United States Patent Office

3,746,645

Patented July 17, 1973

3,746,645

POLYETHER SERIES SYNTHETIC LUBRICATING OIL COMPOSITIONS

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No Drawing. Filed Nov. 26, 1971, Ser. No. 202,652
Claims priority, application Japan, Dec. 4, 1970, 45/107,264
Int. Cl. C10m 3/30
U.S. Cl. 252—51.5 A 4 Claims

ABSTRACT OF THE DISCLOSURE

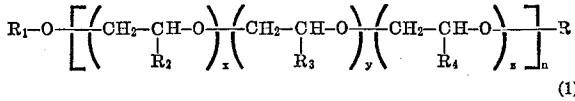
Lubricating oil composition for an engine oil is obtained by adding a polyoxyalkylene glycol ether N-amine substituted succinimide to a polyoxyalkylene glycol ether.

The present invention relates to lubricating oil compositions obtained by compounding a polyether N-amine substituted succinimide to a polyether series synthetic lubricating oil.

Polyoxyalkylene glycol ethers (abridged as "polyether" hereinafter) have been broadly used as in petroleum series lubricating oil but have not been suitable for engine oil of motorcars. This is because the additives compatible to the polyethers have not been fully developed as compared with the petroleum series lubricating oil. Accordingly, when the polyethers containing no detergent or dispersant are used for an engine oil of motorcars, they are poor in the function for dispersing completely carbon, varnish and slag formed by the incomplete combustion of fuel into the oil and such substances deposit on piston ring groove or clog the oil filter resulting into an interference of the driving of engine.

The inventors have found that when the polyether series lubricating oils are used as a lubricating oil of an internal combustion engine, for example, an engine oil of motorcars, the excellent lubricating activity can be attained by compounding the dispersant of the present invention which has a high compatibility and does not form ashes, to the polyether and accomplished the present invention.

The polyethers having a viscosity of a lubricating oil have the following formula.



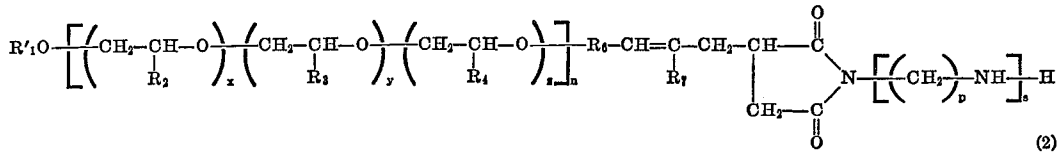
(1)

R_1 and R_5 are hydrogen or hydrocarbon groups of C_mH_{2m+1} or C_kH_{2k-1}, R_2, R_3 and R_4 are hydrogen or alkyl group of C_jH_{2j+1}, m is an integer of 1 to 18, k is an integer of 3 to 18, j is an integer of 1 or 2, and x, y, z and n are 0 or an integer of 1 to 100.

The polyethers having the above Formula 1 are obtained by subjecting to an addition polymerization propylene oxide or butylene oxide alone and an aliphatic alcohol (ROH) or subjecting to a random or block-copolymerization two or more these oxides or ethylene oxide simultaneously and said alcohol and if necessary, the end OH group may be alkyl etherified.

Illustrative of the polyethers is butoxypolyoxypropylene glycol having a molecular weight of 500 to 3,000 obtained by the addition polymerization of propylene oxide and butanol and further alkoxypolyoxypropylene glycol obtained by using the aliphatic alcohols, such as methanol, ethanol, propanol, 2-ethyl-hexanol, Ziegler alcohol and oxo alcohol known as derivatives of petroleum chemistry and the like, may be mentioned. In addition, alkoxypolyoxyethyleneoxypropylene glycol, alkoxypolyoxypropyleneoxybutylene glycol, alkoxypolyoxyethyleneoxypropyleneoxybutylene glycol, butoxypolyoxypropylene glycol mono ether having the above described hydrocarbon groups may be cited.

Polyether N-amine substituted succinimides have the following formula.



(2)

In the above formula, R_2, R_3, R_4, x, y, z and n have the same meanings as in the above Formula 1, R'_1 is C_mH_{2m+1} (m is an integer of 1 to 18), R_6 is C_gH_{2g} (g is 0 or an integer of 1 to 15) and R_7 is hydrogen or a hydrocarbon group of C_fH_{2f+1} (f is 0 or an integer of 1 to 3) and p and s are an integer of 1 to 6.

As the dispersant for petroleum series lubricating oil, alkenyl succinimides have been known but these substances are not at all dissolved in the polyethers or even if dissolved, these substances have no excellent cleaning and dispersing ability. On the contrary, the compounds having the above Formula 2 are different from the alkenylsuccinimides and have a compatibility with the polyethers and a high cleaning and dispersing ability.

