# Europäisches Patentamt **European Patent Office** Office européen des brevets



EP 0 796 908 A1 (11)

(12)

### **EUROPEAN PATENT APPLICATION**

(43) Date of publication: 24.09.1997 Bulletin 1997/39

(21) Application number: 97200253.9

(22) Date of filing: 30.01.1997

(51) Int. Cl.<sup>6</sup>: **C10M 111/04**, C10M 169/04 // (C10M111/04, 105:06, 105:18, 107:34), (C10M169/04, 107:34, 127:06, 129:16), C10N30:10

(84) Designated Contracting States: CH DE ES FR GB IT LI NL SE

(30) Priority: 20.02.1996 US 603730

(71) Applicants:

• UNILEVER N.V. NL-3000 DK Rotterdam (NL) **Designated Contracting States:** CH DE ES FR IT LI NL SE

 UNILEVER PLC London EC4P 4BQ (GB) **Designated Contracting States:** 

(72) Inventor: Rodenberg, Douglas G. Sharonville 0410 45241 (US)

(74) Representative: Rosen Jacobson, Frans Lucas M. et al Unilever N.V.. Patent Division. P.O. Box 137 3130 AC Vlaardingen (NL)

#### (54)**Oxidation resistant lubricant**

A synthetic lubricant composition having greatly improved oxidation resistance, compatibility with petroleum lubricants, good corrosion resistance, and hydrolytic stability, is formed by combining one or more polyalkylene glycols, singly or in combination, with an effective amount of one or more alkylated aromatic compound such as alkylated naphthalene. Polyalkylene glycols initiated with mono and polycyclic aromatic compounds such as alkyl phenol, cresol, and alkyl naphthol further enhance performance when used singly or in combination with other hydroxyl or alkyl initiated polyalkyene glycols. The blends are compounded with corrosion inhibitors, metal deactivators, dispersants, thickeners, and other additives known in the art of lubrication to produce a superior lubricant for air compressors, turbines, hydraulics, gears, bearings, fuel engines, textiles, textile machinery, and greases.

#### Description

5

10

#### Field of the invention

The present invention relates to synthetic lubricant compositions having good oxidation resistance, compatibility with petroleum lubricants, good corrosion resistance and hydrolytic stability, and being suitable for use in air compressors, turbines, hydraulics, gears, bearings, fuel engines, textile machinery and greases.

#### **Background of the Invention**

Different lubricants possessing a variety of characteristics are required for use in different applications.

Characteristics which are essential to certain applications include lubricity, seal compatibility, low volatility, low pour point temperature, anti-wear/extreme pressure, high thermal conductivity, thermal stability, corrosion resistance, hydrolytic stability, varnish and deposit control, and oxidation stability or resistance. Oxidation stability and related varnish/deposit control is very important for most applications and is essential for a good general purpose, long life synthetic lubricant.

The most common types of synthetic lubricant base stocks are polyalphaolefin (referred to as "PAO"), esters (referred to as diesters), polyol esters and polyalkylene glycols. These synthetic base stocks are used independently but are commonly used in combinations with each other to enhance their performance. Generally, esters are added at 20-30% to PAO to improve additive solubility and varnish/deposit control such as in synthetic motor oil lubricants, and at 20-30% to polyalkylene glycols to improve corrosion protection such as in air compressor lubricants. Esters are commonly used independently but perform best at higher temperatures or in clean, low humidity applications such as in chain lubricants and aircraft turbine lubricants. Because of their relatively poor hydrolytic stability and chemical resistance, they can cause premature degradation. Degradation of the ester through oxidation or hydrolysis by moisture results in corrosive acidic by-products. When esters are blended with either PAO or polyalkylene glycol, hydrolytic stability and chemical resistance of the blend is reduced and therefore the life of the lubricant based on that blend. Polyglycols by themselves exhibit excellent varnish/deposit control and hydrolytic stability and produce little acidic by-products upon oxidation. However, they exhibit very poor corrosion protection and they generally are not compatible with petroleum lubricants.

PAO's, by themselves, offer good oxidation stability;

however, they exhibit poor solubility characteristics, which results in poor seal compatibility, additive solubility, and varnish/deposit control.

