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(71) Applicant
Produits Chimiques Ugine Kuhlmann, Tour Manhattan—La Defense 2, 5 & 6 Place de L'Iris, 92400 Courbevoie, France
(72) Inventors
Francis Defretin, Jean-Paul Eudeline, Elisabeth Schoch, Alain Voisin
(74) Agent
Page, White & Farrer

(54) Additive for Oil for Internal Combustion Engines

(57) An additive for oil for internal combustion engines, comprises at least one dithiophosphate, at least one fatty amide, and a fluorographite CF_x where x is from 0.6 to 1. The amide may be replaced by a mixture of a fatty acid and an amine, or by the corresponding salt.

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SPECIFICATION

Additive for Oil for Internal Combustion Engines

This invention relates to additives for mineral or synthetic oils for internal combustion engines.

One of the major preoccupations of manufacturers of internal combustion engines and producers of motor oil is to perfect new mechanical techniques and new lubricant compositions for reducing fuel consumption.

In particular, efforts have been made to reduce the viscosity of the lubricating oil base, but there is then a risk of premature wear of the motors. To reduce this wear, it has been proposed to use products which adjust the viscosity, such as polymethacrylates, polyisobutylenes, and so-called anti-wear additives based on sulphur, phosphorus and a heavy metal, such as metal dithiophosphates.

Viscosity regulators have the disadvantage of shearing when used, which reduces their effectiveness, and decomposing thermally to form varnishes which are prejudicial to the service life of the engine. Moreover, the anti-wear additives based on sulphur, phosphorus and heavy metal have a limited service life.

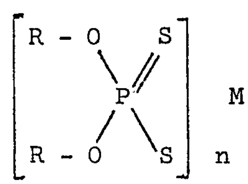
It has also been proposed to add microdispersions of solid lubricants such as molybdenum bisulphide MoS_2 and graphite to the oils, as anti-wear additives, but the results are still poor as regards the fuel saving obtained.

An appreciable improvement has been achieved by reinforcing the action of additives based on sulphur, phosphorus and heavy metal with polar derivatives such as esters of fatty acids and alcohols, e.g. isopropyl oleate.

We have now perfected a composition which considerably increases the lubricant properties of oils, thus resulting in fuel savings which may be from 5 to 12%, depending on the type of engine, and the stabilisation of the temperatures of the oil and water at a value which is 5°C to 10°C lower than the temperatures obtained with the oils used at present.

According to the present invention, there is provided an additive for oil for internal combustion engines, comprising simultaneously at least one dithiophosphate, at least one fatty amide, and a fluorographite CF_x wherein x is from 0.6 to 1.

The dithiophosphates (DTPM) are preferably compounds having the chemical formula:



(I)

wherein each R independently represent an organic alkyl or aryl radical, M is a metal cation such as Cu_{II}, Ag_{I}, Zn_{II}, Cd_{II}, Pb_{II}, or a non-metallic or organic radical derived from ethylene diamine, for example.

The use of dithiophosphates wherein M is a metal is particularly recommended owing to the performance of these products at high temperatures, and the use of zinc dithiophosphates is particularly recommended. The other products of formula I which are particularly recommended include the dithiocarbamates and dialkylphosphorodithioates.

The amounts of dithiophosphate to be added to motor oils containing the additive compositions according to the invention vary according to the type of oil. It is generally recommended to use from 0.05% to 0.2% of dithiophosphate, expressed in M cations by weight of the base oil. It should be noted that these amounts are larger than those used at present in the commercial anti-wear oils, namely 0.03% to 0.07% expressed in M cations which makes it necessary to add dithiophosphate to the compositions according to the invention.

The second constituent of the compositions claimed is a fatty amide and more particularly an aliphatic amide the fatty chain of which contains 8 to 36 carbon atoms. Particularly good results have been obtained with oleic diamide, but lauric laurylamide, alkanol-amides and oxo acid amides are also suitable for use. The fatty amide content to be added to the composition varies according to the type of oil to which the additive is to be added, but should generally correspond to 0.05% to 1% by weight of the base oil.

For reasons of economy, it is generally preferable to replace the amide in the composition by the products form which it is prepared, namely the fatty acid and the amine, or the corresponding salt. From the first few hours of operation of internal combustion engines wherein the oil contains the additive proposed by the applicants, these products are converted into the corresponding amide. The amount of fatty amine salt to be used is advantageously from 0.05% to 1% by weight of the basic motor oil.

The third constituent of the additive is a fluorographite, a solid lubricant of the formula CF_x, wherein the carbon used for the synthesis of the CF_x is natural or artificial graphite, coke or active charcoal, and wherein x is from 0.6 to 1, preferably from 0.8 to 1.

