



(11) **EP 2 497 818 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
12.09.2012 Bulletin 2012/37

(51) Int Cl.:
C10M 163/00 (2006.01)

(21) Application number: **12158753.9**

(22) Date of filing: **09.03.2012**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

- **Zhang, Jie**
100007 Beijing (CN)
- **Liu, Gonde**
100007 Beijing (CN)
- **Ma, Yuli**
100007 Beijing (CN)

(30) Priority: **10.03.2011 CN 201110058054**

(74) Representative: **Meyer-Dulheuer, Karl-Hermann**
Dr. Meyer-Dulheuer & Partner
Patentanwaltskanzlei
Mainzer-Landstrasse 69-71
60329 Frankfurt am Main (DE)

(71) Applicant: **Petrochina Company Limited**
Dongcheng District
Beijing 100007 (CN)

(72) Inventors:
• **Zhai, Yueki**
100007 Beijing (CN)

(54) **A marine cylinder oil composite additive**

(57) The present invention relates to a marine cylinder oil composite additive. Based on the total weight of the composite additive, said marine cylinder oil composite additive comprises: 15-25% sulfonate detergent with superhigh base number, 35-45% phenolate detergent with superhigh base number, 20-30% naphthenate detergent with superhigh base number, 0-8% dispersing agent, 0-4% antiwear agent, and 10-20% Group I base oil with high viscosity index which is selected from the group consisting of 400SN, 500SN and 650SN. The benefit of the present invention lies in the fact that the composite additive can satisfy the requirement of BOB system about the viscosity and base number, and can be

blended with many system oils under a number of domestic and foreign brands so as to provide cylinder lubricating oils with different base numbers. The composite additive according to the present invention has good adaptability and excellent performances in terms of antiwear, antioxidization and high temperature detergency, which meet the requirement of marine engines about the performance of cylinder oils. Moreover, the composite additive according to the present invention is able to maintain good stability in the base oil of the system oil as well as good compatibility, and thus the lubricating performance of the cylinder oil will not be adversely affected.

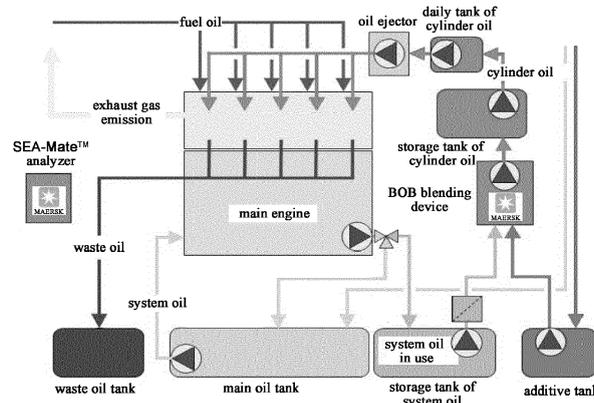


Figure 1

EP 2 497 818 A1

Description**FIELD OF THE INVENTION**

5 [0001] The present invention relates to a marine cylinder oil composite additive formulation, and more particularly to a composite additive designed for cylinder oils which is applied in shipborne BOB systems.

BACKGROUND OF THE INVENTION

10 [0002] The current BOB (Blender-on-Board) online blending system equipped on ocean vessels is an automatic control system that blends the marine system oil with a composite additive which is designed for the marine lubricating oils in the BOB system so as to provide a cylinder oil that have an optional target base number, and such cylinder oil can be rapidly transferred to the engine in order to meet the different requirements for the base number of the cylinder oil in cases of using fuels with different sulfur contents. A schematic diagram for the operating principle of BOB online blending system is shown in Figure 1.

15 [0003] The operating procedure of the BOB system is as follows: the system oil is pumped from the main oil tank to each lubrication point of the engine so as to provide lubrication and thereafter recycled back to the main oil tank, wherein part of the system oil is side-drawn and then blended with a composite additive in the BOB blending device to form a cylinder oil with required base numbers, which is burned off after fulfilling lubrication, and the residue thereof flows into a waste oil tank.

20 [0004] The composite additives designed for the BOB system are remarkably different from the traditional marine lubricating oils. The later are lubricating oil products with fixed base numbers, which are produced in blending plants and may be directly used by adding into the oil tank of vessels, whereas the former are additives produced by blending plants and blended with the system oil before adding into a tank of vessels so as to provide marine cylinder oils with different base numbers in order to meet the requirement of the use in engines. Therefore, the composite additives designed for the BOB system have several features in terms of the technical requirement:

1. Sufficient antiwear and antioxidization properties should be preserved when relatively low dosage is used;
2. Good compatibility to system oils under different brands;
- 30 3. The composite additive should satisfy the requirement of being pumped within the BOB system and fit with the blending system.