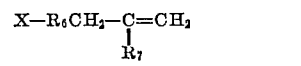
The amount of the compounds having the above Formula 2 added based on the polyethers is 0.1–10% (by weight), preferably 0.5–5% by weight. In less than 0.1% the activity is low, while even if more than 10% is added, the property is not very improved.

The compounds having the above Formula 2 include alkoxypolyoxyalkylene glycol monoallyl ether N-amine substituted succinimide, alkoxypolyoxyalkylene glycol β-methallyl ether N-substituted succinimide and the like and alkoxypolyoxyalkylene glycols are the compounds cited in the Composition 1 of the polyethers of the base oil.

The polyether N-amine substituted succinimides (PASI) having the above Formula 2 are produced in the following manner.

Namely, olefin ether of alkoxypolyoxyalkylene glycol is reacted with maleic anhydride and then with a polyamine to form imides.

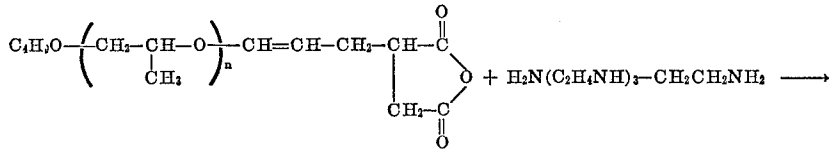
The above described olefin ethers are produced in the following manner. Alkoxypolyoxyalkylene glycol is added with metallic sodium or sodium methylate (CH_3ONa) to convert the end OH group into —ONa, to which a monohaloolefin is reacted. The monohaloolefin has the following formula.



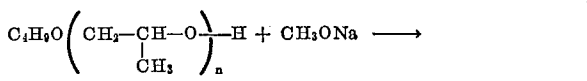
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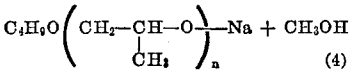
In the above formula, X is chlorine, bromine or iodine and R_6 and R_7 have the same meanings as described above. Illustrative of the monohaloolefin is allyl chloride and β-methallyl chloride.

For example, butoxypolyoxypropylene glycol is reacted

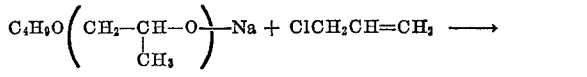


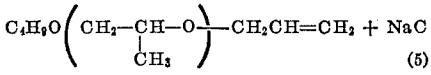
with allyl chloride.





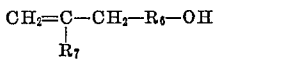
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(5)

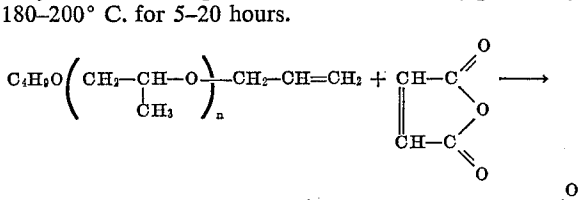
Alternatively, an alcohol having the following Formula 6

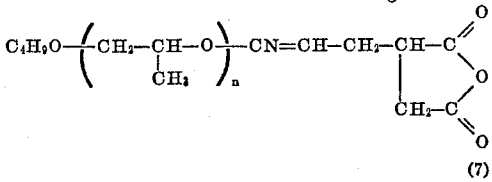


(6)

is polymerized with alkylene oxides and then the end OH group is reacted with alkylmonochloride (R'_1X) to form an alkylether.

1 mole of the olefin ether having the above Formula 5 is reacted with 1–7 moles, preferably 1–3 moles of maleic anhydride at a temperature of 150–230° C., preferably 180–200° C. for 5–20 hours.

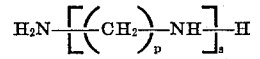




(7)

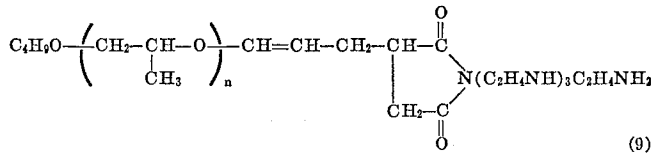
Less than 2% by weight of organic peroxide may be added as the reaction catalyst. In order to prevent the thermal decomposition of the reaction product, the reaction may be effected in gaseous nitrogen by adding xylol, toluene and the like as a diluting solent. After the reaction, unreacted maleic anhydride and xylol are removed by a distillation under a reduced pressure.

Thereafter, 1 mole of the compound having the above described Formula 7 is dissolved in xylol and then 1–7 moles, preferably 1–3 moles of a polyamine is added thereto gradually and the reaction mixture is heated at 120–180° C. to effect dehydration while refluxing xylol, whereby imide is formed. The progress of the reaction can be observed by the amount of water formed. After the reaction, the unreacted polyamine and the solvent are distilled off to obtain the product. The polyamines have the following formula



(8)

and include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, trimethylenediamine and tetramethylenediamine.



