Patented July 1, 1952

2,602,048

UNITED STATES PATENT OFFICE

2,602,048

LUBRICATING OIL ADDITIVES

Adlai E. Michaels, Cranford, and Niilo V. Hakala, Rahway, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application March 8, 1951, Serial No. 214,652

6 Claims. (Cl. 252—32.7)

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This invention relates to methods of preparing improved lubricating oil compositions containing different additives having some degree of incompatibility. More particularly, it relates to methods of improving the compatibility of metallo-organic additives and polymeric additive materials in lubricating oil compositions. It relates also to lubricating compositions containing different additive materials exhibiting some degree of incompatibility to which have been added compounds which will be designated "compatibility improvers."

Lubricating oils manufactured by conventional methods are often unsuited for use under conditions encountered in internal combustion engines and for diverse industrial purposes. Satisfactory lubricating can be generally given by almost any type of lubricant of the proper viscosity for brief periods of time. However, for a sustained service under normal operating conditions the quality of lubricants becomes important and it is necessary for the lubricant not only to carry out the primary functions but also to exhibit the following advantages: (1) the lubricant should operate satisfactorily over a wide temperature range and (2) the deleterious effects of excessive engine deposits should be countered. In order to achieve these performance objectives, important characteristics of lubricating oils must be enhanced, especially viscosity, viscosity index, and ability to remove carbonaceous deposits. To obtain these and other desirable results, various additive materials have been blended with lubricating oils to extend the quality of lubricants for specific purposes beyond the level which can be reached by known manufacturing methods.

Generally, additives have been developed for specific purposes, for example, pour point depressants, viscosity index improvers, sludge dispersers, detergents, and the like. To obtain a general purpose lubricant having a high level of performance with respect to pour point, viscosity index, sludge dispersion, and the like, it is necessary to incorporate in the lubricating oil base stock many varied additive materials. Because of the diverse nature of many of these materials, it is not surprising that a certain incompatibility among them exists. For example, metallo-organic compounds used as detergent additives are frequently incompatible with high molecular weight polymeric materials used primarily as thickeners and viscosity index improvers. Lubricating oils having incorporated therein both of the above-mentioned additive materials are frequently unacceptable because of turbidity

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It has now been discovered that the addition of certain oxygenated organic compounds of the glycol ether type improves the compatibility of metallo-organic additives and highly polymeric additives, particularly the alkyl dibasic acid ester-vinyl ester copolymeric additives, and corrects thereby the unacceptable turbidity of a lubricant using the two additives.

These oxygenated organic compounds may be represented by the formula:

$$R—O—(CHR'—CHR''—O—)_nR'''$$

where R is H or an alkyl group having 1 to 8 carbon atoms, R' and R'' are H or an alkyl group having 1 to 3 carbon atoms, R''' is an alkyl group having 1 to 8 carbon atoms and n is an integer from 1 to 8.

The polyalkylene glycol ethers, especially the mono- and di-alkyl ethers of polyethylene glycol and of polypropylene glycol, are preferred, in particular the methyl, ethyl, propyl and butyl ethers thereof. It has been found that the polyethylene and polypropylene glycol mono-alkyl ethers or ester-ethers obtainable under the trade names "Carbitol" and "Dowanol" are particularly useful in improving the compatibility of copolymeric additives and metallo-organic additives.

Oxygenated organic compounds of the class enumerated may be dissolved in oil mixtures or solutions which contain incompatible additive materials for the purpose of minimizing or eliminating said incompatibility. These oxygenated compounds may be added (1) to the base oil before the addition of the polymeric additive or the metallo-organic additive (2) to the oil blend after the addition of either the polymeric additive or the metallo-organic additive (3) to the oil blend after the addition of the polymeric additive and the metallo-organic additive (4) to the metallo-organic additive.

To summarize briefly, the oil compositions of this invention consist essentially of a mineral lubricating oil containing combined therein (1) a copolymeric material which imparts desirable properties of viscosity index improving and/or pour depression to the blend, (2) a metallo-organic additive which is useful for improving the detergency characteristic of the oil blend, and (3) a compatibility improver which serves to minimize or eliminate any turbidity caused by a mixture of the metallo-organic additive and the copolymeric material.

