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(54) Lubricant composition

(57) The present invention relates to a lubricant composition comprising at least one oil-soluble organic molybdenum compound and at least one oil-soluble tungsten compound, with the proviso that the weight ratio of molybdenum to tungsten in the lubricant is at least 2.5:1. The compositions provide unexpected and substan-

tially improved friction and abrasion properties over related compositions devoid of the invention. When using these lubricant compositions, for example in internal combustion engines, the engine power can be increased and the fuel consumption can be reduced.

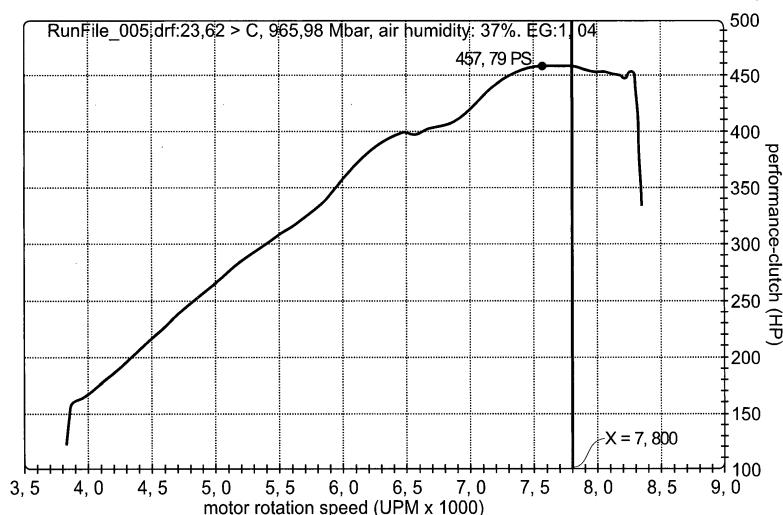


Fig. 1

Description

[0001] The present invention claims priority of U.S. Provisional Patent Application Serial No. 61/779563, filed March 13, 2013, and German Patent Application 10 2013 112 454.2, filed November 13, 2013, the disclosure of each of which is incorporated by reference herein in their entirety.

[0002] The Kyoto Protocol provides for a reduction in the annual greenhouse gas emissions of the industrialized countries within the so-called first commitment period (2008-2012) by an average of 5.2 percent compared to the level of 1990.

[0003] The greenhouse gases regulated by the Kyoto Protocol include the greenhouse gas carbon dioxide (CO₂). The CO₂ emissions are mainly produced by burning fossil fuels, such as gasoline and diesel fuel. For this reason, the global transportation sector, which is expected to be dependent on fossil fuels for the foreseeable future, plays an important and significant role.

[0004] For this reason, the Association of European Automobile Manufacturers ACEA (Association de Constructeurs Européens d'Automobiles) has pledged to the European Union to reduce the average CO₂ emissions from the European vehicle fleet by 25% by the year 2008 compared to 1995.

[0005] Assuming that an average car emitted 186 grams of CO₂/km in 1995, this means for the year 2008 a reduction of emissions to 140 grams of CO₂/km (2008), which is equivalent to a reduction the average fuel consumption to 6.0 liters per 100 kilometers for gasoline vehicles and 5.3 liters for diesel vehicles per 100 kilometers according to the New European Vehicle Cycle (NEFC/NEDC). Binding limits for CO₂ emissions of new cars were agreed to at the EU level at the end of 2008. The corresponding EU Regulation 443/2009 provides that starting in 2012 an average of at least 65 percent of the European new car fleet must not emit more than 130 grams of CO₂/km. By 2015, this limit is applied in several stages to the total fleet with the target of reducing emissions to 95 grams of CO₂/km by 2020.

[0006] An emission standard for motor vehicles sets limits for carbon monoxide (CO), nitrogen oxides (NO_x), hydrocarbons (HC) and particulate matter (PM) and subdivides the vehicles into pollutant classes, to which certain emission code numbers are assigned, which are used, *inter alia*, to calculate the road tax and the assignment to pollutant groups for environmental zones. The limits differ for both the type of the engine (gasoline or diesel) as well as for the type of vehicle (cars, trucks and buses, cycles and mopeds) and are subject to increasing scrutiny in the European Community.

[0007] Since September 1, 2009, the Euro-5 standard is applied throughout Europe to the type test for new passenger cars, which is binding since January 1, 2011 for all newly registered vehicles.

[0008] For trucks, the Euro 6 standard is applied from January 1, 2013 throughout Europe to the type test, which is binding since January 1, 2014 for all newly registered vehicles.

[0009] The types of vehicles found today in all areas of the transportation sector, such as passenger cars, commercial vehicles and buses, motorcycles and mopeds, stationary facilities and marine propulsion and auxiliary machinery, use as an energy source fossil fuels, such as gasoline and diesel fuel, light and heavy fuel oils or gases. The combustion of these fossil fuels produces greenhouse gases, in particular carbon dioxide (CO₂) as a reference value. The road traffic in Germany contributes to about 20% of the CO₂ emissions, making it one of the largest producers of CO₂ emissions.

[0010] The engines used in the transportation sector are subject to extreme demands and operating conditions. Many factors affect the service life, the performance, the driving characteristics, the emissions and much more. A key component for the optimal operation of the engines is the appropriate selection of the engine oil (lubricant).

