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(54) Use of Lubricating Oil for Reducing Fuel Consumption

Verwendung Schmieröls zur Reduzierung des Kraftstoffverbrauchs

L'utilisé d'huile lubrificante pour réduire la consommation de carburante

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Description

[0001] The present invention relates to lubricating compositions capable of guaranteeing an improvement in the fuel economy performances of internal combustion engines, also without resorting to specific additives conventionally known as friction modifiers or reducers. The above compositions envisage the presence of particular deterging additives selected from the group of sulfophenates, preferably superbasic, and particular anti-wear additives having the general formula $ZnP_2S_4O_4R_4$.

[0002] The request for lubricating products with fuel economy (f.e.) performances has been a fundamental demand for car manufacturers for a long time. This necessity has recently been further re-evaluated, not only with respect to the opportunity of reducing the consumption of limited energy sources, but also for the necessity of reducing environment pollution. At present, the most advanced formulations in the field of engine oils must therefore also satisfy this requirement.

[0003] From a technical point of view, lubricants serve to protect metallic surfaces from direct contact, and this role, at hydrodynamic or elasto-hydrodynamic lubrication regimes (hereinafter indicated as H regimes), is effected thanks to a fundamental characteristic of the oil, i.e. its viscosity. In principle, in fact, the higher the viscosity, the more the presence of thick lubricating layers on the metallic surface, for its protection, is guaranteed. It is well known, on the other hand, that the use of high viscosity values, which is a representative parameter of intermolecular friction leads to a more difficult flow of the lubricating layers and to the generation of passive friction which dissipates useful mechanical energy. For this reason, tendentially more fluid oils have already been in use for a long time. This system, however, creates drawbacks linked to a closer distance between the moving solid surfaces, more specifically, the severer lubrication regimes, or "mixed" (M) and "boundary" (B) regimes, become more critical. In correspondence with these regimes, there is the presence of increasingly thinner lubricating layers, until a situation is reached in which the surface roughness of the solid creates a direct contact which can lead to high friction and wear phenomena.

[0004] In internal combustion engines, there are mechanical contacts in movement which operate at various lubrication regimes. A minimization of the passive friction consequently inevitably requires an accurate balancing-reduction in friction at all the various lubrication regimes. In particular, at H lubrication regimes, the friction coefficient, essentially due to the shearing of the lubricating molecules in motion, is in the order of 0.001-0.08, but at severer regimes (M, B), with increasing partial contacts between the solids in movement, it passes to a range of 0.08-0.3, and consequently the optimization of the latter is extremely important in the final f.e. performance.

[0005] The greater fluidity of the oils at H regimes is obtained by improving the characteristics of the base oils and polymeric additives, particularly viscosity modifier and/or viscosity index enhancer additives.

[0006] The minimization of the friction at the other severer regimes is much more complex, as the level of knowledge on the functioning mechanisms of the relative additives is still modest; furthermore, as the additives used in the lubricants sometimes differ greatly from each other, many interpretations which are valid in one context, are not so in another.

[0007] Measurement of the friction coefficient variations at the various lubrication regimes, with particular reference to the regimes responsible for generally higher friction, is a useful method for identifying new and advantageous solutions for the formulation of f.e. products. These measurements can be conveniently effected by means of a ball-on-disk tribometer which operates under mixed movement conditions of the rolling/sliding type. With this apparatus and a suitable method, it is possible to trace friction coefficient curves vs. rolling rate, also called Stribeck-Like Curves (SLC), which take into account the behaviour of the lubricant at H, M, B regimes. The definitive validation of the above tribological measurements is obtained by means of engine tests required by specifications on the part of European, American and Japanese organisms and manufacturers.

[0008] Among the most well-known additives with declared anti-friction properties, organometallic additives with Molybdenum (for example dithiophosphates, dithiocarbamates, dithioamides) described for example in US-A-6,174,842, US-A-6,010,987 and US-A-6,034,038, can be mentioned. These additives allow the friction coefficient to be reduced between the surfaces in movement, but their effectiveness is conditioned by chemical reactions in the solid-solid contact area ("tribo-reactions") which can be inhibited by specific unfavourable "local" conditions or by antagonism with other additives.

[0009] There are also other effective anti-friction additives for providing lubricating oils with f.e. performances. Among these, there is the group of polar esters (see for example US-A-4,304,678, US-A-4,683,069 and US-A-5,962,381). In particular, US-A-5,962,381 describes a special group of polar esters which can exert a friction-reducing action at mixed and hydrodynamic regimes. This behaviour has also been measured with an analogous method to that indicated above (rolling/sliding tribometry).

[0010] The combined use of specific anti-friction additives and additives traditionally present in the basic formulation is also indicated (see for example US-A-6,143,701 which describes synergies between Molybdenum compounds and detergents). EP-A-0913455 discloses a lubricant composition comprising sulfurized phenates and ZnDTP which are P esters, used to improve fuel economy.

[0011] There are consequently numerous possible methods for obtaining the desired performance. In any case, it should be remembered that with each further addition of additives, unexpected unbalances can be created in the equilibrium existing between the various properties of the final mixture and their duration with time.

[0012] Furthermore, the addition of Molybdenum increases the content of ashes, metals, sulfur and (at times) phosphorous of the mixture, and these variations are not coherent with the necessity of improving the compatibility of the oils with post-treatment systems of the exhaust gases of vehicles. The use of polar ester products, on the other hand, can generally create a negative competition with respect to the solid to defend, obstructing the action of the anti-wear additive.

