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(54) **LUBRICATING COMPOSITION**

(57) The invention relates to lubricating compositions based on base oils containing a metal film-forming, multi-functional composition for enhanced antifriction, anti-seize, antioxidant and cleaning/dispersant properties.

The present lubricating composition includes a base oil and a metal salt of an organic acid, and further contains a metal salt of an organic acid, an aromatic amine, a succinimide derivative, and an oil-soluble organic acid.

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Description**Technical field**

5 **[0001]** The invention relates to lubricating compositions based on base oils, which contain a metal-plating, multifunctional composition that improves antifriction, extreme pressure, antioxidant, as well as detergent and dispersant properties, and may be used in internal combustion engines (ICE) of trucks and cars, locomotives, river and marine fleet, as well as in transmission and industrial oils.

10 **Prior art**

[0002] From the "Prior art", a composition is known, which contains, wt%: metal salt of an organic acid: 10-90; metal salt of an inorganic acid: 1.5-25; aliphatic alcohol: 3-55; aromatic amine: 1-8; epoxy resin: 2-10; succinimide polymer: 2-8; 2-imino-substituted indoline: 0.5-6 (see Russian Federation patent No. 2 277 579, cl. C10M 141/06, publ. on 10 June 2006).

15 **[0003]** In addition, a lubricating composition is known from the "Prior art", which includes a basic oil component, at least one metal salt of an organic acid and at least one metal salt of an inorganic acid, as well as additionally includes the epoxy aliphatic resin DEG-1 (see patent No. EP2626405A, cl. C10M141/00, publ. on 14 August 2013).

20 **[0004]** The technical problem of known analogues is that, due to the presence of metal salts of inorganic acids, in the process of working on friction surfaces, metals are reduced, and a "strong" inorganic acid is formed; the presence of epoxy resin makes it difficult to form a metal protective film on the friction surface, and the presence of abrasive materials leads to clogging of the oil channels of the lubrication system of internal combustion engines.

Disclosure of invention

25 **[0005]** The task of this invention is to eliminate the above disadvantages.

[0006] The technical result consists in eliminating the clogging of the oil channels of the lubrication system of internal combustion engines, as well as improving anti-wear and detergent properties.

30 **[0007]** The technical result is achieved by the fact that the lubricating composition includes a base oil and a metal salt of an organic acid, while it additionally contains a metal salt of an organic acid, an aromatic amine, a succinimide derivative, an oil-soluble organic acid, wherein the following ratio of components is used, wt%:

	base oil:	97.3-97.8;
	metal salt of an organic acid:	0.06-0.27;
35	aromatic amine:	0.33-0.945;
	succinimide derivative:	0.99-1.755;
	organic acid:	0.11-0.405.

40 **[0008]** According to particular embodiments, the base oil is a synthetic base oil or a mineral oil.

[0009] The lubricating composition contains an oil-soluble metal-plating additive, the components of which are a metal salt of an organic acid, an aromatic amine, a succinimide derivative, an oil-soluble organic acid, wherein the following ratio of components is used, wt%:

45	metal salt of an organic acid:	3-10;
	aromatic amine:	15-35;
	succinimide derivative:	45-65;
	organic acid:	5-15.

50 **[0010]** As a metal salt of an organic acid, it contains metal salts of organic acids with a carbon number of C₁₅-C₁₈, as aromatic amines, it contains diphenylamine or its homologues, and as a succinimide polymer, it contains industrially manufactured additives: C-5A, or C-5AB, or C-1500B, or C-2500.

[0011] Synthetic base oils are, for example, polyalphaolefins, gas-to-liquids (GTL) base oils, such as those obtained from the Fischer-Tropsch process, or certain esters.

55 **[0012]** Another category of synthetic base oils is formed by polyalkylene glycols (PAGs). These base oils are obtained, for example, by the polymerisation or copolymerisation of alkylene oxides, preferably containing from 2 to 8 carbon atoms.