[0011] High-quality engine oils, especially partially and/or fully synthetic formulations have a positive impact on all relevant factors. In addition to the now well-known beneficial effects, such as reducing the internal friction, reliable lubrication of the moving parts, long-term aging stability (Long-Life), build-up of wear-resistant coatings, good cold start behavior, prevention of deposits and good transport of contaminants, the viscosity gains increasing importance.

[0012] Nearly all European vehicle manufacturers today use engine oils with the viscosity grade 5W-30 (range for passenger cars) and 10W-40 (range for trucks).

[0013] To meet the increasingly stringent demands on the reduction of CO₂ emissions, increasingly developments of ever thinner engine oils are also promoted in addition to structural design measures. Lower viscosity grades, such as e.g. 0W-20 or even 0W-16 are under discussion. However, this may result in a failure/breakage of the lubricating film under severe thermal engine loads, which could cause engine damage.

[0014] Oil-soluble liquid organic molybdenum compounds are known for use as additives for lubricant compositions. Organic molybdenum amide complexes are known, for example, from EP 0 546 357 B1, which can be prepared by the reacting fatty oils with an amino compound and a molybdenum source.

[0015] These organic molybdenum complexes are used due to their friction-reducing (antifriction) and wear-reducing properties and as antioxidants in lubricant additives, for example for engine oils.

[0016] A commercially available lubricant additive is MOLYVAN® 855 distributed by Vanderbilt Chemicals, LLC, which comprises molybdenum complexes of N, N-bis(hydroxyethyl) cocoalkyl amides. The oil soluble molybdenum additive MOLYVAN® 855 is also mentioned in patent US 5,641,731 A, which teaches as preferred a total content of 0.1 wt.-% to 2 wt.-% of molybdenum in the lubricant. Patent US 4,889,647 discloses organic molybdenum complexes of the

aforementioned type as well as structural chemical formulas and manufacturing methods for these compounds; for example, the compounds can be produced from seed oils such as coconut oil, diethanolamine, and molybdenum trioxide. Organic molybdenum complexes that are chemically very similar to these compounds are described in EP 0 546 357 B1. These are also fatty oil amides, wherein the fatty oil is reacted with a 2-(2-aminoethyl) amino ethanol.

5 [0017] Lubricating oil compositions containing alkyl ammonium tungstate compounds having anti-friction and abrasion-reducing properties are described in EP 1 618 172 B1. These are organo-ammonium metal compounds consisting of polytungstate ions and dialkyl-ammonium ions of the type $R_2NH_2^+$, wherein the radicals -R are long-chain alkyl groups. One example for such group is di-tridecyl ammonium tungstate, which can be prepared by reacting tungstic acid hydrate with di-tridecylamine. In the teaching of EP 1 618 172 B1, it is recommended to add this additive based on organo-ammonium tungsten in a sufficient amount so as to produce a final concentration of 0.05 wt.-% to 2.0 wt.-% in the lubricant.

10 [0018] A dialkyl ammonium tungstate compound of the aforementioned type as a lubricant additive is offered by the company Vanderbilt Chemicals, LLC. under the product name VANLUBE® W 324.

15 [0019] US 7,879,777 B2 describes an additive for a lubricating composition which contains a combination of three components, namely a secondary diarylamine antioxidant, an organic molybdenum compound and an organo-ammonium tungsten compound. The organic molybdenum compound may be, for example, a dialkyl-dithio-carbamate or the aforementioned MOLYVAN® 855 (Vanderbilt Chemicals, LLC). Various organo-ammonium tungsten compounds may be used. However, for this known additive for lubricants, weight ratios of these compounds are recommended, wherein the amount of tungsten in the additive is greater than the amount of molybdenum. The recommended weight ratio of molybdenum to tungsten in the additive is 1:2 to 1:8.5, assuming the indicated lower limit and upper limits, respectively.

20 [0020] Even if one selects the maximum amount of the specified range for molybdenum (350 ppm) and the minimum amount of the specified range for tungsten (100 ppm), the ratio of molybdenum: tungsten is about 3.5:1. Furthermore, for this conventional lubricant composition, a maximum content of 350 ppm (0.035 wt.-%) is recommended; larger amounts of molybdenum are viewed as critical to avoid, because they cause formation of deposits in the lubricant so that the lubricant no longer meets the required standards (GF-5 specification).

25 [0021] It is therefore the object of the invention to further improve a lubricant composition of the aforementioned type with respect to reduction of friction, reduction of abrasion, increase in the engine power and reduction of fuel consumption.

[0022] This problem is solved with a lubricant composition according to the invention of the aforementioned type having the features of claim 1.

30 [0023] According to the invention, the lubricant composition is a composition which in addition to other components, is comprised of at least one organic molybdenum compound, also at least one alkyl- or aryl-substituted ammonium tungstate, with the proviso that the ratio by weight of molybdenum to tungsten in the lubricant is at least 2.5:1. Preferably, the lubricant composition has a minimum amount of Mo at greater than 350 ppm, and more preferably, at a maximum of 700 ppm.