[0013] In any case, the addition of further components, as well as making a mixture which already contains about 10-15 different active species, even more complex, also increases the costs.

[0014] Lubricating compositions for engine oils have now been found, which are capable of improving the f.e. performance of an internal combustion engine lubricated with the above lubricating compositions, which overcome the drawbacks indicated above.

[0015] More specifically, the present invention relates to lubricating compositions for internal combustion engines capable of reducing the fuel consumption of engines lubricated by the compositions themselves, the above lubricating compositions comprising:

(a) base oil having a viscosity suitable for lubricating;
(b) detergent additives in a quantity ranging from 0.5% to 5.0% by weight, preferably from 1.0% to 4.0% by weight, with respect to the total weight of the lubricating composition;
(c) anti-wear additives in a quantity ranging from 0.3% to 5.0% by weight, preferably from 0.8% to 3.0% by weight with respect to the total weight of the lubricating composition; the above lubricating compositions being characterized in that:

** at least 60% by weight, preferably at least 70% by weight, of the detergent additives is selected from sulfophenates having general formula (I) RΦ (OH) $-S_n-$ (OH) ΦR', wherein R and R', the same or different, are alkyl radicals having from 1 to 16, preferably from 9 to 12, carbon atoms, n ranges from 1 to 5, preferably from 1 to 4; and wherein both the hydroxyls, preferably both in para position with respect to R and R', are salified with one or more alkaline-earth metals, preferably with calcium;
** the anti-wear additives are selected from zinc dithiophosphates having general formula (II) $ZnP_2S_4O_4R_4$, wherein R_4 is an alkyl radical having the formula $-CH_2R_5$, wherein R_5 is a linear and/or branched saturated alkyl radical, having from 2 to 15, preferably from 2 to 7, carbon atoms.

[0016] The sulfophenates (I) salified with calcium can be neutral or superbasic, preferably superbasic. The term superbasic means that the above sulfophenates are treated with a quantity of base which is higher than the stoichiometric value. The above excess normally ranges from about 125% to about 220% molar. Superbasic sulfophenates having a TBN of 50 to 400, preferably from 100 to 300, are particularly preferred. TBN (total base number) is the quantity of base equivalent to mg of KOH in a sample, and is measured according to the regulation ASTM D-2896.

[0017] The detergent additives comprise (i) from 60 to 100% by weight of sulfophenates having general formula (I) and may comprise (ii) from 0 to 40% by weight of other detergents selected from calcium sulfonates, calcium alkylbenzene sulfonates, calcium salicylate.

[0018] The anti-wear additives used have a general formula of the type $ZnP_2SgO_4R_4$, wherein R_4 is an alkyl radical having the formula $-CH_2R_5$, wherein R_5 is a linear and/or branched saturated alkyl radical, having from 2 to 15, preferably from 2 to 7, carbon atoms. R_5 is preferably selected from $-(CH_2)_3CH_3$, $-CH(CH_3)CH_3$, $-C(CH_3)_3$, and relative mixtures.

[0019] The fuel economy performances of the lubricating compositions used in the present invention can also be obtained using compositions which contain, in addition to components (a)-(c), friction modifying or reducing additives, provided they are compatible with the same components (a) - (c).

[0020] As far as the base oils (a) are concerned, these are selected from one or more of mineral or synthetic oils (among synthetic oils, poly α-olefins (PAO) and ester bases can be mentioned), typically used in lubricating oils for internal combustion engines fed by both gasoline and gas oil. The base oils can come from various processings, for example from hydro-refining or conversion processes of heavy waxes. Mixtures of mineral or synthetic oils can obviously be used. The viscosity of the above base oils can fall within a range of 2.0 to 10.0 mm^2/s, preferably from 2.5 to 8.0 mm^2/s, measured at 100°C. These bases, also possibly mixed with each other, are contained in a predominant quantity, reaching, in relation to the remaining group of additives necessary, up to 95-98% w; their concentration is typically equal to about 85% w.

[0021] An object of the invention also relates to the fuel economy upgrading of secondary synergic properties of the above detergent and anti-wear additives, as these additives are typically used in the formulation of lubricating oils for internal combustion engines, to guarantee compliance with various specifications.

[0022] A further object of the invention relates to a method which allows convenient and economical f.e. products to be formulated, without resorting to potentially critical variations to the already complex lubricating mixture.

[0023] Another important object of the invention relates to the possibility of ensuring a high duration of the f.e. performances, due to the fact that said performances are guaranteed by additives traditionally used for long durations, as a much greater duration range of the oil must be guaranteed with respect to the range required by the f.e. engine test.

[0024] The invention is the use of anti-wear additives of the zinc alkyl dithiophosphate type and detergents of the sulfophenate type which, when mixed in suitable ratios in a typical formulation for engine oils, give the mixture an evident fuel economy advantage.

[0025] The f.e. performance can be obtained within a range of concentrations which, for anti-wear, varies from 0.3 to 5.0 %w, preferably from 0.8 to 3.0 %w; for the sulfophenate detergent from 0.5 to 5.0%w, preferably from 1.0 to 4.0%w.

[0026] It has been surprisingly found that said mixture significantly reduces the friction coefficient at regimes closest to boundary conditions, and in particular, also the friction coefficient at regimes closest to M and H conditions.

[0027] It has also been found that this reduction in various regimes is also maintained when all the other typical components of a formulation for engine oil are added.

[0028] Furthermore, it has been found that, after laboratory aging tests, the SLC only undergoes slight modifications.

