

UNITED STATES PATENT OFFICE

2,637,698

MINERAL OIL LUBRICATING COMPOSITION
CONTAINING A COPOLYMER OF AN ALKYL
ESTER OF ITACONIC ACID AND AN ALKYL
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4 Claims. (Cl. 252—56)

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The present invention relates to copolymers of unsaturated dibasic acid esters and their derivatives with acrylic esters and related compounds. The present invention further relates to the use of polymeric materials of this general type as additives for lubricating oils and analogous compositions, and to the formulation of oil compositions, and the like, containing said additives as new products of manufacture. The invention further relates to the processes for producing the products of the character referred to above.

It has now been found, and is the subject matter of the invention, that alpha-methylene dicarboxylic acid esters readily copolymerize with alpha, beta unsaturated monocarboxylic compounds to yield shear stable and thermally stable oil soluble products which are particularly valuable as lubricating oil additives such as viscosity index improvers, pour depressants, and the like.

It is well known in the prior art that mineral base lubricating oils and, particularly, lubricating oils such as those used in the crank cases of automotive engines, have serious limitations with respect to pour point and viscosity-temperature relationships unless they are prepared from carefully selected materials or are modified to improve their viscosity and/or their pour characteristics. The present invention has, as a major object, the production of an improved additive material for oils which is suitable both for improving the viscosity index and for lowering the pour point.

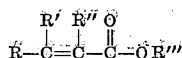
While reference is made above to lubricants for automotive crank cases, it will be understood that the invention has application to other type lubricants and is applicable generally to hydrocarbon oil fractions such as hydraulic oils and in some instances to synthetic oils which are employed similarly to naturally occurring mineral oils.

An important object of this invention is to produce polymeric materials which are stable at high rates of shear and are stable when employed in internal combustion engines as a constituent of the lubricating oil. A further object of this invention is to produce a polymeric material which is useful for improving the viscosity-temperature characteristics of oils without excessively increasing the viscosity thereof, and which may be used in various hydrocarbon base stocks derived from various crude oils, such as paraffinic, naphthenic, asphaltic or mixed base. A still further object is to prepare a material which does not lose its properties of depressing the pour

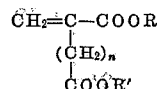
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points of oils upon repeated cycles of temperature change above and below the normal pour points. Many materials which are effective pour point depressors in lubricating oils, for example, become unsatisfactory after being subjected to a large number of temperature changes. This property which is commonly referred to as pour instability is highly objectionable under many conditions where low temperatures are encountered and an object of this invention is to prepare materials and lubricating oils containing such materials which are free from pour instability.

As an important aspect of the present invention, it has been discovered that excellent shear stable and thermally stable polymeric lubricating oil additives may be produced by copolymerizing alpha-methylene unsaturated dicarboxylic acid esters, wherein the esterifying group contains 6 or less carbon atoms, with compounds having the formula



wherein R is hydrogen or an alkyl group, R' is hydrogen or a halogen, R'' is hydrogen, a halogen or an alkyl group, and R''' is an alkyl, alicyclic aralkyl or aliphyl group containing at least 8 carbon atoms. In general, when R and R' are alkyl, it is preferred that they be relatively small, for example, methyl, ethyl, propyl, isopropyl, etc. Among the compounds of this type are esters of acrylic acid, methacrylic acid, alpha-chlor acrylic acid, crotonic acid, alpha chlor crotonic acid, beta chlor crotonic acid and mixtures thereof. The alpha-methylene dicarboxylic acid esters which are copolymerized with the alpha, beta-unsaturated compounds have the following general formula:



wherein $n=0, 1, 2$ or 3 or mixtures thereof, and R and R' are the same or different alkyl, alicyclic, aralkyl or aliphyl group usually containing no more than 6 carbon atoms. Examples of these esters are alpha-methylene malonic esters, itaconic esters, alpha-methylene glutaric esters and alpha-methylene adipic esters.