35 [0024] Extensive tests in conjunction with the present invention have shown that the combination of organic molybdenum compounds, in particular of the above-mentioned type with organically substituted ammonium tungsten compounds in lubricating compositions have surprisingly lead to unexpected effects, significantly improving various properties of the lubricant composition. Here, surprisingly synergistic effects have been observed, i.e. the combination of the above compounds results in a significantly greater improvement in the desired lubricating properties than would be the case if only one of the two components in the form of additives were added to a lubricant, as long as the two components are admixed to the lubricant with specific relative weight ratios.

40 [0025] It was also found that adding solely the tungsten compound to the lubricant composition does not result in any significant improvement in the desired properties, especially in a reduction of the coefficient of friction and abrasion. The addition of the tungsten compound is only effective when additionally an organic molybdenum compound is also added to the lubricant composition. However, the simultaneous addition of the tungsten compound and the organic molybdenum compound result in a significant improvement in the performance of the lubricant composition in comparison to the exclusive addition of an equivalent amount of the molybdenum compound, which means that the tungsten compound produces an effect when being added simultaneously with the molybdenum compound. This provides clear evidence that the simultaneous addition of the tungsten compound and the molybdenum compound results in a synergistic effect.

45 [0026] In addition, varying degrees of improvements are also attained with the simultaneous addition of both compounds to the lubricating composition, which leads to the conclusion that the ratio of the amounts of molybdenum to tungsten in the lubricant composition affects their preferred properties. It has been observed that there is a range of an optimal ratio for both compounds. The improved properties occur to a lesser extent outside this range, meaning that further addition of one or the other compound to increase or decrease the weight ratio of the two compounds in the lubricant composition produces a less apparent synergistic effect.

50 [0027] The lubricant composition according to the invention can be used, for example, for engine oils, but applications as transmission oil or hydraulic oil may also be considered.

55 [0028] According to a preferred embodiment of the present invention, the weight ratio of molybdenum to tungsten in the lubricant may be between about 3:1 and about 10:1. Preferably, a weight ratio of molybdenum to tungsten in the

lubricant is between about 4:1 and about 8:1. Particularly preferred, the weight ratio of molybdenum to tungsten in the lubricant is in the order of at least about 5:1.

[0028] As already mentioned above, the experiments in the context of the present invention have led to the realization that not only the relative ratio of the two compounds is important, but that also the respective absolute amount of these compounds in the lubricant composition is a factor affecting the properties of the lubricant. For example, the beneficial properties do surprisingly not improve further when the amount of the one or the other compound is increased beyond a certain percentage. Without being restricted to theory, the reason for this may be that the respective organic compounds of molybdenum and tungsten decompose or oxidize when present in larger weight proportions, causing deposits of decomposition and/or oxidation products of these compounds in the lubricant, which may significantly diminish their properties by, for example, causing increased abrasion and increased coefficients of friction or adherence of such products to engine parts. Furthermore, the maximum solubility of the organic molybdenum and tungsten compounds in the lubricant may also play a role. The compounds of the invention have good initial oil solubility; however, chemical changes can be introduced in these compounds by aging and/or temperature effects during operation, also in conjunction with other components of the lubricant, which could then lower the solubility in the lubricant.

[0029] Preferably, in another embodiment of the present invention, the organic molybdenum compound may be added to the lubricant in an amount such that the amount of molybdenum in the lubricant is less than 0.1 wt.-% Mo based on the total weight of the lubricant composition. More preferably, the amount of molybdenum in the lubricant is less than about 0.07 wt.-% (700 ppm) and greater than about 0.038 wt.-% (380 ppm) Mo based on the total weight of the lubricant composition. It has been shown within the context of the present invention that contrary to the information in the prior art, an amount of more than 400 ppm of molybdenum in the lubricant produces particularly advantageous properties of the lubricant, when a comparatively small amount of ammonium tungstate is added within the range of the aforementioned weight ratios of Mo and W. This was by no means expected based on the disclosure of the above-mentioned US 7,879,777 B2.

[0030] The ammonium tungstate is preferably added to the lubricant composition in an amount such that the amount of tungsten in the lubricant is less than 0.05 wt.-% based on the total weight of the lubricant composition. More preferably, the amount of tungsten in the lubricant is less than or equal to 0.02 wt.-% (200 ppm) based on the total weight of the lubricant composition. The amount of tungsten in the lubricant may, for example, only be about 0.01 wt.-% (100 ppm) or below 100 ppm, for example in the range from about 50 ppm to about 95 ppm.

[0031] Preferably, within the context of the present invention, an organic molybdenum compound in the form of an organic molybdenum complex is used, which is prepared starting from at least one long chain fatty oil, diethanolamine or 2-(2-aminoethyl) amino ethanol, and molybdenum trioxide. Particularly preferred are compounds wherein the long chain fatty acid oil is an oil of a saturated fatty acid having 8 to 18 carbon atoms, in particular selected from the group comprising caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid or stearic acid, or an unsaturated fatty acid with up to 18 C-atoms, in particular oleic acid or linoleic acid, or a mixture of two or more fatty acid oils of the aforementioned type. Within the context of the invention, for example organic molybdenum compounds of the aforescribed type can be used, as are present in the additive having the trade name MOLYVAN® 855 manufactured by the company Vanderbilt Chemicals, LLC, which has been mentioned above, as well as in the corresponding cited patents.