[0005] According to the novelty search within Chinese and worldwide patents, no related reference documents are found in the field of both shipborne BOB online blending system and the composite additive designed the BOB system.

35 [0006] It can be known from the corresponding Chinese and worldwide patents that the sulfonate detergent with superhigh base number has excellent detergency and dispersion performances and the sulfurized calcium phenolate has excellent antiwear and antioxidization performances, and thus the cylinder oil formulation is commonly composed by the sulfonate detergent and the sulfurized calcium phenolate; the naphthenate has good oil film diffusibility, and the burned residue thereof is relatively soft and readily cleaned by the lubricating oil. Such combustion behavior of the naphthenate is particularly important for the "disposable" cylinder oil, and its relatively fast diffusion rate on the cylinder wall could just compensate for the lacking of oil film strength at low injection rate. The application of the cylinder oil composite additive formulation comprising three detergents of the sulfonate detergent, sulfurized calcium phenolate detergent and naphthenate detergent can not only enhance the performance of the cylinder oil but also utilize the abundant naphthenate resource of PetroChina so as to build significant superiority in the technology of marine oil self-owned by PetroChina.

SUMMARY OF THE INVENTION

50 [0007] The purpose of the present invention is to provide a marine cylinder oil composite additive that can not only satisfy the requirement of the marine BOB online blending system but also have wide adaptability.

[0008] The marine lubricating oil composite additive is characterized in that, based on the total weight of the composite additive, it comprises: 15-25% sulfonate detergent with superhigh base number, 35-45% phenolate detergent with superhigh base number, 20-30% naphthenate detergent with superhigh base number, 0-8% dispersing agent, 0-4% antiwear agent, and 10-20% Group I base oil with high viscosity index which is selected from the group consisting of 400SN, 500SN and 650SN.

55 [0009] Said sulfonate detergent with superhigh base number is C₂₂-C₃₀ linear alkyl benzene calcium sulphonate, wherein the base number thereof is 395-430 mgKOH/g.

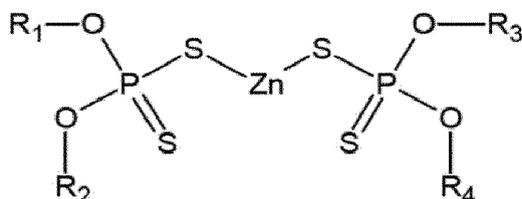
[0010] Said phenolate detergent with superhigh base number is C₁₈-C₂₄ alkyl sulfurized calcium phenolate, wherein

the base number thereof is 290-310 mgKOH/g.

[0011] Said naphthenate detergent with superhigh base number is C_{20} - C_{30} long chain alkyl calcium naphthenate, wherein the base number thereof is 390-420 mgKOH/g.

[0012] Said dispersing agent is selected from the group consisting of mono-polyisobutylene succinimide, bis-polyisobutylene succinimide and multi-polyisobutylene succinimide.

[0013] Said antiwear agent is zinc long-chain alkyl thiophosphate with the structure corresponding to the following formula,



wherein R_1 , R_2 , R_3 and R_4 are long-chain primary alkyl groups each comprising 12-18 carbon atoms, or R_1 , R_2 , R_3 and R_4 are long-chain secondary alkyl groups each comprising 12-16 carbon atoms.

[0014] Said base oil is Group I base oil with high viscosity index which is selected from the group consisting of 400SN, 500SN and 650SN, the kinematic viscosity of which is 8.0-11.0 cst at 100°C. The appropriate base oils are commercially available from PetroChina Company.

[0015] The marine cylinder oil composite additive provided by the present invention employs three composed detergents, wherein the sulfonate detergent with superhigh base number has excellent detergency and dispersion performances but relatively poor antiwear and antioxidization performances; the sulfurized calcium phenolate has excellent antiwear and antioxidization performances but relatively poor detergency and dispersion performances; the naphthenate has good oil film diffusibility but relatively poor detergency and antiwear performances. The above three detergents are composed so as to allow full play to their advantages and compensate for their shortages.

[0016] The technical features of the present invention are as follows: the requirement of the BOB system process for the viscosity and base number can be satisfied by the composite additive, which can be online blended and widely applied. The cylinder oils with different base numbers can be formulated based on system oils under a number of domestic and foreign brands. The composite additive according to the present invention has good adaptability and excellent performances in terms of antiwear, antioxidization and high temperature detergency, which meet the requirement of marine engines. Moreover, the composite additive according to the present invention can remain good stability in solution as well as good compatibility, and thus the lubricating performance of the cylinder oil would not be adversely affected. Such composite additive has been tested by sailing over 4000 hours, and has been technically certified by MAN B&W, the engine OEM (original equipment manufacturer).

DESCRIPTION OF DRAWINGS

[0017]

Figure 1 shows a schematic diagram for the operating principle of BOB online blending system.