It is important in the preparation of copolymers of the type described herein that there be present at least one long chain hydrocarbon radical containing from about 8 to about 24 carbon atoms. These long chains are supplied by the

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alpha-beta unsaturated compound. The presence of these relatively long chains is of value in providing oil solubility and also for imparting desirable properties to the copolymer. For the production of pour depressants, it is essential that there be side chains containing 10 or more carbon atoms. These long chains may be supplied by the alcohols which are used to prepare the esters of the alpha-beta unsaturated compounds.

For the production of unusually effective V. I. improvers, it is necessary to have short side chains such as methyl, ethyl, butyl, etc. present in the copolymer in addition to the long side chains necessary to give oil solubility. These short side chains are supplied by the alpha-methylene dicarboxylic esters. It has been found that copolymers containing methyl side chains are usually more effective V. I. improvers than similar copolymers containing ethyl, butyl or longer side chains, and that, in general, the V. I. improving potency of similar copolymers decreases as side chain length, as supplied by the alpha-methylene dicarboxylic ester, is increased. This is illustrated as follows:

Copolymer	3.6 Wt. Percent Copolymer in Oil B ¹	
	Viscosity, S. U. S./210° F.	V. I.
Dimethyl Itaconate, 2%-----	64.0	147
C ₈ Oxo Acrylate, 98%-----		
Diethyl Itaconate, 4%-----		
C ₈ Oxo Acrylate, 96%-----		
Dibutyl Itaconate, 5%-----		
C ₈ Oxo Acrylate, 95%-----	62.7	146
C ₈ Oxo Acrylate, 95%-----	62.8	145
C ₈ Oxo Acrylate-----	63.4	143

¹ Oil B=lubricating oil having 45 S. U. S. viscosity at 210° F. and 115 V. I.

One commercially available alcohol mixture suitable for the preparation of the esters may be obtained from the hydrogenation of coconut oil. Such a product is sold under the trade name "Lorol" and is a mixture of saturated straight chain alcohols ranging from 10 to 18 carbon atoms and having a major proportion of lauryl alcohol which has 12 carbon atoms. Other related products are made by separating this material, which may be considered as a crude mixture, into several different fractions having a relatively higher proportion of the higher, lower, or medium constituent thereof. The composition of Lorol per se and related products, "Lorol B" and "Lorol R," is approximately as follows:

	Compositions of Mixtures of Commercial Alcohols		
	Lorol	Lorol B	Lorol R
C ₁₀ -----percent--	4	3	1
C ₁₂ -----do-----	55.5	46	85
C ₁₄ -----do-----	22.5	24	13
C ₁₆ -----do-----	14	10	1
C ₁₈ -----do-----	4	17	-----
Average Number of Carbon Atoms.	12.8	13.5	12.2

In addition to straight chain alcohols such as those contained in Lorol, branched chain alcohols can be employed. A source of branched chain alcohols which are suitable for the invention are those produced from olefins, carbon monoxide, and hydrogen by the "Oxo" reaction. Aliphatic alcohols produced as a by-product in the synthesis of hydrocarbons from carbon monoxide and hydrogen may also be used. Primary

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aliphatic alcohols are preferred, although secondary alcohols may be employed.

Also, alicyclic alcohols such as cyclohexanol, methylcyclohexanol and hydrogenated alkyl phenols, aralkyl alcohols such as phenylethanol, and aliphatic alcohols such as alkylated phenols, cresols, etc., can be employed. The above-mentioned alcohols may contain functional groups such as halogen, —NH₂, —CN, —NO₂, —OR, —O—(CH₂)_n—O—R, etc., provided they do not interfere with copolymerization or render the copolymer insoluble. Whereas straight chain and slightly branched aliphatic primary alcohols give excellent results and are therefore preferred, the other types of alcohols and their derivatives mentioned above can be employed for preparing the ester monomers which are copolymerized according to the invention. It will be understood that mixtures of alcohols of the same type or of different types can be employed. In the case of esters prepared from the alpha-methylene dicarboxylic acid, mixed esters such as methyl decyl itaconate can be copolymerized with the alpha, beta-unsaturated monocarboxylic compound with good results.