[0029] It has also been discovered, from engine tests, that the advantage measured in laboratories on an SLC level can be found in terms of f.e. at the end of the test, also confirming the performance duration.

[0030] In addition to the essential components (a), (b) and (c), the lubricating composition used in the present invention can contain one or more components normally used in formulations for engines oils, for example viscosity index enhancers and/or viscosity modifiers, dispersing agents, antioxidants, anti-rust agents, anti-foam agents, demulsifiers, pour point depressants.

[0031] Ashless nitrogenated dispersing agents typically used normally comprise oil-soluble polymeric structures functionalized with nitrogenated substituents capable of aggregating with polar particles or substances to be dispersed. The dispersing agents typically contain one or more nitrogenated parts bound to the polymeric skeleton, often by means of a bridge, and can be selected from all the known oil-soluble derivates, such as salts, amides, imides, amino-esters, oxyazolinic derivatives of mono or dicarboxylic acids with a long hydrocarbon chain and relative hydrocarbon anhydrides; long-chain thiocarboxylates of hydrocarbons to which a polyamine is directly bound; Mannich condensation products formed by condensation between long-chain substituted phenols with formaldehyde and polyalkylene polyamines. Numerous examples of dispersing agents are indicated in patent literature, for example in US-A-5,962,381.

[0032] Non-nitrogenated dispersing agents also exist, for example esters prepared by reaction between functionalized oil-soluble polymeric hydrocarbons and hydroxyl compounds, such as mono or polycarboxylic alcohols, or with aromatic compounds such as phenols and naphthols. Ester dispersing agents can also be prepared starting from unsaturated alcohols such as allyl alcohol, or starting from ether-alcohols.

[0033] Convenient viscosity modifiers (or viscosity index enhancers) which can be added to the lubricating composition of the present invention comprise oil-soluble polymers having an weight average molecular weight ranging from about 10,000 to about 1,000,000, preferably from about 20,000 to about 500,000, as determined by gel permeation chromatography or light scattering methods. Typical examples of these polymers comprise polyisobutene, ethylene/propylene/alphaolefin copolymers, (co)polymethacrylates, copolymers of styrene and acrylic esters, copolymers of vinyl compounds and unsaturated carboxylic acids; partially hydrogenated copolymers of styrene and isoprene, styrene and butadiene, isoprene and butadiene; partially hydrogenated homopolymers of butadiene and isoprene.

[0034] Viscosity modifying compounds also exist, which act as dispersing agents - viscosity modifiers, see for example US-A-4,089,794; US-A-4,160,739 and US-A-4,137,185. Other dispersing agents - viscosity modifiers are ethylene or propylene copolymers grafted with nitrogenated compounds, see for example US-A-4,068,056, US-A-4,146,489 and US-A-4,149,984.

[0035] The f.e. lubricating composition of the present invention can also contain antioxidants, which reduce the tendency of mineral oils to degrade by thermo-oxidation during their use. Typical examples of these antioxidants are hindered phenols, variously substituted aromatic amines, salts of alkaline-earth metals of alkylphenol thioesters having C_5 to C_{12} side chains, calcium nonylphenol sulfide, oil-soluble phenates, sulfurized phenates.

[0036] Typical anti-rust compounds which can be used in the lubricating composition of the present invention are polyoxyalkylene polyols and relative esters, and polyoxyalkylene phenols.

[0037] In the present invention, it is also possible to use small quantities of demulsifying agents. Preferred demulsifying agents can be obtained by the reaction between an alkylene oxide and an adduct obtained by reacting a bis-epoxide with a polyhydroxyl alcohol (see EP-A-330,522).

[0038] Anti-foam agents which can be used are compounds of the polysiloxane type, for example silicon oil or polydimethyl siloxanes.

[0039] Other additives are pour point depressants which lower the minimum temperature at which the fluid flows and can be poured. Typical examples of these additives which improve the fluidity at low temperatures of the lubricating composition are the well-known dialkyl fumarate/vinyl acetate copolymers and polyalkyl methacrylates.

[0040] The lubricating composition of the present invention is prepared by the conventional mixing of the various components, both essential and complementary.

[0041] In a complete formulation for engine oil, the lubricating composition of the present invention is characterized by a more favourable SLC with respect to the corresponding formulation without these specific detergent and anti-wear additives. This advantage can be observed along the whole measurement rate range, thus being indifferently apparent in one or more of the "hydrodynamic", elasto-hydrodynamic", "mixed" and "boundary" conditions.

[0042] The following examples are provided for a better understanding of the present invention.

EXAMPLES

Method for evaluating the lubricating compositions

[0043] The friction coefficient measurements on lubricating compositions were effected by the application of a special measurement method under rolling-sliding conditions. A brief description is provided, for example, in the article of G. Tripaldi, S. Fattori, R. Nodari, A. Vettor "An Investigation on the Antifriction Performance of Some Organo-molybdenum Additives", Lubrication at the frontier, D. Dowson et al. Editors, 1999 Elsevier Science B.V. pages 751-758. This method envisages the use of a ball-on-disk tribometer capable of subjecting the test-samples to independent rotation rates, thus varying the ratio between the sliding rate and rolling rate [slide-to-roll (S/R) ratio]. A preparative operating sequence of the instrument was prepared, gradual heating from a low to high temperature (from 40 to 135°C), friction coefficient measurements by curves at various S/R values, and the construction of the SLC. As an example, an SLC curve of this type (obtained in the final phase at 135°C), useful for evaluating potential energy dissipations, is indicated in Figure 1. In terms of reliability, each curve is constructed with average data of at least two tests and the standard deviation is always lower than 10%. The friction coefficient values are extracted from these curves at the inlet rates of 0.01 - 0.1 - 1.0 m/sec (figure 1); these values were considered, for the sake of comparison, as being representative of the boundary, mixed and hydrodynamic (or elasto-hydrodynamic) lubrication regimes (B, M, H) respectively. The relative comparison between the terns of friction coefficient values thus obtained on the various mixtures, rather than their absolute value, allows a conclusion to be reached as to their fuel economy potentiality.