[0032] Preferably, within the context of the present invention, an ammonium tungstate in the form of an organo-ammonium metal compound is used, including polytungstate ions and dialkyl-ammonium ions of the type $R_2NH_2^+$, wherein the radicals -R are long chain alkyl groups, for example, tridecyl groups.

[0033] Another object of the present invention is a method for preparing a lubricant composition of the aforementioned type, wherein the lubricant composition is prepared by adding one or more additives to a base lubricant composition.

[0034] The lubricant composition according to the invention may be prepared, for example, by adding to a lubricant base composition a first additive containing the organic molybdenum compound in a higher concentration and a second additive containing the ammonium tungstate in a higher concentration, wherein the first additive and the second additive are each added to the lubricant composition in a suitable amount resulting in the respective percentages of molybdenum and tungsten and the weight ratio of molybdenum to tungsten in the final lubricating composition commensurate with the above results.

[0035] Alternatively, however, the lubricant composition can also be prepared by using only a single additive, wherein in this variant the additive includes both the organic molybdenum compound in a higher concentration as well as the ammonium tungstate in a higher concentration, wherein the additive contains the molybdenum compound and the ammonium tungstate in a defined relative weight ratio and wherein the additive with the aforementioned combined ingredients is added to the lubricant composition in such an amount so that the respective percentage of molybdenum and tungsten, as well as the weight ratio of molybdenum to tungsten, results in the final lubricant composition commensurate with the above discussion.

[0036] The features recited in the dependent claims relate to preferred further developments of the solution of the object according to the invention. Further advantages of the invention will become apparent from the following detailed description.

[0037] Exemplary embodiments of the present invention will now be described with reference to the appended drawings, which show in:

5 Figure 1 a diagram illustrating the engine power in hp of a test vehicle which was tested with an engine oil according to the present invention, as a function of engine speed;

Figure 2 a diagram illustrating in a comparison the coefficients of friction for various engine oil compositions measured in a test apparatus.

10 **Example 1:**

[0038] Engine oils prepared by adding additives based on a combination of the organic ammonium tungsten compound (VANLUBE® W 324) and the organic molybdenum compound (MOLYVAN® 855, both available from Vanderbilt Chemicals, LLC, Norwalk Connecticut, USA) to a freely selected standard engine oil formulation for internal combustion engines, were tested with regard to a reduction of fuel consumption (fuel economy) and CO₂ emission levels and compared in each case with a reference oil.

[0039] The following reference oil was used: Castrol Edge FST 5W-30.

[0040] Two oil formulations according to the invention with the designation "Pantere Speed 5W-30" by the Applicant were compared therewith, wherein one oil with the test number T0438-13/0003 contained the aforementioned molybdenum compound and the tungsten compound in a ratio of 5:1 and the other oil with the test number T0438-13/0004 contained the aforementioned molybdenum compound and the tungsten compound in a ratio of 6:1. The aforementioned molybdenum compounds and tungsten compounds were added to the reference oil in the form of additives. It should be noted that the reference oil is a recommended oil meeting the highest standards, which is regarded in the industry as an already-optimized oil in terms of friction properties. The fuel consumption was compared in each case with the fuel consumption when using the reference oil.

[0041] The experiments were performed at the internationally recognized and accredited company ISP Salzbergen GmbH & Co. KG, wherein the strict driving conditions according to the NEDC cycle (New European Driving Cycle) were applied. A BMW 520d (F10) was used as a test vehicle. The results are listed in Table 1 below. A chassis dynamometer of the type ECDM 48L-4x4 from the company MAHA-AIP GmbH & Co. KG and a gas sampling and analysis system from the company Horiba MEXA-7400HLE and Horiba CVS-7400S were used for the experiments, with the gases CO/CO₂, NO_x and HC being analyzed.

Table 1

Summary of test results					
Test No.	Oil Designation	Fuel Consumption [L/100km]	Average Fuel Consumption [L/100 km]	Minimum Consumption Compared to T0438-13/0002 [%]	Scattering [%]
T0438-13/0002	Castrol Edge FST 5W-30	4.85	4.85	---	0.00
		4.85			
T0438-13/0003	Pantere Speed 5W-30	4.79	4.78	1.44	0.42
		4.77			
T0438-13/0004	Pantere Speed 5W-30	4.80	4.77	1.65	1.25
		4.74			
		4.76			
		4.78			

[0042] The results listed in the table above indicate that the oil formulations according to the invention reduce the fuel consumption of a warm engine by 1.44% and 1.65%, respectively, compared to the reference oil. These values were obtained under strict experimental test conditions, simulating ideal driving conditions of the engine, which is usually not attainable under actual traffic conditions. The experience gained by the applicant has demonstrated that significantly greater fuel economy can be attained with common driving in traffic.

Example 2:

[0043] It could be demonstrated with a sports car Model GT 3 from the company Porsche having a standard rated power of 420 hp that the use of a lubricant composition according to the invention as engine oil results in a significant increase in the engine power. This is illustrated in the graph of Figure 1. The engine power of the test vehicle was measured on a dynamometer. The nominal power of this individual test vehicle measured by the manufacturer during a factory acceptance test was 435 hp. Figure 1 shows that a nominal power of about 458 hp was measured when a lubricant composition according to the invention with the designation Pantere Racing 10W60 was used in the vehicle, which represents an increase of power of more than 5%, which is due solely to the use of the lubricant.

