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2,694,685

MALEINOID-VINYL COPOLYMER AND ITS USE
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This invention relates to novel chemical copolymers and to methods of preparing and using same, and more particularly to using them as lubricating oil additives, especially as pour depressors and V. I. (viscosity index) improvers. The invention may be typified by making a copolymer of 20% by weight of vinyl acetate with 80% by weight of dialkyl maleic acid ester of substantially saturated alcohols having an average of 12 to 18 carbon atoms, and using a small amount of such copolymer as a pour depressor and V. I. improver in a waxy mineral lubricating oil.

The hydrocarbon base stocks which may be used according to this invention may preferably be any of the waxy or paraffinic hydrocarbon oil fractions such as those derived from petroleum, or synthetic oils made by polymerization of olefins or other unsaturated aliphatic hydrocarbons or other synthetic oils, and such fractions may be either relatively narrow cut fractions separated from petroleum or other crude hydrocarbon mixtures by distillation or other suitable means, and they may be used in the relatively crude state or after refining by suitable methods such as clay treating, acid treating, solvent extraction, cracking, hydrogenation as well as treatment by various chemical refining agents such as aluminum chloride, etc. The invention is especially applicable to mineral oil base stocks of the lubricating oil boiling range, or to lower boiling fractions such as those of the kerosene or gas oil boiling range which it is desired to thicken to viscosities within the lubricating oil range, as for use in gun recoil oils, shock absorber oils, etc. especially when these are to be used in very cold climates. However, it is to be understood that the invention may also be applied to other paraffinic oils and for other purposes, by using as the base stock lighter mineral oil fractions such as gasoline or naphtha, or by using gas oil fractions such as diesel fuel, or even solid waxy petroleum fractions such as paraffin wax and petrolatum.

When the copolymer additive is used essentially only as a V. I. improver or as a thickener, the hydrocarbon base stocks may be derived from mixed base, naphthenic, or even asphaltic crudes.

Many types of materials, a few natural ones and many synthetic ones, including many types of polymerized esters have been used, or suggested, as pour point depressors and viscosity index improvers in lubricating oils. The primary purpose of these additives is to prepare a lubricant which will be as fluid as possible at cold temperatures and yet will not thin out or have too low viscosity at high temperatures. However, many of these previously suggested materials either are not as satisfactory from a technical point of view as is desired, or they are too difficult to make or are too expensive for practical use. Vinyl ester polymers are disclosed in U. S. Patent 2,020,714 as additives for lubricating oils. Other polymerized esters are disclosed as being V. I. improvers but not as pour depressors. Furthermore, some polymerized esters have relatively good pour depressing properties as measured by the A. S. T. M. pour point test but do not have satisfactory pour stability, which means remaining in a stable fluid condition in spite of alternate cycles of warming and cooling such as occurs during storage at atmospheric temperature. Numerous other polymers and copolymers of esters and other materials are known which are either totally insoluble in mineral lubricating oils, especially in waxy lubricating oils, or have such a low solubility therein as would be impractical for use as pour depressors and V. I. improvers, even

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though they may be satisfactory for use as a synthetic resin or plastic or for other purposes. For instance, U. S. Patent 1,945,307 discloses copolymers of olefin dicarboxylic acids and vinyl esters, for example, diethyl fumarate and vinyl acetate, but such products are insoluble in lubricating oils.

Broadly, the present invention comprises copolymerizing at least one maleinoid ester with at least one vinyl compound containing oxygen, there being an average of about 4 to 18, preferably 6 to 16, carbon atoms in the side chains of the copolymer of the maleinoid ester and the vinyl compound.

The maleinoid ester to be used may consist either of a single compound or mixtures as will be more fully explained later. When a dialkyl maleate is polymerized, the alkyl groups appear as side chains in the polymer structure.

Alkyl esters of maleic acid polymerize much more slowly than corresponding esters of fumaric acid. They also copolymerize with other materials at different rates and produce copolymers having different properties.

The alcohols which are particularly useful in the present invention for esterifying either or both of the carboxyl ($-\text{COOH}$) groups of maleic acid, are the primary straight chained alcohols, preferably saturated alcohols. Nevertheless, secondary alcohols, branched chain alcohols and cyclic alcohols, e. g. cyclohexanol, cyclohexyl methanol or other naphthenyl alcohols, may be used, particularly when there is present a long straight chain of 10 to 22 carbon atoms in the reaction mixture. The alcohols are generally preferred free of substituents. However, the alkyl or naphthenyl residues may contain various substituents such as alkoxy, thioalkoxy, halogen, NH_2 , NO_2 , SO_3H , CN , and other groups as long as these do not interfere with the polymerization or render the polymers insoluble or otherwise unsuitable in lubricating oils.

