United States Patent Office

2,995,587
Patented Aug. 8, 1961

2,995,587

CARBALKOXYALKYL DIPHENYL ETHERS

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No Drawing. Filed May 29, 1958, Ser. No. 738,649
3 Claims. (Cl. 260—410.9)

This invention is directed to new compositions of matter; that is, the new compounds, carbalkoxyalkyl diphenyl ethers.

The new compounds of this invention can be used as base oils for lubricants in general, including use as hydraulic fluids and as base oils for grease compositions. When used as base oils for greases, for example, carbalkoxyalkyl diphenyl ethers can be heated with grease thickening agents to a temperature sufficient to form a uniform blend, followed by cooling. High shearing forces, such as obtained by the Manton-Gaulin homogenizer, can also be used to disperse the thickening agents in these new base oils.

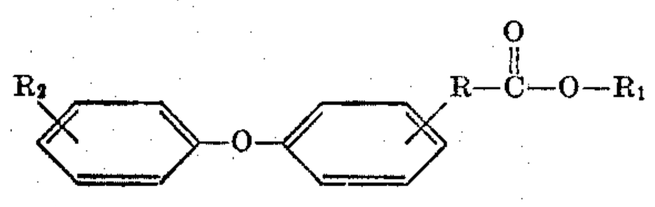
In addition to the above, these new compounds are particularly useful as base oils wherever lubricants are exposed to radiation. The irradiation of organic liquids by means of neutrons, X-rays, or gamma rays increases the viscosity of organic liquids. This viscosity increase is believed to be due to polymerization and cross-linking. In the application of nuclear energy for the generation of electric power, there are numerous frictional surfaces which require lubrication. It is essential to use mechanical equipment containing gears, bearings, journals, etc., all of which require lubrication. Irradiation of the usual lubricants results in the formation of heavy, viscous, or solid materials which are ineffective as lubricants. Furthermore, oxidation of lubricants in general is greatly increased by irradiation.

It is an object of this invention to provide new compositions of matter which are useful as base oils for lubricating compositions.

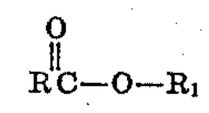
In accordance with this invention, it has been discovered that the new compounds, carbalkoxyalkyl diphenyl ethers, are useful as base oils for lubricating compositions.

The new compounds described herein are liquid at normal temperatures and they are particularly useful as lubricating oils, such as hydraulic fluids; as base oils for lubricating compositions used in the lubrication of internal combustion engines; base oils for grease compositions; and lubricants in general. These new oils are particularly resistant to radiation.

The carbalkoxyalkyl diphenyl ethers of the present invention are represented by the following formula:



wherein R is a divalent, straight-chain or branched chain, saturated hydrocarbon radical containing from 2 to 17 carbon atoms, and R_1 is a straight-chain or branched chain, saturated hydrocarbon radical containing from 1 to 18 carbon atoms, and R_2 is hydrogen or the radical



wherein R and R_1 are the same as described hereinabove.

Examples of the R radical include divalent radicals derived from propane, butane, isobutane, pentane, 2-methyl butane, 2,3-dimethyl propane, hexane, heptane, octane, decane, dodecane, tetradecane, hexadecane, octadecane, etc.

Examples of the R_1 radicals include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, anyl, octyl, decyl, dodecyl, etc.

The compounds described herein can be prepared as follows:

Diphenyl ether and an acid catalyst (e.g., anhydrous aluminum chloride) are mixed in a vessel equipped with a mixing means. To this mixture is slowly added a monoester of an olefinically unsaturated monocarboxylic acid (e.g., ethyl undecylenate). The whole mixture is heated for a period of time sufficient to complete the reaction; then diluted with a hydrocarbon solvent (e.g., benzene) and poured onto ice-diluted hydrochloric acid. The hydrocarbon fraction is washed with water, followed by neutralization. The mixture is dried, and the solvent removed by distillation.

The following examples illustrate the preparation of carbalkoxyalkyl diphenyl ethers.

EXAMPLE I

Preparation of carbethoxy decyl diphenyl ether and bis(carbethoxy decyl) diphenyl ether

A mixture of 170 grams (1.0 mol) of diphenyl ether and 133 grams (1.0 mol) of anhydrous aluminum chloride was charged to a reaction vessel. To this mixture was slowly added (dropwise) 212 grams (1.0 mol) of ethyl undecylenate. The reaction temperature was maintained at 45° to 50° C., using ice water as an external coolant until all of the undecylenate had been added. The whole mixture was then heated at a temperature of 60°–70° C. for a period of five hours, after which the mixture was diluted with 1 volume of benzene, then poured onto ice-diluted hydrochloric acid. When the mixture had been warmed, the benzene layer separated from the aqueous phase. This benzene layer was washed with water until neutral, then dried over anhydrous sodium sulfate, and filtered. The benzene was removed by distillation, after which carbethoxydecyl diphenyl ether and bis(carbethoxydecyl) diphenyl ether were recovered by distillation at reduced pressures.