Dow manufactures an air compressor lubricant that incorporates 30% ester with polyglycol. Overall, it is a good, cost effective lubricant, offering competitive oxidation life compared to PAO/ester and ester containing air compressor lubricants. However, its' water separation property is relatively poor and its' ester content tends to hydrolyze. This is disclosed, for example, in US Patent 4,302,343.

Most major oil companies as well as some oil blending companies now produce various synthetic motor oils that are formulated with 20-30% ester in PAO. PAO and ester blends are also commonly found in lubricants formulated for hydraulics, turbines, bearings, gears, and general purpose lubricant applications such as Mobil's SHC series of synthetic lubricants. Overall, such formulations are good, cost effective lubricants. However, oxidation resistance, varnish/deposit control, and resistance to moisture and combustion by-products or chemicals needs to be improved to extend lubricant life. Also, efforts to reduce additive content and improve pollution controls is intensifying.

Other synthetic lubricants include alkylated aromatic compounds such as those disclosed is US Patent 5,457,254, US Patent 5,414,174, US Patent 5,302,769, US Patent 5,235,115, US Patent 5,191,135, US Patent 5,191,134, US Patent 5,177,284, US Patent 5,171,904, US Patent 5,043,508, and US Patent 5,034,563. These are, however, more expensive and do not offer equivalent oxidation stability, varnish/deposit control, seal compatibility, and lubricity, and are not generally as suitable per se with applications such as compressors and the like.

Hatco Corp., Henkel Corp., and several major oil corporations manufacture ester based lubricants. These lubricants perform very well in jet turbines, high temperature chains, and other applications where high temperatures or extreme cleanliness eliminates moisture and chemical contaminants. Performance of esters in industrial applications such as air compressors, hydraulics, and gears is marginal for a synthetic lubricant due to moisture and chemical contaminants and poor seal compatibility.

Other lubricants include silicones, polyaryl (biphenyl) ethers, fluorinated organics, and phosphate esters that are extremely expensive and are suitable to only very special applications where unique performance characteristics are required and cost is not of foremost concern.

#### **Definition of the Invention**

The present invention is premised upon the realization that a lubricant exhibiting excellent lubricity, oxidation resistance, hydrolytic stability, and varnish/deposit control can be formed by combining a polyalkylene glycol with an alkylated

55

35

#### EP 0 796 908 A1

aromatic compound or an alkoxylated aromatic compound. Such a lubricant is relatively inexpensive, but retains all the advantages of the polyalkylene glycol, in particular, excellent lubricity, hydrolytic stability and varnish/deposit control. Further, this overcomes the deficiencies of polyalkylene glycols, providing compatibility with various types of petroleum lubricants, good corrosion resistance, and drastically improving oxidation resistance. Accordingly, the present invention provides a lubricant composition comprising a polyalkylene glycol compound in combination with an aromatic compound selected from the group consisting of alkylated aromatic lubricants and alkoxylated aromatic lubricants in an amount effective to improve the oxidation resistance of said polyalkylene glycol compound.

Preferably, the lubricant of the present invention is formed from one or more alkylated naphthalenes in combination with one or more polypropylene or polybutylene glycols initiated preferably with either an alkyl or aromatic alcohol. The objects and advantages of the present invention will be further appreciated in light of the following detailed description.

#### **Detailed Description**

The present invention is a lubricant or base stock blend formed by combining a polyalkylene glycol with an alkylated or alkoxylated aromatic composition. For purposes of the present invention, the aromatic portion of the aromatic composition can be a phenyl group, a naphthyl group or a fused aromatic compound such as a bis-phenyl or phenathrene group.

The aromatic moeity is desirably substituted with one or more alkyl groups. Specifically, the aromatic group is substituted with at least one alkyl group which is  $C_3$  alkyl or higher, generally  $C_5$  -  $C_{24}$ . In addition, or alternately, the aromatic group can be substituted with an alkoxy group to form, for example, an alkoxy naphthalene wherein the alkyl portion of the alkoxy group is  $C_3$  - $C_{24}$ . The method of manufacturing such compositions is relatively well known but is disclosed in particular in US Patent 5,191,135, US Patent 5,177,284, US Patent 5,191,134, and US Patent 5,043,508.

