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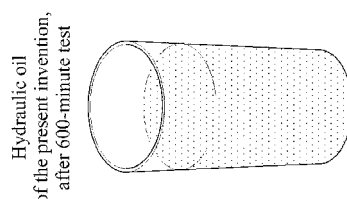
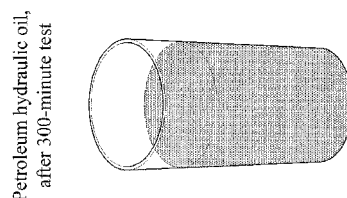
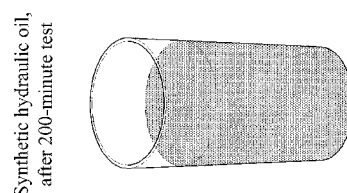
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(54) **FIRE-RESISTANT HYDRAULIC OIL**

(57) Provided is a flame-retardant hydraulic oil prepared by mixing 25 to 97 % by weight (wt%) of a petroleum lubricating base oil, 1 to 20 wt% of a phosphorus or halogen flame-retardant additive, 1 to 35 wt% of an ester compound, and 0.05 to 20 wt% of a performance enhancer.

FIG 1

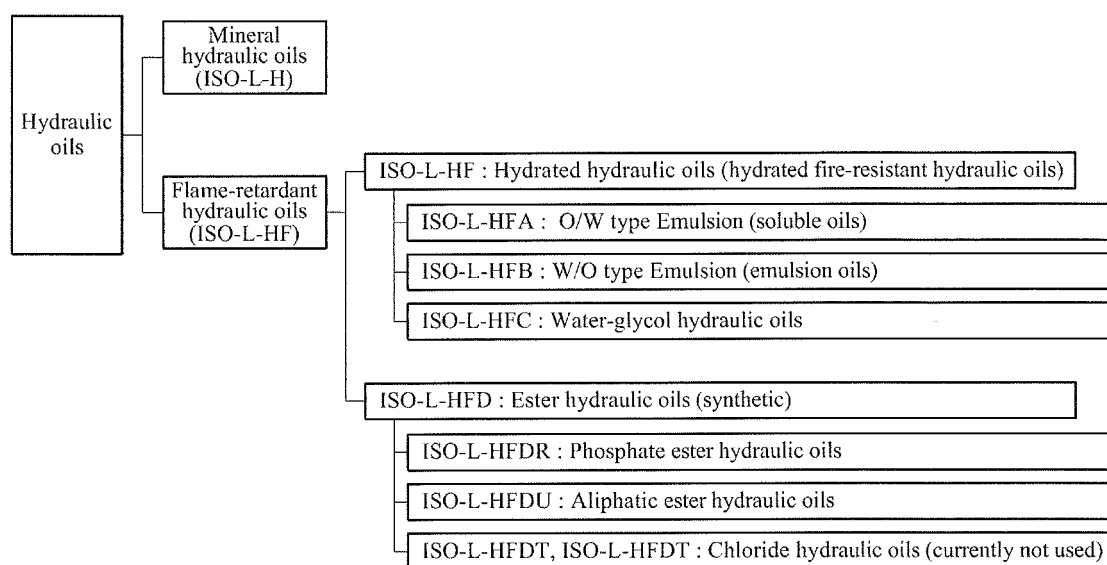


DescriptionTechnical Field

[0001] The present invention relates to a new type of flame-retardant hydraulic oil which is impervious to fire and has heat and oxidation stability to lengthen a life, contributing to social development and stability.

Background Art

[0002] As an increasing number of high-temperature and high-pressure devices are being used in a variety of industrial facilities, it is necessary to supply a lubricating oil, in particular, hydraulic oil which may actively contribute to addressing a risk of fire. A hydraulic oil which contributes to dealing with a risk of fire is referred to as a flame-retardant hydraulic oil and is classified as follows in Table 1, according to the International Organization for Standardization (ISO) standards ISO classification system.

Table 1

[0003] A flame-retardant hydraulic oil collectively refers to products which cause small flames, does not allow a fire to quickly spread, and is self-extinguishable when a fire breaks out.

[0004] Various types of hydraulic oils are currently being developed and used, wherein petroleum hydraulic oils including mineral oils as lubricating base oils are mostly used. However, the petroleum, that is, mineral hydraulic oils are inappropriate for use at high-temperatures due to a great risk of fire. In contrast, the flame-retardant hydraulic oil is safe from a fire and is very expensive, for example, 3 to 10 times a price of petroleum oils and needs to be handled in a special environment, for example, for sealing and packing. Thus, many facilities use petroleum hydraulic oils in a dangerous environment in which exposure to a fire is prevalent.