Table I hereinbelow presents physical properties of the carbethoxydecyl diphenyl ether and bis(carbethoxydecyl) diphenyl ether of Example I hereinabove.

TABLE I

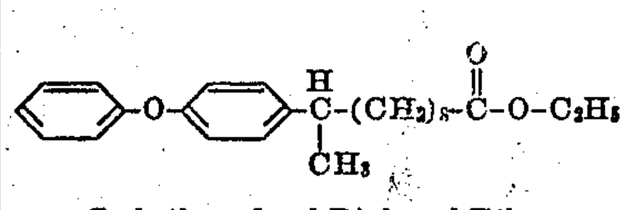
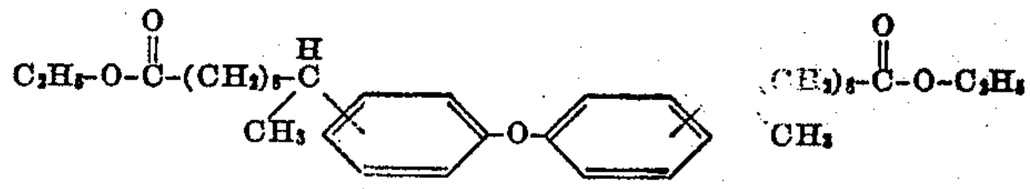
Structure		
Compound	Carbethoxydecyl Diphenyl Ether	Bis(carbethoxydecyl) Diphenyl Ether
Distillation Fraction:		
(a) Boiling Range, ° F., at 0.5 mm. Hg	374–410	554–603
(b) Description	Heart Cut	Heart Cut
Physical Properties:		
(a) Viscosity, cs.—		
at 100° F.	25.7	87.4
at 210° F.	4.53	10.6
(b) Temperature, ° F., for Viscosity (extrapolated)—		
of 1 cs.	458	611
of 2,500 cs.	−13	+16
of 13,000 cs.	−34	−8
(c) ASTM Slope (100° F. to 210° F.)	0.768	0.686
(d) Viscosity Index	98	111
(e) Pour Point, ° F.	−60	−55
(f) Viscosity at Pour Point, cs. (extrapolated)	170,000	1,000,000
(g) Refractive Index, n_D^{20}	1.5187	1.5038

Table II hereinbelow presents the results of radiation stability tests of the new compounds described herein.

The stability of the carbalkoxyalkyl diphenyl ethers to irradiation was determined by subjecting these new compounds to gamma radiation. A 10 ml. sample of the material to be tested was sealed in a stainless steel capsule in an atmosphere of helium. The fluids were irradiated at two dosage levels at 60° F., and the viscosity changes were noted.

The gamma radiation source used herein was the spent nuclear reactor fuel canal facility located at the Materials Testing Reactor, National Reactor Testing Station, Idaho.

TABLE II

Radiation stability	Hydrocarbon Oil [1]	Carbethoxydecyl Diphenyl Ether	Bis(carbethoxydecyl) Diphenyl Ether
A. Viscosity Change at 100° F., Percent:			
(a) Dosage 10^{10} ergs/g. Carbon—			
1.13	+37.7	+2.53	+5.25
5.31	+187.0	+19.2	+106.0
B. Viscosity Change at 210° F., Percent:			
(a) Dosage 10^{10} ergs/g. Carbon—			
1.13	+24.4	−0.88	+3.49
5.31	+93.0	+11.2	+29.2

[1] A California naphthenic base white oil having a viscosity of 70 cs. at 100° F.

The new lubricating base oils of this invention may be blended with oxidation inhibitors (e.g., organo selenides, dihydroxy anthraquinones, etc.), extreme pressure agents (e.g., organo sulfides), oiliness agents, viscosity index improving agents (e.g., olefin polymers), detergents (e.g., metal sulfonates), etc.

Grease thickening agents useful herein are illustrated by silica, metal salts of fatty acids (e.g., sodium stearate); metal salts of organic phosphonates (e.g., sodium polyethylene phosphonate); metal salts of terephthalamic acids (e.g., sodium N-octadecyl-terephthalamate), etc.

I claim:

1. A carbalkoxyalkyl diphenyl ether selected from the group consisting of 1-carbethoxy-methylnonyl diphenyl ether and bis(carbethoxy-methylnonyl) diphenyl ether.
2. 1-carbethoxy-methylnonyl diphenyl ether.
3. Bis(carbethoxy-methylnonyl) diphenyl ether.

References Cited in the file of this patent

UNITED STATES PATENTS

2,621,192 Haslam ---------- Dec. 9, 1952

OTHER REFERENCES

Van Loon: Chem. Abst., 44, 7058 (1950).
Mincher: KAPL–731, Apr. 2, 1952, pages 3, 4 and 7.