Examples of some of the alcohol radicals which may be used include first the preferred ones having 10 to 16 carbon atoms, e. g. normal decyl, normal dodecyl (lauryl), tetradecyl, cetyl, as well as branched homologs thereof, and also the intermediate alkyl groups or alcohol radicals having an odd number of carbon atoms, e. g. 11, 13 and 15, although such groups are not as available in nature as the even ones. Alcohol radicals having less than 10 carbon atoms which may be used in admixture or conjunction with higher ones as explained above include octyl, heptyl, hexyl, amyl, butyl, as well as various branched and primary, secondary and tertiary homologs thereof, normal propyl and isopropyl, ethyl and even methyl. Higher alcohol radicals which may be used, particularly in admixture or in conjunction with some of the lower ones just mentioned, to obtain the desired average of 10 to 16 carbon atoms, include stearyl (normal octadecyl), eicosyl, docosyl, ceryl (having 26 carbon atoms), etc. As indicated, instead of using single pure alcohol compounds, other commercially available mixtures may be used as for instance those having 10 to 16, or 10 to 18 carbon atoms, and derived by hydrogenation of coconut oil. In the range of a lower number of carbon atoms, a commercial mixture of isomeric amyl alcohols is available.

Thus if the resulting copolymer is desired to be both a pour depressor and V. I. improver the maleinoid ester should contain at least one long chain having at least 10 carbon atoms, even though other side chains present in the maleinoid ester monomer may have a number of carbon atoms ranging widely from 1 to about 30. However, if the copolymer is desired to be essentially a V. I. improver, with relatively little or no pour depressing properties, there should be some solubilizing side chains preferably of at least about 4 carbon atoms in the maleinoid ester to obtain good solubility in lubricating oils. Present indications are that the only way it is possible to make an oil-soluble maleinoid ester having only side chains of less than 6 carbon atoms, e. g. from 1 to 5 carbon atoms is to copolymerize therewith a large proportion of a vinyl compound having a side chain of enough carbon atoms to make a total average of 4 to 18, preferably 6 to 16, carbon atoms for all the side chains in the copolymer. Thus if a maleinoid ester is used hav-

ing only 1 or 2 carbon atoms in the side chain (a methyl or ethyl ester), the vinyl compound used should preferably have a relatively long chain, i. e. at least 10 carbon atoms and be used in a proportion of at least about 75% by weight or about 3 mols per mol of maleic ester. On the other hand, if a dibutyl maleic acid ester is used, the vinyl compound used should preferably have a side chain of about 8 to 10 or so carbon atoms, and should be used in a proportion of about 60 to 75% by weight or 2 to 3 mols per mol of butyl maleate.

Although the maleate esters of the above described alcohols are preferred, one may also use esters which have been derived from other maleinoid dibasic acids in which the carboxyl groups are attached to 2 carbon atoms of an ethylenic group. The homologs of maleic acid or maleic anhydride would fall in this group; these include citraconic acid or citraconic anhydride. Also falling in this group would be the derivatives of the above acids and anhydrides, such as monochlormaleic acid or anhydride, dichlormaleic acid or anhydride, monochlorcitraconic acid or anhydride, etc. It is to be noted that one of the characteristics of the maleinoid dibasic acids is that they are capable of forming anhydrides. The anhydrides are particularly valuable in many cases, such as in the preparation of half esters from alcohols and in the preparation of mixed esters. Mixtures may be used containing 2 or more different maleinoid acids or anhydrides. These combinations may be used in the preparation of the esters, or the esters may be produced from the pure acids or anhydrides and later combined.

Instead of using maleinoid esters made by reacting a maleinoid acid or anhydride with an alcohol, similar esters made in any other manner may be used.

For simplicity and reference purposes, these various maleinoid ester monomers may be referred to by the general formula $R-M-R'$ where M is a maleinoid acid radical, and R and R' are like or unlike saturated hydrocarbon groups, such as alkyl, cycloalkyl or naphthenyl, preferably for pour depressing purposes averaging about 10 to 16 carbon atoms, at least one group having at least 10 carbon atoms. Thus a suitable simple ester is RMR where R has 10 to 16 carbon atoms. Mixtures of simple esters are mixtures of RMR and $R'MR'$ or R^xMR^x where all R's average 10 to 16 carbon atoms but the overall range limits are from 1 to 30 carbon atoms, R^x representing a mixed alcohol group. A true mixed ester is RMR' where R and R' are different. Also one could use mixtures of two or more mixed esters, e. g. RMR' , RMR'' , $R'MR''$, or any such mixed esters in admixture with one or more simple esters.

A procedure found to be useful in the preparation of the esters consists in heating one mol of the dibasic acid or anhydride with approximately 2 mols of alcohols in the presence of a catalyst such as H_2SO_4 , toluene sulfonic acid, HCl , $SnCl_2$, etc. An entraining agent such as an inert gas, naphtha, etc. is helpful in the removal of water. It is often unnecessary to use a catalyst for the preparation of half esters from the anhydrides with alcohols.

It is generally preferable that the monomeric esters be essentially neutral, although small quantities of half esters or free maleinoid acids appear to have no harmful effect and may even be helpful. Small quantities of unreacted alcohols may also be present, even though they retard polymerization and tend to cause the formation of low molecular weight copolymers from the esters.

