement as set forth in Society of Automotive Engineers (SAE) J300, namely maximum CCS viscosity of 3500 10^{-3} Pa.s @ -25°C, and minimum kV of 3.8 $mm^2 S^{-1}$ @ 100°C.

Various components of the composition, essential as well is optimal and customary, may react under the conditions of formulation, storage or use; the invention also provides the product obtainable or obtained as a result of any such reaction.

The features of the invention will now be discussed in more detail as follows:

Metal Salt

Processes for the manufacture of metal detergents used in the present invention are known to those skilled in the art. The concentration of metal salt is preferably no lower than 3 or 4, or 5, more preferably between 8 and 13, mmol per kg oil. The metal detergent typically has a metal: metal salt molar ratio between 1 to 10. Examples of metal detergents that may be used in accordance with the invention include calcium or magnesium alkyl salicylates, preferably C_{14-24} alkyl salicylates. The total base number (TBN) of a salicylate detergent, if used, measured by ASTM D2896, is preferably 50 to 450 such as 80 to 450.

Lubricating Oil Base Stock

This may be mineral or synthetic or both.

The improved viscosity control achieved by the present invention is further enhanced if the oil of lubricating viscosity (or base stock), used in the manufacture of the composition is a mineral oil base stock containing high levels (>85%) of saturates (as measured by the ASTM method D2007).

Anti-oxidant

Reducing the metal salt content in the composition may limit the antioxidative properties of the metal detergents. It may therefore be preferable that antioxidants are added to the lubricant formulations to counter this effect. Anti-oxidants (or oxidation inhibitors) increase the composition's resistance to oxidation and may work by combining

with and modifying peroxides to render them harmless, by decomposing peroxides, or by rendering an oxidation catalyst inert. Antioxidants that may be used in the present invention include amine anti-oxidants such as those based on aryl or alkyl-substituted amines, for example Irganox L57 (tertiary -C_{12} alkyl diphenylamine), or phenolic anti-oxidants, such as hindered phenols, for example Irganox L135 (2,6-ditertiary-butyl-4-(2-carboxy (alkyl) ethyl) phenol) (CIBA Speciality Chemicals).

Further additives, as co-additives, may be incorporated in the composition to enable it to meet particular requirements. Examples include, additional to those hereinbefore mentioned in connection with this invention, corrosion inhibitors, anti-oxidants, friction modifiers, dispersants, detergents/rust inhibitors, anti-wear agents, pour point depressants, anti-foaming agents, and viscosity modifiers.

Dispersants have been noted hereinbefore and are additives for holding solid and liquid contaminants in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge formation. Ashless dispersants may comprise a long-chain hydrocarbon, eg polymeric, conferring oil-solubility, with a polar head, eg in the form of a functional group, for associating with particles to be dispersed. A noteworthy class of ashless dispersants is constituted by the hydrocarbon-substituted succinimides, which may be used borated or unborated.

The additives for the composition of the invention are typically blended into a base stock in amounts to enable them to provide their desired functions. Concentrates, ie concentrated dispersions or solutions of one or more additives, are known in the art and may be used in known manner to prepare the compositions of the invention.

The compositions are to lubricate mechanical engine components, particularly of an internal combustion engine, by supplying the composition thereto. A preferred engine is a diesel (compression-ignited) engine. A particular preferred composition is a heavy-duty diesel engine lubricating oil composition, ie for application in large diesel engines.

EXAMPLES

The following Examples illustrate the invention.

The lubricating oil compositions used in the examples comprised the following components: an overbased calcium C_{14-18} alkyl salicylate detergent, a calcium sulphonate

detergent, a calcium phenate, a dispersant, an antiwear agent e.g. a zinc diaryl or dialkyl dithiophosphate, and an antioxidant. Selected components were blended to give five different fully formulated oils having the viscosity specifications corresponding to the Society of Automotive Engineers (SAE) requirements for a 15W40 multigrade oil. The oils were identical other than for their detergent type and/or concentration.

The oils were each tested in the Mack T8 engine test. Table 1 shows the rate of viscosity increase at different concentrations of metal salts (or surfactants), where specific oils are identified by the code letters A to F.