Organization of the formulations used

[0044] In the following examples, the formulations indicated, object of the claim, are cited with the abbreviations F1 to F17; in the case of Comparative Formulations, this abbreviation is accompanied by a C. The compositions of the same and the overall results of the friction coefficient measurements are indicated in Table 1. The structures of the additives of interest are specified in the footnotes. All the formulations, as well as the additives and base oils explicitly mentioned, contain the same additional components, added to complete the necessary performances of a high quality engine oil without additives with a specific antifriction action.

TABLE 1

Ex. Nr	Formulations	Detergents % w/w	Antiwear % w/w	Friction % w/w	Base oil	Friction coefficients		
						B	M	H
1	F1-C	SF 2.6	DTP1-A 1.3	-	PAO	0.1291	0.1127	0.0537
	F2	SFF1 2.9	"	-	"	0.1135	0.0698	0.0150
	F3-C	SL 2.7	"	-	"	0.1249	0.1178	0.0644
2	F4-C	SF 2.6	DTP2-A 1.3	-	"	0.1330	0.1256	0.0736
	F5-C	SFF1 2.9	"	-	" 0.1280	0.1280	0.1163	0.0543
	F6-C	SL 2.7	"	-	"	0.1302	0.1202	0.0644
3	F7-C	SF 2.6	DTP1-B 1.3	-	XHVI	0.1301	0.1205	0.0487
	F8	SFF1 2.9	"	-	"	0.0950	0.0611	0.0238
	F9-C	SL 2.7	"	-	"	0.1201	0.1121	0.0458

(continued)

Ex. Nr	Formulations	Detergents % w/w	Antiwear % w/w	Friction % w/w	Base oil	Friction coefficients		
						B	M	H
4	F10-C	SFF2 2.8	DTP2-B 1.3	-	PAO	0.1330	0.1256	0.0636
	F11	SFF2 2.8	DTP1-A 1.3	-	"	0.1030	0.0593	0.0144
5	F12	SFF1 2.9	DTP1-A 1.3	MoDTC 1.6	"	0.0501	0.0592	0.0177
	F13	SFF1 2.9	"	GMO 1.0	"	0.1101	0.0558	0.0123
	F14-C	SF 2.6	"	GMO 1.0	"	0.1202	0.0702	0.0320
	F15-C	SL 2.7	"	GMO 1.0	"	0.1104	0.0689	0.0490
6	F16-C	SF 2.6	DTP2-A 1.3	MoDTC 1.6	XHVI	0.0580	0.0601	0.0511
	F17	SFF2 2.9	DTP1-B 1.3	-	"	0.0910	0.0570	0.0105

Note to Table 1:
- SF = superbasic calcium alkylbenzene sulfonate (TBN = 300), wherein the alkyl grouping is C_{15};
- SFF1 = superbasic calcium sulfophenate (TBN = 250), having general formula (I) wherein n = 1.8; R=R'=C_{12} in a prevalently para position with respect to the -OH groups;
- SFF2 = superbasic calcium sulfophenate (TBN = 150), having general formula (I) wherein n = 1.8; R=R'=C_9 in a prevalently para position with respect to the -OH groups;
- SL = superbasic calcium salicylate, TBN = 280
- DTP1-A alkyl zinc dithiophosphate from primary C_4/C_5 alcohols;
- DTP2-A alkyl zinc dithiophosphate from secondary C_3/C_6 alcohols;
- DTP1-B alkyl zinc dithiophosphate from primary C_8 alcohols;
- DTP2-B alkyl zinc dithiophosphate from secondary C_4 alcohols;
- MoDTC = molybdenum dithiocarbamate;
- GMO = glycerin mono-oleate.

EXAMPLE 1

[0045] The formulations relating to this example (F1-C, F2, F3-C), together with the common complementary components, all envisage the use of an anti-wear additive zinc dithiophosphate of primary alcohols (DTP1-A), as per Table 1. For the formulation F1-C, a sulfonate detergent (SF) however was used, for F2, a sulfophenate (SFF1), and for F3-C a salicylate (SL), all superbasic.

[0046] The results of the SLC are indicated in Table 1.

Comments

[0047] The considerable advantage in terms of low friction, resulting from the data of the F2 formulation containing the additive sulfophenate/dithiophosphate of primary alcohols, is evident.

EXAMPLE 2

[0048] The formulations relating to this comparative example (F4-C, F5-C, F6-C) were prepared with the same procedure as the previous ones, only varying the anti-wear additive: DTP2-A was selected, see the Note to Table 1, which is a zinc dithiophosphate of secondary alcohols. The results of the SLC are indicated in Table 1.

Comments

[0049] These results show that by substituting the dithiophosphate of primary alcohols (DTP1-A) of the present invention with dithiophosphate of secondary alcohols (DTP2-A), the friction coefficients remain higher not only with the sulfonate and salicylate detergents, but also in the presence of sulfophenate.