(9)

When PASI of the present invention is added to the polyether, this dispersant shows an excellent lubricating property and cleaning and dispersing ability and does not form ashes and is suitable for the use for an engine oil of an internal combustion engine.

The following examples are given for the purpose of illustration of this invention and are not intended as limitations thereof.

In the examples, "part" and "percent" mean by weight.

EXAMPLE 1

100 parts of butoxypolyoxypropylene glycol allyl ether having a molecular weight of about 1,000 is added with 10.5 parts of maleic anhydride and 1.5 parts of perbutyl D (ditert.-butyl peroxide, made by Nippon Oils and Fats Co., Ltd.) and the resulting mixture was reacted at 180–190° C. for 5 hours to obtain butoxypolyoxypropylene glycol allyl ether succinic anhydride in a reaction ratio of more than 95%.

110 parts of said succinic anhydride is dissolved in 130 parts of xylol and 10.5 parts of tetraethylenepentamine is added dropwise thereto at 160° C. in 2 hours. The reaction mixture is cured for 3 hours and then xylol and the unreacted polyamine are distilled off to obtain 120 parts of butoxypolyoxypropylene glycol allyl ether succinimide.

EXAMPLE 2

100 parts of lauroxypolyoxyethyleneoxypropylene glycol methallyl ether (molar ratio of EO to PO; 1:9) having a molecular weight of 1,200 is added with 12 parts of maleic anhydride and the mixture is reacted at 180–190° C. for 20 hours. As the amine, 8.5 parts of triethylenetetramine is used and the reaction is effected in the same manner as in Example 1 to obtain 117 parts of lauroxypolyoxyethyleneoxypropylene glycol methallyl ether succinimide.

EXAMPLE 3

The reaction is effected in the same manner as described in Example 1 except that methoxypolyoxyethyleneoxypropyleneoxybutylene glycol allyl ether (molar ratio of EO:PO:BO; 1:8:1) having a molecular weight of about 1,000 is used and 5.0 parts of tetramethylenediamine is used as the polyamine, to obtain 114 parts of methoxypolyoxyethyleneoxypropyleneoxybutylene glycol allyl ether succinimide.

In each example, EO is ethylene oxide, PO is propylene oxide and BO is butylene oxide.

EXAMPLE 4

The composition of samples of engine oil is shown in the following Table 1.

TABLE 1

Sample	Dispersant Name	Dispersant Part	Polyether Name (viscosity)	Polyether Part	P-α-NA (part)
A	Butoxypolyoxypropylene glycol allyl ether succinimide.	2	Butoxypolyoxypropylene glycol (SAE-40)	96	2
B	Lauroxypolyoxyethyleneoxypropylene glycol methallyl ether succinimide.	5	Lauroxypolyoxyethyleneoxypropylene glycol (molar ratio of EO to PO, 1:9) (SAE-40).	93	2
C	Methoxypolyoxyethyleneoxypropyleneoxybutylene glycol allyl ether succinimide.	3	Methoxypolyoxyethyleneoxypropyleneoxybutylene glycol (molar ratio of EO:PO:BO, 1:8:1) (SAE-40).	95	2
D	No		Butoxypolyoxypropylene glycol (molecular weight 1,200) (SAE-40).	98	2

P-α-NA is an antioxidant of phenyl-α-naphthyl amine.

Test manner

The dispersant was added to an engine oil of motorcar and the runnnig test was made. A common motorcar having a displacement of 2,000 cc. was used and the running test was effected based on the following standard of the exchange of the sample oil.

Sample oil

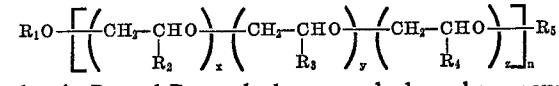
A, B, C, D of the Table 1, fuel: L.P.G.
Standard of exchange, 30,000 km./3 months.

Four new cars were charged with the sample oils separately and the cars were run under usual running condition and after about 240,000 km. was run for 2 years, each portion of the engine was checked based on C.R.C. estimation standard.