Half esters of alpha-methylene dicarboxylic acids may also be used in the preparation of copolymers. The resulting products contain free carboxyl groups which may be used as such or which may be neutralized by reacting with an alcohol, a primary or secondary amine or with ammonia or with a metal-containing compound to obtain an esterified, amidized or imidized product or an ammonium or a metallic salt.

Various conditions of copolymerization may be used in this invention involving either bulk or emulsion techniques. In bulk polymerization diluents may or may not be used. Temperatures may vary from 25° C. to 150° C. for periods ranging from 5 minutes to 100 hours and in the presence of various types of catalysts such as benzoyl peroxide, t-butyl hydroperoxide, cumene hydroperoxide, and other peroxides, aluminum chloride, boron fluoride, activated clays, ultra-violet light, and the like.

The oil solubility of the finished copolymeric material is governed to a considerable extent by the ratio of the alpha methylene dicarboxylic esters, which supply short side chains to the copolymer, to the alpha, beta unsaturated monocarboxy esters, which supply long side chains to the copolymer, employed in the copolymerization reaction. Examples of approximate maximum ratios giving copolymeric materials soluble in a lubricating oil consisting of 94% solvent extracted Mid-Continent stock and 6% solvent extracted bright stock are as follows:

I	II	Wt. Ratio I/II
Itaconate Ester.	Acrylate Ester	
Dimethyl-----	C ₈ Oxo-----	2/98
Do-----	Decyl-----	15/85
Do-----	Lauryl-----	20/80
Do-----	Lorol-----	20/80
Diethyl-----	C ₈ Oxo-----	4/96
Dibutyl-----	do-----	5/95
Do-----	Decyl-----	20/80

Copolymers of higher ratios of short chain esters to long chain esters may be soluble in other types of lubricating oil stocks.

The average molecular weight of the finished polymeric material should not be less than 1,000 or more than 50,000. The preferred range is

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about 5,000 to 20,000, a molecular weight of 7,000 to 17,000 being especially preferred.

The copolymers which are produced according to this invention not only are suitable pour depressants and viscosity index improvers but also are rust inhibitors, detergents, and generally improve the condition of the engines in which they are used. These copolymers may also be used in compounding greases, waxes, and the like, and may also be used in conjunction with other additive materials such as pour depressants, viscosity index improvers, rust inhibitors, detergents, extreme pressure agents, dyes, and the like.

The invention will better be understood from the specific examples described hereinafter which are illustrative only and are not to be construed as limiting the scope of the applicant's invention.

EXAMPLE I

To 20 g. of dimethyl itaconate were added 180 g. of octyl, decyl methacrylate (a mixture of octyl and decyl methacrylates) and 164 g. of a white oil having a 43 S. U. S. viscosity at 210° F. in a 3-liter stirring flask contained in an oil bath. The mixture was then heated for 48 hours at 70° C. in a nitrogen atmosphere adding 1 gram of benzoyl peroxide at the start and 1 gram of benzoyl peroxide after heating the mixture for 1 hour. A clear homogeneous copolymer was obtained which was blended to 20% concentration in a lubricating oil having a viscosity of 43-44 S. U. S. at 210° F. and this oil concentration was employed directly as a V. I. improver.

EXAMPLE II

To 100 g. of dimethyl itaconate were added 900 g. of octyl, decyl methacrylate and 755 g. of a white oil having 43 S. U. S. viscosity at 210° F., in a 3-liter stirring flask contained in an oil bath. The mixture was then heated for 27 hours at 70° C. in a nitrogen atmosphere, adding 5 grams of benzoyl peroxide at the start and 5 grams of benzoyl peroxide after heating the mixture for 1 hour. A clear, homogeneous copolymer was obtained which was blended to 40% concentration in a mineral lubricating oil having 43-44 S. U. S. viscosity at 210° F. and this oil concentrate was employed directly as a V. I. improver.