In some cases it may be desirable to copolymerize a maleinoid half ester with the vinyl compound, and then convert the resulting copolymer into the corresponding metal salt thereof and use such metal salt as lube oil additive, for instance, as a polyfunctional additive having pour depressing, V, I.-improving and engine-detergent characteristics. If desired, some of the vinyl-maleinoid half ester copolymer may be used as lube oil additive directly without conversion into the corresponding metal salt. The maleinoid half ester may also be first mixed with a maleinoid diester before copolymerization with the vinyl compound.

The other primary reactant to be copolymerized with the above described maleinoid ester is a vinyl compound containing oxygen, and this should preferably be one having the general formula $CH_2=CH-Y$, where Y is a radical composed essentially of C, H, and O, such as ester radicals having the general formula $-OOCR$ and ether radicals having the formula $-OR$, where R in the formulas represents a straight, branched, or cyclic hydro-

carbon radical which may or may not contain relatively inert substituents such as NH_2 , NO_2 , HSO_3 , CN , etc. which do not interfere with the use of the resulting copolymer as a lube oil additive. It is preferred that Y consist only of carbon, hydrogen and oxygen, and it is preferred that the group Y, which appears in the polymeric material as a side chain, should have less than 10 carbon atoms, and preferably, especially for V. I.-improving properties, contains only 1 to 4 carbon atoms. General indications at present are that if Y contains only 1 to 4 carbon atoms then the side chains in the maleinoid ester should ordinarily contain at least 4 carbon atoms and the vinyl compound should generally be used in a relatively low proportion of only about 0.5 to 2 mols per mol of maleinoid ester, or about 10 to 30% by weight in the monomeric mixture. However, larger numbers of carbon atoms ranging even up to 30 or so may be used in the group Y, and in such case, proportionately fewer carbon atoms may be used in the side chains of the maleinoid ester, and a proportionately higher concentration of the final compounds can be used in the monomeric copolymerization feed.

Some specific examples of suitable vinyl compounds will now be mentioned. A preferred vinyl ester is vinyl acetate which has 2 carbon atoms in the acetate radical which is considered the side chain in the final copolymer. Vinyl propionate, vinyl butyrate and other higher vinyl fatty acid esters may be used such as vinyl caproate, vinyl laurate, vinyl myristate, vinyl palmitate, vinyl stearate, etc. Various derivatives of such vinyl esters may be used such as the vinyl ester of phenyl stearic acid, vinyl chloracetate, etc.

A preferred ether is vinyl butyl ether, although one may also use vinyl ethers of other lower alkyl alcohols, e. g. methyl, ethyl, propyl, isopropyl, amyl octyl, cyclohexyl, or decyl, lauryl, tetradecyl, cetyl, octadecyl, and even higher alcohols having up to 30 or so carbon atoms.

In some cases it is preferred to use more than one monomeric vinyl compound, and in such cases one may use two or more monomers of any one class of vinyl compounds, such as a mixture of vinyl acetate and vinyl propionate, or a mixture of vinyl butyl ether and vinyl isopropyl ether or a mixture of vinyl ethyl ether and vinyl iso-octyl ether; or one or more monomers of two or more classes of such vinyl compounds, such as a mixture of vinyl acetate and vinyl isobutyl ether.

As in the case of the maleinoid esters, the side chains of the vinyl compound may consist of mixtures derived from commercially available natural or synthetic mixed fatty acids, or alcohols, such as the vinyl ester of coconut oil fatty acids or the vinyl ester of mixed fatty acids as present in natural vegetable, animal or fish oils and waxes, or the vinyl ether of the mixed isomeric amyl alcohols or the vinyl ether of the mixed C_{12} to C_{18} alkyl alcohols obtained by hydrogenation of coconut oil.

The preparation of the copolymers of this invention is not limited to any particular method and may be carried out in the presence or absence of diluents. It is generally preferred to use no diluent if it is desired to obtain products of highest molecular weight, but it is more practical to use about .01 to 5, preferably 0.1 to 1.0, volumes of diluent per volume of mixed maleinoid and vinyl monomers, and suitable materials for use as diluent include refined petroleum hydrocarbon solvents such as heavy naphtha or kerosene fractions, naphthenes, aromatics, etc. Peroxide type catalysts are especially suitable for the copolymerization reaction. Among the suitable peroxides are benzoyl peroxide, acetyl peroxide, lauroyl peroxide, urea peroxide, etc. Valuable polymers or copolymers are also produced by other catalysts, e. g. BF_3 , $AlCl_3$, clay, alumina, oxygen, ozone and other polymerizing materials. Heat, light, pressure, and/or volatilization may also be used alone or with any of the above catalysts. Furthermore, it is possible to use a mixture of catalysts, or to polymerize the esters in steps, such as starting the reaction by one method and completing it by another. The catalyst may also be added gradually or all at once.