Example	Surfactant (Soap) Concentration mmol/kg oil	Inorganic Base Concentration mmol/kg oil	VK increase @ 3.8% soot, mm^2s^{-1} at 100?C
A	13 (salicylate)	39	15.9
B	20 (13 salicylate) (7 phenate)	54	29.7
C	20 (10 salicylate) (10 phenate)	52	25.1
D	13 (salicylate)	54	15.4
E	10 (salicylate)	56	11.5
F	20 (13 salicylate) (7 sulphonate)	54	15.0

A comparison of the results from Examples A and D shows that the level of inorganic base had no effect on the overall viscosity level. It is apparent also that reducing the surfactant concentration resulted in improvements in the reduction of viscosity levels in the lubricating oil composition. The most marked effect was achieved using a salicylate surfactant concentration of 10 mmol/kg of lubricating oil composition.

Table 2 illustrates the effect of antioxidants, added in combination with the metal detergents, on the increase in viscosity in the Mack T8 engine test.

Soap mmol/kg oil	Inorganic Base mmol/kg oil	Antioxidant And mass %	VK increase @ 3.8% soot, mm^2s^{-1} at 100?C
13 Salicylate	54	None	15.02
13 Salicylate	54	0.5% Phenolic	10.63
13 Salicylate	54	0.5% Aminic	11.86

As shown, the addition of a phenolic or aminic antioxidant results in a reduction in the rate of viscosity increase when compared with metal detergents lacking an antioxidant.

Table 3 illustrates the performance of a lubricating oil composition comprising a metal detergent consisting of 10 mmol salicylate surfactant per kg oil and 61 mmol inorganic base per kg oil, in a range of standard US and European engine cleanliness tests.

Table 3

A. Maintained European diesel engine cleanliness performance (CE-L-42-A-92).

	Test Result	Recognised Permitted Levels MB228:1/ACEA E2
Average bore polish	3.3%	=8%
Average cylinder wear	4.1 ìm	=7 ìm
Piston cleanliness	31.9 merit	=31 merit
Average Engine Sludge	9.7	>9
Oil consumption (total), kg (start of test oil Consumption, g/hr 0.67)	17.61	>18 kg

B. US diesel cleanliness performance. Caterpillar 1N.

	Test Result	Recognised Permitted Level 1st time pass CG-4
Top Groove Fill (TGF)	8%	20% max
Weighted Demerits CAT-N1 (WDN)	254.6 demerits	286.2 demerits max
Top Land Heavy Carbon (TLHC)	0.0	3% max
Average Oil Consumption	0.21	0.5 max (g/kw/hr)

C. Caterpillar 1K.

	Test Result	Recognised Permitted Level 1st time pass CF-4
Weighted Demerits CAT-K1	299 demerits	322 demerits max
Top Groove Fill (TGF)	8.5%	24% max
Top Land Heavy Carbon (THLC)	0.0	4.0% max
Average Oil Consumption	0.14	0.27 max (g/kw/hr)

The results show that lubricating oil compositions comprising metal detergents of the present invention are able to achieve acceptable levels of performance in each of the cleanliness tests.

CLAIMS

1. A lubricating oil composition comprising, as a detergent, one or more metal salts of long chain hydrocarbyl-substituted organic acids, such as selected from aromatic carboxylic acids, sulfonic acids or phenol derivatives, the total concentration of said metal salts being not more than 15 mmol/kg of the composition, provided that the composition is not an SAE 5W composition whose base stock comprises less than 5, such as less than 6 or 10, wt. % non-conventional lubricant.

2. A lubricating oil composition comprising, as a detergent, one or more overbased metal salts of long chain hydrocarbyl-substituted acids selected from aromatic carboxylic acids or phenol derivatives, the total concentration of said metal salts being not more than 15 mmol/kg of the composition, provided that the composition is not an SAE 5W composition whose base stock comprises less than 5, such as less than 6 or 10, wt. % non-conventional lubricant.

3. The composition as claimed in claim 1 or claim 2 wherein the concentration is between 5 and 15, such as between 8 and 13, mmol/kg of the composition.

4. The composition as claimed in any preceding claim wherein the metal salt is a calcium alkyl salicylate.

5. The composition as claimed in any preceding claim wherein the carboxylic acid is a C_{14-24} alkyl salicylic acid.

6. The composition as claimed in any preceding claim further comprising an anti-oxidant comprising an aminic, such as an aryl- or alkyl-substituted amine, anti-oxidant or comprising a phenolic, such as a hindered phenolic, anti-oxidant.