Example 3:

[0044] Friction and wear characteristics were measured in tests with a vibration-friction-wear tester (SRV), whereby different oils for truck engines having compositions according to the invention were tested with the two molybdenum and tungsten compounds mentioned in Example 1 and having varying composition ratios and compared with a reference oil LSAP 10W-40, which did not contain these compounds. In this SRV test, a steel ball was moved back and forth under pressure on a steel plate with an oscillating motion.

[0045] The test results are shown in the following Table 2 and illustrated in the graph of Figure 2. Two experiments were performed for each oil composition, with minimum, maximum and final friction values shown in Figure 2. Figure 2 clearly shows that the coefficients of friction for all oil compositions according to the invention 2 to 8 are improved over those of the reference oil 1. Particularly advantageous are the values for the oil 2, which has a ratio of Mo:W in the oil of about 6:1, and the absolute amounts of the Mo-compound were 505 ppm and of the tungsten compound 84 ppm.

Table 2

Determination of friction and wear characteristics in Oscillation friction wear tester (SRV)										
Sample	Run	Wear Scar Diameter [\emptyset , μm]			Friction Coefficient [μ]			Mo:W ppm	Mo:W	
		\emptyset_1	\emptyset_2	$\emptyset_{\text{Average}}$	μ_{min}	μ_{max}	μ_{end}			
oil 1	1	495	484	490	0.11	0.12	0.12	---	---	
	2	484	482	483	0.11	0.13	0.17			
oil 2	1	523	478	501	0.06	0.09	0.07	505:84	6:1	
	2	512	488	500	0.06	0.10	0.07			
oil 3	1	511	509	510	0.07	0.10	0.07	492:98	5:1	
	2	518	495	507	0.07	0.09	0.07			
oil 4	1	535	505	520	0.07	0.10	0.07	482:118	4:1	
	2	516	514	515	0.07	0.11	0.07			
oil 5	1	500	484	492	0.07	0.10	0.07	442:148	3:1	
	2	500	493	497	0.07	0.10	0.07			
oil 6	1	515	495	505	0.07	0.10	0.08	393:197	2:1	
	2	530	523	527	0.08	0.11	0.08			
oil 7	1	516	495	506	0.08	0.13	0.09	295:295	1:1	
	2	505	497	501	0.08	0.10	0.08			
oil 8	1	514	493	504	0.09	0.11	0.09	197:393	1:2	
	2	499	466	483	0.1	0.11	0.10			
Date of test		: October 2013				Normal force		: 300 N		
Tester		: Rigo				Frequency		: 20 Hz		
Test Specimen		: Disc 100Cr6; \emptyset 24 x 7.9 mm [Rz 0.5 μm] lapped				Temperature		: 40-140°C		
		: Ball 100Cr6, \emptyset 10 mm, DIN 51401-2, polished				Time		: 100 min		

[0046] The improvement over the reference oil becomes gradually smaller with decreasing molybdenum content and increasing tungsten content. Very good results are obtained with the oils 2 to 5. For the oil 5, the ratio of molybdenum to tungsten is 3:1 and the absolute amount of molybdenum was 442 ppm.

Example 4:

[0047] The ability of the inventive combination to retain or improve the frictional performance of an aged lubricating oil was tested. The aforementioned molybdenum compound and the tungsten compound were combined with the reference oil of Example 1. To simulate aging, oils were subjected to a modified High Temperature Corrosion Bench Test (HTCBT). In this test, oil is exposed to oxidative conditions in the presence of four catalytic metals: lead copper, tin and phosphor bronze. The HTCBT test herein was based on the ASTM test method D6594, but modified such that the temperature was increased to 165°C, and test length reduced to 48 hours. The friction response of the oxidatively aged oil was measured using a PCS Instruments MTM2 Mini-Traction Machine. The friction versus velocity (Stribeck curve) was determined for each fresh and aged oil at temperatures of 60°C- 140°C in 20 °C intervals.

[0048] A comparison of oil performance across boundary, and elastohydrodynamic lubricating regimes was made by integrating the area under each Stribeck curve. This integral is commonly referred to as the Stribeck Friction Coefficient (SFC). Lower values of SFC indicate that less energy is absorbed by the lubricant across all lubrication regimes. Lower values relative to the baseline formulation would therefore be expected to correlate with better performance in fuel economy engine tests. SFC results are shown in Table 3.

Table 3

Determination of friction at various temperatures in aged oils under slip/roll conditions using Mini Traction Machine (MTM)							
Sample	Relative Change in Stribeck Friction Coefficient (SFC-SFC ₀)/SFC ₀					Mo:W	Mo:W
	60°C	80 °C	100 °C	120 °C	140 °C	ppm	ratio
Castrol Edge FST 5W-30	0%	0%	0%	0%	0%	0:0	0
Oil 9 comparative	3.60%	7.50%	6.70%	0.07%	2.66%	250:100	2.5
Oil 10	0.13%	-5.64%	-13.67%	-14.75%	-16.41 %	500:50	10
Oil 11	1.21%	-5.24%	-12.96%	-23.75%	-17.64%	500:200	2.5
Oil 12	2.27%	-2.10%	-4.72%	-12.83%	-15.02%	700:100	7
Slide:Roll Ratio	: 50%	Load	:35N				
Sliding Velocity Profile	: 1000 mm/s - 100 mm/s, step 100 mm/s, hold 2 min/step						
	: 100 mm/s - 10 mm/s, step 10 mm/s, hold 2min/step						