Figure 2 shows the monitoring data for samples of the fresh/waste cylinder oils using the composite additive of the present application during the sailing.

DETAILED DESCRIPTION OF THE INVENTION

Example 1:

[0018] The composite additive used in BOB system may be prepared from the components mentioned below (their contents in weight percentage are also given in detail) by means of normal blending process. The blending process is as follows: the base oil is firstly added into a blending barrel/tank, and then the temperature is raised to $65 \pm 5^\circ\text{C}$, wherein the base oil should have a kinematic viscosity of 7.0-12.0 mm^2/s at 100°C; the antiwear agent, the dispersing agent and the detergents are subsequently introduced into said blending barrel/tank, and stirring is carried out at $65 \pm 5^\circ\text{C}$ for 2 hours until completely homogeneous. The above process is implemented in every example hereafter.

[0019] In this example, the sulfonate with superhigh base number is long-chain linear C_{22} -alkyl benzene calcium sulphonate with superhigh base number and its base number is 430 mgKOH/g, the sulfurized alkyl phenolate with superhigh base number is long-chain C_{25} -alkyl sulfurized calcium phenolate and the base number thereof is 290 mg-

EP 2 497 818 A1

KOH/g, and the naphthenate detergent with superhigh base number is C₂₀-alkyl calcium naphthenate with superhigh base number and the base number thereof is 390 mgKOH/g. The antiwear agent is zinc long-chain primary alkyl thiophosphate wherein the long-chain primary alkyl group comprises 12 carbon atoms. The dispersing agent is mono-polyisobutylene succinimide. The base oil is group I base oil 400SN available from PetroChina Daqing Petrochemical Company.

Components	Contents (%)
Linear alkyl (C22) calcium sulfonate with superhigh base number	15
Sulfurized calcium alkyl (C25) phenolate with superhigh base number	45
Alkyl (C20) calcium naphthenate with superhigh base number	20
Zinc primary alkyl (C12) thiophosphate	2
Mono-polyisobutylene succinimide	8
Group I base oil of 400SN	10

Example 2:

[0020] The composite additive used in BOB system may be prepared from the components mentioned below (their contents in weight percentage are also given in detail) by means of normal process.

[0021] In this example, the sulfonate with superhigh base number is long-chain linear C₃₀-alkyl benzene calcium sulphonate with superhigh base number and its base number is 395 mgKOH/g, the sulfurized alkyl phenolate with superhigh base number is long-chain C₁₈-alkyl sulfurized calcium phenolate and the base number thereof is 310 mg-KOH/g, and the naphthenate detergent with superhigh base number is C₃₀-alkyl calcium naphthenate with superhigh base number and the base number thereof is 420 mgKOH/g. The antiwear agent is zinc long-chain secondary alkyl thiophosphate wherein the long-chain secondary alkyl group comprises 16 carbon atoms. The dispersing agent is bis-polyisobutylene succinimide. The base oil is group I base oil 500SN available from PetroChina Daqing Petrochemical Company.

Components	Contents (%)
Linear alkyl (C30) calcium sulfonate with superhigh base number	15
Sulfurized calcium alkyl (C20) phenolate with superhigh base number	35
Alkyl (C30) calcium naphthenate with superhigh base number	27
Zinc secondary alkyl (C16) thiophosphate	4
Bis-polyisobutylene succinimide	4
Group I base oil of 500SN	15

Example 3:

[0022] The composite additive used in BOB system may be prepared from the components mentioned below (their contents in weight percentage are also given in detail) by means of normal process.

[0023] In this example, the sulfonate with superhigh base number is long-chain linear C₂₆-alkyl benzene calcium sulphonate with superhigh base number and its base number is 410 mgKOH/g, the sulfurized alkyl phenolate with superhigh base number is long-chain C₂₂-alkyl sulfurized calcium phenolate and the base number thereof is 300 mg-KOH/g, and the naphthenate detergent with superhigh base number is C₂₆-alkyl calcium naphthenate with superhigh base number and the base number thereof is 405 mgKOH/g. The antiwear agent is zinc long-chain primary alkyl thiophosphate wherein the long-chain primary alkyl group comprises 18 carbon atoms. The dispersing agent is multi-polyisobutylene succinimide. The base oil is group I base oil 500SN available from PetroChina Daqing Petrochemical Company.

Components	Contents (%)
Linear alkyl (C26) calcium sulfonate with superhigh base number	25

EP 2 497 818 A1

(continued)

Components	Contents (%)
Sulfurized calcium alkyl (C22) phenolate with superhigh base number	35
Alkyl (C26) calcium naphthenate with superhigh base number	20
Zinc primary alkyl (C18) thiophosphate	2
Multi-polyisobutylene succinimide	6
Group I base oil of 500SN	12

Example 4:

[0024] The composite additive used in BOB system may be prepared from the components mentioned below (their contents in weight percentage are also given in detail) by means of normal process.