Generally, for use in the present invention, the aromatic composition will be an effective lubricant and will have a viscosity of at least about 10-220 cSt at  $40^{\circ}$  C. One preferred alkylated aromatic is a monoalkylated naphthalene ( $C_{16}$ ). Mobil Chemical Co. sells such an alkylated naphthalene under the trademark Mobil MCP917. Di and tri alkylated naphthalenes and mixtures are also available and can be used.

The level of the alkylated or alkoxylated aromatic compound will be from 5% to 90% by weight of the lubricant composition of the present invention and preferably from 10% to 30% by weight. The remaining primary portion of the lubricant, other than minor lubricant additives and the like, known to the art of lubrication, will be the polyalkylene glycol. The polyalkylene glycol can be manufactured with a single or a random or block mixture of two or more of the following oxides: ethylene, propylene, 1-2 or 2-3 butylene, hexa-1-ene, or dodec-lene glycols initiated with either an alkyl or aromatic alcohol. The polyalkylene glycol, also referred to as polyoxyalkylene glycol or polyglycol ethers, will generally be defined by the following formula:

#### R-[- ( A )n - R' ]m

#### wherein

35

40

45

50

R is hydrogen or an organic substituent having from 1 to 24 carbon atoms which functions as the initiator for the alkylene oxide polymer. Preferably, the organic substituents encompassed by R are derived from linear or branched alkyl alcohols and polyols, as well as aromatic alcohols and polyols. Alkyl initiator compounds include water, methanol, ethanol, propanol, butanol, ethylene glycol, propylene glycol, butylene glycol, 1,6 hexane diol, glycerine, trimethylolpropane, pentaerythritol, and mixtures thereof and the like. Aromatic initiator compounds include monohydric phenols and dihydric phenols and their alkylated derivatives such as o, m, and p cresol, guaiacol, saligenin, carvacrol, thymol, o and p-hydroxy diphenyl, catechol, resorcinol, hydroquinone, pyrogallol, and phloroglucinol.

- a) R', which end blocks or caps the poly alkylene glycol backbone, can comprise a hydroxyl group or it may be further reacted with organic acids to form esters or with alkyl or aryl halides to form alkyl or aryl ether capped polyoxyalkylene glycols.
- b) In Formula 1, m is an integer having a value of from 1 to 8 and n is a positive number, typically not exceeding 1,000.
- c) A is an ethylene oxide, propylene oxide, butylene oxide, hexa-1-ene oxide, or a dodec-1-ene oxide, reacted singly or in random or block combinations with one or more other alkylene oxides.

The viscosity of the polyalkylene glycols of the present invention typically ranges from about 10 to 680 centistokes (cSt) at 40° C, depending on the lubricant application viscosity requirements.

As used herein, the term "viscosity" refers to each polyalkylene glycol used in the composition on an individual basis. Those skilled in the art can determine the viscosities of mixtures of PAGs suitable for use in accordance with the

3

55

present invention.

30

35

40

45

50

55

As noted above, methods for preparing the PAGs of the present invention are known to those skilled in the art. Ethylene oxide, propylene oxide, and butylene oxide are the three most common commercially available alkylene oxides used in the manufacture of polyalkylene glycols. These alkylene oxides are polymerized singly or in random or block combinations with one or more other alkylene oxides. They are initiated most often with a hydroxyl or an alkyl or aryl alcohol such as butanol or nonylphenol, respectively. A preferred polyalkylene glycol is that initiated with an alkyl aryl alcohol such as a C<sub>3</sub>-C<sub>20</sub> alkyl phenol with the nonylphenol initiated polyalkylene glycol preferred. This can be used in combination with water and alkyl alcohol initiated polyalkylene glycols as desired to form a suitable economical blend. Preferably about 0-100%, preferably 5-80% and most preferably 20-60% of the polyalkylene glycol will be the alkyl aryl alcohol initiated poly alkylene glycol Branched polyethers of alkylene oxides, formed from trimethylol or other polyol initiators are also commercially available. Polyalkylene glycols are commonly used as surfactants, process chemicals, and lubricants. Thus, the present invention will incorporate from 10% to 95% by weight of the polyalkylene glycol, and preferably from 60% to 90% by weight.