EXAMPLE 3

[0050] The formulations of this example all contain a primary zinc alkyl dithiophosphate anti-wear additive, but with a different organic structure from the previous one (DTP1-B, see the Note to Table 1). The formulation F7-C contains the detergent SF, F8 the detergent SFF1, F9-C the detergent SL. A "non-conventional" base oil XHVI obtained from the hydroisomerization process of waxes, was also used.

Comments:

[0051] Although varying the structure of the anti-wear additive and the type of base oil, also in this case, the results show the greater antifriction validity of the combination of sulfophenate/primary dithiophosphate additives (F8) with respect to those with SF and SL detergents (F7-C and F9-C respectively), with a differentiated action in the three regimes.

EXAMPLE 4

[0052] Both of the formulations F10-C and F11 were prepared with PAO bases and with superbasic sulfophenate detergent SFF2, having a different structure with respect to that used in the other examples (see the Note to Table 1). Furthermore:

** F10-C contains an anti-wear additive zinc dithiophosphate of secondary alcohols (DTP2-B) with different organic structures from the previous one;
** F11 contains the same anti-wear additive zinc dithiophosphate of primary alcohols already used in Example 1 (DTP1-A).

Comments

[0053] Also in this case, with a different superbasic sulfophenate, the friction coefficient data confirm the synergic action of the sulfophenate/primary dithiophosphate pair, with respect to the analogous sulfophenate/secondary dithiophosphate pair.

EXAMPLE 5

[0054] As the sulfophenate/primary dithiophosphate pair shows unexpected antifriction performances, it is important to verify that said performances are compatible and coherent with respect to additives specifically commercialized as antifriction agents, particularly with respect to Molybdenum additives and ashless additives of an ester nature (see the state of the art). For this purpose, 4 formulations were prepared, all containing an anti-wear agent zinc dithiophosphate of primary alcohols DTP1-A. Of these, the first two (F12, F13) also contain the other component which serves for the antifriction synergy claimed (a sulfophenate, SFF1). Furthermore, the first (F12) also contains a Molybdenum anti-wear additive (MoDTC), whereas the second (F13) contains an ashless ester antifriction additive (GMO).
[0055] The further formulations F14-C and F15-C, both containing the antifriction additive GMO, contain a sulfonate (SF) and salicylate (SL) detergent, respectively.

Comments

[0056] With respect to the formulation F2, object of the invention, the addition of the two antifriction additives described (F12 and F13) allows some of the friction coefficient values to be improved, demonstrating a good compatibility, from this point of view, of the synergic pair towards additives of both species. The results obtained from the further comparative formulations F14-C and F15-C show, on the other hand, that the specific addition of the anti-friction additive GMO, in formulations without the pair of synergic additives claimed, does not provide better results with respect to the F2, object of the invention.

EXAMPLE 6

[0057] The formulations F16-C and F17 are based on XHVI.

[0058] The formulation F16-C is characterized by a detergent addition to the superbasic sulfonate (SF), anti-wear agent dithiophosphate of secondary alcohols DPT2-A, but with the addition of Molybdenum antifriction agent to try and recuperate a low friction performance on a formulation which does not contain the synergic pair, object of the invention. The formulation F17 of the present invention, on the other hand, contains the synergic pair (SFF2/DTP1-B) but without antifriction agent.

Comments

[0059] The results obtained with the formulation F16-C illustrate a case of partial functioning of the Molybdenum additive, probably due to antagonism with other additives; good results from the SLC are in fact only obtained at boundary regimes (with respect to the corresponding F4-C). The formulation F17, without Molybdenum antifriction additive, shows less attractive friction coefficients at boundary regime with respect to the previous one with Molybdenum, however it recovers better values at less severe regimes (above all H regimes).

Engine evaluations

[0060] Various compositions with significant SLC friction curves, inserted in the same formulation context, were subjected to engine fuel economy evaluation, according to methods prescribed by performance specifications of engine oils.

[0061] For this purpose, the following tests were used: ASTM Sequence VIB engine test, required by ILSAC (International Lubricant Standardization and Approval Committee) and API (American Petroleum Institute) specifications, and the fuel economy test with a Mercedes M111 engine, required by ACEA (Association des Constructeurs Européens d'Automobiles) specifications.

[0062] Both tests measure, in different engines and operating conditions, the improvement in the fuel economy (Fuel Economy Improvement, FEI) with respect to a specific reference oil of the single tests.

[0063] In the Sequence VIB test, the fuel economy measurement takes place in two distinct phases, one which precedes the aging of the oil (phase I) and the other which follows it (phase II), so that the fuel economy retention can also be evaluated; in the case of the test with an M111 engine, on the other hand, the measurements only refer to the non-aged oil.

[0064] The results obtained are indicated in Table 2 below.

TABLE 2

Formulation	Detergent w%	Antiwear w%	Anti-friction w %	Base oil	FEI %		
					Sequence VIB		M111 FE
					PHASE 1	PHASE 2	
F7-C	SF 2.6	DTP1-B 1.3	—	XHVI	1.2	0.9	
F8	SFF1 2.9	"	—	"	1.6	1.3	2.64
F16-C	SF 2.6	DTP2-A 1.3	MoDTC 1.6	"	1.1	0.7	
F18	SFF1 2.9	DTP1-B 1.3	MoTA 1.5	"	1.7	1.3	2.76

[0065] As can be observed from Table 2, the formulation which in the group of additives contains the superbasic sulfophenate/primary zinc dithiophosphate pair (F8), object of the present invention, with the Mercedes M111 test, has an FEI value which exceeds the limit of the ACEA A1-B1 specifications (2.5%).