[0025] In this example, the sulfonate with superhigh base number is long-chain linear C₂₂-alkyl benzene calcium sulphonate with superhigh base number and its base number is 430 mgKOH/g, the sulfurized alkyl phenolate with superhigh base number is long-chain C₂₄-alkyl sulfurized calcium phenolate and the base number thereof is 290 mg-KOH/g, and the naphthenate detergent with superhigh base number is C₂₀-alkyl calcium naphthenate with superhigh base number and the base number thereof is 390 mgKOH/g. The antiwear agent is zinc long-chain secondary alkyl thiophosphate wherein the long-chain secondary alkyl group comprises 12 carbon atoms. The dispersing agent is bis-polyisobutylene succinimide. The base oil is group I base oil 400SN available from PetroChina Daqing Petrochemical Company.

Components	Contents (%)
Linear alkyl (C26) calcium sulfonate with superhigh base number	20
Sulfurized calcium alkyl (C22) phenolate with superhigh base number	42
Alkyl (C26) calcium naphthenate with superhigh base number	20
Zinc secondary alkyl (C12) thiophosphate	0
Bis-polyisobutylene succinimide	8
Group I base oil of 400SN	10

Example 5:

[0026] The composite additive used in BOB system may be prepared from the components mentioned below (their contents in weight percentage are also given in detail) by means of normal process.

[0027] In this example, the sulfonate with superhigh base number is long-chain linear C₂₀-alkyl benzene calcium sulphonate with superhigh base number and its base number is 410 mgKOH/g, the sulfurized alkyl phenolate with superhigh base number is long-chain C₂₄-alkyl sulfurized calcium phenolate and the base number thereof is 300 mg-KOH/g, and the naphthenate detergent with superhigh base number is C₂₆-alkyl calcium naphthenate with superhigh base number and the base number thereof is 405 mgKOH/g. The antiwear agent is zinc long-chain secondary alkyl thiophosphate wherein the long-chain secondary alkyl group comprises 16 carbon atoms. The dispersing agent is multi-polyisobutylene succinimide. The base oil is group I base oil 650SN available from PetroChina Daqing Petrochemical Company.

Components	Contents (%)
Linear alkyl (C20) calcium sulfonate with superhigh base number	16
Sulfurized calcium alkyl (C24) phenolate with superhigh base number	40
Alkyl (C26) calcium naphthenate with superhigh base number	20
Zinc secondary alkyl (C16) thiophosphate	4
Multi-polyisobutylene succinimide	0

EP 2 497 818 A1

(continued)

Components	Contents (%)
Group I base oil of 650SN	20

Example 6:

[0028] The composite additive used in BOB system may be prepared from the components mentioned below (their contents in weight percentage are also given in detail) by means of normal process.

[0029] In this example, the sulfonate with superhigh base number is long-chain linear C₂₀-alkyl benzene calcium sulphonate with superhigh base number and its base number is 410 mgKOH/g, the sulfurized alkyl phenolate with superhigh base number is long-chain C₂₄-alkyl sulfurized calcium phenolate and the base number thereof is 300 mg-KOH/g, and the naphthenate detergent with superhigh base number is C₂₆-alkyl calcium naphthenate with superhigh base number and the base number thereof is 405 mgKOH/g. The antiwear agent is zinc long-chain secondary alkyl thiophosphate wherein the long-chain secondary alkyl group comprises 16 carbon atoms. The dispersing agent is multi-polyisobutylene succinimide. The base oil is group I base oil 650SN available from PetroChina Daqing Petrochemical Company.

Components	Contents (%)
Linear alkyl (C20) calcium sulfonate with superhigh base number	19
Sulfurized calcium alkyl (C24) phenolate with superhigh base number	40
Alkyl (C26) calcium naphthenate with superhigh base number	25
Zinc secondary alkyl (C16) thiophosphate	2
Multi-polyisobutylene succinimide	4
Group I base oil of 650SN	10

[0030] The present invention provides a tri-detergent composite additive designed for the BOB system, and the physical and chemical properties of such composite additive are able to satisfy the requirement of Maersk Fluid Co. about the composite additive designed for the BOB system. The physical and chemical properties of the composite additives obtained by the above examples are listed in Table 1.