The copolymeric materials useful as viscosity index improvers or pour depressors and contemplated in this invention are preferably the di-

basic acid ester-vinyl ester copolymers. These copolymers may be formed by copolymerizing a di-alkyl maleate or fumarate ester with vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl caproate, vinyl laurate, and the like. The di-alkyl dibasic acid ester may be prepared by simply heating the desired dibasic acid or anhydride with approximately a double molar proportion of the desired alcohol in the presence of an esterification agent such as sulfuric acid, hydrochloric acid, toluene sulfonic acid, and the like. It is preferred that the alcohol used as the esterification agent have an average of from 10 to 16 carbon atoms. An entraining agent such as an inert gas, naphtha and so forth is helpful for the removal of the water of esterification.

The copolymerization reaction taking place between the dibasic acid ester and the vinyl ester is ordinarily enhanced by the use of a polyoxide type catalyst among which may be mentioned benzoylperoxide, cumene hydroperoxide, tertiary butyl hydroperoxide, and the like.

In the preferred embodiment of this invention there is contemplated the use of a dialkyl dibasic acid ester-vinyl acetate copolymer in which the alkyl groups average from between 10 to 16 carbon atoms. An oil composition containing from 0.05% to 10% of the dibasic acid ester-vinyl acetate copolymer, preferably from 0.1% to 2.0%, percentages being by weight based on the weight of the total composition, is contemplated.

The metallo-organic additive material having the desirable detergency improving characteristics are preferably the metal salts of alkylated phenol sulfides or the reaction products of these sulfides and phosphorus sulfide. With these materials may be combined a minor amount of a petroleum sulfonate such as calcium petroleum sulfonate, calcium mahogany soaps, and the like. The barium salt of an alkyl phenol sulfide is particularly useful either alone or reacted with phosphorus sulfide. These materials are well known in the art of their preparation and are described in detail in United States Patent No. 2,362,291. It has been found that oil compositions containing from 0.2% to 0.3% by weight, based on the weight of the total composition, impart desirable detergent properties. A preferred range is from 0.8% to 2% by weight.

The compatibility agent, as described above, preferably diethylene glycol monoethyl ether is efficacious in amounts varying between 0.001% to 1.0% by weight, preferably 0.006% to 0.3% by weight.

In order to more explicity define the invention outlined above the following examples are given, it being understood that these examples are only illustrative of the inventive concept and not considered to be limiting in any way.

Preparation of Di-Alkyl Maleate Ester

A 3-liter flask equipped with a water trap and a reflux condenser was washed with 294 g. of maleic anhydride, 1118 g. of the alcohol obtained by hydrogenation of coconut oil and containing an average of 13.5 carbon atoms per molecule, 2 g. of sulfo-salicylic acid, 400 c. c. of xylene, and 200 c. c. of naphtha. The above mixture was refluxed for a total of 14 hours during which time 58 c. c. of water were collected. The reaction product was diluted with about 1,000 c. c. of benzol and then given four washes with 5% to 10% sodium carbonate solution and two with water. The sulfides were removed by evaporation on a steam bath. The resulting maleate ester had a saponification number of 230, a neutralization number of 0.5, and a viscosity of 210° F. of 41.7 S. U. S. and an average molecular weight of about 495.

Copolymerization of Vinyl Acetate With Maleate Ester

A 1-liter 3-necked flask equipped with a condenser, stirrer, and a thermometer was charged with 200 g. of a lubricating oil having a viscosity at 210° F. of 44 S. U. S. and 300 g. of the maleate ester as prepared above. This mixture was heated to about 80° C. after which it was blown with nitrogen for about 5 minutes. There was then added 4 g. of benzoyl peroxide and the mixture was again blown with nitrogen for about 5 minutes. Vinyl acetate addition was saturated with stirring about 45 minutes after the addition of the benzoyl peroxide and a total of 100 g. of vinyl acetate was added during the course of 1½ hours. The reaction mixture was maintained at 80° C. with stirring for 20 hours from the first addition of the vinyl acetate. The resulting copolymer had a viscosity at 210° F. of 3042 S. U. S.

Example I

A solvent extracted Mid-Continent paraffinic oil having a Saybolt viscosity of 46 seconds at 210° F. and a viscosity index of 110 had added thereto 0.2% of an alkyl maleate-vinyl acetate copolymer prepared according to the technique outlined above. Ten separate samples of the above lubricating oil composition were set aside. To five of these samples were added 0.8% of five separate samples of inhibitor-detergents consisting of the barium salt of alkyl phenol sulfide reacted with phosphorus sulfide. All five blends were hazy or turbid initially and on several days standing, all blends were very turbid with a precipitate settling out in one blend. To the remaining five samples were added the same inhibitor-detergent additives but in this case the inhibitor-detergent additives contained diethylene glycol mono-ethyl ether (sufficient quantities to give a concentration of 0.02% in the final blend). After standing two and a half months, the latter samples were found to be perfectly clear.

