

1

3,346,496

**LUBRICANTS CONTAINING CARBODIIMIDES
AS ANTIOXIDANTS**

Wolfram Neumann and Walther Lohmar, Leverkusen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

No Drawing. Filed May 13, 1965, Ser. No. 455,606

Claims priority, application Germany, June 16, 1964, F 43,191

5 Claims. (Cl. 252—50)

The present invention relates to lubricant additives; more particularly it concerns lubricant additives which consist essentially of carbodiimides.

The carbodiimides to be used as lubricant additives may be mono- or poly-carbodiimides and may belong to the aliphatic, cycloaliphatic or aromatic series. Examples of monocarbodiimides are the following: di-isopropyl-carbodiimide, di-n-butyl-carbodiimide, methyl-tert.-butyl-carbodiimide, dicyclohexyl - carbodiimide, diphenyl-carbodiimide, di-p-tolyl-carbodiimide and 4,4'-didodecyl-diphenyl-carbodiimide. Of special advantage are diphenyl-monocarbodiimides which carry in the phenyl radicals in ortho-position to the carbodiimide group substituents, e.g. alkyl, alkoxy, aryl and aralkyl radicals, such as 2,2'-diethyl-diphenyl - carbodiimide, 2,2'-di-isopropyl-diphenyl-carbodiimide, 2,2'-diethoxy-diphenyl-carbodiimide, 2,6,2',6'-tetraethyl - diphenyl-carbodiimide, 2,6,2',6'-tetraisopropyl-diphenyl-carbodiimide, 2,6,2',6'-tetraethyl-3,3'-dichloro-diphenyl-carbodiimide, 2,2'-diethyl-6,6'-dichloro-diphenyl-carbodiimide, 2,6,2',6'-tetra-isobutyl-3,3'-dinitro-diphenyl-carbodiimide and 2,4,6,2',4',6'-hexaisopropyl-diphenyl-carbodiimide. Suitable polycarbodiimides are, for example, tetramethylene- ω,ω' -bis-(tert.-butyl-carbodiimide), hexamethylene- ω,ω' -bis-(tert.-butyl-carbodiimide), tetramethylene- ω,ω' -bis-(phenyl-carbodiimide) and those compounds which may be obtained by heating aromatic polyisocyanates such as 1,3-di-isopropyl-phenylene-2,4-di-isocyanate, 1-methyl-3,5-diethyl-phenylene-2,4-diisocyanate and 3,5,3',5'-tetra-isopropyl-diphenylmethane-4,4-di-isocyanate, in the presence of tertiary amines, basically reacting metal compounds, carboxylic acid metal salts or non-basic organometal compounds at a temperature of at least 120° C., according to the process of German Patent No. 1,156,401.

With the aid of carbodiimides it is possible to improve substantially lubricants of a great variety of types, in particular their resistance to oxidative attacks. This applies in the first instance to lubricants which are produced from mineral oils, but also to lubricating oils of synthetic origin which are polyethers or polyether esters, but especially to lubricating oils based on synthetic polyethers or polyether esters which contain $-(CH_2)_4-O-$ groups alternating several times with one another or with other alkylene- $O-$ groups and which are described in German Patent No. 1,071,872. The carbodiimides are, at the same time, also effective as protective agents against corrosion and are, moreover, capable of keeping the decomposition products formed during the lubricating process in solution. The amounts of carbodiimides required in each case can be easily determined in preliminary experiments; in general, additives of 1 to 2 percent by weight, referred to the lubricant, have proved to be sufficient.

It is noteworthy that the lubricant additives to be used according to the present invention are compatible with other lubricant additives, e.g. with detergents, agents for increasing the resistance of the lubricating film, and also agents for improving the solidification point and the viscosity. An especially advantageous embodiment of the present invention consists in that the carbodiimides can be added to the lubricants in combination with diphenyl-

2

amines known as antioxidants, such as 4,4'-di-(methylbenzyl)-diphenylamine, and/or hydroxyquinolines such as 8-hydroxyquinoline. Thus, surprisingly, a synergistic effect is achieved. The following examples serve to illustrate the invention without, however, limiting its scope; the parts given are parts by weight.