Table 1 Comparison of the physical and chemical properties of the tri-detergent cylinder oil composite additives designed for the BOB system

Item	Sample						Technical requirement	Method
	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6		
Kinematic viscosity (100°C), mm ² /s	93.68	89.64	90.52	88.78	91.38	92.80	<95 according to OEM	GB/T 265
Base number, mgKOH/g	308	298	302	295	298	306	≥285 according to OEM	SH/T 0251
Density (20°C), kg/m ³	1095.2	1082.5	1090.6	1080.8	1092.6	1098.7	Report	SH/T 0604
Flash point (closed), °C	188	192	186	191	188	195	≥150	GB/T 261
Moisture, %	0.10	0.06	0.03	0.06	0.05	0.08	<0.2	GB/T 260

EP 2 497 818 A1

(continued)

Item	Sample						Technical requirement	Method
	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6		
Mechanical impurity, %	0.030	0.020	0.018	0.028	0.015	0.020	<0.1	GB/T 511
Sulfated ash, %	38.62	33.54	35.86	34.62	37.54	36.91	Report	GB/T 2433

[0031] The composite additive designed for the BOB system using triple detergents provided by the present invention is well compatible with system oil products under typical domestic and foreign brands, for example Exxon-Mobile Company, BP Company and PetroChina. The performances of the formulated cylinder oils with different base numbers are individually studied by simulated experiments, and the results demonstrate that the cylinder oils with different base numbers maintain good combination property as for lubricating oil, for example the antioxidization, antiwear, detergency and water resisting performances and etc. Herein, the antioxidization performance of the cylinder oil is evaluated according to the oxidative induction time which is measured by differential scanning calorimetry (PDSC). The antiwear performance is evaluated by the Pb value and the long wear extent which are obtained by four-ball test. The coking tests are carried out in order to test the detergency performance of the cylinder oil, while the gel tests are carried out so as to test the storage stability.

[0032] The tri-detergent composite additive designed for the BOB system formulated according to the formulation of Example 6 is blended with Exxon-Mobile system oil Mobilgard M300, BP system oil Energol OE-HT30 and Kunlun system oil DCC3008, respectively, so as to provide cylinder oils with the base numbers of 70 mgKOH/g, 60 mgKOH/g, 50 mgKOH/g and 40 mgKOH/g as shown in Tables 2, 3, 4 and 5.

Table 2 Physical and chemical properties of the cylinder oil with the base number of 70 mgKOH/g and the simulated performance thereof

Item	Unit	Mobilgard M300	Energol OE-HT30	KUNLUN DCC3008	Method
Dosage of the composite additive, %		22	22	21.2	
Viscosity, 100°C	mm ² /s	14.12	14.72	13.81	GB/T 265
Viscosity coefficient	-	105	102	104	ISO2909
Base number	mgKOH /g	69.2	70.2	69.8	SH/T 0251
Flash point	°C	252	250	258	GB/T 261
Sulfated ash, %	w%	7.82	7.72	7.68	GB/T 2433
Oxidative induction time by PDSC	min	14.72	13.98	13.20	SH/T 0719, the test condition is: 200°C, 3.0MPa, O ₂
Pb value by four-ball test	N	1254	1186	1186	GB/T 3142
Long wear extent by four-ball test	mm	0.34	0.33	0.34	SH/T 0189
Coking test	mg	21	20	18	SH/T 0300

EP 2 497 818 A1

(continued)

Item	Unit	Mobilgard M300	Energol OE-HT30	KUNLUN DCC3008	Method
Gel test	ml	0.3	0.5	0.25	1 % of water and 99% of oil are blended in the test tube, stirred by an agitator blade (2000rpm) for 60 sec and stored at 70°C for 96 h. The precipitation amount at tube bottom is observed.

Table 3 Physical and chemical properties of the cylinder oil with the base number of 60 mgKOH/g and the simulated performance thereof

Item	Unit	Mobilgard M300	Energol OE-HT30	KUNLUN DCC3008	Method
Dosage of the composite additive, %		18.64	18.64	17.8	
Viscosity, 100°C	mm ² / s	13.86	14.35	13.47	GB/T 265
Viscosity coefficient	-	102	100	108	ISO2909
Base number	mgK OH/g	59.2	59.8	60.2	SH/T 0251
Flash point	°C	250	258	252	GB/T 261
Sulfated ash, %	w%	7.36	7.40	7.35	GB/T 2433
PDSC	min	14.14	13.08	12.89	SH/T 0719, the test condition is: 200°C, 3.0MPa, O ₂
Pb value by four-ball test	N	1186	1117	1186	GB/T 3142
Long wear extent by four-ball test	mm	0.34	0.34	0.33	SH/T 0189
Coking test	mg	19	20	16	SH/T 0300

EP 2 497 818 A1

(continued)

Item	Unit	Mobilgard M300	Energol OE-HT30	KUNLUN DCC3008	Method
Gel test	ml	0.5	0.2	0.25	1 % of water and 99% of oil are blended in the test tube, stirred by an agitator blade (2000 rpm) for 60 sec and stored at 70°C for 96 h. The precipitation amount at tube bottom is observed.