Example II

Two samples were prepared as in Example I with the exception that a different alkyl dibasic acid ester-vinyl acetate copolymer was employed. The blend without the compatibility improver turned cloudy immediately, but the blend containing the diethylene glycol mono-ethyl ether (0.02% in final blend) was still clear at the end of the two and a half months examination period.

Example III

Two samples were prepared as in Example II except that in the one blend 0.04% diethylene glycol mono-ethyl ether was added directly to the oil blend before the addition of the detergent additive instead of as a component of the latter additive. The blend without the compatibility improver was cloudy immediately whereas the blend containing the diethylene glycol monoethyl ether was still clear at the end of two and a half months.

Example IV

Example III was repeated except that a different sample of alkyl dibasic acid ester-vinyl

ester copolymer was employed and 0.02% instead of 0.04% compatibility improver was employed. Results were identical with those observed in Example III.

Example V

Eight oil blends were prepared using the same test oil and the same polyester copolymer (0.2%) described in Example I. To four of the blends were added 2.0% of 4 separate samples of the detergent inhibitor employed in Example I plus calcium petroleum sulfonate. All four blends exhibited some haziness in one day. To the remaining four samples were added the same inhibitor-detergent additives but in this case the latter additives contained diethylene glycol mono-ethyl ether sufficient to give a final blend concentration of 0.025%. All of the latter blends were clear after two and a half months standing.

Example VI

Two oil blends were prepared using the same test oil and same polyester copolymer (0.2%) described in Example I. To one blend was added 1.0% of a detergent-inhibitor comprising the metal salt of alkylated phenol sulfide and to the second blend was added 1.0% of the same additive containing diethylene glycol mono-ethyl ether (0.006% concentration in final blend). The first blend exhibited a slight haze in one week whereas the blend containing the compatability improver was clear at the end of two and a half months.

Example VII

Two oil blends were prepared using the same test oil and same polyester copolymer (0.2%) described in Example I. To one blend was added 0.8% of calcium isooctyl phenol sulfide and to the second blend was added 0.8% of the same additive containing diethylene glycol mono-ethyl ether (0.006% concentration in final blend). The first blend exhibited a haze in several days and was cloudy in 2 weeks whereas the blend containing the compatibility improver was clear at the end of two and a half months.

Example VIII

Three oil blends composed of 0.2% alkyl dibasic acid ester-vinyl acetate copolymer and the same base stock described in Example I were prepared. To one blend was added 0.8% of P_2S_5 treated barium isooctyl phenol sulfide, to the second blend was added 0.04% methoxy triglycol and 0.8% of the same detergent additive and to the third blend was added 0.8% of the same detergent additive which contained methoxy triglycol (0.02% concentration in final blend). The first blend was cloudy immediately while the two blends containing the compatibility improver were clear at the end of two and a half months.

Example IX

Two blends were prepared using the same base stock, same polyester copolymer and same detergent additive described in Example VIII. To one of the blends was added 0.04% dimethoxy-tetraethylene glycol. The blend without the compatibility improver was cloudy initially whereas the latter blend was clear initially but showed a slight haze at the end of a 40-day low temperature (40° F.) storage test.

The results of the above experiments may be summarized as follows:

COMPATIBILITY OF POLYESTER COPOLYMERS WITH METALLO-ORGANIC ADDITIVES

[Blends contain 0.2% copolymer in extracted Mid-Continent oil having a Sayholt viscosity of 46 seconds at 210° F. and a viscosity index of 110.]