EXAMPLE III

To 0.2 grams of dimethyl itaconate were added 9.8 grams of octyl Oxo acrylate, 10.0 grams of a white oil having a 43 S. U. S. viscosity at 210° F. and 0.10 gram of 100 mesh benzoyl peroxide in a 30 cc. test tube. The tube was flushed with nitrogen, stoppered, agitated to effect complete solution, then heated for 30 hours at 70° C. in an oil bath. A clear, homogeneous copolymer was obtained which was blended to 20% concentration in a lubricating oil having a viscosity of 43-44 S. U. S. at 210° F. and this oil concentration was employed directly as a viscosity index improver. The octyl alcohol from which the acrylate was prepared was made by the Oxo reaction in the presence of a cobalt catalyst of CO, hydrogen and a C₇ olefin fraction, obtained from the polymerization of C₃-C₄ refinery gases in the presence of phosphoric acid catalyst, forming octyl aldehyde which was then hydrogenated to the alcohol.

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EXAMPLE IV

A copolymer of 1.7 g. of dimethyl itaconate with 9.3 g. of decyl acrylate was prepared in a similar manner to Example III, employing 9.0 g. of white oil diluent and 0.11 g. of 100 mesh benzoyl peroxide.

EXAMPLE V

A copolymer of 2.0 g. of dimethyl itaconate with 8.0 g. of lauryl acrylate was prepared in a similar manner to Example III, employing 7.0 g. of white oil diluent and 0.10 g. of 100 mesh benzoyl peroxide.

EXAMPLE VI

A copolymer of 3.2 g. of dimethyl itaconate with 12.8 g. of Lorol R acrylate was prepared in a similar manner to Example III, employing 11.1 g. of white oil diluent and 0.16 g. of 100 mesh benzoyl peroxide. This copolymer was also useful as a pour depressant.

EXAMPLE VII

A copolymer of 0.4 g. of diethyl itaconate with 9.6 g. of octyl Oxo acrylate was prepared in a similar manner to Example III, employing 10.0 g. of white oil diluent and 0.10 g. of 100 mesh benzoyl peroxide.

EXAMPLE VIII

A copolymer of 0.5 g. of dibutyl itaconate with 9.5 g. of octyl Oxo acrylate was prepared in a similar manner to Example III, employing 10.0 g. of white oil diluent and 0.10 g. of 100 mesh benzoyl peroxide.

The following table illustrates the superiority of examples of copolymers prepared according to this invention over acrylate and methacrylate polymers per se and a commercial viscosity index improver as regards lower thickening power and/or greater viscosity index improving power in motor oil blends.

Copolymer	S. U. S. Vis./210° F., 20 Wt. Percent Copolymer in Oil A	3.6 Wt. Percent Copolymer in Oil B	
		S. U. S. Vis./210° F.	V. I.
Dimethyl Itaconate, 10%-----	323	61.4	147
Octyl, decyl Methacrylate, 90%-----			
Example I			
Dimethyl Itaconate, 10%-----	352	62.3	149
Octyl, decyl Methacrylate, 90%-----			
Example II			
Dimethyl Itaconate, 2%-----	433	64.0	147
Octyl Oxo Acrylate, 98%-----			
Example III			
Dimethyl Itaconate, 15%-----	660	74.1	154
Decyl Acrylate, 85%-----			
Example IV			
Dimethyl Itaconate, 20%-----	501	68.1	152
Lauryl Acrylate, 80%-----			
Example V			
Dimethyl Itaconate, 20%-----	401	63.8	150
Lorol R acrylate, 80%-----			
Example VI			
Diethyl Itaconate, 4%-----	373	62.7	146
Octyl Oxo Acrylate, 96%-----			
Example VII			
Dibutyl Itaconate, 5%-----	385	62.8	145
Octyl Oxo Acrylate, 95%-----			
Example VIII			
Octyl Oxo Acrylate, 100%-----	362	63.4	143
Octyl, decyl Methacrylate, 100%..	566	71.7	147
Lauryl Acrylate, 100%-----	335	66.1	141
Commercial V. I. Improver X-----	651	72.5	147

Oil A—solvent extracted lubricating oil having 43-44 S. U. S. vis. at 210° F., 112 V. I.
Oil B—solvent extracted lubricating oil having 45 S. U. S. vis. at 210° F., 115 V. I.

