United States Patent Office 3,010,906 Patented Nov. 28, 1961

3,010,906
LUBRICATING OIL ADDITIVES

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No Drawing. Filed Jan. 26, 1956, Ser. No. 561,676
Claims priority, application France Mar. 9, 1955
5 Claims. (Cl. 252—56)

The present invention relates to a new class of lubricating oil additives which impart improved properties to lubricating oils containing them, and particularly relates to such additives which comprise the polymers or copolymers of alkoxy esters, and to lubricating oils containing them.

It is often desirable to improve the physical properties of lubricating oils, and one of the most useful ways of doing so is to incorporate additive compounds into the lubricating oils.

The use of additives to improve the detergency of lubricating oils is well-known. Such detergent oils when used in internal combustion engines inhibit corrosion, piston ring sticking, cylinder wear, and the formation of varnish on metal engine parts, as well as preventing the formation of sludge deposits within the engine. Well known types of detergents for lubricating oils are alkaline or alkaline earth metal-containing compounds. While such metal containing compounds generally have good detergency properties, their use under certain conditions, such as severe engine conditions or when oil-consumption is high, may cause an undesirable residue of ash in and adjacent to the combustion chamber of the engine. The presence of such ash may reduce the engine efficiency by causing pre-ignition, valve-burning or other undesirable effects.

It is the object of the present invention to provide an additive material which imparts good detergent properties to lubricating oils, but which does not result in the formation of harmful ash deposits within engines, and which also provides other useful properties, including raising the value of the viscosity index without unduly increasing the viscosity, and lowering the pour-point of lubricating oils in which the additive of the present invention is incorporated.

The additive compounds of the present invention are polymeric or copolymeric materials derived from partly esterified and alkoxylated unsaturated dibasic acids. While generally any unsaturated dibasic acid, may be used, it is preferred to use substituted or unsubstituted monoethylonic acids, such as fumaric or maleic acids which are alpha beta unsaturated or butenedioic acids or their alkyl derivatives.

The unsaturated dibasic acid is partly esterified with any aliphatic alcohol, although such alcohols having from 3 to 20 carbon atoms per molecule are preferred, and those having from 9 to 18 carbon atoms per molecule particularly preferred. The alcohols may be of straight-chain or branched configuration, and those alcohols produced by the "Oxo" process are preferred. It is within the scope of the invention to use a mixture of such alcohols.

By the term "partly esterified" it is meant that less than two gram molecules of alcohol is reacted with a gram molecule of organic dibasic acid during the esterification process. Particularly useful proportions of reactants include 1 gram molecule of dibasic acid with about 1.6 gram molecules of alcohol.

The partly-esterified dibasic acid is reacted with any alkylene oxide to produce the alkoxy-ester compounds. The alkylene oxido used is preferably one which contains from 2 to 6 carbon atoms per molecule, and is particularly ethylene oxide or propylene oxide. It is within the scope

of the present invention that the partly esterified acid may have some residual free acid hydrogen atoms left after reaction with the alkylene oxide, or it may be neutral, all the residual free acid hydrogen being reacted with the alkylene oxide. The reaction of the partially esterified acid with the alkylene oxide may be carried out by any well-known chemical method, for instance at temperatures of about 140° C. and in the presence of traces of boron tri-fluoride-phenol complex.

The additive compounds of the present invention are obtained by polymerising the alkoxy-ester compounds described above, or by copolymerizing such compounds with an unsaturated organic compound.

The preferred unsaturated organic compounds include unsaturated hydrocarbons, such as styrene, unsaturated esters derived from either unsaturated alcohols such as vinyl alcohols, or unsaturated acids such as fumaric or maleic acids, or methacrylic acid. Other unsaturated organic compounds include nitriles, e.g., acrylonitrile, or the anhydrides of unsaturated dibasic acids, such as maleic anhydride. While the above unsaturated organic compounds are the preferred compounds the alkoxy-esters may be copolymerized with any other copolymerizable organic compound.

The present invention therefore comprises an oil-soluble lubricating oil additive comprising a polymer or coplomer of an alkoxy-ester, said alkoxy ester being derived from a partly esterified unsaturated dibasic acid further reacted with an alkylene oxide.

The polymerization or coploymerization reaction of the alkoxy esters carried out by any well-known chemical process, such as low-temperature Friedel-Crafts processes, or ionic, free radical or radiation polymerization processes.

It is preferred that the polymerization or copolymerization process be carried out with the aid of a peroxide type of catalyst, preferably benzoyl peroxide, at temperatures ranging from 50° to 150° C., for periods of time ranging from 2 to 100 hours. It may be convenient to carry out the polymerization or copolymerization process in the presence of an inert solvent, such as gasoline, light lubricating oils, or chloroform. By the use of such solvents it is possible to control the reaction velocity and the molecular weights of the products.

To ensure that the final additive products are readily soluble in lubricating oils, it is preferable to carry out the polymerization or copolymerization reaction in the presence of an ester of maleic or fumaric acid with a C_3–C_{20} alcohol, preferably a C_{16}–C_{17} "Oxo" alcohol.

The additive compounds of the present invention are intended to be used in any lubricating oil, whether derived from animal, vegetable or mineral sources, and including synthetic lubricating oils especially those comprising complex esters, diesters, formals, methacrylates, or blends thereof.

The additive compounds of the present invention may be incorporated in lubricating oils in proportions from 0.01% to 20% by weight.

It is understood that the additive compounds of the present invention are restricted to those compounds which are soluble in the lubricating oil in which they are incorporated. Such solubility may be determined by a simple test.

The lubricating oils containing the additive compound of the present invention may also contain other additive compounds, such as oxidation inhibitors, extreme-pressure additives and anti-frothing agents.