[0013] Mineral base oils of the compositions include all types of base oils obtained by atmospheric and vacuum

distillation of crude oil followed by refining processes, such as solvent extraction, deasphalting, solvent dewaxing, hydrotreating, hydrocracking and hydroisomerisation, as well as hydrotreating.

Carrying out the invention

[0014] The lubricating composition is obtained as follows. In an unsaturated carboxylic acid, selected from the number of fractions C₁₅-C₁₈, for example, the technical oleic one of grade B-115, which is a mixture of unsaturated carboxylic acids C₁₅-C₁₈, monovalent copper oxide is introduced, mixing is carried out, for example, passing the mixture through a hydrodynamic apparatus, with mixing criteria Re=10,000-60,000 and the temperature range from 30 °C to 180 °C. Dispersion and dissolution is carried out for 30-60 min., while salts of unsaturated carboxylic acids are formed. After dissolving the oxides in the acid, the unreacted oxides are separated by filtration.

[0015] As a result of auto-oxidation and auto-reduction (disproportionation) reaction, monovalent and divalent salts of unsaturated carboxylic acids are formed, the ratio between which is regulated by the process duration and the value of the Reynolds number. Then, an aromatic amine (diphenylamine), an unsaturated carboxylic acid (selected from the number of fractions C₆-C₂₂), and a succinimide derivative (C-5A, or C-5AB, or C-1500B, or C-2500), at room temperature, are introduced into the purified solution with stirring.

[0016] The quality control of the oil-soluble metal-plating additive is carried out by the percentage of copper, which is determined by dissolving a sample of the product in glacial acetic acid, followed by iodometry titration. The content of copper, Cu⁺¹ and Cu^{+II}, in the additive may be determined by X-ray photoelectron spectroscopy (XPS). The base oil and the oil-soluble metal-plating additive are heated during mixing, for example, for 5-48 hours at a temperature of approximately 30 °C to approximately 70 °C, for example, for approximately 24 hours at a temperature of approximately 60 °C. Mixing is carried out at speeds from approximately 2,000 rpm to approximately 5,000 rpm. Prior to the examination and use, mixtures are usually cooled for 10-24 hours to a temperature of approximately 25 °C.

[0017] The use of unsaturated carboxylic acids makes it possible to obtain the necessary molecular structure of a metal-plating additive to lubricating compositions, which ensures the achievement of the required physical and chemical properties.

[0018] The use of a metal-plating additive to lubricating compositions makes it possible to significantly reduce the friction coefficient for various friction pairs, including those with a high degree of loading and high frequencies of mutual displacement, as well as to eliminate damage to the oil channels of the lubrication system of internal combustion engines and to improve anti-wear and detergent properties.

[0019] The invention is illustrated by the following examples of implementation of the invention.

Example 1

[0020] The lubricating composition contains a polyalkylene glycol base oil, a metal salt of an organic acid, an aromatic amine, and a succinimide derivative, while it additionally contains an oil-soluble organic acid, wherein the following ratio of components is used, wt%:

polyalkylene glycol base oil:	97.3;
salt of copper and carboxylic acid (C ₁₅ -C ₁₈):	0.20;
diphenylamine:	0.40;
succinimide derivative (C-5A):	1.70;
oleic acid:	0.40.

Example 2

[0021] The lubricating composition contains a synthetic base oil in the form of polyalphaolefins, a metal salt of an organic acid, an aromatic amine, and a succinimide derivative, while it additionally contains an oil-soluble organic acid, wherein the following ratio of components is used, wt%:

synthetic base oil in the form of polyalphaolefins:	97.8;
salt of copper and carboxylic acid (C ₁₅ -C ₁₈):	0.2;
diphenylamine:	0.3;
succinimide derivative (C-1500):	1.3;
oleic acid:	0.4.

Example 3

[0022] The lubricating composition contains a hydrocracking mineral base oil, a metal salt of an organic acid, an aromatic amine, and a succinimide derivative C-5AB, which is a solution of boron-modified alkenyl succinimide in mineral oil. At the same time, the composition additionally contains an oil-soluble organic acid, wherein the following ratio of components is used, wt%:

hydrocracking mineral base oil:	97.5;
salt of copper and carboxylic acid (C ₁₅ -C ₁₈):	0.25;
diphenylamine:	0.6;
succinimide derivative (C-5AB):	1.35;
oleic acid:	0.3.