In addition to the alkylated aromatic compounds and the polyalkylene glycols, the present invention can incorporate the following additives in well known standard amounts: anti-wear/extreme pressure additives, antioxidants, metal deactivators, detergents, dispersants, corrosion inhibitors, defoamers, dyes or such additives as may be required for the lubricant application. The lubricant of the present invention can also include 1% to 20% of various components which may affect various physical characteristics of the lubricant such as viscosity, Viscosity index, solvency, and low temperature characteristics and the like. Such components would include polyalphaolefins, polyol esters and diesters, silicone lubricating fluids, as well as modified or grafted versions such as esters grafted onto polyalphaolefins. Other polymer fluids which are typically used in the manufacturing of lubricants can also be incorporated such as polyisobutylene, polybutylene, olefinic copolymers, styrene and styrene copolymers, branches parafinic polymers and polymethacrylates. These are all components that are well known for use with motor oils and industrial lubricants.

The lubricant of the present invention is formed by simply adding the base fluid and additive components together in a blender and mixing until completely solubilized. Due to their nature, they will remain solubilized without further mixing or treatment.

For use in the present invention, preferred alkylated aromatic compounds include: alkylated naphthalene sold by Mobil under the trade designation Mobil MCP 917. Further, preferred polyalkylene glycols include Dow Chemical L-series such as Dow L910 or Union Carbide LB series or a propoxylated nonylphenol (5 mole).

In order to test the formulation of the present invention, two lubricants having the following specific components were prepared:

Additive:	Weight %	
	Α	В
Dow Polyglycol L910 (Dow Chem. Co.)	78.00	58.00
Propoxylated nonylphenol (5-10 mole)		20.00
Mobil MCP 917 (Mobil Chemical Co.)	20.00	20.00
Irgalube 349 (Ciba Geigy)*	0.30	0.30
Lubrizol 859 (Lubrizol Corp.)*	0.10	0.10
Irgamet 39 (Ciba Geigy)*	0.10	0.10
Irganox L-57 (Ciba Geigy)*	1.00	1.00
Irganox L-135 (Ciba Geigy)*	<u>0.50</u>	<u>0.50</u>
	100.00	100.00

<sup>\*</sup>Additives for an anti-wear hydraulic or gear lubricant. (Modification of additives is necessary for other applications.)

These formulations were then tested and compared with commercially available lubricants, specifically Sullube 32, sold by Sullair, manufactured by Dow Chemical, and Summa Rotar, sold by Diversey. These were then tested for viscosity, total acid number, and oxidation resistance using a rotary bomb test. The results of these tests are shown below.

#### EP 0 796 908 A1

5	Physical & Chemical Char- acteristics	IASTM Method	Sullube 32	Lubricant A	Lubricant B	Summa Rotar Oil	
	VISCOSITY						
			D-445				
10	40° C		38.2 cSt	28.7 cSt	40.9 cSt	27.5 cSt	
10	100° C		7.2 cSt	7.4 cSt	7.3 cSt	5.3 cSt	
	Viscosity Index	D-2270	157	161	144	131	
	TAN						
15	(Total Acid Number)	NEW OIL	0.83	0.82	0.68	0.11	
	Specific Gravity	D-287	0.981	0.962	0.98	0.911	
	Emulsion Charact	teristics					
20	D-1401 After 1 Hr. @ 130°F		2-06-72	2-32-46	5-35-40	8-17-55	
	D-1401 After 1	6 Hrs @ 70° F		4-14-62	5-34-41	8-38-34	10-35-25
	FOUR BALL WEA	R					
25	(1800rpm, 20k	g, 1 hr, 167° F)	0.50 mm	0.30 mm	0.30 mm	0.30 mm	
	(1800rpm, 40kç	g, 1 hr, 167° F)	1.90 mm	0.40 mm	0.50 mm	0.80 mm	
	TAN						
		Rota	ary Bomb Test	: 275° F, 130ps	i O <sub>2</sub> , 5ml H <sub>2</sub> O		
30	30 hours:		8.976	⟨2	<2	8.48	
	72 hours:		N/A	4.51	<2	N/A	
	120 hours:		N/A	N/A	4.49	N/A	

35

As the data shows, oxidation resistance of the two lubricants in the present invention are vastly superior to the two commercial lubricants which represent the industry standard for synthetic air compressor lubrication. The test is stopped after 30 hours for Sullube 32 and Summa Rotar after a 25 PSI pressure decrease in the test bomb. The test is also stopped if the TAN values of the lubricant exceed 10.0 because this can result in excessive corrosion of the test bomb copper catalyst. However, Lubricant A and B of the present invention lasted 72 and 120 hours, respectively. Also, the TAN values were better. The lubricants of the present invention provided 2.5 to 4 times the oxidation life of two commercially available synthetic compressor lubricants.