7. The composition as claimed in claim 6 wherein the anti-oxidant is an alkyl-substituted amine and is a tertiary C_{4-12} alkyl diphenylamine.

8. The composition as claimed in claim 6 wherein the anti-oxidant is a phenol and is a 2,6-ditertiary-butyl-4-(2-carboxy(alkyl) ethyl) phenol.

9. The composition as claimed in any of the preceding claims wherein the detergent has a metal:metal salt ratio of between 1 to 10.

10. The composition as claimed in any preceding claim comprising a base stock in the form of a mineral oil base stock containing greater than 85% of saturates, as measured by ASTM method D2007.

11. The composition as claimed in any preceding claim further comprising a dispersant, for example at a concentration of 3 to 10 mass % based on the mass of the composition.

12. The composition as claimed in any preceding claim free of a magnesium salt detergent.

13. The composition as claimed in any preceding claim in the form of a heavy duty diesel lubricating oil composition.

14. A method of making a lubricating oil composition comprising admixing a major amount of an oil of lubricating viscosity and minor amounts of metal salt and, optionally, of an anti-oxidant as defined in any preceding claims.

15. A method of lubricating a diesel engine which comprises supplying to the engine a lubricating oil composition as claimed in any of claims 1 to 13 or a lubricating oil composition made by the method of claim 14.

16. A method of alleviating viscosity increase in a lubricating oil composition due to the presence of increasing levels of soot when the composition is lubricating a diesel engine, which comprises using, in the composition, one or more metal salts as defined in claim 1 or claim 2.

INTERNATIONAL SEARCH REPORT

Internati· ·l Application No
PCT/Ep 99/02842

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10M159/20 C10M163/00 C10M129/10 C10M129/54 C10M135/10
//(C10M163/00,129:10,133:12,137:10,159:20),C10N30:04

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	GB 709 587 A (NAAMLOOZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ) 26 May 1954 (1954-05-26) page 3, line 87-90; table A page 6, line 9-87 ---	1,3,6, 9-16
X	US 4 729 848 A (YAMAGUCHI ELAINE S ET AL) 8 March 1988 (1988-03-08) example 5; table II ---	2,9-15
P,X	EP 0 884 378 A (TONEN CORP) 16 December 1998 (1998-12-16) page 2, line 4-35 page 3, line 28-38; tables 1,2 ---	1-6,9-14

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 September 1999	27/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Kazemi, P

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Internati[illegible] Application No
PCT/Er 99/02842

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 0 881 277 A (TONEN CORP) 2 December 1998 (1998-12-02) page 7, line 5-35; examples 1-3; tables 1,2	1,3,9-14
X	EP 0 604 218 A (LUBRIZOL CORP) 29 June 1994 (1994-06-29) examples 6,8,9,21,22,34	1-3,5,6, 9,12
A	US 3 903 151 A (LOWE WARREN) 2 September 1975 (1975-09-02) column 7, line 30-50	2,3,9, 13-15
A	US 5 558 802 A (DOWLING MICHAEL) 24 September 1996 (1996-09-24) column 5, line 41-44 column 12, line 64 - column 13, line 10 column 14, line 49 - column 15, line 10; claims 1-9	1-16

1

INTERNATIONAL SEARCH REPORT

rmation on patent family members

Internat al Application No
PCT/EP 99/02842

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 709587 A		DE 947416 C	
		FR 1058832 A	19-03-1954
US 4729848 A	08-03-1988	NONE	
EP 0884378 A	16-12-1998	JP 11061165 A	05-03-1999
		CA 2235292 A	12-12-1999
EP 0881277 A	02-12-1998	JP 11043687 A	16-02-1999
EP 0604218 A	29-06-1994	AU 665879 B	18-01-1996
		AU 5254693 A	07-07-1994
		BR 9304553 A	26-07-1994
		CA 2112187 A	24-06-1994
		JP 6220477 A	09-08-1994
		ZA 9309526 A	08-08-1994
US 3903151 A	02-09-1975	NONE	
US 5558802 A	24-09-1996	AU 6340496 A	01-04-1997
		CA 2222373 A	20-03-1997
		EP 0876449 A	11-11-1998
		WO 9710317 A	20-03-1997