The invention having now been generally described, it may be further understood by reference to the following examples:

EXAMPLE I

One gram molecule of maleic acid was partly esterified

with 1.6 gram molecules of a C_9 "Oxo" alcohol in the presence of 1% paratoluene sulphonic acid as a catalyst. After removal of reaction water the resulting ester had an acid number of 40.

This ester was condensed at 140° C. with ethylene oxide in the presence of traces of a BF_3/phenol complex. After 16 hours' reaction the acid number of the ester was 6, the weight of ethylene oxide combined with the ester being equal to 8% by weight of the said ester.

The ethoxylated ester thus obtained was copolymerized with 25% by weight of vinyl acetate at 70° C. for an hour in the presence of 2 grammes benzoyl peroxide.

The resulting copolymer (copolymer A) when added to a paraffinic oil having a viscosity index of 113, yielded the following results given in Table I.

Table I

Percentage of copolymer A	Characteristics of oil according to percentage of copolymer A		
	Viscosity Index	Viscosity in centistokes	
		at 37.8° C.	at 99° C.
0	113	32.1	5.8
2	129	35.4	6.2
4	136.5	41	7.1

EXAMPLE II

One gram molecule of maleic acid was partly esterified with 1.5 gram molecules of a C_9 "Oxo" alcohol in the presence of paratoluene sulphonic acid as catalyst, and 100–220% of gasoline. After washing in water and distilling the gasoline off, an ester was obtained having an acid number of 30.

This ester was condensed with gaseous ethylene oxide at 140° C. in the presence of traces of the BF_3/ether complex. After 18 hours' reaction, the acid number was 1.1: the weight of ethylene oxide combined with the ester being equal to 7% of the weight of the said ester.

After blowing with CO_2 at 110° C. and treating with 2% Actisil earth the acid number of the ester was 0.8.

The ester was then polymerized at 70° C. in the presence of 0.5% benzoyl peroxide with 50% by weight of vinyl acetate in the presence of an equal quantity of C_{16} "Oxo" alcohol maleofumarate.

The copolymer thus obtained when added to a paraffinic oil of viscosity index 112.5, yields the following results given in Table II.

Table II

Percentage of copolymer B	Characteristics of oil according to precentage of copolymer B		
	Viscosity index	Viscosity in centistokes at 99° C.	Pour point, ° C.
0	112.5	5.4	−9
0.2			−18
1	122.5	5.8	
2	126	6.1	
3.25			−27
4	135	6.9	
8	146	9.0	

The lubricant composition obtained by addition to the above paraffinic oil was stable at low temperature. After holding test at −5° C. for 48 hours with up to 20% of copolymer B the composition remained clear.

EXAMPLE III

An engine test was carried out with a mineral oil containing copolymer B, and with the same mineral oil without any additive.

The test was carried out according to the standard CRC

FL–2 adapted for a Peugeot 203 engine (4 cylinder, bore 75 mm., stroke 73 mm., total stroke capacity 1290 cc., volumetric compression 6.8, speed 2500 r.p.m., length of test 50 hours, output 20 H.P.

	° C.
Temperature of oil	55
Temperature of water:	
Inlet	33
Outlet	35

This test is of the type known as "cold test."

Composition of oils by weight	Without Additive	According to the invention
Paraffinic oil of viscosity 35 centistokes at 37.8° C. viscosity index 112, percent	99.1	95.85
Copolymer B, percent		3.25
Anti-oxidising agent: polymer of di-isobutylene phenol with formaldehyde and ammonia, percent	0.4	0.4
Anti-corrosion additive: alpha pinene phosphosulphide, percent	0.5	0.5
Chief characteristics of these oils—Viscosity index	112	131
Pour point, ° C	−9	−27

The results of the engine test are as follows:

(1) *Cleanliness.*—The cleanliness of the parts of the engine enumerated below is given points from 0 to 10, the point 10 being given to parts having no deposit and 0 to parts totally covered with deposit.

	Oil without additive	Oil of invention
Combustion chamber (deposits)	6.9	9.3
Skirts (varnish)	7.0	9.4
2. Deposits of mud:		
grammes on oil filter	32	9
grammes in connecting rod	17	2.3

What we claim is:

1. An oil-soluble lubricating oil additive having detergency and viscosity index improving properties prepared by partially esterifying, in the presence of a sulfonic acid catalyst, one mole of maleic acid with from about 1.5 to about 1.6 moles of an alcohol having about 9 carbon atoms per molecule, condensing the partial ester thereby formed with ethylene oxide in sufficient amount to incorporate about 7 to 8 weight percent of ethylene oxide into the partial ester, and thereafter copolymerizing the resulting ethoxylated ester within the range of 25 to 50 weight percent of vinyl acetate in the presence of a peroxide type catalyst.

2. An oil-soluble lubricating oil additive having detergency and viscosity index improving properties prepared by partially esterifying one mole of a butenedioic acid with from about 1.5 to about 1.6 moles of an aliphatic alcohol having in the range of 3 to 20 carbon atoms per molecule, condensing the partial ester thereby formed with an alkylene oxide having in the range of 2 to 6 carbon atoms per molecule in sufficient amount to incorporate about 7 to 8 weight percent of alkylene oxide into the partial ester, and thereafter copolymerizing the resulting alkoxylated ester within the range of from 25 to 50 weight percent of vinyl acetate.

3. An additive as defined by claim 2 wherein said alkoxylated ester has been additionally copolymerized with an ester of a butenedioic acid.

4. An additive as defined by claim 2 wherein said alkoxylated ester has been copolymerized with said vinyl acetate in admixture with a C_{16} alcohol maleofumarate.

5. A lubricating composition consisting essentially of a major proportion of a lubricating oil and from 0.01 to 20 weight percent of the additive defined by claim 2.

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