[0005] Therefore, a need exists for a new, inexpensive type of flame-retardant hydraulic oil that does not need to be handled in a special environment, and is usable for a long period of time.

Disclosure of InventionTechnical Goals

[0006] An aspect of the present invention provides a flame-retardant hydraulic oil which is fire resistant, inexpensive, does not need to be handled in a special environment, and has a long life.

Technical solutions

[0007] According to an aspect of the present invention, there is provided a flame-retardant hydraulic oil prepared by mixing 25 to 97 % by weight (wt%) of a petroleum lubricating base oil, 1 to 20 wt% of a phosphorus or halogen flame-re-

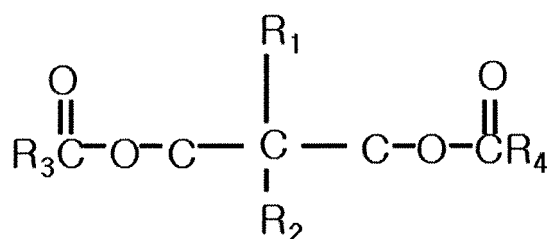
tardant additive, 1 to 35 wt% of an ester compound, and 0.05 to 20 wt% of a performance enhancer.

[0008] The petroleum lubricating base oil may include most refined petroleum lubricating base oils provided domestically and internationally, wherein a petroleum lubricating base oil having a dynamic viscosity of 5 to 1,000 millimeters/second (mm²/sec) at 40 °C and a paraffin content of 50 to 90 wt% is preferably used since petroleum lubricating base oils having excessively high or excessively low viscosity may cause a problem in operation.

[0009] The flame-retardant additive used for the flame-retardant hydraulic oil may include phosphorus or halogen flame-retardant additives, wherein a compound including both phosphorus and halogen additives further enhances flame retardancy. The flame-retardant additive is obtained by introducing phosphorus and a halogen, which are flame retardant, into an aryl or allyl group and is selected from the group consisting of tricresyl phosphate, tributyl phosphate, tris(β-chloroethyl) phosphate, tris(β-chloropropyl) phosphate, tris(dichloropropyl) phosphate, trioctyl phosphate, triphenyl phosphate, octyl diphenyl phosphate, tris(isopropylphenyl) phosphate and tributoxyethyl phosphate.

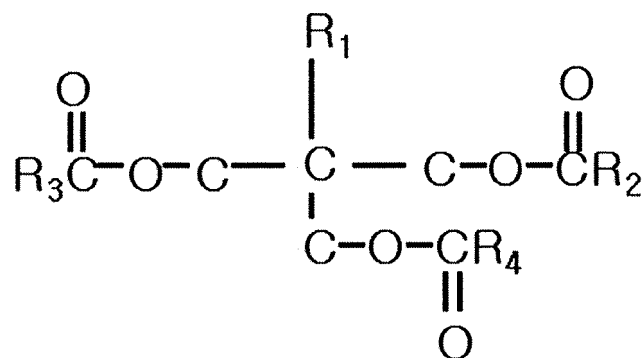
[0010] The ester compound used for the flame-retardant hydraulic oil may include at least one selected from the group consisting of compounds represented by Formulas 1 to 3:

[Formula 1]



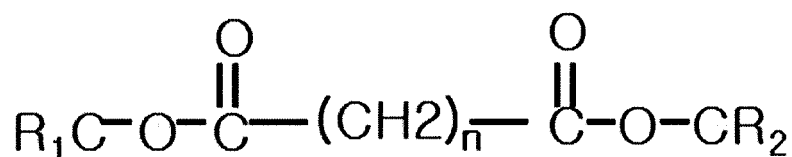
where R₁ and R₂ are the same or different and each represent a C1 to C2 alkyl group, and R₃ and R₄ are the same or different and each represent a C6 to C22 saturated or unsaturated alkyl group;

[Formula 2]



where R₁ represents a C1 to C2 alkyl group, and R₂, R₃ and R₄ are the same or different and each represent a C6 to C22 saturated or unsaturated alkyl group; and

[Formula 3]



where n is an integer from 2 to 12, and R₁ and R₂ are the same or different and each represent a C2 to C 18 alkyl group.

[0011] The ester compound may include polyol esters disclosed by the inventor of the present invention in KR Patent Registration No. 88842, No. 169565 and No. 0201759 and may include at least one of dibasic esters, such as adipates, azelates, sebacates and phthalates.