In order to obtain a good dispersion of the fluorographite, it is recommended to microdisperse it beforehand in an oil-miscible dispersing medium, particularly in polyglycol ethers or mineral oils. Polyglycol ethers with a viscosity of 20 to 400 centistokes at 40°C, and particularly with a viscosity of 100 centistokes, have proved especially suitable.

The CF_x content of the compositions may vary depending on the desired effect, but generally corresponds to 0.01% to 1% by weight of CF_x in the basic motor oil which is to contain the additive, and preferably from 0.02% to 0.5%.

The synergy found to exist between the various constituents of the additive compositions for engines claimed is particularly important.

Comparative tests have shown, for example, that the addition to the primary constituents of the composition, namely the dithiophosphate and the fatty amide or fatty amine salt, of a well known solid lubricant such as molybdenum sulphide, which is very often used in conjunction with graphites, produces results which are greatly inferior to those obtained by the addition of the said fluorographite to these same constituents.

The compositions according to the invention are prepared by simply mixing the constituents together. The addition of these compositions to motor oils is effected without difficulty by simply adding the additive composition, prepared beforehand, or the constituents thereof, to these oils.

The following Examples illustrate the present invention.

The tests in the Examples are tests carried out in the laboratory using conventional oil testing apparatus, namely the 4 ball apparatus and the Faville and Reichert devices, or practical tests carried out on the road using petrol or diesel engine vehicles of current types.

Example 1
Laboratory Tests

Lubricant compositions having the formulae shown in table I are prepared from the following constituents:

A—*Base oil* consisting of a mixture of:

500 neutral petroleum fraction	95% by weight
Bright stock solvent (BSS)	5% by weight

B—*Additive 1:*
2% by weight of zinc dithiophosphate containing 10% zinc
1% of a mixture of 70% BSS
30% oleic diamine dioleate

C—*Additive 2:*
microdispersion of fluorographite $CF_{0.9}$ in an amount of 10% by weight in a polyglycol ether with a viscosity of 100 centistokes at 40°C or, for test 8, microdispersion of 10% molybdenum bisulphide in a polyglycol ether.

Table I
Composition of Lubricants Studied, in % by weight

Compositions	A *Base oil*	B *Additive 1*	C *Additive 2*
1	100	0	0 CF_x
2	99	0	1 "
3	98.5	1.5	0 "
4	97	3	0 "
5	97.5	1.5	1 "
6	96	3	1 "
7	92	3	5 "
8	97.5	1.5	1 MoS_2

Composition 1 is the base oil on its own, without additives. Compositions 3 and 4 contain the base oil and additive 1 (zinc dithiophosphate and amine salt), composition 2 contains the base oil and the additive 2 (fluorographite), compositions 5, 6 and 7 contain the base oil, the additive 1 (dithiophosphate and amine salt) and additive 2 (fluorographite), and in composition 8 the fluorographite of composition 5 is replaced by molybdenum bisulphide.

The various compositions of Table I are easily prepared by simply adding the various additives to the base oil. Their properties are investigated in conventional manner, using tests carried out with the 4 ball apparatus, the Faville apparatus and the Reichert apparatus.

1.1—Tests Using the Shell 4 Ball Apparatus

This apparatus indicates the effectiveness of a lubricant in preventing wear under the loads applied.

Three balls blocked in position in a dish containing the lubricant are subjected, via the 4th ball which is integral with the spindle of a motor rotating at a fixed speed, to a known variable vertical load. The trace of the wear formed on the three fixed balls is measured, and as a function of the load the wear load index (WLI) is determined according to the standard ASTM D 2783; the higher the WLI the better the lubricant.

The jamming load in kg, corresponding to a sudden increase in wear beyond the expected value, is also noted, as is the welding load in kg which is defined as the pressure at which the 4 balls become welded together.

All the tests were carried out by applying increasing loads for 10 seconds each.

The results of the tests carried out on the various compositions are given in Table II.

Table II
Study of Lubricants Using the 4 Ball Apparatus

Compositions	*Wear load index (WLI)*	*Jamming load in kg*	*Welding load in kg*
1	32.5	100	160
2	31.2	80	250
3	40.9	100	200
4	43.2	100	250
5	44.3	100	315
6	44.2	100	315
7	47.1	100	400
8	39.4	100	250

The effect of the fluorographite on the welding load will be noted; whereas the addition of 0.1% of molybdenum sulphide to the base oil (composition 8) results in a welding load of 250 kg, the addition of 0.1% of fluorographite, namely 1% of additive 2 (composition 5) gives a welding load of 315 kg. It will also be noted that the wear load index increases very subtantially when fluorographite is added. With composition 3, in which the base oil is already doped with an additive of zinc dithiophosphate and diamine oleate, the wear load index is 40.9 and increases to 44.3 when 0.1% of fluorographite is added (composition 5).