Example 1

100 parts of a naphthene-basic mineral oil are mixed with 1 part of 2,6,2',6'-tetra-isopropyl-diphenyl-carbodiimide. The resistance of the mineral oil to oxidative attacks is thus substantially improved; the action of the carbodiimide used is further increased by the addition of 0.2 part 4,4'-(dimethylbenzyl)-diphenylamine and/or 8-hydroxyquinoline. This is evident from appropriate comparative experiments, the results of which are given in Table I, where the neutralisation numbers (mg. KOH/g. oil) of the oils mixed with the various additives are listed after oxidative action.

In the table the letters have the following significance:

A oil without additive

B oil with 1% 2,6,2',6'-tetra-isopropyl-diphenyl-carbodiimide

C oil with 0.2% 4,4'-dimethylbenzyl-diphenylamine

D oil with 1% 2,6,2',6'-tetra-isopropyl-diphenyl-carbodiimide and 0.2% 4,4'-dimethylbenzyl-diphenylamine

E oil with 1% 2,6,2',6'-tetra-isopropyl-diphenyl-carbodiimide and 0.2% 8-hydroxyquinoline

F oil with 0.2% 4,4'-dimethylbenzyl-diphenylamine and 0.2% 8-hydroxyquinoline

G oil with 1% 2,6,2',6'-tetra-isopropyl-diphenyl-carbodiimide, 0.2% 4,4'-dimethylbenzyl-diphenylamine and 0.3% 8-hydroxyquinoline.

TABLE I

Duration of the oxidative action in hours	Neutralisation numbers						
	A	B	C	D	E	F	G
0	0.07	0.05	0.08	0.05	0.12	0.14	0.01
50	2.88	0.20	0.40	0.16	0.04	0.07	0.06
100	---	0.34	0.66	0.24	0.02	0.12	0.08
200	---	0.70	1.06	0.24	0.16	0.25	0.09
300	---	1.00	1.55	0.80	0.20	0.43	0.11
400	---	1.39	2.48	1.20	0.28	0.65	0.16
500	---	1.92	---	1.43	0.57	0.99	0.30
600	---	3.10	---	1.60	2.46	1.17	0.54
700	---	---	---	1.79	---	1.40	0.86
800	---	---	---	1.89	---	1.60	1.06
900	---	---	---	1.97	---	1.79	1.19
1,000	---	---	---	2.20	---	1.96	1.25

The comparative experiments were carried out according to the instruction of ASTM-oxidising test D 943-54: 300 ml. of the oil to be tested were filled, together with 60 ml. distilled water, into a 60 cm.-high glass cylinder of 4.5 cm. diameter, and iron and copper spirals were introduced into the oil/water mixture in accordance with the conditions prevailing in the lubricating processes. Three litres oxygen per hour were then blown at 95° C. through the oil/water mixture via a tube which extended almost to the bottom of the test cylinder. At specified time intervals, 10 ml. of the oil were withdrawn to determine the neutralisation number. When the neutralisation number reached a value above 2 or when the duration of the oxidative action amounted to 1000 hours, the test was interrupted.

Example 2

100 parts of a polyether oil obtained according to Example 2 of German patent specification No. 1,120,139 by polymerisation of a mixture of tetrahydrofuran, ethylene oxide and propylene oxide in the presence of formaldehyde-dimethyl acetate and boron trifluoride compounds of tetrahydrofuran, are mixed with 2 parts of one

of the additives listed in Table II. It is apparent from the neutralisation numbers given therein and determined according to the data of Example 1 that the resistance of the oil to oxidative attacks is likewise substantially improved in this way. The letters in the following table have the meaning:

- A oil without additive
 B oil with 2% di-n-butyl carbodiimide
 C oil with 2% di-cyclohexyl-carbodiimide
 D oil with 2%, 2,6-2',6'-tetraethyl-4,4'-dimethyl-diphenyl-carbodiimide
 E oil with 2% 2,6,2',6'-tetraethyl-diphenyl-carbodiimide
 F oil with 2% 2,6,2',6'-tetra-isopropyl-diphenyl-carbodiimide