When a catalyst such as benzoyl peroxide is used for the copolymerization, the amount of it may be varied over a rather wide range of about 0.1% to about 5% based on the reactants, but preferably from about 0.5% to 2.0%. The preferred temperature of copolymerization is from 50° to 120° C., although 20° to 200° C. or even a wider spread may be used. Generally, a non-oxidizing

atmosphere is desirable although not necessary. A suitable non-oxidizing atmosphere may be through the use of N_2 , H_2 , CO_2 , SO_2 , hydrocarbon gases such as methane, ethane, etc.

The copolymers produced according to this invention are valuable additives for lubricating oils, especially waxy or paraffin base lubricating oils, because they have pour depressing properties when prepared with at least one long side chain of at least 10 carbon atoms. They are also V. I. improvers, and in some instances have other valuable characteristics. Generally they are viscous liquids, although in some cases of particularly high molecular weight they more nearly resemble a plastic solid. The average molecular weight, as estimated from the Staudinger equation using intrinsic viscosity measurement in diisobutylene, of these copolymers generally ranges from about 1,000 to 100,000 or so, and preferably should be about 2,000 to 20,000 when used essentially as a pour depressor, or about 5,000 to 50,000 when used essentially as a V. I. improver, the molecular weight range of about 5,000 to 25,000 being preferred when the copolymer is to be used simultaneously for its pour depressing and V. I.-improving properties. As the viscosity of the copolymer is so high as to be difficult to make quick determinations, it is preferable, for comparative purposes, to make a 20% or a 50% solution of the copolymer in a mineral lubricating oil base stock, and in fact the polymerization raw materials may desirably be reacted directly in such a mineral lubricating oil as a diluent, and then the viscosity of the resulting solution may readily be determined, and the average molecular weight may, if desired, be roughly estimated from the viscosity of such solution. The Saybolt viscosity of a 20% by weight solution of the copolymer in a paraffinic lubricating oil base stock having per se a viscosity of 44 seconds Saybolt at 210° F., should be about 100 to 5,000 seconds Saybolt at 210° F. These copolymers are generally substantially non-volatile up to about 200° C. under a vacuum corresponding to about 1 mm. mercury absolute pressure. They show satisfactory performance when used as additives in crankcase lubricants for internal combustion engines.

From a theoretical point of view it is quite surprising that the two primary types of reactants used in this invention can be successfully copolymerized to form products of the desired high molecular weight range, yet with good oil-solubility and good pour depressing and V. I.-improving properties, because maleic acid esters per se respond only very slowly to polymerization, as compared to fumaric or itaconic acid esters, and vinyl acetate polymerizes very rapidly, yet the mixture copolymerizes at a good rate and with satisfactory uniformity. The copolymer is better than a polymer of either monomer.

The amount of these copolymers to be used in blending with lubricating oils may vary over a rather wide range, depending upon the particular purposes for which they are used. Small quantities in the range of 0.01% may be sufficient in some cases such as for obtaining slight but effective pour depressing properties or an improvement in pour stability, while for other purposes, especially V. I. improvement much larger amounts, e. g. up to 5% or more may be used. Generally about 0.1% to 2.0% will suffice for most purposes.

The copolymers of this invention may be used in conjunction with other lubricating oil additives, e. g. dyes, antioxidants, sludge dispersers or detergents, or other pour depressors or V. I.-improvers, fatty oils, esters, etc. One such suitable combination may comprise a lubricating oil base stock containing a small amount, e. g. 0.1 to 1% of a pour depressor made by Friedel-Crafts condensation of chlorinated paraffin wax containing about 10 to 15% chlorine with naphthalene, which is very potent in reducing the A. S. T. M. pour point of the waxy lube oil, and adding to the resulting blend a small amount, e. g. 0.1 to 0.5% of a copolymer made according to the present invention, which is especially potent in lowering the stable pour point of the lube oil blend. A larger amount of this copolymer may be used for imparting even better V. I.-improving properties if desired.

The advantages and details of the invention will be better understood from a consideration of the following experimental data.

EXAMPLES 1 to 6

Preparation of di-coconut maleate

- 10 A 3-liter flask equipped with a water trap and a reflux condenser was charged with the following:

1118 g. coconut oil alcohols¹
294 g. maleic anhydride
15 2 g. sulfosalicylic acid
400 cc. xylene
200 cc. naphtha

¹ Chiefly mixed C_{12} to C_{18} saturated straight chain alcohols made by hydrogenation of coconut oil, and comprising about:

20 3% C_{10}
46% C_{12}
24% C_{14}
10% C_{16}
17% C_{18} alcohols

- 25 The above mixture was refluxed for a total of 14 hours, during which time 58 cc. of water were collected. The reaction product was diluted with about 1000 cc. of benzol and then given 4 washes with 5 to 10% Na_2CO_3 solution and two with water. Most of the solvents was removed by evaporation on a steam bath, although the final traces were removed by the use of nitrogen and laboratory vacuum at 100° C. The resulting di-coconut maleate (or di- C_{12-18} maleate) ester had a saponification number of 230, neutralization number of 0.50, a viscosity at 210° F. of 41.7 Saybolt seconds, and an average molecular weight of about 495.