The lubricants of this invention provide superior lubrication and extended service life without the problems of varnish and deposits found with other petroleum and synthetic lubricants when used in air compressors, hydraulics, turbines, bearings, and gears. For example, this lubricant can be used in air compressors for more than 8,000 hours without being replaced.

Further, this can be used in other applications including self-lubricating compressed or sintered porous metal parts such as brass and bronze, as well as self-lubricating porous plastic parts.

The lubricant of this invention provides excellent oxidation stability, varnish and deposit control, and resistance to catalysis from combustion by-products and moisture when used in fuel engines. Also, because of its inherent solubility characteristics and lubricity, engine oil formulations are less dependent on lubricity additives and detergents/dispersants.

The lubricant of the present invention can further be formulated into grease by adding appropriate thickeners in the amount of 6 to 14% depending on the thickener and the desired amount of thickening. The ratio of the polyalkylene glycols and alkylated aromatic compounds should remain substantially the same with simply the addition of thickener. Typical thickeners include polyurea, modified clays, soap thickeners such as calcium complex, calcium sulfonate, lithium, lithium complex, and aluminum complex. A typical formulation of such a grease is disclosed below.

5

10

15

20

ADDITIVE:		WEIGHT %
Base Fluid		
Dow Polyglycol L910	Dow Chemical Company	78.00
Mobil MCP 917	Mobil Chemical Co.	20.00
Irgalube 349*	Ciba Geigy	0.30
Lubrizol 859*	Lubrizol Corp.	0.10
Irgamet 39*	Ciba Geigy	0.10
Irganox L-57*	Ciba Geigy	1.00
Irganox L-135*	Ciba Geigy	<u>0.50</u>
		100.00
Thickener		
Polyurea		8-10 percent

<sup>\*</sup> Additives for an anti-wear hydraulic or gear lubricant. (Modification of additives is necessary for other applications.)

The grease lubricant of the present invention can be used in a wide variety of applications including general lubrication and in any application where grease is employed.

Particularly, the present invention can be used in high speed bearings, electric motor bearings, high temperature bearings, and sealed for life bearing where extremely long lubricant life and resistance to varnishing is desired. These applications are particularly subject to oxidation and therefore requires a lubricant that is oxidation resistant. Whether formulated as a grease or an oil, the lubricant of the present invention provides exceptional oxidation resistance while, at the same time, providing excellent lubricity, hydrolytic stability and varnish/deposit control. This has been a description of the present invention, along with the preferred method of practicing the invention presently known to the inventor. It is noted in this respect that various alternatives will be immediately evident to the person skilled in the art, without departing from the scope of the invention.

#### **Claims**

35

40

50

55

- 1. A lubricant composition comprising a polyalkylene glycol compound in combination with an aromatic compound selected from the group consisting of alkylated aromatic lubricants and alkoxylated aromatic lubricants in an amount effective to improve the oxidation resistance of said polyalkylene glycol compound.
- 1. The lubricant composition claimed in claim 1, wherein said alkylated aromatic lubricant is a C5-C24 alkyl substituted aromatic compound.
- 2. The lubricant composition claimed in claim 2, wherein said aromatic compound is an alkylated naphthalene.
  - 4. The lubricant composition claimed in claim 1, wherein said polyalkylene glycol has the following general formula:

wherein:

- (a): R is selected from the group consisting of hydrogen and an organic substituent having from 1 to 24 carbon atoms;
- (b): R' is selected from the group consisting of hydroxyl, alkyl ether, and aryl ether;
- (c): m is an integer having a value of from 1 to 8, n is a positive number less than 1,000;