Table 4 Physical and chemical properties of the cylinder oil with the base number of 50 mgKOH/g and the simulated performance thereof

Item	Unit	Mobilgard M300	Energol OE-HT30	KUNLUN DCC3008	Method
Dosage of the composite additive, %		15.25	15.25	14.38	
Viscosity, 100°C	mm ² /s	13.46	13.98	13.06	GB/T 265
Viscosity coefficient	-	105	100	102	ISO2909
Base number	mgK OH/g	49.8	49.2	49.7	SH/T 0251
Flash point	°C	246	258	250	GB/T 261
Sulfated ash, %	w%	6.97	6.86	6.94	GB/T 2433
PDSC	min	13.86	13.04	11.95	SH/T 0719, the test condition is: 200°C, 3.0MPa, O ₂
Pb value by four-ball test	N	1049	1117	1117	GB/T 3142
Long wear extent by four-ball test	mm	0.35	0.34	0.34	SH/T 0189
Coking test	mg	26	18	20	SH/T 0300

EP 2 497 818 A1

(continued)

Item	Unit	Mobilgard M300	Energol OE-HT30	KUNLUN DCC3008	Method
Gel test	ml	0.45	0.32	0.50	1 % of water and 99% of oil are blended in the test tube, stirred by an agitator blade (2000 rpm) for 60 sec and stored at 70°C for 96 h. The precipitation amount at tube bottom is observed.

Table 5 Physical and chemical properties of the cylinder oil with the base number of 40 mgKOH/g and the simulated performance thereof

Item	Unit	Mobilgard M300	Energol OE-HT30	KUNLUN DCC3008	Method
Dosage of the composite additive, %		11.86	11.86	10.96	
Viscosity, 100°C	mm ² / s	12.92	13.62	12.67	GB/T 265
Viscosity coefficient	-	100	108	102	ISO2909
Base number	mgK OH/g	39.6	40.1	39.8	SH/T 0251
Flash point	°C	246	250	258	GB/T 261
Sulfated ash, %	w%	6.50	6.36	6.58	GB/T 2433
PDSC	min	12.82	13.41	11.98	SH/T 0719, the test condition is: 200°C, 3.0MPa, O ₂
Pb value by four-ball test	N	1117	1117	1186	GB/T 3142
Long wear extent by four-ball test	mm	0.35	0.34	0.35	SH/T 0189
Coking test	mg	21	24	18	SH/T 0300

(continued)

Item	Unit	Mobilgard M300	Energol OE-HT30	KUNLUN DCC3008	Method
Gel test	ml	0.4	0.25	0.5	1 % of water and 99% of oil are blended in the test tube, stirred by an agitator blade (2000 rpm) for 60 sec and stored at 70°C for 96 h. The precipitation amount at tube bottom is observed.

[0033] The composite additive designed for the BOB system using triple detergents provided by the present invention can be blended with system oils so as to provide cylinder oils that can satisfy the requirement of the engine. Such composite additive has been tested by sailing over 4000 hours wherein BP Energol OE-HT30 is used as the system oil by the vessel, and has been technically certified by MAN B&W. Samples of the fresh/waste cylinder oils using such composite additive during the sailing were monitored, and the data are illustrated in Figure 2.

[0034] Throughout the test of 4000 hours, the base number of the cylinder oil formulated from the composite additive decreased from 70 mgKOH/g at the beginning, through 60 mgKOH/g and 50 mgKOH/g, to 40 mgKOH/g at the end. The entire sailing test could be divided into four stages according to the base number of the cylinder oil, and each stage lasted about 1000 hours.

[0035] It can be clearly seen from Figure 2 that the residual base number in the waste oil was not notably decreased, and the Fe content resulted from the wear was not notably increased, either, that is, the both important index fluctuated within normal ranges.

1. The Fe content in the waste oil was never abnormally high, and the Fe content of all the samples was always less than 150 ppm, which satisfied the requirement of the engine OEM about the performance of cylinder oils;

2. The residue base number of the waste oil from the four different stages tended to decrease due to the decrease of the base number of fresh oils. Furthermore, even if the cylinder oil with a base number of 40 mgKOH/g was used, the residue base number in the waste oil was still above 15 mgKOH/g. It is shown that the composite additive has strong ability to "store" the base number, and thus effectively prevent the wear of engine parts to occur.

[0036] In conclusion, the cylinder oil maintained steady combination performance in case that the variation of the dosage of the composite additive reached the extent close to 50%, especially in terms of the antiwear performance under extreme pressure and the ability to preserve the base number. The test results sufficiently satisfied the requirement of the engine about the lubricating oil performance and were technically certified by the engine OEM.