Copolymerization of vinyl acetate with di-coconut maleate

- 40 A 1 liter, 3 necked flask equipped with a condenser, stirrer and a thermometer was charged with the following:

45 200 g. lubricating oil (vis. 210—44 Saybolt seconds, paraffinic)
300 g. di-coconut maleate

- The above mixture was heated to 80° C. after which it was blown with nitrogen for about 5 minutes in order to replace the air with a more inert gas. There was then added 4 g. of benzoyl peroxide and the mixture was again blown with nitrogen for about 5 minutes. Stirring was then started and continued throughout the course of the reaction. Vinyl acetate addition was started about 45 minutes after adding of the benzoyl peroxide and a total of 100 g. 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 vinyl acetate. The resulting copolymer which had a slight odor of vinyl acetate, was blown with nitrogen for 3 hours at the temperature of a steam bath causing a 9 g. loss in weight. This copolymer (66% by weight in the oil solution) has a viscosity of 3402 Saybolt seconds at 210° F.

- 65 Similarly five other copolymerization runs were made in which the concentration of vinyl acetate in the admixture of vinyl acetate and di-coconut maleate ranged from 15 to 50% by weight of vinyl acetate. This corresponded to a molar ratio of 1 to almost 6 mols of vinyl acetate to 1 mol of the di-coconut maleate. The viscosities of the resulting copolymer solutions in the same lubricating oil, are shown in the following table, together with the A. S. T. M. pour points of blends obtained by dissolving 0.1% of the copolymer in 3 different paraffinic reference oils, which were solvent extracted Mid-Continent neutral lube oil base stocks of SAE 10 grade, containing about 3 to 8% bright stock, and the table also shows how the blends of 0.1% of the copolymers in reference oil C behaved in the pour stability test, which was described in a paper by McNab, Rogers, Michaels, and Hodges presented at the National Fuels and Lubricants Meeting of the Society of Automotive Engineers, on November 7 and 8, 1946, at Tulsa, Oklahoma.

TABLE I

Ex- ample	Ratio of Vinyl Acetate to Di- coconut Maleate		Vis. at 210° F. of Copolymer in Oil Solution (Saybolt Secs.)	A. S. T. M. Pour Pts. of Refer- ence Oil Blends ¹			Solid Pt. (°F.) of 0.1% Blend in Oil C in Severe Temp. Cycles ²
	Wt. Ratio	Mol Ratio		A	B	C	
1.....	15:85	1.02:1.0	639	+5	+15	+30	>+20
2.....	20:80	1.44:1.0	1,493	-20	-15	-15	-23
3.....	25:75	1.92:1.0	3,402	-15	-30	-25	DNGS
4.....	30:70	2.46:1.0	7,095	-15	-20	-15	DNGS
5.....	35:65	3.10:1.0	24,351	-15	-25	-20	DNGS
6.....	50:50	5.76:1.0	57,704	-10	-15	-15	DNGS

¹ 0.1% concentration of actual copolymer in reference oils.² DNGS means Did Not Go Solid at -23° F. (lowest temperature tested).

The above table shows that all these particular copolymers containing from 15% to 50% of vinyl acetate with 85% to 50% of the di-coconut maleate had good pour stability.

With lower proportions of vinyl acetate, e. g. 5 to 10% by weight of vinyl acetate and 90 or 95% of the maleate, the copolymers have satisfactory A. S. T. M. pour depressing properties but the pour stability is not satisfactory. On the other hand, if the proportion of vinyl acetate is raised to much above 50% by weight, or above a molar ratio of 6 to 1, the resulting copolymer tends to become less soluble in highly paraffinic lubricating oil, and therefore cannot be used satisfactorily as a pour depressor, either in regard to A. S. T. M. pour point or as to pour stability. However, such copolymers having a relatively high proportion of vinyl acetate, even up to 60% by weight or up to a molar ratio of 10 mols of vinyl acetate per mol of di-coconut maleate, may be dissolved satisfactorily in low V. I. lubricating oil base stock made from naphthenic or mixed base crudes, and have good V. I.-improving properties when used in such oils. If the concentration of vinyl acetate is raised above about 65% by weight in admixtures with the di-coconut maleate, or above about 12 mols of vinyl acetate per mole of di-coconut maleate, the resulting copolymers are substantially insoluble in lubricating oils of all types.

An examination of the A. S. T. M. pour point data in Table I show that Example 2, namely the copolymer of 20% by weight of vinyl acetate and 80% by weight of di-coconut maleate, which represents a molar ratio of 1½ mols of vinyl acetate per mol of the maleate, gave the best A. S. T. M. pour depressing characteristics, because the 0.1% blend of the copolymer in reference oil B gave -30° F. pour point and in oil C gave -25° F. pour point, which was the best in either of those two reference oils, and was almost as good as the best in reference oil A.