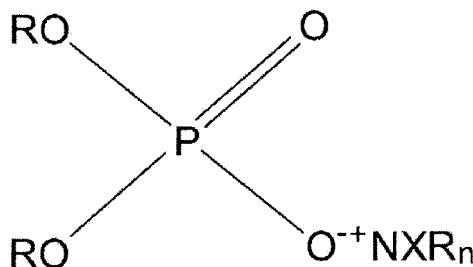
[0012] The hydraulic oil is inexpensive, does not need to be handled in a special environment and has excellent flame retardancy by adding the phosphorus or halogen flame-retardant additive to the petroleum lubricating base oil. Conventionally, the phosphorus or halogen flame-retardant additive is not properly mixed into the petroleum lubricating base oil, but the present invention solves such a problem by adding the ester compound.

[0013] According to an aspect of the present invention, the performance enhancer includes an antioxidant, an anti-load and anti-abrasive additive, a viscosity enhancer, an anticorrosive agent and an antifoaming agent.

[0014] The antioxidant may include metal salts of phenyl naphthylamine, phenyl, and phosphate ester and be used in an amount of 0.1 to 10 wt%.

[0015] The anti-load and anti-abrasive additive is preferably amine salts of phosphate ester neutralized and represented by Formula 4, has a synergy effect in combination with metal salts of phosphate ester, allyl phosphate ester and a sulfide as additives, and is added in an amount of 0.05 to 7.0 wt%:

[Formula 4]



where R represents hydrogen or a C1 to C10 alkyl or aryl hydrocarbon compound, X represents hydrogen or C1 to C4 hydrocarbon, and n is an integer from 1 to 10.

[0016] The viscosity enhancer may include an olefin copolymer, polymethacrylate or the like, preferably polymethacrylate exhibiting excellent shear stability and less change in viscosity and having a molecular weight of 200,000 or less. Here, a combination of a low molecular weight viscosity enhancer and a high molecular weight viscosity enhancer may improve low-temperature fluidity as well as viscosity index. The viscosity enhancer is added in an amount of 0.1 to 5.0 wt%.

[0017] 0.01 to 2.0 wt% of the anticorrosive agent or the antifoaming agent may be added, as necessary.

[0018] Although the foregoing additives are necessary for the lubricating oil composition, excessive amounts thereof may reduce flame retardancy or decrease in viscosity by shear, generation of dregs or discoloration of the oiling agent. Thus, it is needed to mix proper amounts of the base oil and the additives.

Advantageous effects

[0019] A flame-retardant hydraulic oil according to the present invention is safe from a fire, inexpensive, does not need to be handled in a special environment, and has a long life.

Brief Description of Drawings

[0020] FIG. 1 is a diagram illustrating occurrences of sludge in examples of the present invention and comparative examples after an oxidation stability test.

Best Mode for Carrying Out the Invention

[0021] Reference will now be made in detail to embodiments of the present invention.

Preparation of petroleum (mineral) lubricating base oil

[0022] As a petroleum lubricating base oil, general lubricating base oils available from oil companies were used in view of a flash point, heat and oxidation stability, and impurities content as illustrated in Table 2.

Table 2

	Dynamic viscosity (mm ² /sec)	Color (KS M 2106)	Flash point (in open cup, °C)	Hydrocarbon composition	
				C _p	C _A
Petroleum lubricating base oil A	15.0 ± 2.0	2.5 or lower	200 or higher	50 or higher	3 or lower
Petroleum lubricating base oil B	20.0 ± 2.0		200 or higher		
Petroleum lubricating base oil C	30.0 ± 2.0		220 or higher		
Petroleum lubricating base oil D	35.0 ± 2.0		220 or higher		
Petroleum lubricating base oil F	50.0 ± 2.0		240 or higher		
Petroleum lubricating base oil H	100.0 ± 5.0		240 or higher		
Petroleum lubricating base oil G	120.0 ± 10.0		260 or higher		
Petroleum lubricating base oil H	200.0 ± 10.0		260 or higher		
Petroleum lubricating base oil I	480.0 ± 20.0		300 or higher		
Petroleum lubricating base oil J	1000.0 ± 100.0		300 or higher		
The closer to 0.0 C _A is, the more appropriate.					

Preparation of ester lubricating base oil

[0023] Ester compounds used to prepare mixed flame-retardant hydraulic oils according to the present invention were prepared as listed in Table 3 and may be used independently or as mixtures.