TABLE II

Duration of the oxidative action in hours	Neutralisation numbers					
	A	B	C	D	E	F
0.....	0.02	0.00	0.00	0.01	0.01	0.03
50.....	0.2	0.00	0.00	0.01	0.01	0.03
100.....	0.58	0.00	0.00	0.01	0.01	0.03
200.....	1.35	0.01	0.00	0.02	0.01	0.03
300.....	1.67	0.06	0.00	0.02	0.01	0.05
400.....	2.50	0.15	0.00	0.05	0.01	0.12
500.....	-----	0.21	0.03	0.15	0.01	0.20
600.....	-----	0.29	0.08	0.34	0.02	0.28
700.....	-----	0.38	0.14	0.58	0.12	0.36
800.....	-----	0.48	0.21	0.90	0.30	0.47
900.....	-----	0.53	0.29	0.95	0.54	0.49
1,000.....	-----	0.53	0.39	0.95	0.84	0.49

We claim:

1. A lubricating composition comprising
 (a) an oil base selected from the group consisting of a mineral oil and a synthetic polyether containing $-(CH_2)_4-O-$ groups and
 (b) an oxidation-inhibiting amount of a member selected from the group consisting of an aliphatic monocarbodiimide, aliphatic polycarbodiimide, aromatic monocarbodiimide and aromatic polycarbodiimide.

2. A lubricating composition of claim 1 wherein the carbodiimide is a member selected from the group consisting of di-isopropyl-carbodiimide, di-n-butyl-carbodiimide, methyl-tert.-butyl-carbodiimide, dicyclohexyl-carbodiimide, diphenyl-carbodiimide, di-p-tolyl-carbodiimide, and 4,4'-didodecyl-diphenyl-carbodiimide, 2,2'-diethyl-diphenyl-carbodiimide, 2,2'-di-isopropyl-diphenyl-carbodiimide, 2,2'-diethoxy-diphenyl-carbodiimide, 2,6,2',6'-tetraethyl-diphenyl-carbodiimide, 2,6,2',6'-tetraisopropyl-diphenyl-carbodiimide, 2,6,2',6'-tetraethyl-3,3'-dichloro-diphenyl-carbodiimide, 2,6,2',6'-tetra-isobutyl-3,3'-dinitro diphenyl-carbodiimide, and 2,4,6,2',4',6'-hexaisopropyl-diphenyl-carbodiimide, tetramethylene- ω,ω' -bis-(tert.-butyl-carbodiimide), hexamethylene- ω,ω' -bis-(tert.-butyl-carbodiimide), tetramethylene- ω,ω' -bis-(phenyl-carbodiimide).

3. A lubricating composition of claim 1 wherein the carbodiimide is the reaction product of a lower alkyl substituted phenylene or diphenyl methane diisocyanate in the presence of a member selected from the group consisting of a tertiary amine, a basically reacting metal compound, a carboxylic acid metal salt and a non-basic organo-metal compound, the reaction being effected at a temperature of at least 120° C.

4. A lubricating composition of claim 1 containing an effective amount of an antioxidant selected from the group consisting of diphenylamine and hydroxy quinoline.

5. A lubricating composition of claim 2 containing about 1-2% carbodiimide by weight of lubricant.

References Cited

UNITED STATES PATENTS

2,298,636	10/1942	Prutton	252—51.5
2,458,526	1/1949	Oberright	252—51.5
2,654,680	10/1953	Goppel et al.	260—45.9 X
2,776,994	1/1957	Wolfe et al.	252—401 X
2,948,680	8/1960	Fields	252—51.5 X
3,004,916	10/1961	Ertelt	252—50 X
3,193,522	7/1965	Neumann et al.	252—50 X
3,193,523	7/1965	Neumann et al.	252—401 X

DANIEL E. WYMAN, *Primary Examiner*.

P. P. GARVIN, *Assistant Examiner*.