Subsequent tests have shown that if the copolymer used in Example 2, namely containing 20% by weight of vinyl acetate, is prepared in 20% by weight concentration in a lubricating oil diluent, instead of in 66⅔% by weight concentration, the viscosity of the resulting solution is only 115 seconds Saybolt at 210° F. as compared to 1493 as is shown in the above Example 2, Table I. For the purposes of this invention it is preferred to make the copolymer in about 50 to 95% by weight concentration in a diluent, such as a mineral lubricating oil base stock.

As to the optimum degree of polymerization, it is clear from the above Table I that copolymers having good pour depressing properties can be made over a wide range of molecular weight, as indicated by the viscosity of the copolymer concentrate in the lubricating oil diluent; however, for V. I.-improving properties, and particularly when it is desired to have both V. I.-improving properties and pour depressing properties, it is preferred that the copolymerization be continued until a 20% concentrate in a lubricating oil basestock of the general nature of that used in the above table, have a viscosity of about 500 to 1,000 seconds Saybolt at 210° F. This is equivalent to a molecular weight of about 10,000 to 20,000 in the copolymer per se.

For comparison it should be noted that a simple polymer of di-coconut maleate made under substantially identical polymerization conditions as used for the above described copolymers, had substantially comparable pour depressing properties as determined by the A. S. T. M.

pour test, but did not have good pour stability because a blend of 0.1% of it in reference oil C has a solid point of 0° F., whereas all of the copolymers shown in Table I have a solid point at least as low as -23° F.

EXAMPLE 7

The following comparative data are given to show the surprising advantage of the copolymer of the present invention, namely a dialkyl maleate-vinyl acetate copolymer, as compared to a copolymer similar except in substitution of a corresponding fumarate instead of maleate. The di-coconut maleate-vinyl acetate copolymer used in this test was made by the general procedure explained above under Examples 1 to 6, using 80% by weight of the maleate ester monomer and 20% by weight of the vinyl acetate monomer, copolymerizing the monomer mixture in a concentration of 66⅔% in a diluent consisting of lubricating oil having a viscosity at 210° F. of 44 Saybolt seconds, and using a reaction temperature of 80° F. for 20 hours. The product, in the paraffinic lube oil basestock of 44 seconds Saybolt at 210° F., had a viscosity of 1493 seconds Saybolt at 210° F. On the other hand, the corresponding di-coconut fumarate-vinyl acetate copolymer which was made in identically the same way had a viscosity of 3392 seconds Saybolt at 210° F.

When these two copolymers were blended in the concentration of about 0.1% of active ingredients in three different paraffinic lubricating oil basestocks, the resulting blends had A. S. T. M. pour points as indicated in the following table:

BASE OILS

	A	B	C	Stable Pour Pt. (° F.)
Maleate.....	-15	-30	-25	<-23
Fumarate.....	-10	-10	-20	-15

The above table shows that the maleate copolymer is more effective than the corresponding fumarate copolymer in regard to pour depressing properties as determined by the A. S. T. M. pour point method, and also has better pour stability.

EXAMPLE 8

The following data are given to show the pour depressing effectiveness, as determined by A. S. T. M. pour point, of the copolymer of this invention when used in a wide range of different concentrations in a waxy mineral lubricating oil base stock. The copolymer used in this test was made by copolymerizing 20 parts of vinyl acetate with 80 parts of di-coconut maleate in 75% concentration in a petroleum oil for a period of 40 hours at 70° C. 1% benzoyl peroxide was used as a catalyst which was added in 6 equal portions during the first 5 hours.

The resulting copolymer, in 20% by weight concentration in a lube oil base stock having a viscosity of 44 seconds Saybolt at 210° F., had a viscosity of about 600 seconds Saybolt. This copolymer was blended in concentrations ranging from .01% by weight up to about 0.25% by weight in a Mid-Continent neutral lubricating oil base stock and tested for A. S. T. M. pour points with the following results.

Percent Copolymer	A. S. T. M. Pour Point (° F.)
0.....	+30
0.01.....	10
0.02.....	0
0.05.....	-10
0.10.....	-23
0.15.....	-29
0.20.....	-32
0.25.....	-35

The above table shows that the copolymer of this invention is an extremely potent pour depressor as determined by the A. S. T. M. pour point test, even when used in extremely small concentrations.

EXAMPLE 9

The following data are given to illustrate a V. I. (viscosity-index) improving characteristic and the viscosity of the blends at 210° F. of the copolymer of this invention, when blended in small concentrations in several different lubricating oil basestocks. The particular copolymer used in these tests was made with 20% vinyl acetate and 80% di-coconut maleate.

Test	Basestock	Vis. 210° F.			V. I.		
		10	10.4	13.3	10	10.4	13.3
1.....	Mid-Continent, SAE-10 (#1).	44.2	46.2	-----	91	105	-----
2.....	Mid-Continent, SAE-10 (#2).	44.6	45.4	-----	95	110	-----
3.....	Pennsylvania 180 neutral	45.6	47.6	-----	100	111	-----
4.....	Solvent extracted Mid-Continent oil.	46.2	-----	72.0	114	-----	144

¹ Percent copolymer added.