Analysis of the sample oil

After about 30,000 km. was run for 3 months, the total amount of oil was discharged and exchanged. The analyzed value is shown in Table 2.

having the following formula



wherein R_1 and R_5 are hydrogen or hydrocarbon groups of C_mH_{2m+1} or C_kH_{2k-1}, R_2, R_3 and R_4 are hydrogen or alkyl groups of C_jH_{2j+1}, m is an integer of 1–18, k is an integer of 3–18, j is an integer of 1–2, all except one of x, y and z are 0 or any of x, y, and z are integers of 1–100, and n is an integer of 1–100, 0.1–10% by weight of a polyoxyalkylene glycol ether N-amine substituted succinimide having the following formula

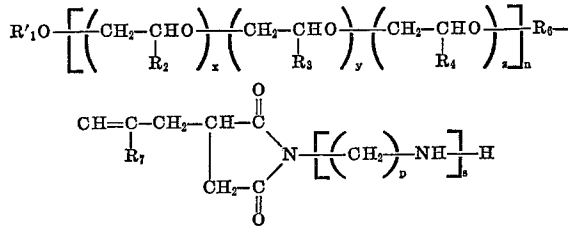


TABLE 2

Item	Sample oil A Before use	A After use	B Before use	B After use	C Before use	C After use	D Before use	D After use
Viscosity, 98.9° C. (cst.)	15.6	15.8	15.6	15.6	15.2	15.5	14.1	13.6
Viscosity, 37.8° C. (cst.)	96.5	101.1	96.5	99.8	94.1	99.6	86.0	87.1
Viscosity index number	141.0	139.6	141.0	139.6	141.5	139.4	141.5	138.8
PH (isopro water)	9.1	4.1	10.3	4.0	9.2	3.8	6.5	3.4
Remaining carbon, percent		1.3		1.3		1.3		1.68
Heptane, insoluble percent portion		3.0		2.9		3.2		4.5
Carbon dispersibility		Good		Good		Good		Bad
Oil element condition		Good		Good		Good		(1)

[1] Fairly bad.

NOTE.—Isopro water means a solution of 10 g. of sample dissolved in 60 ml. of a mixture of isopropyl alcohol and water (mixture ratio of isopropyl alcohol to water is 10:6 by volume).

The estimation of each portion of engine is shown in the following Table 3.

TABLE 3

	A	B	C	D
Running distance of sample oil, km.	239,372	236,579	230,370	239,671
Item:				
Cleaning ability of piston:				
Deposit of carbon on top ring groove	9.63	8.39	8.36	4.24
Deposit on ring groove	2.96	2.59	1.87	1.44
Deposit on ring land	2.79	3.50	2.47	1.74
Agglomeration on ring	10.00	10.00	10.00	8.00
Deposit on piston crown	9.07	8.99	8.59	7.84
Deposit on under crown	2.75	3.55	2.00	1.00
Deposit on piston skirt	4.85	5.63	2.88	2.05
Cleaning ability of lubricating oil system:				
Varnish	2.95	2.75	2.15	2.25
Slag	8.67	8.05	8.23	7.23
Condition of valve lifter:				
Abrasion	(1)	(1)	(1)	(1)
Corrosion	No	No	No	No
Abrasion of connecting rod bearing metal	No	No	No	No

[1] Small.

As seen from the above data, the dispersant of the present invention is more excellent in the properties than the comparative sample.

What is claimed is:

1. Polyether series synthetic lubricating oil composition obtained by adding to a polyoxyalkylene glycol ether wherein R_2, R_3, R_4, x, y, z and n have the same meanings as described above, R'_1 is C_mH_{2m+1} (m is an integer of 1–18), R_6 is C_gH_{2g} (g is 0 or an integer of 1–15), R_7 is hydrogen or a hydrocarbon group of C_fH_{2f+1} (f is 0 or an integer of 1–3) and p and s are an integer of 1–6.

2. Polyether series synthetic lubricating oil composition as claimed in claim 1, wherein the polyoxyalkylene glycol ether N-substituted succinimide is butoxypolyoxypropylene glycol allyl ether succinimide.

3. Polyether series synthetic lubricating oil composition as claimed in claim 1, wherein the polyoxyalkylene glycol ether N-substituted succinimide is lauroxypolyoxyethyleneoxypropylene glycol methallyl ether succinimide.

4. Polyether series synthetic lubricating oil composition as claimed in claim 1, wherein the polyoxyalkylene glycol ether N-substituted succinimide is methoxypolyoxyethyleneoxypropyleneoxybutylene glycol allyl ether succinimide.

References Cited

UNITED STATES PATENTS

3,312,619 4/1967 Vineyard ..... 252—51.5 A
3,361,673 1/1968 Stuart et al. ..... 252—51.5 A

WERTEN F. W. BELLAMY, Primary Examiner

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,746,645 Dated November 26, 1971

Inventor(s) SAITO, ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 35 "NaC"" should be -- NaCl --
Column 3, line 56 "Cn"" should be -- CH --
Column 6, line 44 "138.8"" should be -- 138.5 --
Column 6, line 45 "3.4"" should be -- 3.8 --
Column 6, line 46 "1.68"" should be -- 1.64 --
Column 6, line 47 "4.5"" should be -- 4.8 --

Signed and sealed this 29th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.