The following table illustrates the pour depressing properties of copolymers prepared according to this invention.

Pour depressant properties of copolymers

Copolymer	Percent Concentration of Active Ingredient	A. S. T. M. Pour Point, ° F. of Blends in—	
		Oil C	Oil D
None.....	None	+5	+20
Dimethyl Itaconate, 20%.....	0.2	-25	-15
Lorol R Acrylate, 80%..... Example VI.			

Oil C—conventionally refined Pennsylvania 180 Neutral.
Oil D—solvent extracted Mid-Continent +Bright Stock—S. A. E. 10 grade.

The following tables illustrate the superior polymer stability characteristics of copolymers prepared according to the present invention as compared to the stability characteristics of other type methacrylate-itaconate ester copolymers and a current commercial V. I. improver in both laboratory tests and automotive enging tests.

Polymer breakdown characteristics[McIntyre pump test.¹]

Copolymer	Vis. 20% Copolymer Conc. in Oil A	New Oil			Used Oil 4 Hr. Sample	
		Wt. per-cent, Copol.	Vis., 210° F.	V. I.	Loss in V. I.	Percent Loss, Vis./210° F., Based on Polymer
Dimethyl Itaconate, 10%.....	323	2.75	75.8	122	2.0	16
Octyl, decyl Methacrylate, 90%..... Example I						
Decyl Itaconate, 80%.....	356	3.40	76.1	134	7.0	39
Methyl Methacrylate, 20%.....						
Commercial V. I. Improver X.....	651	2.05	77.0	123	4.8	31

¹ Copolymer oil blend circulated through McIntyre gear pump at 200° F. and 1000 p. s. i. g.

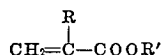
Polymer breakdown characteristics

[32 hr. Chevrolet engine test.]

Copolymer	New Oil			Used Oil—32 Hr. Sample	
	Wt. per-cent Copol.	Vis./210° F., S. U. S.	V. I.	Loss in V. I.	Percent Loss in Vis./210° F., Based on Polymer
Dimethyl Itaconate, 10%.....	1.2	52.0	127.2	5.5	12
Octyl, decyl Methacrylate, 90%..... Example II					
Commercial V. I. Improver X.....	1.2	52.1	125.6	7.9	24

What is claimed is:

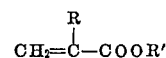
1. A lubricating oil composition consisting essentially of a major proportion of a mineral oil base stock and a small but viscosity index improving amount of a copolymer of an alkyl ester of itaconic acid wherein the esterifying group contains from 1 to 4 carbon atoms and a compound having the formula



wherein R is selected from the class consisting of hydrogen and a methyl group and R' is selected from the class consisting of the alkyl group containing from 8 to 24 carbon atoms.

2. A lubricating oil composition consisting es-

entially of a major proportion of a mineral oil base stock and a small but viscosity index improving amount of a copolymer of dimethyl itaconate and a compound having the formula



wherein R is selected from the class consisting of hydrogen and a methyl group and R' is selected from the class consisting of the alkyl group containing from 8 to 24 carbon atoms.

3. A lubricating oil composition consisting essentially of a major proportion of a mineral oil base stock and a small but viscosity index improving amount of a copolymer of dimethyl itaconate and mixtures of octyl and decyl methacrylate.

4. A lubricating oil composition consisting essentially of a major proportion of a mineral oil base stock and a small but viscosity index improving amount of a copolymer of 1 mol of di-

methyl itaconate and 0.1 to 2.0 mols of mixtures of octyl and decyl methacrylate.

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