The above data show that the copolymer of this invention is a very effective V. I.-improver, since even a very small concentration of 0.4% of copolymer per se raises the V. I. of a Mid-Continent lubricating oil basestock from 91 to 105 or from 95 to 110, and raises the V. I. of a Pennsylvania 180 neutral from 100 to 111. When used in a much larger concentration namely 3.3% of copolymer, it raises the V. I. of a solvent-extracted Mid-Continent neutral oil from 114 up to 144.

Thus, even when the copolymer is used in concentrations which are normally used merely for pour depressing properties, this copolymer has substantial V. I.-improving characteristics. Even when used in larger amounts such as 3% or so for obtaining very high V. I.-improvement, the copolymer still possesses good pour-depressing characteristics.

Chemical analysis of a copolymer similar to that made in Example 1 by the use of about 85% by weight of di-coconut maleate ester monomer with about 15% by weight of vinyl acetate monomer, and reacted at about 175° F. for about 20 hours gave the following results:

ANALYSES

Theoretical	Actual	
	(1)	(2)
C=72.33	C=72.60	72.06
H=11.10	H=11.09	11.19
O=16.57	O=16.31	16.75

¹ By difference.

It should be understood that a number of variations in the procedure of this invention can be carried out without departing from the general spirit of the invention.

For instance, the catalyst may be added either all at once, or as preferred, by addition in small charges over several hours during the initial part of the copolymerization, as this appears to give better catalyst efficiency.

EXAMPLE 10

A simple way to change the relative number of carbon atoms in the alkyl groups of the side chains in the maleate ester monomer, is to use along with the di-coconut maleate a small amount of some other dialkyl maleate, as for instance a didecyl maleate. For instance, two different copolymers were made from monomeric mixtures both of which contained 20% by weight of vinyl acetate and 80% of maleate ester monomer, but in the one mixture the maleate ester monomer consisted entirely of di-coconut maleate (referred to as copolymer A) while in the other mixture the maleate ester consisted of a mixture of 20% by weight of didecyl maleate and 80% by weight of di-coconut maleate (referred to as copolymer B). Both copolymerizations were carried out with 66⅔% by weight of monomer in 33⅓% by weight of paraffinic lubricating oil as diluent, and using 1% of benzoyl peroxide catalyst at 80° C. for 20 hours. The resulting copolymers were tested in four different concentrations, both as to A. S. T. M. pour point (in three different reference oils), and as to pour stability as deter-

mined by measuring the highest solid point in a cold box test using alternate warming and cooling.

Copolymer	Concentration of Active Ingredient, Weight Percent	ASTM Pour Pt., ° F., in Indicated Base Stocks ¹			Solid Point, ° F., in Cold Box Test C
		A	B	C	
5	None	+5	+15	+30	>+20
10	0.025	-10	-20	-20	-20
A	0.05	-10	-20	-20	<-20
	0.1	-15	-25	-25	<-20
	0.2	-20	-25	<-35	<-20
	0.025	-15	-25	-10	-15
	0.05	-25	-30	-20	-15
15	0.1	-25	-30	-25	<-20
B	0.2	-30	-30	<-35	<-20

¹ Same as used in earlier tests.

The above table shows that in regard to A. S. T. M. pour point copolymer B which contained the vinyl acetate along with a mixture of decyl maleate and coconut maleate, was slightly superior to the copolymer of vinyl acetate and coconut maleate alone, thereby indicating that for A. S. T. M. pour point effectiveness, the ester copolymer containing a slightly higher proportion of C₁₀ (decyl) side chains gives better results. However, when used in extremely small proportions, e. g. 0.025%, or 0.05% by weight of active ingredients, the stable pour point was not quite as good as in the case of copolymer A which did not contain the extra proportion of C₁₀ (decyl) side chains. On the other hand, when used in the larger and more conventional proportions of 0.1% or 0.2% by weight, the resulting blends were substantially equivalent in regard to stable pour point.

EXAMPLE 11

Another way in which the present invention shows entirely unexpected results, and great superiority over other polyester type pour depressors, is when used as pour depressor in a diluted aviation lubricating oil. Some recent specifications for such oils call for a diluted pour point maximum of -65° F.; this is to permit proper lubrication of aircraft engines when flying at very high altitudes or in cold climates. A diluted aviation oil blend was made by mixing together 67.6% by weight of bright-stock and 32.4% by weight of a solvent refined paraffinic lubricating oil having a viscosity of 52 seconds Saybolt at 210° F., and then blending with 70% by volume of that lubricating oil mixture, 30% by volume of a relatively low boiling or volatile diluent composed of a mixture of 80% by volume of standard solvent naphtha and 20% by volume of xylene. To the resulting diluted aviation oil were added, in small concentrations of 0.1 to 0.4%, by weight of active ingredient, a di-coconut maleate-vinyl acetate copolymer. The A. S. T. M. pour point tests obtained were as follows:

Wt. Percent Active Ingredient	A. S. T. M. Pour Point (° F.)
0.....	-25
0.1.....	-60
0.2.....	-70

The tremendous potency of this pour depressor in diluted aviation lubricating oils is entirely unexpected, and thus far unaccountable because some other types of polyester materials, when similarly blended, obtain pour points of only -20 to -30° F. Apparently for some reason, the presence of 30% by volume of relatively volatile diluent in the lubricating oil makes the di-coconut maleate-vinyl acetate copolymer exceptionally potent.