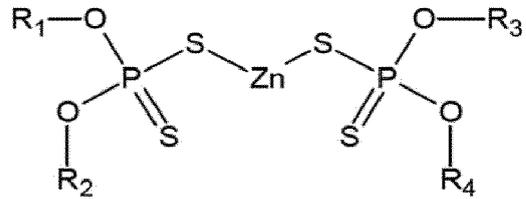
Claims

1. A marine cylinder oil composite additive, **characterized in that**, based on the total weight of the composite additive, it comprises: 15-25% sulfonate detergent with superhigh base number, 35-45% phenolate detergent with superhigh base number, 20-30% naphthenate detergent with superhigh base number, 0-8% dispersing agent, 0-4% antiwear agent, and 10-20% Group I base oil with high viscosity index which is selected from the group consisting of 400SN, 500SN and 650SN;
said sulfonate detergent with superhigh base number is C₂₂-C₃₀ linear alkyl benzene calcium sulphonate, wherein the base number thereof is 395-430 mgKOH/g;
said phenolate detergent with superhigh base number is C₁₈-C₂₄ alkyl sulfurized calcium phenolate, wherein the base number thereof is 290-310 mgKOH/g;
said naphthenate detergent with superhigh base number is C₂₀-C₃₀ long chain alkyl calcium naphthenate, wherein the base number thereof is 390-420 mgKOH/g;

EP 2 497 818 A1

said dispersing agent is selected from the group consisting of mono-polyisobutylene succinimide, bis-polyisobutylene succinimide and multi-polyisobutylene succinimide;
said antiwear agent is zinc long-chain alkyl thiophosphate with the structure corresponding to the following formula,

5



10

wherein R_1 , R_2 , R_3 and R_4 are long-chain primary alkyl groups each comprising 12-18 carbon atoms, or R_1 , R_2 , R_3 and R_4 are long-chain secondary alkyl groups each comprising 12-16 carbon atoms.

15

2. The marine cylinder oil composite additive according to claim 1, **characterized in that**, the kinematic viscosity of said base oil is 8.0-11.0 cst at 100°C.

