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ESTERIFIED ALLYL ESTER-POLYCARBOXYLIC ACID COPOLYMERS

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1 Claim. (Cl. 260—78.5)

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This invention relates to improved lubricating oil compositions and, more particularly, to lubricating oil compositions improved by the addition of small percentages, sufficient to improve the characteristics of the oil, of products formed by copolymerizing alpha, beta-unsaturated polycarboxylic acids or acid anhydrides with esters of allyl alcohol, and thereafter esterifying the products with normal aliphatic alcohols, or mixtures of normal aliphatic alcohols, containing between about eight and about eighteen carbon atoms per molecule.

Prior to this invention alpha, beta-dicarboxylic acids, their anhydrides, and their esters have been mentioned in the literature as being copolymerizable with unsaturated compounds. However, insofar as is known, it has never before been suggested that alpha, beta-polycarboxylic acids or their anhydrides could be copolymerized with allyl esters and that the copolymers so formed could thereafter be esterified with relatively long chained, normal aliphatic alcohols to yield oil-soluble products which could be added to lubricating oils to lower the pour points or improve the viscosity indexes thereof.

According to the present invention, it has been found that alpha, beta-polycarboxylic acids or their anhydrides will react with allyl esters to produce copolymers, which copolymers are still capable of reacting with normal aliphatic alcohols to form new compositions of matter. It has further been discovered that at least certain of the compositions of matter so formed can be added to lubricating oils in minor proportions and that the addition will lower the pour points and improve the viscosity indexes of the lubricating oils.

REACTANTS

The reaction products of this invention are prepared from three basic reactants, a polycarboxylic acid material, an allyl ester material, and a normal aliphatic alcohol material. To these three basic reactants a fourth material, which may be designated as a vinyl monomer, may be added.

The polycarboxylic acid material may consist of a single chemically pure alpha, beta-unsaturated polycarboxylic acid such as maleic acid, fumaric acid, itaconic acid, glutaconic acid, mesaconic acid, citraconic acid, or aconitic acid. It may instead, consist of a single, pure anhydride of such an acid, except fumaric acid, which does not form an anhydride, or a mixture of such acids or anhydrides, or a single commercial quality acid or anhydride or a mixture of such acids or anhydrides. In general, the use of the anhydrides is preferred.

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Substituted acids such as chloromaleic acid may also be used. Maleic and fumaric acids, and particularly maleic anhydride, are preferred because of their availability, and the ease with which they react.

The allyl ester material may similarly be either of chemically pure quality or of commercial quality and may consist of either a single allyl ester or a mixture of allyl esters. These may be derived either from mono- or polybasic acids including aliphatic straight or branched chain acids, or from aromatic acids. Examples are allyl acetate, allyl-2-ethyl hexoate, allyl stearate, diallyl sebacate, allyl benzoate and diallyl phthalate. Preferably this material contains between about eight and about eighteen carbon atoms per molecule and, better still, an average of about fourteen carbon atoms per molecule, that is to say, an average of not less than twelve nor more than sixteen.

The normal aliphatic alcohol material used for the final esterification may be either a single, chemically pure, normal, aliphatic alcohol, a commercial grade of normal, aliphatic alcohol, or a mixture of chemically pure or commercial grade normal aliphatic alcohols. The average number of carbon atoms per molecule of alcohol should preferably be not less than about eight nor more than about eighteen, and better still about fourteen, that is to say, not less than twelve nor more than sixteen. A technical grade of lauryl alcohol as sold by Eastman Kodak Company may be named as a preferred example. Commercial alcohol mixtures such as "Lorol-B" and "Lorol-5," manufactured by E. I. du Pont de Nemours & Company, have also been found very satisfactory. These alcohol mixtures contain alcohols ranging from ten to eighteen carbon atoms per molecule in approximately the following proportions:

	Lorol-B	Lorol-5
	Percent	*Percent*
C_{10}	2.5	2.8
C_{12}	55.0	61.0
C_{14}	20.5	21.0
C_{16}	9.0	11.0
C_{18}	13.0	2.2
Av. No. C Atoms	13.5	12.7

REACTION CONDITIONS

The copolymerization of the allyl ester material and the polybasic acid material, may be accomplished by heating at temperatures ranging

from about 50° C. to about 150° C. for a period of time sufficient to accomplish the desired reaction. Periods of from one to twenty-four hours have been found satisfactory. The reaction can be accomplished either in the presence or the absence of solvent. Among the preferred polymerization catalysts is benzoyl peroxide in a proportion of about 0.10 to about 5.0% by weight. Solvents, such as benzene, xylene, or dioxane, may be added to reduce the viscosity and to control the reaction more efficiently.

In the case of a peroxide catalyzed polymerization, according to the literature (P. D. Bartlett and Kenzie Nozaki, "The polymerization of allyl compounds—The peroxide induced copolymerization of allyl acetate with maleic anhydride"—J. A. C. S., August 1946, page 1495) a 1:1 polymer composition always results.