[0049] In Table 3, the reference oil is a recommended oil meeting the highest standards, which is regarded in the industry as an already-optimized oil in terms of friction properties. Oil 9 is a comparative composition using molybdenum and tungsten values described in US 7,879,777 B2. As can be seen from the table, Comparative Oil 9, which has less than the required inventive amount of molybdenum (i.e. at least 350 ppm) does not impart improved frictional performance by reducing the SFC relative to the reference oil. In contrast to this, oils 10-12 show that the inventive combinations of molybdenum and tungsten impart improved frictional performance to the oils, even after the oils have been severely oxidatively stressed. It is noteworthy that in comparing Oils 11 and 9, each with the same Mo:W ratio, it is the critical minimum amount of Mo that is responsible for the large improvement, despite the prior art recommendation to avoid such a high amount. This benefit is particularly substantial at elevated working temperatures.

Claims

1. Lubricant composition containing at least one oil-soluble organic molybdenum compound, **characterized in that** this compound further contains at least one alkyl- or aryl-substituted ammonium tungstate, wherein the weight ratio of molybdenum to tungsten in the lubricant is at least 2.5:1, and the amount of molybdenum in the lubricant composition is at least 350 ppm based on the total weight of the lubricant composition.
2. Lubricant composition according to claim 1, **characterized in that** the weight ratio of molybdenum to tungsten in the lubricant is between about 3:1 and about 10:1.
3. Lubricant composition according to claim 1, **characterized in that** the weight ratio of molybdenum to tungsten in the lubricant is between about 4:1 and about 8:1.
4. Lubricant composition according to one of the claims 1 to 3, **characterized in that** the amount of molybdenum in

the lubricant is less than 0.1 wt.-% Mo based on the total weight of the lubricant composition.

5 5. Lubricant composition according to one of the claims 1 to 4, **characterized in that** the amount of molybdenum in the lubricant is less than or equal to 700 ppm and greater than 350 ppm Mo based on the total weight of the lubricant composition.

10 6. Lubricant composition according to one of the claims 1 to 5, **characterized in that** the amount of tungsten in the lubricant is less than or equal to 500 ppm based on the total weight of the lubricant composition.

15 7. Lubricant composition according to one of the claims 1 to 6, **characterized in that** the amount of tungsten in the lubricant is less than or equal to 200 ppm based on the total weight of the lubricant composition.

20 8. Lubricant composition according to one of the claims 1 to 7, **characterized in that** the weight ratio of molybdenum to tungsten in the lubricant is at least about 5:1.

25 9. Lubricant composition according to one of the claims 1 to 8, **characterized in that** the organic molybdenum compound is an organic molybdenum complex, prepared from at least one long chain fatty acid oil, diethanolamine or 2-(2-aminoethyl) amino ethanol, and molybdenum trioxide.

30 10. Lubricant composition according to claim 9, **characterized in that** the long chain fatty acid oil is an oil of a saturated fatty acid having 8 to 18 carbon atoms, in particular selected from the group consisting of caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid and stearic acid, or an unsaturated fatty acid with up to 18 carbon atoms, in particular oleic acid or linoleic acid, or a mixture of two or more fatty acid oils of the aforementioned type.

35 11. Lubricant composition according to one of the claims 1 to 10, **characterized in that** the ammonium tungstate is an organo-ammonium metal compound comprising polytungstate ions and dialkyl-ammonium ions of the type $R_2NH_2^+$, wherein the radicals -R are long-chain alkyl groups.

40 12. Method for preparing a lubricant composition according to one of the claims 1 to 11, **characterized in that** the lubricant composition is prepared by adding to a lubricant base composition a first additive containing the organic molybdenum compound in a higher concentration and a second additive containing the ammonium tungstate in a higher concentration, wherein the first additive and the second additive are each added to the lubricant composition in such an amount that the respective percentages of molybdenum and tungsten and the weight ratio of molybdenum to tungsten in the final lubricating composition are obtained in accordance with one of the claims 1 to 11.

45 13. Method for preparing a lubricant composition according to one of the claims 1 to 11, **characterized in that** the lubricant composition is prepared by adding to a lubricant base composition an additive which contains the organic molybdenum compound in a higher concentration as well as the ammonium tungstate in a higher concentration and which contains the molybdenum compound and the ammonium tungstate in a defined relative weight ratio to one another, wherein the additive with the aforementioned combined ingredients is added in each case to the lubricant composition in an amount such that the respective percentages of molybdenum and tungsten and the weight ratio of molybdenum to tungsten in the final lubricating composition are obtained according to one of the claims 1 to 11.