20

25

30

35

40

45

50

55

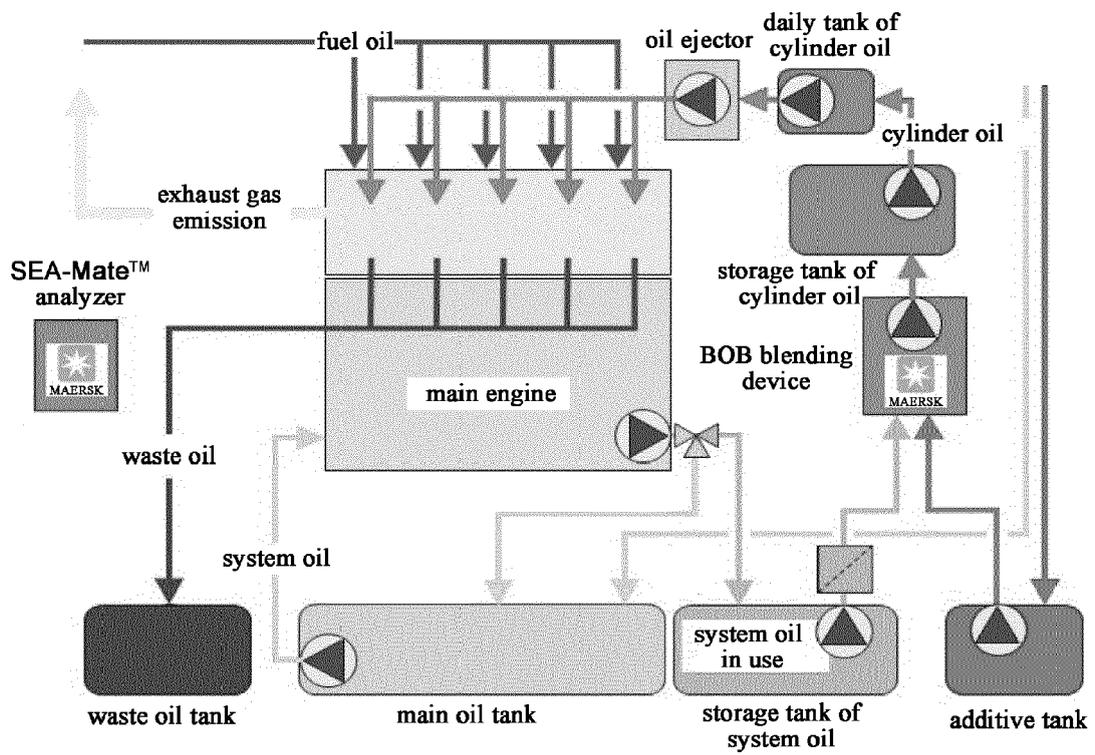


Figure 1

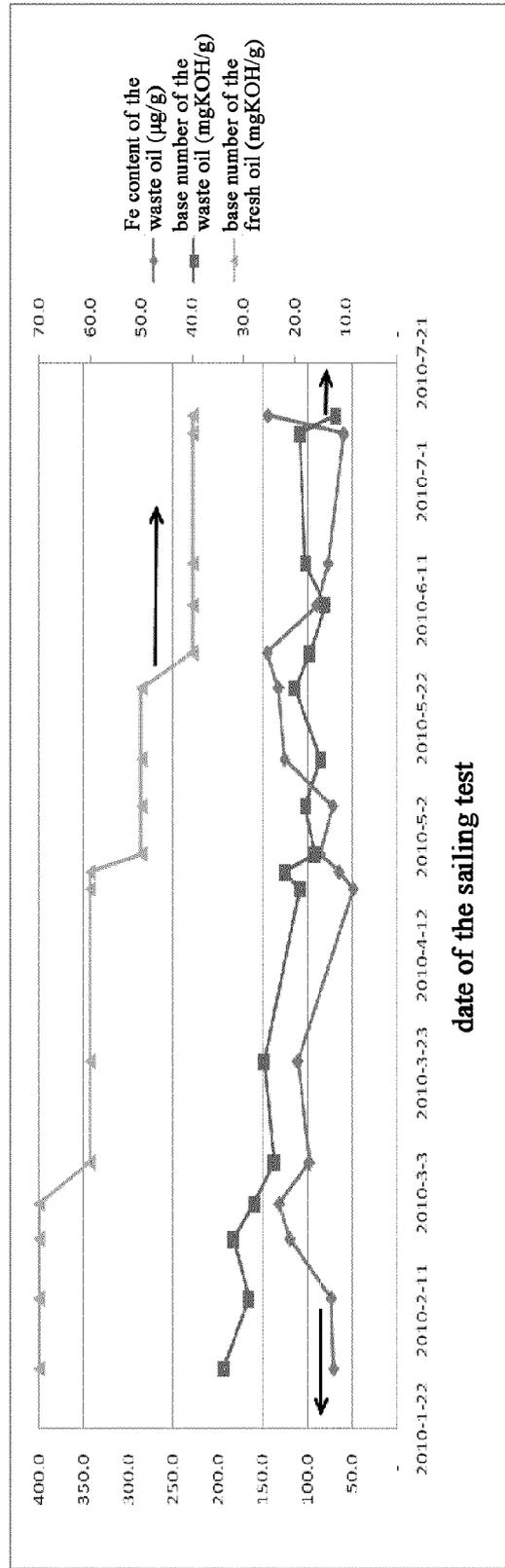


Figure 2 Monitoring data of the samples during the sailing test for the bis-detergent composite additive designed for the BOB system



EUROPEAN SEARCH REPORT

Application Number
EP 12 15 8753

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	EP 1 126 010 A1 (CHEVRON ORONITE JAPAN LTD [JP]) 22 August 2001 (2001-08-22) * paragraph [0012] - paragraph [0035]; claims 1,2,3,4,7,13-23; examples 1-6 *	1,2	INV. C10M163/00
Y	US 2008/287327 A1 (MAYHEW ALEXANDRA [GB] ET AL) 20 November 2008 (2008-11-20) * sentences 68,78, paragraph 23; tables 2,3 *	1,2	
Y	EP 0 331 359 A1 (EXXON CHEMICAL PATENTS INC [US]) 6 September 1989 (1989-09-06) * page 4, line 34 - line 35; claims 1-7,19-21; tables 1-3 *	1,2	
Y	CN 101 161 798 A (WUXI HUIYUAN ADVANCED LUBRICAT [CN]) 16 April 2008 (2008-04-16) * abstract; example 1 *	1,2	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
			C10M
1	Place of search Munich	Date of completion of the search 10 July 2012	Examiner Pöllmann, Klaus
CATEGORY OF CITED DOCUMENTS 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		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	

EPO FORM 1503 03.02 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 12 15 8753

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.

10-07-2012

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1126010	A1	22-08-2001	CA 2336505 A1	14-08-2001
			EP 1126010 A1	22-08-2001
			JP 4011815 B2	21-11-2007
			JP 2001226691 A	21-08-2001
			SG 95628 A1	23-04-2003
			US 2001019999 A1	06-09-2001

US 2008287327	A1	20-11-2008	EP 1963469 A1	03-09-2008
			JP 2009511718 A	19-03-2009
			US 2008287327 A1	20-11-2008
			WO 2007047446 A1	26-04-2007

EP 0331359	A1	06-09-1989	DE 68901549 D1	25-06-1992
			EP 0331359 A1	06-09-1989
			ES 2033089 T3	01-03-1993
			GR 3005497 T3	24-05-1993
			HK 99894 A	23-09-1994
			JP 2008296 A	11-01-1990
			US 4948522 A	14-08-1990

CN 101161798	A	16-04-2008	NONE	