Although the ratio of reactants in the copolymer may remain constant, the reaction conditions will affect the length of the copolymer chain. For example, the use of low temperatures, small amounts of peroxide catalyst and long reaction times will result in higher molecular weight copolymers. By conducting the reaction in the absence of solvents or in the presence of solvents, such as dioxane, which do not tend to cause chain transfer, there is an increased tendency toward the formation of higher molecular weight polymers.

The esterification of the copolymer with the alcohol material may be accomplished by simply heating the copolymer and the alcohol material in the presence of a small amount of concentrated sulfuric acid or p-toluene sulphonic acid. It is preferred in this reaction to utilize a high-boiling solvent such as xylene and azeotropically distill the water formed in the reaction.

In another embodiment of the present invention, a vinyl monomer such as vinyl acetate, styrene, various vinyl esters or ethers, is copolymerized with an allyl ester and maleic anhydride, for example, and the copolymer thus obtained is then esterified with the alcohol material. A fairly wide range of proportions of vinyl monomer to copolymer may be used, for example, from none at all up to at least 50% by weight of the weight of the copolymer. Preferably, if a vinyl monomer is to be used at all, it will be used in the proportion of about 15 to 30% based on the weight of the copolymer.

OIL BASE

The reaction products of this invention are particularly adapted for use as pour point depressants and viscosity index improvers in lubricating oils. They may be incorporated in any type of lubricating oil ranging from gasoline and kerosene to petrolatum and petroleum wax. They may also be used in synthetic lubricating oils or even in lubricating oils or other lubricants derived from animal or vegetable sources. The reaction products of this invention are particularly adapted for use in petroleum oils of the type normally used for the lubrication of internal combustion engines.

CONCENTRATION IN OILS

The reaction products of this invention will normally be incorporated in lubricating oils in concentrations ranging from 0.01% to 20%. Normally, a higher concentration will be required to effect a satisfactory improvement in viscosity index than will be required to effect a satisfactory lowering of the pour point of the oil. In many cases, therefore, where viscosity index improvement is not the major function of the new products in the oil, a concentration of 0.01% to 2.0% is preferred.

It is within the concept of this invention to incorporate the new reaction products in oils containing other improving agents such as pour depressants, detergents, extreme pressure lubrication improvers, viscosity index improvers, stabilizing agents, rust inhibitors and the like.

It is further contemplated that the reaction products of this invention may be prepared and marketed in their pure form, that is, without admixture with lubricating oils, or may be prepared and marketed in concentrated solutions in oil, which concentrated solutions are adapted to be added to further quantities of oil to improve its characteristics.

Further details of this invention and further advantages may be understood from the following detailed examples and results of tests.

EXAMPLE I

A copolymer of allyl laurate and maleic anhydride was prepared by first preparing allyl laurate from allyl alcohol and a technical grade of lauric acid and reacting 50.0 g. of this allyl laurate with 20.2 g. of maleic anhydride in the presence of 0.7 g. of benzoyl peroxide and 200 cc. of xylene. The reactants were mixed and slowly heated to xylene reflux temperature and held at that temperature for four hours. The xylene and unreacted materials were removed by distillation at 125° C. under 0.5 mm. mercury pressure. The copolymer was an amber-colored resin.

20.0 g. of the copolymer and 60.0 g. of "Lorol-B" were reacted in the presence of 0.8 g. of p-toluene sulphonic acid and 100 cc. of xylene by heating to xylene reflux temperature in a flask equipped with a side arm water trap and condenser. After heating for 1 hour the xylene was slowly removed by distillation, raising the temperature to 160° C. and heating for an additional ½ hour. The solution was transferred to a distilling flask and the remaining xylene and unreacted alcohol removed by distillation at 250° C. under 1 mm. pressure of mercury. The viscous polymer which resulted was readily soluble in lubricating oil.

Instead of distilling at high temperatures to remove unreacted high molecular weight alcohols, extraction with hot alcohol may be used. For example the copolymer, after removal of solvent, may be extracted several times with about 3 to 5 volumes of hot alcohol, preferably ethyl alcohol. The high molecular weight alcohols are soluble in the hot alcohol while the copolymers are insoluble therein. Traces of entrained alcohol are removed by evaporation on a steam bath.

EXAMPLE II

A copolymer of allyl acetate and maleic anhydride was prepared by reacting 50.0 g. of allyl acetate and 49.0 g. of maleic anhydride in the presence of 3.0 g. of benzoyl peroxide in 400 cc. of toluene. The reactants were mixed and heated to reflux temperature as before. After about 15 minutes, the copolymer began to precipitate from the solution. The mixture was heated for 3 hours, cooled and filtered. The copolymer was dissolved in dioxane and reprecipitated by pouring into water. It was then vacuum filtered and dried to a white resin.