[0023] The effect of the composition on the friction coefficient at different temperatures in the area of friction and pressure for various friction pairs is presented in Table 1.

Table 1

Example No.	Friction pair: Cast Iron (SCh 18-36) - Steel A (A-18)					
	Pressure (P), 25 kg/cm ²		Pressure (P), 50 kg/cm ²		Pressure (P), 100 kg/cm ²	
	f, friction coefficient	T, °C Temperature in the friction area	f, friction coefficient	T, °C Temperature in the friction area	f, friction coefficient	T, °C Temperature in the friction area
1	0.14	26	0.18	50	0.24	62
2	0.11	22	0.13	45	0.17	50
3	0.10	21	0.12	40	0.16	46

[0024] By using other ratios of the composition components within the claimed ranges, a reduction in the friction coefficient is also achieved.

[0025] The use of the lubricating composition makes it possible to significantly reduce the friction coefficient for various friction pairs, including those with a high degree of loading and high frequencies of mutual displacement.

[0026] Tribological tests of lubricants are carried out using a friction machine that simulates the operation of a heavily-loaded friction unit under slippage conditions.

[0027] For comparative tests, the following was used:

- Sample 1: composition according to Russian Federation patent No. 2 277579;
- Sample 2: composition according to example No. 1;
- Sample 3: composition according to example No. 2;
- Sample 4: composition according to example No. 3.

[0028] The tests were carried out using a friction machine with the maximum load $G_{\max, \text{start}} = 2,600$ MPa for 1 hour at a washer rotation speed of 50-3,500 rpm.

[0029] The main criteria for comparing the performance of the lubricants were:

- the ball contact patch diameter;
- the ball temperature increment during testing;
- the change in friction coefficients during testing.

[0030] The values of the contact patch diameter, the friction coefficients and the temperature characteristics of friction

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pairs are given in Table 2.

Table 2

5	Names of lubricants, speed/linear speed	Contact patch diameter, μm	Friction coefficient, $\mu=\text{kM start/set mode}$	T°C increase
	50 rpm Vlin. = 0.044 m/s			
10	Sample 1	478.85	15/15	0.263
	Sample 2	469.66	13/13	0.82
	Sample 3	474.95	13/12	-1.27
	Sample 4	567.25	16/15	0.26
15	500 rpm Vlin. = 0.44 m/s			
	Sample 1	475.93	15/14	3.34
	Sample 2	826.95	14/13	3.24
20	Sample 3	705.29	12/12	2.43
	Sample 4	666.24	11/11	2.16
	1,000 rpm Vlin. = 0.88 m/s			
25	Sample 1	681.28	14/14	4.32
	Sample 2	707.01	14/14	7.99
	Sample 3	777.25	12/12	3.76
30	Sample 4	713.27	12/12	3.62
	1,500 rpm Vlin. = 1.32 m/s			
35	Sample 1	818.26	16/13	9.16
	Sample 2	791.46	16/14	10.6
	Sample 3	749.84	14/13	7.2
	Sample 4	719.7	11/12	6.96
40	2,000 rpm Vlin. = 1.64 m/s			
	Sample 1	1669.68	destruction of	the friction pair
45	Sample 2	867.41	15/13	11.47
	Sample 3	907.85	13/13	10.44
	Sample 4	857.93	13/13	8.86
	2,500 rpm Vlin. = 2.05 m/s			
50	Sample 1	0	0	0
	Sample 2	718.58	15/13	10.17
	Sample 3	939.76	15/14	15.2
55	Sample 4	1653.93	destruction of	the friction pair

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(continued)

3,000 rpm Vlin. = 2.46 m/s			
Sample 1	0	0	0
Sample 2	1,895.94	destruction of	the friction pair
Sample 3	671.44	12/11	8.19
Sample 4	0	0	0

[0031] The contact (specific) load P_c , kg/mm², is calculated according to the formula:

$$P_c = P_{\text{total}}/S, \text{ kg/mm}^2$$

where

P_{total} : load on the sample, kg;

S : ball contact patch area, mm²; $S = \pi D^2/4$ where D : ball contact patch diameter, mm.