1.2—Tests Using the Faville Apparatus

This machine is used to determine the anti-wear and extreme pressure properties of a lubricant.

A cylindrical test piece connected to the spindle of a motor rotating at variable speed (from 120 to 3,000 rpm) is inserted between two bits on which a variable pressure is exerted. The assembly of the test piece and bits is either immersed in the liquid to be tested or is sprinkled with this same liquid. During the application of the load, the tangential resistance force is recorded and from this the coefficient of friction is deduced. The loss of weight of the test piece and bits is also determined. The test carried out is a test of endurance in which increasing loads are applied over a given period.

—speed: 178 rpm
—test piece and bits: 16 NC6 steel
—application of loads:

9 bars:	3 min
15 bars	1 min
23 bars:	1 min
30 bars:	40 min

—quantity of oil used: 80 cm^3.

The assembly of the test piece and bits is continuously sprinkled with the oil. The oil circulates at a constant speed.

The results obtained with the Faville apparatus are given in Table III.

Table III
Study of Lubricants Using the Faville Apparatus

Compositions	Coefficient of friction 9 bars	15 bars	23 bars	30 bars	Loss in mg Testpiece	Bits	
1	0.135	0.110	0.130	0.130	10.5	2.7	3
2	0.140	0.124	0.130	0.120	7.5	0.4	0
3	0.120	0.120	0.120	0.115	3.8	1.4	1
4	0.110	0.100	0.200	0.115	5	0.8	1
5	0.120	0.124	0.133	0.140	2.1	0.2	0.5
6	0.105	0.105	0.115	0.110	1.5	0.4	0
7	0.090	0.100	0.110	0.105	0.2	0	0.2
8	0.135	0.124	0.150	0.140	9	1	0.5

It will be noted that the simultaneous presence of zinc dithiophosphate, amine oleate and fluorographite (compositions 6 and 7) substantially reduces the value of the coefficient of friction and considerably decreases the wear measured by the loss in weight of the test piece and the two bits.

Whereas, with zinc dithiophosphate and amine oleate (composition 3), there are weight losses of 3.8, 1.4 and 1, respectively, when fluorographite is added (composition 5) the losses are only 2.1, 0.2 and 0.5, respectively.

It should also be noted that the addition of molybdenum sulphide gives mediocre results.

1.3—Test Using the Reichert Apparatus

This apparatus is used to study the wear by friction of metal parts, i.e. the resistance of the film of lubricant.

A ring, half immersed in the fluid which is to be tested, rotates at a fixed speed of 900 rpm; it is in contact with a fixed cylinder to which a load of 1,500 g is applied (i.e. 15,000 kg/cm^2 of Hertz contact pressure). The ring rotates for a specified time corresponding to 100 m of linear travel of the ring (or corresponding to 1 minute, in terms of time). After this period, an elliptical wear imprint is formed on the cylinder. The surface area of the imprint is measured and from this the load capacity of the lubricant is deduced.

The load capacity is determined, which is the ratio of the load in kg/surface area of the imprint in cm^2.

The results of the test are given in Table IV.

Table IV

Compositions	Imprints mm^2	Load kg	Load capacity kg/cm^2
1	35.3	30	90
2	29	30	104
3	17.7	30	170
4	10	30	300
5	14.3	30	210
6	9.5	30	316
7	7.5	30	400

It will be noted that the load capacity of the base oil, which increases considerably when the zinc dithiophosphate and diamine oleate are added, is further increased by the introduction of fluorographite. Thus, for example, it passes from a load capacity of 90 kg/cm^2 in the base oil (composition 1) to 170 kg following the addition of zinc dithiophosphate and oleate (composition 3) and to 210 kg following the supplementary addition of 0.1% of fluorographite (composition 5). Composition 7, containing 3% of additive 1 and 5% of additive 2, i.e. 0.5% by weight of fluorographite, results in a remarkable load capacity of 400 kg/cm^2.

All the tests carried out show that the additive compositions for motor oil according to the invention have a set of particularly interesting properties, namely an increase in the welding load and load capacity of the lubricant, a reduction in the wear of metal parts under friction which leads to a lowering of the coefficient of internal friction in engines, and a reduction in the wear of the engine.

Example 2
Tests on a Motor Vehicle having a Petrol Engine

A standard Renault 16 TS car with an engine which had completed 9,000 km was used, carrying two passengers, to carry out a test on the consumption of super-grade petrol with a standard commercial engine oil, then a comparative test was carried out using this same oil to which a lubricant additive composition according to the invention had been added.