Detergent Additive	Appearance of Blend (Without Compatibility Improver)	Compatibility Improver	Appearance of Blend Containing Compatibility Improver
0.8% Metal salt of alkyl phenol sulfide+phosphorus sulfide.	Turbid initially; precipitate on standing.	0.02% Diethylene glycol mono-ethyl ether.	Clear end of 2½ months.
0.08% Metal salt of alkyl phenol sulfide+phosphorus sulfide (4 samples).	Haze initially; very turbid in several days.	0.02% Diethylene glycol mono-ethyl ether.	All clear end of 2½ months.
1.0% Metal salt of alkyl phenol sulfide	Slight haze in one week	0.006% Diethylene glycol mono-ethyl ether.	
0.8% Metal salt of alkyl phenol sulfide	Slight haze in several days; cloudy—2 wks.	0.006% Diethylene glycol mono-ethyl ether.	Clear end of 2½ months.
2.0% Metal salt of alkyl phenol sulfide+phosphorus sulfide+calcium mahogany soap (4 samples).	Slight haze initially	0.025% Diethylene glycol mono-ethyl ether.	All clear end of 2½ months.
0.8% Metal salt of alkyl phenol sulfide+phosphorus sulfide.	Turbid initially; very turbid on standing.	0.04% Methoxy triglycol [1]	Clear end of 2½ months.
0.8% Metal salt of alkyl phenol sulfide+phosphorus sulfide.	do	0.02% Methoxy triglycol	Clear end of 2½ months.
0.8% Metal salt of alkyl phenol sulfide+phosphorus sulfide.	do	0.04% Dimethoxytetra ethylene glycol.[1]	Clear initially.[2]
0.8% Metal salt of alkyl phenol sulfide+phosphorus sulfide.	Cloudy initially	0.02% Diethylene glycol mono-ethyl ether.	Clear end of 2½ months.
0.8% Metal salt of alkyl phenol sulfide+phosphorus sulfide.	do	0.04% Diethylene glycol mono-ethyl ether.[1]	Clear end of 2½ months.
0.8% Metal salt of alkyl phenol sulfide+phosphorus sulfide.	do	0.02% Diethylene glycol mono-ethyl ether.	Clear end of 2½ months.

[1] Compatibility improver added directly to oil blend.
[2] Slight haze at end of 40-day low temperature (40° F.) storage test.

An examination of the data appearing in the table above points out the efficacy of the compatibility improver of this invention. In all instances the initial turbidity was removed by the addition of minor amounts of a material selected from the class consisting of diethylene glycol monoethyl ether, methoxy triglycol, and dimethoxy tetraethylene glycol.

To summarize briefly this invention relates to an oil composition having no turbidity which consists essentially of a mineral lubricating oil from 0.5% to 10% of a copolymer of a dibasic acid ester containing from 10 to 16 carbon atoms in the ester portion thereof with a vinyl ester, from 0.2 to 3.0% of a metallic salt of an alkylated phenol sulfide or the phosphorus sulfide reaction product of such metallic salt of an alkylated phenol sulfide and from .001% to 1.0% of a compatibility improver selected from the class consisting of diethylene glycol monoethyl ether, methoxy triglycol, and dimethoxy tetraethylene glycol. The preferred embodiment contemplates the use of a copolymer of a maleic acid ester containing from 10 to 16 carbon atoms in the ester portion thereof, the barium salt of an alkylated phenol sulfide, and diethylene glycol ether.

This application is a continuation-in-part of Serial No. 67,085, now abandoned.

What is claimed is:

1. A non-turbid lubricating oil blend having a high viscosity and exhibiting a high degree of detergency which consists essentially of a mineral oil base stock having combined therein about 0.05% to about 10% by weight of a copolymer of a maleate ester containing from 10 to 16 carbon atoms in the ester portion thereof and vinyl acetate, from about 0.2% to 3.0% by weight of a detergent inhibitor selected from the class consisting of metal salts of alkylated phenol sulfides and reaction products of metal salts of alkylated phenol sulfide, and a phosphorus sulfide, and from about 0.01% to 1.0% by weight of a compatibility improver of the class consisting of diethylene glycol monoethyl ether, methoxy triglycol, and dimethoxy tetraethylene glycol.

2. A non-turbid lubricating oil blend having a high viscosity index and exhibiting a high degree of detergency which consists essentially of a mineral oil base stock having combined therein about 0.1% to about 2.0% by weight of a copolymer of a maleate ester containing from 10 to 16 carbon atoms in the ester portion thereof and vinyl acetate, from about .08% to 2.0% by weight of a detergent inhibitor selected from the class consisting of metal salts of alkylated phenol sulfides and reaction products of metal salts of alkylated phenol sulfide, and a phosphorus sulfide, and from about 0.06% to 0.30% by weight of a compatibility improver of the class consisting of diethylene glycol monoethyl ether, methoxy triglycol, and dimethoxy tetraethylene glycol.

3. A lubricating oil blend according to claim 2 wherein the detergent inhibitor is the barium salt of an alkylated phenol sulfide.

4. A lubricating oil blend according to claim 2 wherein the compatibility improver is diethylene glycol monoethyl ether.

5. A lubricating oil blend according to claim 2 wherein the compatibility improver is methoxy triglycol.

6. A lubricating oil blend according to claim 2 wherein the compatibility improver is dimethoxy tetraethylene glycol.

ADLAI E. MICHAELS.
NIILO V. HAKALA.

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