EXAMPLE 12

To investigate the effect of increasing the chain length of the vinyl ester component of the copolymers of the invention, additional copolymers of the "Lorol B" ester of maleic acid were prepared with vinyl acetate, vinyl butyrate, and vinyl laurate, that is, using as the second monomer vinyl esters of fatty acids containing 2, 4, and 12 carbon atoms respectively. The copolymers were prepared using equal mols of maleic ester, and the vinyl ester, using a white oil as a diluent (a 4:1 weight ratio of monomers to diluent) using as a catalyst 1.0 weight per

cent benzoyl peroxide, a temperature of 75° C., and a reaction time of 18 hours.

The resulting copolymers were separated from the unreacted ester and diluent and blended in 0.1 weight per cent and 0.2 weight per cent in Oil A' and Oil C. Oil A' was identical with Oil A above except that it had not been so stringently dewaxed and had a pour point of +15° F. instead of the +5° F. of Oil A. Standard A. S. T. M. pour point determinations were made on the blends and the results are set out below.

Vinyl Ester Used	A. S. T. M. Pour Points (° F.)					
	Oil A'			Oil C		
	0.0	0.1	0.2	0.0	0.1	0.2
Vinyl Acetate.....	+15	-20	-25	+30	-15	-25
Vinyl Butyrate.....	+15	-25	-25	+30	-15	<-35
Vinyl Laurate.....	+15	-15	-15	+30	-10	-15

It is not intended that this invention be limited to the specific examples which have been given merely for the sake of illustration but only by the appended claims in which it is intended to claim all novelty inherent in the invention as well as all modifications coming within the scope and spirit of the invention.

This application is a continuation-in-part of Serial No. 728,727, filed February 14, 1947, for the same inventor, now abandoned.

What is claimed is:

1. A lubricating oil composition comprising a major proportion of a lubricating oil and a small amount, sufficient to depress the pour point thereof, of an oil-soluble copolymer of a vinyl ester of a fatty acid having from 2 to 18 carbon atoms and a dialkyl maleate wherein each alkyl group ranges from not less than 10 to not more than 18 carbon atoms.

2. A lubricating oil composition comprising a major proportion of mineral oil and a small amount, sufficient to depress the pour point thereof, of an oil-soluble copolymer of vinyl acetate and a dialkyl maleate wherein each alkyl group ranges from not less than 10 to not more than 18 carbon atoms.

3. A lubricating oil composition comprising a major proportion of a lubricating oil and a small amount, sufficient to depress the pour point thereof, of an oil-soluble

copolymer of vinyl butyrate and a dialkyl maleate wherein each alkyl group ranges from not less than 10 to not more than 18 carbon atoms.

4. A lubricating oil composition comprising a major proportion of a lubricating oil and a small amount, sufficient to depress the pour point thereof, of an oil soluble copolymer of a vinyl laurate and a dialkyl maleate wherein each alkyl group ranges from not less than 10 to not more than 18 carbon atoms.

5. A lubricating oil composition consisting essentially of a major proportion of waxy hydrocarbon oil having dissolved therein 0.01 to 5%, based on the weight of the total composition, of a copolymer of 50 to 85% by weight of dialkyl maleate wherein each alkyl group ranges from not less than 10 to not more than 18 carbon atoms and average 12 to 16 carbon atoms, with 50 to 15% of vinyl acetate, said copolymer having a molecular weight Staudinger of between 1000 and 100,000 and having the property of substantially depressing the normal pour point of said oil.

6. Composition according to claim 5 in which the pour depressor is a copolymer of 80% by weight of dialkyl maleate, wherein the alkyl esterifying groups are the alkyl radicals of commercial coconut oil alcohols ranging from C₁₀ to C₁₈, with 20% by weight of vinyl acetate.

7. A composition consisting essentially of a waxy mineral base lubricating oil containing a pour point depressing amount, between 0.01% and 5%, based on the weight of the final composition, of a copolymer of about 80% by weight of C₁₀ to C₁₈ dialkyl maleate ester copolymerized with about 20% of vinyl acetate to a molecular weight between about 5000 and 25,000 Staudinger.

8. A lubricating oil composition comprising a major proportion of a mineral oil containing combined therein from 0.01% to 10% by weight of an oil soluble copolymer of a vinyl ester of a fatty acid having from 2 to 18 carbon atoms and a dialkyl maleate wherein each alkyl group ranges from not less than 8 to not more than 18 carbon atoms.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
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