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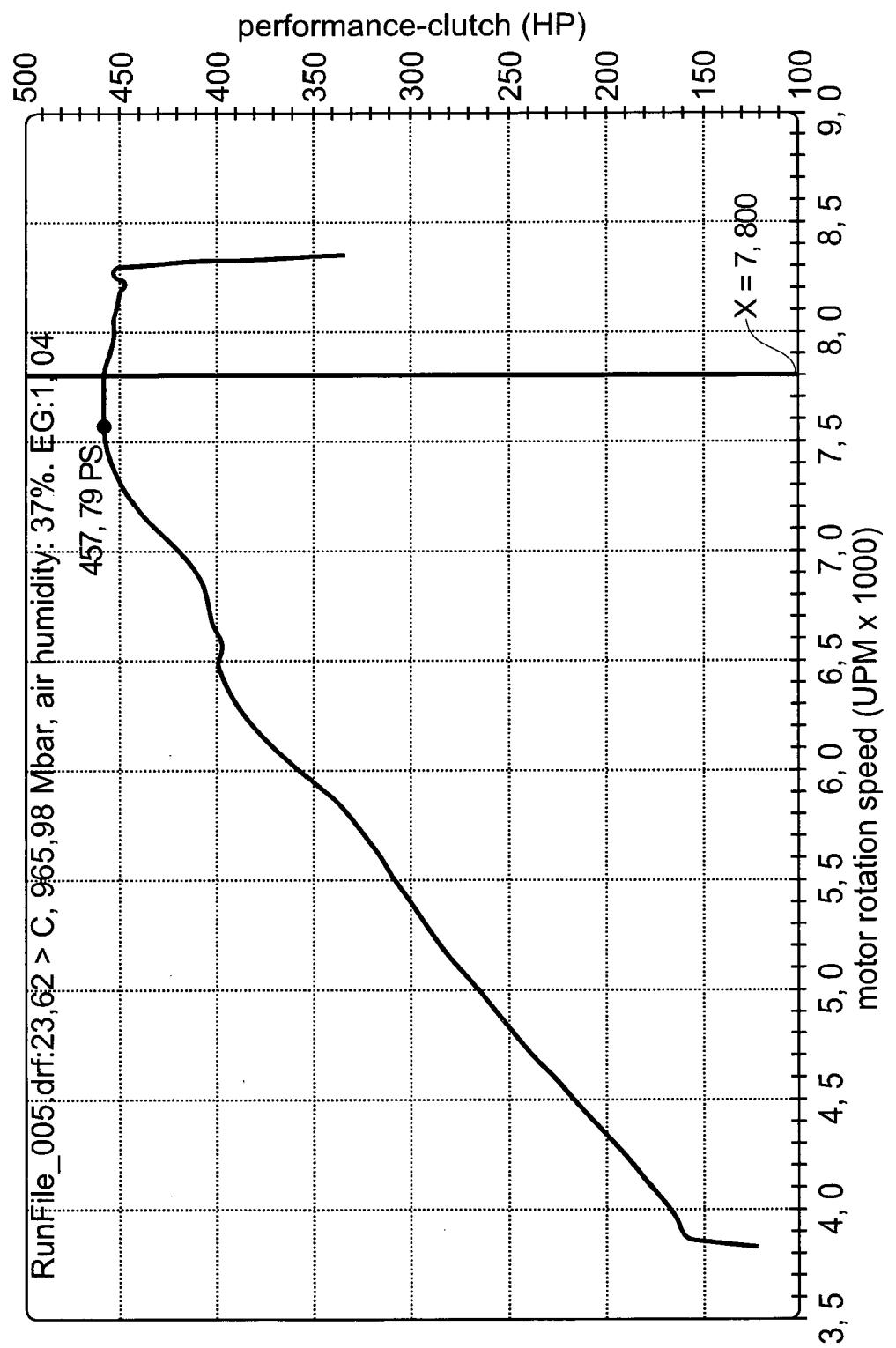