[0066] The same formulation, containing the same pair superbasic sulfophenate/zinc dithiophosphate of primary alcohol, provides good results also with the Sequence VIB test, with FEI values coinciding with the limits of the ILSAC GF3 specification.

[0067] Other compositions tested in this context, containing combinations of detergents/anti-wear agents of a different type (F7-C) from those of the present invention, even with the addition of a molybdenum friction modifying additive (F16-C), provide insufficient results with the Sequence VIB test.

[0068] Finally, the formulation F18 shows a good compatibility of the synergic combination object of the present invention with a Molybdenum friction modifier (MoTA = Mothioamide) which however, in the case of the example, does not lead to any significant improvements in the oil fuel economy.

Claims

1. Use as friction reducing additive for lubricating compositions for internal combustion engines comprising a base oil having a viscosity suitable for lubricating, of an additive composition comprising:

   (i) detergent additives, at least 60% by weight of said detergent additives being selected from sulfophenates having general formula (I) RΦ(OH)-S_n-(OH)ΦR', wherein R and R', the same or different, are alkyl radicals having from 1 to 16 carbon atoms, n ranges from 1 to 5; and wherein both the hydroxyls are salified with one or more alkaline-earth metals;
   (ii) anti-wear additives selected from zinc dithiophosphates having general formula (II) $ZnP_2S_4O_4R_4$, wherein R is an alkyl radical having the formula -CH_2R_5, wherein R_5 is a linear and/or branched saturated alkyl radical, having from 2 to 15 carbon atoms;

   wherein said additive composition is added to the lubricating composition in an amount so as to obtain: a quantity of detergent additives (i) ranging from 0.5% to 5.0% by weight with respect to the total weight of the lubricating composition; a quantity of anti-wear additives (ii) ranging from 0.3% to 5.0% by weight with respect to the total weight of the lubricating composition.

2. The use according to claim 1, wherein said additive composition is added to the lubricating composition in an amount so as to obtain a quantity of the detergent additives (i) from 1.0 to 4%, with respect to the total weight of the lubricating composition.

3. The use according to claim 1, wherein said additive composition is added to the lubricating composition in an amount so as to obtain a quantity of the anti-wear additives (ii) ranging from 0.8 to 3.0%, with respect to the total weight of the lubricating composition.

4. The use according to claim 1, wherein at least 70% by weight of the detergent additives (i) is selected from sulfophenates having general formula (I).

5. The use according to claim 1, wherein, with reference to the compound having general formula (I), n ranges from 1 to 4.

6. The use according to claim 1, wherein, with reference to the compound having general formula (I), both the hydroxyls are in para position with respect to R and R'.

7. The use according to claim 1, wherein, with reference to the compound having general formula (I), both the hydroxyls are salified with calcium.

8. The use according to claim 7, wherein the detergent additive salified with calcium having general formula (I) has a total base number (TBN) ranging from 50 to 400.

9. The use according to claim 8, wherein the detergent additive salified with calcium having general formula (I) has a total base number (TBN) ranging from 100 to 300.

10. The use according to claim 1, wherein the detergent additives (i) comprise from 0% to 40% by weight, of detergents, different from the compounds having general formula (I), selected from calcium sulfonates, calcium alkylbenzene sulfonates, calcium salicylate.

11. The use according to claim 1, wherein, in the compound having general formula (II), R is an alkyl radical having the formula -CH_2R_5, wherein R_5 is a linear and/or branched saturated alkyl radical having from 2 to 7 carbon atoms.

12. The use according to claim 11, wherein R_5 is selected from: -$(CH_2)_3CH_3$, -CH (CH_3) CH_3, -$C(CH_3)_3$, and relative mixtures.

13. The use according to claim 1, wherein the base oils (a) have a viscosity, measured at 100°C, ranging from 2.0 to 10 mm^2/s.

14. The use according to claim 13, wherein the base oil has a viscosity, measured at 100°C, ranging from 2.5 to 8 mm^2/s.

15. The use according to claim 1, wherein the base oil is selected from one or more of mineral or synthetic oils.

16. The use according to claim 1, wherein R and R', the same or different, are alkyl radicals having from 9 to 12 carbon atoms.

Patentansprüche

1. Verwendung einer Additivzusammensetzung als reibungsverringerndes Additiv für Schmiermittelzusammensetzungen für Verbrennungsmotoren, umfassend ein Basisöl mit einer Viskosität, die zum Schmieren geeignet ist, wobei die Additivzusammensetzung umfasst:

   (i) Detergensadditive, wobei mindestens 60 Gew.-% der Detergensadditive ausgewählt sind aus Sulphenaten mit der allgemeinen Struktur (I) $R\Phi(OH)\text{-}S_n\text{-}(OH)\,\Phi R'$, wobei R und R' gleich oder unterschiedlich Alkylreste mit von 1 bis 16 Kohlenstoffatomen sind, n von 1 bis 5 reicht; und wobei beide Hydroxyle mit einem oder mehreren Erdalkalimetallen versalzt sind;
   (ii) Abriebfeste Additive ausgewählt aus Zinkdithiophosphaten mit der allgemeinen Formel (II) $ZnP_2S_4O_4R_4$, wobei R ein Alkylrest mit der Formel $-CH_2R_5$ ist, wobei R_5 ein lineares und/oder verzweigtes gesättigtes Alkylrest ist, mit 2 bis 15 Kohlenstoffatomen;

   wobei die Additivzusammensetzung zu der Schmiermittelzusammensetzung in einer Menge so hinzugefügt wird, dass eine Menge an Detergensadditiven (i) die von 0,5 Gew.-% bis 5,0 Gew.-% bezogen auf das Gesamtgewicht der Schmiermittelzusammensetzung reicht; eine Menge an Abriebfesten Additiven (ii) die von 0,3 Gew.-% bis 5,0 Gew.-% bezogen auf das Gesamtgewicht der Schmiermittelzusammensetzung reicht, zu erhalten.