Table 3

	Type I (self-manufactured ester)	Type II (commercially available ester)
50	Appearance (KS M 2106)	2.5 or lower
	Total acid number (mg KOH/g)	2.0 or lower
	Dynamic viscosity (40°C), mm ² /sec)	10 to 250
55	Flash point (open type, °C)	200 or higher

Preparation of flame-retardant additive

[0024] Flame-retardant additives were prepared as illustrated in Table 4, wherein raw materials having a purity of 80% or higher were used for stability of the hydraulic oils.

Table 4

Flame-retardant additive A	Tricresyl phosphate
Flame-retardant additive B	Tributyl phosphate
Flame-retardant additive C	Tris(β -chloroethyl) phosphate
Flame-retardant additive D	Tris(β -chloropropyl) phosphate
Flame-retardant additive E	Tris(dichloropropyl) phosphate
Flame-retardant additive F	Trioctyl phosphate
Flame-retardant additive G	Triphenyl phosphate
Flame-retardant additive H	Octyl diphenyl phosphate
Flame-retardant additive I	Tris(isopropylphenyl)phosphate)
Flame-retardant additive J	Tributoxyethyl phosphate

Preparation of hydraulic oil

[0025] The lubricating base oils and the flame-retardant additives listed in Tables 2, 3 and 4 were added to suitable amounts of performance enhancers, thereby preparing hydraulic oils as illustrated in Tables 5 and 6. Here, content is expressed as percent by weight (wt%).

Table 5

Ingredients	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Petroleum lubricating base oil A	20.0		40.0				
Petroleum lubricating base oil C		65.0		30.0			
Petroleum lubricating base oil E	60.0	20.0		40.0	70.0		
Petroleum lubricating base oil G			40.0			40.0	10.0
Petroleum lubricating base oil I					10.0	25.0	40.0
Self-manufactured ester 1	5.0		10.0			10.0	
Commercially available ester 2		3.0		5.0			30.0
Flame-retardant additive A	2.0		2.0		5.0		
Flame-retardant additive B	5.0	3.0					
Flame-retardant additive C			1.0				

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(continued)

Ingredients	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Flame-retardant additive D				10.0			
Flame-retardant additive E		3.0					
Flame-retardant additive F						10.0	
Flame-retardant additive G						10.0	
Flame-retardant additive H			2.0	5.0			
Flame-retardant additive I					5.0		
Flame-retardant additive J							10.0
Antioxidant	1.0	0.5	2.0	1.0	0.5	2.0	0.5
Anti-abrasive additive	1.0	0.5	2.0	2.0	2.0	2.0	
Viscosity enhancer	Suitable	Suitable	Suitable	Suitable	Suitable	Suitable	Suitable
Antifoaming agent and etc.	Suitable	Suitable	Suitable	Suitable	Suitable	Suitable	Suitable

Table 6

Ingredients	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
Petroleum lubricating base oil B	60.0		20.0				
Petroleum lubricating base oil D		50.0		30.0			
Petroleum lubricating base oil F		20.0		20.0	45.0		
Petroleum lubricating base oil H	10.0		50.0			40.0	
Petroleum lubricating base oil J							15.0
Self-manufactured ester 1	10.0		10.0		35.0	35.0	
Commercially available ester 2		5.0		20.0			20.0
Flame-retardant additive A	5.0			15.0	5.0		15.0
Flame-retardant additive B		5.0					
Flame-retardant additive C			10.0				5.0

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(continued)

Ingredients	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
Flame-retardant additive D	5.0				10.0		
Flame-retardant additive E		5.0					
Flame-retardant additive F				5.0			
Flame-retardant additive G	5.0					20.0	
Flame-retardant additive H			10.0				
Flame-retardant additive I		5.0					
Flame-retardant additive J			5.0				
Antioxidant	1.0	1.0	2.0	1.0	1.5	1.0	0.5
Anti-abrasive additive	2.0	1.0	2.0	2.0	2.0		1.0
Viscosity enhancer	Suitable	Suitable	Suitable	Suitable	Suitable	Suitable	Suitable
Antifoaming agent and etc.	Suitable	Suitable	Suitable	Suitable	Suitable	Suitable	Suitable

Quality test of flame-retardant hydraulic oils

[0026] The hydraulic oils prepared as illustrated in Tables 5 and 6 were evaluated in terms of qualities, and results thereof are listed in Tables 7 and 8.