[0032] Based on the contact load, we estimate the bearing capacity of the friction pair. Table 3.

Table 3

Names of lubricants	Contact patch diameter, μm	Bearing capacity of the friction pair (contact load, P_c , kg/mm ²)
50 rpm		
Sample 1	478.85	35.09
Sample 2	469.66	36.48
Sample 3	474.95	35.67
Sample 4	567.25	25.01
500 rpm		
Sample 1	475.93	35.53
Sample 2	826.95	11.77
Sample 3	705.29	16.18
Sample 4	666.24	18.13
1,000 rpm		
Sample 1	681.28	17.34
Sample 2	707.01	16.1
Sample 3	777.25	13.32
Sample 4	713.27	15.82
1,500 rpm		
Sample 1	818.26	12.02
Sample 2	791.46	12.85
Sample 3	749.84	14.31
Sample 4	719.7	15.54

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(continued)

	2,000 rpm		
5	Sample 1	1669.68	0
	Sample 2	867.41	10.69
	Sample 3	907.85	9.76
10	Sample 4	857.93	10.93
	2,500 rpm		
	Sample 1	0	0
	Sample 2	718.58	15.58
15	Sample 3	939.76	9.11
	Sample 4	1653.93	0
	3,000 rpm		
20	Sample 1	0	0
	Sample 2	1,895.94	0
	Sample 3	671.44	17.85
	Sample 4	0	0

[0033] We estimate the friction power after testing according to the formula:

$$W = P_c \times 10 \times V_{lin.}$$

where

$P_c \times 10$: contact (specific) load, MPa;

$V_{lin.}$: linear speed of the sample displacement, m/s;

$$V_{lin.} = \frac{l \cdot n}{60}$$

where

n: washer revolutions per minute;

l: length of the wear track circumference; $l = \pi \cdot D$ where D is the diameter of the wear track circumference. Under the test conditions when using this friction machine, the track length is conditionally constant and amounts to 0.053 m.

[0034] The calculated value of the friction power characterises the action of the friction force during wear of the contacting surfaces at each stage of this experiment; the data are given in Table 4.

Table 4

Names of lubricants	Bearing capacity of the friction pair (contact load, P_c , kg/mm ²)	Friction power, MPa*m/s
50 rpm; $V_{lin.} = 0.044$ m/s		
Sample 1	35.09	15.44

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(continued)

Names of lubricants	Bearing capacity of the friction pair (contact load, P_c , kg/mm ²)	Friction power, MPa*m/s
Sample 2	36.48	16.05
Sample 3	35.67	15.7
Sample 4	25.01	11
500 rpm; $V_{lin.} = 0.44$ m/s		
Sample 1	35.53	156.31
Sample 2	11.77	51.78
Sample 3	16.18	71.18
Sample 4	18.13	79.77
1,000 rpm; $V_{lin.} = 0.88$ m/s		
Sample 1	681.28	152.57
Sample 2	707.01	141.66
Sample 3	777.25	117.22
Sample 4	713.27	139.19
1,500 rpm; $V_{lin.} = 1.32$ m/s		
Sample 1	818.26	158.64
Sample 2	791.46	169.57
Sample 3	749.84	188.91
Sample 4	719.7	205.07
2,000 rpm; $V_{lin.} = 1.64$ m/s		
Sample 1	Destruction of the pair	0
Sample 2	10.69	175.4
Sample 3	9.76	160.12
Sample 4	10.93	179.29
2,500 rpm; $V_{lin.} = 2.05$ m/s		
Sample 1	0	0
Sample 2	15.58	319.47
Sample 3	9.11	186.79
Sample 4	Destruction of the pair	0
3,000 rpm; $V_{lin.} = 2.46$ m/s		
Sample 1	0	0
Sample 2	Destruction of the pair	0
Sample 3	17.85	439.08
Sample 4	0	0

[0035] The calculation of critical loads for this friction unit when using the Cupper 10W-40 lubricant and the Cupper 10W-40 lubricant modified by using the metal-plating additive (M.-p.) was carried out based on the test data obtained, as well as based on the friction powers calculated and the assumption of a rectilinear dependence ($P_c = W_c/10V_{lin.}$) between P_c (critical load) and W_c (critical friction power) over the entire range of linear speeds.