2. Verwendung nach Anspruch 1, wobei die Additivzusammensetzung zu der Schmiermittelzusammensetzung in so einer Menge hinzugefügt wird, um eine Menge an Detergensadditiven (i) von 1,0 bis 4%, bezogen auf das Gesamtgewicht der Schmiermittelzusammensetzung zu erhalten.

3. Verwendung nach Anspruch 1, wobei die Additivzusammensetzung zu der Schmiermittelzusammensetzung in so einer Menge hinzugefügt wird, um eine Menge von abriebfesten Additiven (ii) reichend von 0,8 bis 3,0% bezogen auf das Gesamtgewicht der Schmiermittelzusammensetzung zu erhalten.

4. Verwendung nach Anspruch 1, wobei mindestens 70 Gew.-% der Detergensadditive (i) ausgewählt ist aus Sulphophenaten mit der allgemeinen Formel (I).

5. Verwendung nach Anspruch 1, wobei bezogen auf die Verbindung mit der allgemeinen Formel (I) n von 1 bis 4 reicht.

6. Verwendung nach Anspruch 1, wobei bezogen auf die Verbindung mit der allgemeinen Formel (I) beide Hydroxyle in der Paraposition bezogen auf R und R' sind.

7. Verwendung nach Anspruch 1, wobei bezogen auf die Verbindung mit der allgemeinen Formel (I) beide Hydroxyle mit Calcium versalzt sind.

8. Verwendung nach Anspruch 7, wobei das mit Calcium versalzte Detergensadditiv mit der allgemeinen Formel (I) eine Gesamtbasenzahl (total base number, TBN) die von 50 bis 400 reicht, aufweist.

9. Verwendung nach Anspruch 8, wobei das mit Calcium versalzte Detergensadditiv mit der allgemeinen Formel (I) eine Gesamtbasenzahl (total base number, TBN) die von 100 bis 300 reicht, aufweist.

10. Verwendung nach Anspruch 1, wobei die Detergensadditive (i) von 0 Gew.-% bis 40 Gew.-% an Detergentien, die sich von den Verbindungen mit der allgemeinen Formel (I) unterscheiden, ausgewählt aus Calciumsulphonaten, Calciumalkylbenzolsulphonaten, Calciumsalicylat umfassen.

11. Verwendung nach Anspruch 1, wobei in der Verbindung mit der allgemeinen Formel (II), R ein Alkylrest mit der Formel $-CH_2R_5$ ist, wobei R_5 ein lineares und/oder verzweigtes, gesättigtes Alkylrest mit 2 bis 7 Kohlenstoffatomen ist.

12. Verwendung nach Anspruch 11, wobei R_5 ausgewählt ist aus: $-(CH_2)_3CH_3$, $-CH(CH_3)CH_3$, $-C(CH_3)_3$, und relativen

Mischungen.

13. Verwendung nach Anspruch 1, wobei die Basisöle (a) eine bei 100°C gemessene Viskosität im Bereich von 2,0 bis 10 mm^2/s aufweisen.

14. Verwendung nach Anspruch 13, wobei das Basisöl eine bei 100°C gemessene Viskosität im Bereich von 2,5 bis 8 mm^2/s aufweist.

15. Verwendung nach Anspruch 1, wobei das Basisöl ausgewählt ist aus einem oder mehreren von Mineralölen oder synthetischen Ölen.

16. Verwendung nach Anspruch 1, wobei R und R' gleich oder unterschiedlich Alkylreste mit von 9 bis 12 Kohlenstoffatomen sind.

Revendications

1. Utilisation comme additif réduisant la friction pour des compositions lubrifiantes pour des moteurs à combustion interne comprenant une huile de base présentant une viscosité adaptée à la lubrification, d'une composition d'additifs comprenant :

   (i) des additifs détergents, au moins 60 % en poids desdits additifs détergents étant sélectionnés parmi des sulfophénates présentant une formule générale (I) $R\Phi(OH)\text{-}S_n\text{-}(OH)\Phi R'$, dans laquelle R et R' sont des radicaux d'alkyle identiques ou différents présentant 1 à 16 atomes de carbone, n allant de 1 à 5 ; et dans laquelle les deux hydroxyles sont salifiés avec un ou plus métaux alcalino-terreux ;
   (ii) des additifs antiusure sélectionnés parmi des dithiophosphates de zinc présentant une formule générale (II) $ZnP_2S_4O_4R_4$, dans laquelle R est un radical d'alkyle présentant la formule $-CH_2R_5$, dans laquelle R5 est un radical d'alkyle saturé linéaire et/ou ramifié présentant 2 à 15 atomes de carbone ;

   dans laquelle ladite composition d'additifs est ajoutée à la composition lubrifiante dans une quantité de sorte à obtenir : une quantité d'additifs détergents (i) allant de 0,5 à 5 % en poids par rapport au poids total de la composition lubrifiante ; une quantité d'additifs antiusure (ii) allant de 0,3 à 5 % en poids par rapport au poids total de la composition lubrifiante.