These tests were performed on a motorway at a constant speed of 120 km/h. The following journeys were made:

—Paris-Poitiers, return, with no additive, after the car had been emptied and filled up with 4 litres of Labo oil; i.e. 557.8 km,

—introduction of 100 g of an additive consisting of a mixture of:

60% of additive 1 as defined in Example 1
40% of additive 2 as defined in Example 1

—journey of 416 km on the Paris-Dieppe motorway in order to attain the optimum effectiveness of the additive.

—Paris-Poitiers, return, with the additive indicated above added to the engine oil beforehand; i.e. 558.9 km.

The results obtained in this test on consumption are given in Table V. It should be noted that, during the two Poitiers-Paris journeys, a stable wind was blowing in the north to south direction.

Table V
Test of Consumption on a Motorway
using a Renault 16TS car with a petrol engine, with and without an additive

Distance in km travelled at 120 km/h	*Time in minutes*	*Consumption of super petrol in litres*	*Average Speed in km/h*	*Consumption of super petrol per 100 km*
		I)—Without Additive		
Outward 315.5	158	36.3	120.00	11.5
Back 242.3	121	33.2	120.06	13.7
Total 557.8	279	69.5	120.03	12.5
		II)—With Additive		
Outward 316.6	158	33.7	120.9	10.6
Back 242.3	121	32.1	120.5	13.3
Total 558.9	279	65.8	120.2	11.8

Fuel Saving:
Outward =7.5%
Back =3.1%
Return trip =5.4%

It will be noted that an average fuel saving of 5.4% was obtained in this test by adding an additive composition of the invention to the engine oil.

Example 3
Test on Motor Vehicle with a Diesel Engine

A standard-type Citreon CX Diesel 2500 D car the engine of which has completed 3,500 km is used to carry out a test on the consumption of gas oil with a standard commercial oil, Total 20W40, and then, by comparison, with this same oil to which a lubricant additive composition according to the invention has been added.

The consumption test is carried out over the return journey from Lille to Le Puy, making a total of 1,300 km on a motorway and 400 km on mountainous main roads, at a speed varying according to the district and the amount of traffic on the roads, but on average 120 km/h on the motorway and 70 km/h on the main roads.

On the outward journey, one person used the car and the consumption of gas oil was 8.1 litres per 100 km. Before the return journey, which was made with 5 people in the car, 200 g of an additive having the following composition were added to the 5 litres of oil:

—75% of the additive 1 defined in Example 1
—25% of the additive 2 defined in Example 1

The consumption of gas oil was 7.2 litres per 100 km, corresponding to a fuel saving of 11%.

Claims

1. An additive for oil for internal combustion engines, comprising simultaneously at least one dithiophosphate, at least one fatty amide, and a fluorographite CF_x wherein x is from 0.6 to 1.
2. An additive according to Claim 1, wherein the dithiophosphate is a metal dithiophosphate.
3. An additive according to Claim 2, wherein the dithiophosphate is zinc dithiophosphate.

4. An additive according to any one of Claims 1 to 3, wherein the fatty amide has the formula:

R—CO—NH—R′ or R—CO—[HN—R″—NH]—CO—R′

wherein each of R and R′ represents an alkyl group having from 8 to 36 carbon atoms and R″ represents an alkyl group having from 2 to 6 carbon atoms.

5. An additive according to any one of Claims 1 to 4, wherein the fatty amide is replaced by a mixture of the corresponding fatty acid and amine, or by the corresponding salt.

6. An additive according to any one of Claims 1 to 5, wherein the fluorographite CF_x is one in which x is from 0.8 to 1.

7. An additive according to any one of Claims 1 to 6, wherein the fluorographite is microdispersed in a dispersing medium which is miscible with oils for internal combustion engines.

8. An additive according to Claim 7, wherein the fluorographite is microdispersed in a polyglycol ether of a viscosity of 100 centistokes at 40°C.

9. An additive according to Claim 1, substantially as described in any one of the foregoing Examples.

10. An oil for an internal combustion engine comprising an additive according to any one of the preceding claims.

11. An oil according to Claim 10, containing from 0.05 to 0.2% by weight of dithiophosphate expressed as dithiophosphate cations.

12. An oil according to Claim 10 or 11, containing from 0.05% to 1% by weight of fatty amide, or fatty amine salt or a mixture of fatty acid and fatty amine.

13. An oil according to any one of Claims 10 to 12, containing from 0.01% to 1% by weight of the fluorographite CF_x.

14. An oil according to Claim 10 substantially as described in any one of the foregoing Examples.

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