Table 5

Name of lubricant	Calculated critical load at revolutions:						
	50 rpm	500 rpm	1,000 rpm	1,500 rpm	2,000 rpm	2,500 rpm	3,000 rpm
Sample 1	360.55	36.05	18.03	12.02	0	0	0
Sample 2	726.07	72.61	36.6	24.20	19.48	15.58	0
Sample 3	997.91	99.79	49.9	33.26	26.77	21.42	17.85
Sample 4	466.07	46.61	23.3	15.54	12.50	10.00	0

[0036] The modification of the lubricant based on a group 3 base oil using the metal-plating additive developed made it possible to ensure the long-term performance of the friction pair at sliding speeds of up to 2.46 m/s.

[0037] The predictive critical load calculation shows a significant (multiple) advantage of the anti-wear properties of the lubricant modified using the additive developed over the entire range of linear speeds.

Claims

1. A lubricating composition, which includes a base oil in the form of a synthetic oil or a mineral oil, which are a polyalkylene glycol base oil, or a synthetic base oil in the form of polyalphaolefins, or a hydrocracking mineral base oil, a salt of copper and carboxylic acid (C₁₅-C₁₈), diphenylamine, oleic acid, and a succinimide derivative in the form of industrially manufactured additives (C-5A, or C-5AB, or C-1500B, or C-2500), wherein the following ratio of components is used, wt%:

base oil:	97.3-97.8;
salt of copper and carboxylic acid (C ₁₅ -C ₁₈):	0.06-0.27;
diphenylamine:	0.33-0.945;
succinimide derivative:	0.99-1.755;
oleic acid:	0.11-0.405.

2. A lubricating composition according to claim 1, **characterised by** that it contains an oil-soluble metal-plating additive, the components of which are a salt of copper and carboxylic acid (C₁₅-C₁₈), diphenylamine, oleic acid, and a succinimide derivative in the form of industrially manufactured additives (C-5A, or C-5AB, or C-1500B, or C-2500), wherein the following ratio of components is used, wt%:

salt of copper and carboxylic acid (C ₁₅ -C ₁₈):	3-10;
diphenylamine:	15-35;
succinimide derivative:	45-65;
oleic acid:	5-15.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/RU 2022/050387

A. CLASSIFICATION OF SUBJECT MATTER

(see supplemental sheet)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10M

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

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

DWPI, E-Library, Espacenet, Google, PATENTSCOPE, PatSearch, USPTO, Yandex

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RU 2737889 C1 (OBSCHESTVO S OGRANICHENNOI OTVETSTVENNOSTIU «KUPPER») 04.12.2020, abstract, p.3 lines 1-3, p.3 line 18 - p.4 line 2, p.4 lines 19-27, p.4 line 32 - p.5 line 7, examples	1-2
A	RU 2741905 C1 (KIREINIKOV ALEKSEI VALEREVICH) 29.01.2021	1-2
A	RU 2398010 C1 (BABEL VALENTINA GRIGOREVNA et al.) 27.08.2010	1-2

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search

24 April 2023 (24.04.2023)

Date of mailing of the international search report

25 May 2023 (25.05.2023)

Name and mailing address of the ISA/

RU

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INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER

C10M169/00 (2006.01)

C10M129/26 (2006.01)

C10M133/12 (2006.01)

C10M133/16 (2006.01)

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Patent documents cited in the description

- RU 2277579 [0002] [0027]
- EP 2626405 A [0003]