#### EP 0 796 908 A1

- (d): A is selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, polyhexa-1-ene oxide, a polydodec-1-ene oxide and combinations thereof.
- 5. The composition claimed in claim 4, wherein said polyalkylene glycol has a viscosity of from about 10 to 680 centistokes (cSt) at 40° C.
- **6.** The lubricant composition claimed in claim 1, wherein said alkoxylated aromatic compound is a phenyl compound.
- 7. The lubricant composition claimed in claim 1, wherein said composition further includes a grease and a thickening agent.
  - **8.** The lubricant composition claimed in claim 1, wherein the alkylated aromatic compound is present at a concentration of from 1 to 90% by weight.
  - **9.** The lubricant composition claimed in claim 1, wherein the polyalkylene glycol is present at a concentration of from 10 to 95% by weight.
  - 10. The lubricant composition claimed in claim 1, which contains in addition:
    - (a) about 0 to 5.0% of one or more anti-oxidant additives;
    - (b) about 0 to 5.0% anti-wear/extreme pressure additives;
    - (c) about 0 to 5.0% corrosion inhibitor;
    - (d) about 0 to 1.0% non-ferrous metal deactivator/corrosion inhibitor;
    - (e) about 0 to 10.0% dispersant and detergent additives.
    - (f) about 0 to 10.0% synthetic base stock selected from the group consisting of PAO, esters and lubricating polymers.

7

20

15

5

25

30

35

40

45

50

55



# **EUROPEAN SEARCH REPORT**

Application Number EP 97 20 0253

Category	Citation of document with in of relevant pas	dication, where appropriate, ssages	Relevant to claim	CLASSIFICATION OF THI APPLICATION (Int.Cl.6)
X	US 2 943 056 A (R.0 * column 2, line 43 claim 1 * * column 4; example	- column 3, line 29		C10M111/04 C10M169/04 //(C10M111/04, 105:06,105:18, 107:34),
X	US 3 377 288 A (A.W * column 7; example	•	1,2,4,5, 8-10	
X	DATABASE WPI Section Ch, Week 91 Derwent Publication Class A28, AN 91-01 XP002031668 & JP 02 286 792 A ( November 1990 * abstract *	s Ltd., London, GB; 2471	1-5,8-10	C10N30:10
X	US 5 368 765 A (M.K * column 3, line 14	•	1,2,4,5, 8-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
P,X	DE 44 31 271 A (IIK GMBH) * column 1, line 62	A MAFA KALTETECHNIK - line 66; claims 1	1,2,4,5, 8,9	
X	DATABASE WPI Section Ch, Week 91 Derwent Publication Class A25, AN 91-01 XP002031669 & JP 02 286 780 A ( 26 November 1990 * abstract *	s Ltd., London, GB;	1,2,4,5, 8-10	
	The present search report has b	-		
	Place of search THE HAGUE	Date of completion of the sear 29 May 1997		genga, K
Y:pa	CATEGORY OF CITED DOCUME! rticularly relevant if taken alone rticularly relevant if combined with and cument of the same category chnological background	NTS T: theory or p E: earlier pat after the fi other D: document	orinciple underlying the ent document, but publ	e invention lished on, or



## **EUROPEAN SEARCH REPORT**

Application Number EP 97 20 0253

	DOCUMENTS CONSII  Citation of document with in		Relevant	CLASSIFICATION OF THE
Category	Citation of document with in of relevant pas		to claim	APPLICATION (Int.Cl.6)
A	US 4 892 680 A (NOBO * column 1, line 9 * column 2, line 10 * column 4, line 3 * column 8, line 58 * column 9, line 13	- line 13 * - line 23 * - line 30 * - line 66 *	1,8-10	
				TECHNICAL FIELDS SEARCHED (Int.Cl.6)
	The present search report has b	een drawn up for all claims		
	Place of search	Date of completion of the sea	rch	Examiner
ı	THE HAGUE	29 May 1997	Hil	lgenga, K
Y:p2 do A:ted O:nd	CATEGORY OF CITED DOCUMENT rticularly relevant if taken alone rticularly relevant if combined with and cument of the same category chnological background n-written disclosure termediate document	NTS T: theory or E: earlier pa after the ther D: documen L: documen date: member of	T: theory or principle underlying the E: earlier patent document, but publis after the filing date D: document cited in the application L: document cited for other reasons  &: member of the same patent family document	