2. Utilisation selon la revendication 1, dans laquelle ladite composition d'additifs est ajoutée à la composition lubrifiante dans une quantité de sorte à obtenir une quantité d'additifs détergents (i) allant de 1,0 à 4 % en poids par rapport au poids total de la composition lubrifiante.

3. Utilisation selon la revendication 1, dans laquelle ladite composition d'additifs est ajoutée à la composition lubrifiante dans une quantité de sorte à obtenir une quantité d'additifs antiusure (ii) allant de 0,8 à 3,0 % en poids par rapport au poids total de la composition lubrifiante.

4. Utilisation selon la revendication 1, dans laquelle au moins 70 % en poids des additifs détergents (i) sont sélectionnés parmi des sulfophénates présentant une formule générale (I).

5. Utilisation selon la revendication 1, dans laquelle en référence au composé présentant une formule générale (I), n varie de 1 à 4.

6. Utilisation selon la revendication 1, dans laquelle en référence au composé présentant une formule générale (I), les deux hydroxyles sont en position para par rapport à R et R'.

7. Utilisation selon la revendication 1, dans laquelle en référence au composé présentant une formule générale (I), les deux hydroxyles sont salifiés avec du calcium.

8. Utilisation selon la revendication 7, dans laquelle l'additif détergent salifié avec du calcium présentant une formule générale (I) a un nombre de base total (TBN) allant de 50 à 400.

9. Utilisation selon la revendication 8, dans laquelle l'additif détergent salifié avec du calcium présentant une formule

générale (I) a un nombre de base total (TBN) allant de 100 à 300.

10. Utilisation selon la revendication 1, dans laquelle les additifs détergents (i) comprennent 0 à 40 % en poids de détergents, différents des composés présentant une formule générale (I), sélectionnés parmi les sulfonates de calcium, les sulfonates de benzène d'alkyle de calcium, le salicylate de calcium.

11. Utilisation selon la revendication 1, dans laquelle dans le composé présentant une formule générale (II), R est un radical d'alkyle présentant la formule $-CH_2R_5$, dans laquelle R_5 est un radical d'alkyle saturé linéaire et/ou ramifié présentant 2 à 7 atomes de carbone.

12. Utilisation selon la revendication 11, dans laquelle R_5 est sélectionné parmi : $-(CH_2)_3CH_3$, $-CH(CH_3)CH_3$, $-C(CH_3)_3$, et des mélanges relatifs.

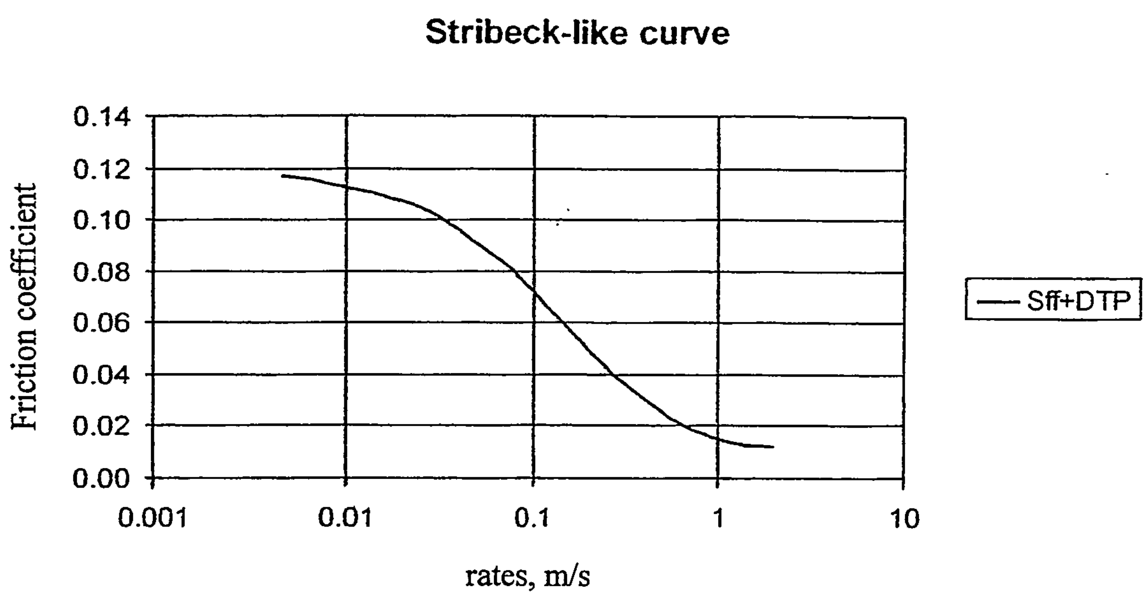
13. Utilisation selon la revendication 1, dans laquelle les huiles de base (a) présentent une viscosité mesurée à 100 °C allant de 2 à 10 mm^2/s.

14. Utilisation selon la revendication 13, dans laquelle l'huile de base présente une viscosité mesurée à 100 °C allant de 2,5 à 8 mm^2/s.

15. Utilisation selon la revendication 1, dans laquelle l'huile de base est sélectionnée parmi une ou plusieurs huiles minérales ou synthétiques.

16. Utilisation selon la revendication 1, dans laquelle R et R' sont des radicaux d'alkyle identiques ou différents présentant 9 à 12 atomes de carbone.

Fig.1


Stribeck-like curve
Friction coefficient
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.001
0.01
0.1
1
10
rates, m/s
Sff+DTP

REFERENCES CITED IN THE DESCRIPTION

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