[0027] The hydraulic oils were generalized in accordance with the International Standards Organization Viscosity Grade (ISO VG). Oxidation stability was evaluated by the rotating bomb oxidation test, ASTM D 2272, while abrasion resistance was evaluated by the shell 4-ball test. Further, flame retardancy was evaluated by the hot manifold test, MIL-F-7100 Fed 6053, in which a sample was dropped on a manifold at a temperature of 374 °C and identified whether to ignite, and by a sprayed fire test, by which a sample is accessed as flame retardant when the sample has an oxygen demand of 50% or higher necessary to catch fire when sprayed.

Table 7

Ingredients	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Dynamic viscosity (ISO VG)	32	32	46	46	68	68	100
Flash point (°C)	250	250	250	260	270	270	300
Pour point (°C)	-30.0	-30.0	-25.0	-25.0	-25.0	-25.0	-20.0
Oxidation stability (RBOT, min)	500	400	400	500	350	400	500

(continued)

Ingredients	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Abrasion resistance (Scar ϕ mm)	0.35	0.35	0.35	0.30	0.30	0.35	0.35
Flame retardancy	Hot Manifold test	Extinguished immediately after ignition					
	Sprayed fire test	Oxygen demand: 50 - 55 %					

Table 8

Test categories	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
Dynamic viscosity (ISO VG)	46	46	68	68	68	100	100
Flash point ($^{\circ}$ C)	250	260	250	270	270	280	280
Pour point ($^{\circ}$ C)	-25.0	-25.0	-25.0	-25.0	-25.0	-20.0	-20.0
Oxidation stability (RBOT, min)	400	400	400	500	600	500	500
Abrasion resistance (Scar ϕ mm)	0.30	0.35	0.35	0.35	0.35	0.35	0.30
Flame retardancy	Hot Manifold test	Extinguished immediately after ignition					
	Sprayed fire test	Oxygen demand: 50 ~ 55 %					

Identification of excellent heat and oxidation stability

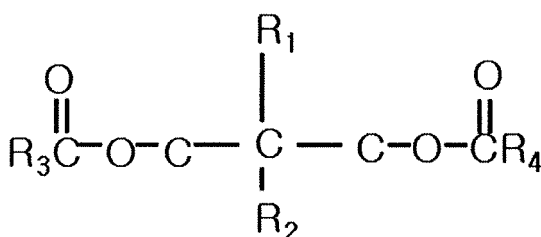
[0028] When a hydraulic oil is subjected to the rotating bomb oxidation test, discoloration and a large amount of precipitate generally occur, and such a precipitate is identified to cause various faults when equipment operates.

[0029] FIG. 1 is a diagram illustrating occurrences of sludge in examples of the present invention and comparative examples after an oxidation stability test.

[0030] Referring to FIG. 1, the flame-retardant hydraulic oils according to the examples of the present invention involve less discoloration and generate a small amount of sludge after being tested over a long period of time when compared to a petroleum hydraulic oil and a synthetic hydraulic oil.

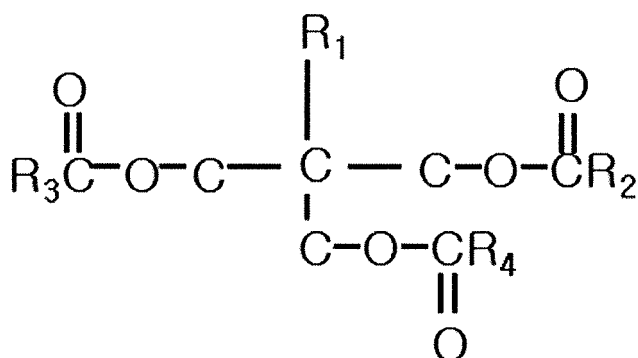
[0031] Although a few embodiments of the present invention have been shown and described, the present invention is not limited to the described embodiments. Instead, it would be appreciated by those skilled in the art that changes may be made to these embodiments without departing from the principles and spirit of the invention, the scope of which is defined by the claims and their equivalents.