Fig. 1

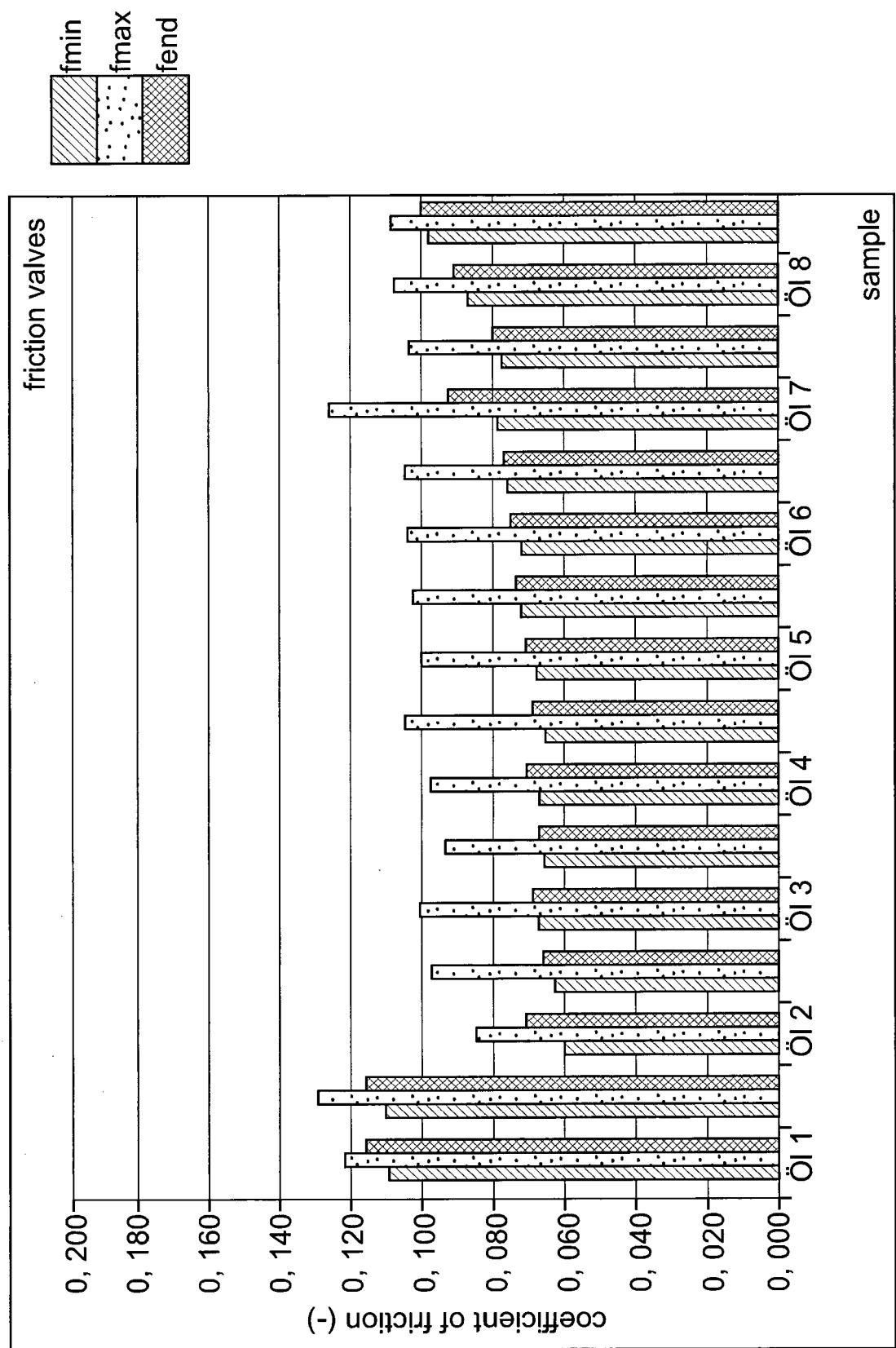


Fig. 2



EUROPEAN SEARCH REPORT

Application Number
EP 14 15 8286

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IPC)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	US 2007/203033 A1 (TYNIK R J; DONNELLY S G; AGUILAR G A) 30 August 2007 (2007-08-30) * paragraphs [0009], [0029]; claims 1,3-5 * * paragraphs [0013], [0018], [0020], [0021]; examples 9-11 *	1,2,4,6,7,9-12	INV. C10M141/06 C10M141/12
X	US 2009/029888 A1 (RAVICHANDRAN RAMANATHAN [US] ET AL) 29 January 2009 (2009-01-29) * paragraphs [0286] - [0291]; examples 30,31; tables 1-3 * * paragraphs [0002], [0007], [0010], [0011], [0238], [0240]; examples 28,29 *	1-13	
A	WO 2004/094574 A1 (VANDERBILT CO R T [US]; TYNIK ROBERT J [US]) 4 November 2004 (2004-11-04) * the whole document *	1-13	
A	US 2011/237475 A1 (DONNELLY STEVEN G [US] ET AL) 29 September 2011 (2011-09-29) * paragraphs [0010] - [0012], [0014], [0047] *	1-13	TECHNICAL FIELDS SEARCHED (IPC)
			C10M C10N
The present search report has been drawn up for all claims			
1	Place of search	Date of completion of the search	Examiner
	Munich	23 June 2014	Bork, Ana-Maria
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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ON EUROPEAN PATENT APPLICATION NO.

EP 14 15 8286

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

23-06-2014

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007203033 A1	30-08-2007	BR PI0708629 A2 CN 101356120 A EP 2021286 A1 JP 5114428 B2 JP 2009521593 A US 2007203033 A1 WO 2007131104 A1	07-06-2011 28-01-2009 11-02-2009 09-01-2013 04-06-2009 30-08-2007 15-11-2007
US 2009029888 A1	29-01-2009	NONE	
WO 2004094574 A1	04-11-2004	AT 541027 T BR PI0409648 A CN 1777666 A EP 1618172 A1 ES 2380691 T3 JP 4232986 B2 JP 2006524191 A US 2004214731 A1 WO 2004094574 A1	15-01-2012 31-10-2006 24-05-2006 25-01-2006 17-05-2012 04-03-2009 26-10-2006 28-10-2004 04-11-2004
US 2011237475 A1	29-09-2011	CN 102812111 A EP 2550346 A1 KR 20130010112 A RU 2012145270 A US 2011237474 A1 US 2011237475 A1 WO 2011119918 A1	05-12-2012 30-01-2013 25-01-2013 27-04-2014 29-09-2011 29-09-2011 29-09-2011

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 61779563 A [0001]
- DE 102013112454 [0001]
- EP 0546357 B1 [0014] [0016]
- US 5641731 A [0016]
- US 4889647 A [0016]
- EP 1618172 B1 [0017]
- US 7879777 B2 [0019] [0029] [0049]