10.0 g. of this copolymer and 22.0 g. of "Lorol-B" were reacted in the presence of 0.3 g.

of concentrated sulphuric acid and 250 cc. of xylene. The reaction was accomplished as in Example I, except that a reaction time of 6 hours was used. The viscous product was readily soluble in lubricating oil.

EXAMPLE III

A copolymer of allyl oleate and maleic anhydride was prepared by reacting 50.0 g. of allyl oleate and 25.0 g. of maleic anhydride in the presence of 1.0 g. of benzoyl peroxide in 200 cc. of dioxane. The solution was heated at 80° C. with stirring for 24 hours. It was then poured into water to precipitate the copolymer which was vacuum filtered and dried.

16.0 g. of this copolymer and 36.0 g. of "Lorol-B" were reacted in the presence of 1.0 g. of concentrated sulphuric acid and 150 cc. of xylene. The reaction was conducted as in Example I. The finished ester was readily soluble in lubricating oil.

EXAMPLE IV

A copolymer of diallyl sebacate and maleic anhydride was prepared by reacting 60.0 g. of diallyl sebacate with 40.0 g. of maleic anhydride in the presence of 1.0 g. of benzoyl peroxide and 200 cc. of dioxane. The reaction was accomplished in the same manner as in Example III.

20.0 g. of this copolymer were reacted with 40.0 g. of "Lorol-B" in the presence of 1.0 g. of concentrated sulphuric acid and 150 cc. of xylene, as in Example I. The ester was readily soluble in lubricating oil.

EXAMPLE V

A copolymer of allyl benzoate and maleic anhydride was prepared by reacting 65.0 g. of allyl benzoate with 40.0 g. of maleic anhydride in the presence of 1.0 g. of benzoyl peroxide and 200 cc. of dioxane. The reaction was accomplished as in Example III.

15.0 g. of the copolymer were reacted with 35.0 g. of "Lorol-B" in the presence of 1.0 g. of concentrated sulphuric acid and 150 cc. of xylene as in Example I. The ester was readily soluble in lubricating oil.

EXAMPLE VI

16.3 g. of maleic anhydride, 20.0 g. of allyl laurate (prepared from allyl alcohol and Eastman's technical lauric acid), 8.3 g. of freshly distilled vinyl acetate and 0.45 g. of benzoyl peroxide were slowly heated to 95° C. At this point vigorous reaction took place, the temperature rising to 155° C. despite the fact that the reaction flask was cooled by means of an ice bath. The reaction product was a sticky, resinous mass which was diluted with 150 cc. of dioxane and heated at reflux for 1 hour. The dioxane was then removed by distillation.

10.0 g. of the above copolymer were mixed with 18.0 g. of "Lorol-B," 0.5 g. of p-toluene sulphonic acid and 200 cc. of xylene and heated at xylene reflux for 3 hours in a flask equipped with a side arm water trap and condenser. The solution was cooled, washed with water and filtered. Solvent and unreacted alcohol were distilled by heating to 280° C. under 1 mm. pressure of mercury.

EXAMPLE VII

A copolymer similar to Example VI was prepared except that the copolymerization was run in the presence of 100 cc. of dioxane at reflux for 8 hours. A "Lorol-B" ester of this copolymer was prepared as described above.

The effectiveness of the reaction products prepared in accordance with the above examples, as depressants of the pour point of lubricating oils, is illustrated by the data of Table I, which follows: These results were obtained by blending 0.25% by weight of the selected reaction product into a furfural-refined Mid-Continent type base oil having an original ASTM pour point of +20° F.

Table I

Compounds Blended in Oil	Concentration, Weight Percent	A. S. T. M. Pour Point, ° F.
None		+20
Example I	0.25	−10
Example II	0.25	0
Example III	0.25	−20
Example IV	0.25	−10
Example V	0.25	−25
Example VI	0.25	−5
Example VII	0.25	−15

The effectiveness of the new reaction products as viscosity index improvers is illustrated by Table II, which follows. These results were obtained by blending 1.0% of the selected reaction product with an acid refined, Mid-Continent type base oil having an original viscosity index of 78.5.

Table II

Compounds Blended in Oil	Concentration, Weight Percent	Kinematic Viscosity at—		Viscosity Index
		100° F.	210° F.	
None		30.55	4.82	78.5
Example III	1.0	31.29	4.95	85.4
Example V	1.0	31.00	4.94	86.9

This application is a division of our copending application, Serial No. 756,316, filed June 21, 1947.

What is claimed is:

As a new composition of matter a reaction product formed by copolymerizing allyl benzoate with maleic anhydride in the presence of a polymerization catalyst at a temperature of from about 50° C. to about 150° C. and reacting the copolymer product thus formed with a mixture of primary, normal, saturated, aliphatic, monohydric, unsubstituted, alcohols having from 8 to 18 carbon atoms and an average of about 14 carbon atoms per molecule.

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