- [Formula 1]



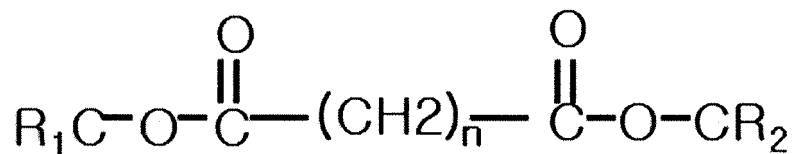
where R₁ and R₂ are the same or different and each represent a C1 to C2 alkyl group, and R₃ and R₄ are the same or different and each represent a C6 to C22 saturated or unsaturated alkyl group;

[Formula 2]



where R₁ represents a C1 to C2 alkyl group, and R₂, R₃ and R₄ are the same or different and each represent a C6 to C22 saturated or unsaturated alkyl group; and

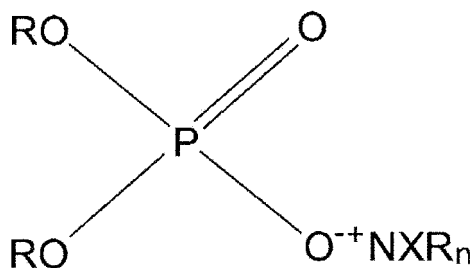
[Formula 3]



where n is an integer from 2 to 12, and R₁ and R₂ are the same or different and each represent a C2 to C18 alkyl group.

6. The flame-retardant hydraulic oil of claim 1, wherein the ester compound comprises at least one selected from the group consisting of adipates, azelates, sebacates and phthalates.
7. The flame-retardant hydraulic oil of claim 1, wherein the anti-load and anti-abrasive additive comprises an amine salt compound of phosphate ester represented by Formula 4:

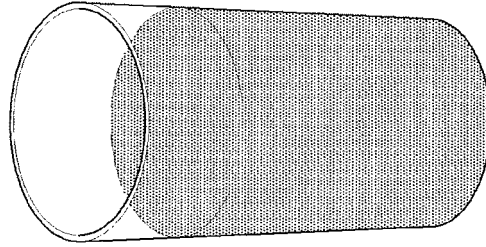
[Formula 4]



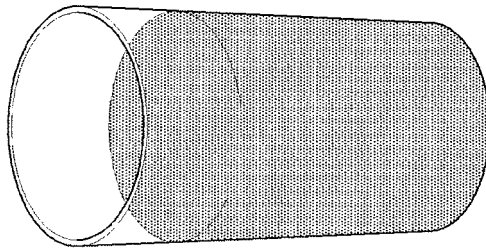
where R represents hydrogen or a C1 to C10 alkyl or aryl hydrocarbon compound, X represents hydrogen or C1 to C4 hydrocarbon, and n is an integer from 1 to 10.

FIG 1

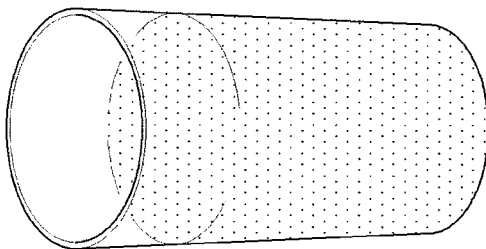
Synthetic hydraulic oil,
after 200-minute test



Petroleum hydraulic oil,
after 300-minute test



Hydraulic oil
of the present invention,
after 600-minute test



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2010/003368

A. CLASSIFICATION OF SUBJECT MATTER <i>C10M 169/04(2006.01)i, C10M 101/02(2006.01)i, C10M 129/72(2006.01)i</i> 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 169/04; C10M 141/10; C10M 169/06; C09K 5/04; C10M 105/42; C10M 119/12; C10M 169/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean Utility models and applications for Utility models: IPC as above Japanese Utility models and applications for Utility models: IPC as above Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS (KIPO internal) & Keywords: fire retardant, base oil, lubrication, phosphorus, ester, load persistent, abrasion persistent, amine salt, oxidation proof, thickener, antifoaming agent		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2002/0010103 A1 (TAKAYAMA, HIMIKO et al.) 24 January 2002 See abstract, pages 2-4, claims 1-18.	1-4,6,7 5
X Y	US 6551523 B1 (SCHNUR, NICHOLAS E.) 22 April 2003 See abstract, columns 4-7, claims 1-20.	1-4,6,7 5
Y	KR 10-2007-0087870 A (KOREA HOUGHTON CORPORATION) 29 August 2007 See abstract, pages 3-4, claims 1-7.	5
Y	KR 10-2008-0020442 A (KOREA HOUGHTON CORPORATION) 05 March 2008 See abstract, tables 1-3, claims 1-7.	5
☐ 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 MAY 2011 (24.05.2011)		Date of mailing of the international search report 25 MAY 2011 (25.05.2011)
Name and mailing address of the ISA/KR  Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140		Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

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INTERNATIONAL SEARCH REPORT Information on patent family members

International application No.

PCT/KR2010/003368

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- KR 0201759 [0011]