

UNITED STATES PATENT OFFICE

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COMPOSITION OF MATTER AND PROCESS

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This invention relates to a method for improving the viscosity-temperature characteristics of lubricating oils, and is concerned more particularly with a method for raising the so-called "viscosity index" of lubricating oils which are essentially of a hydrocarbon nature for the purpose of improving their lubricant qualities.

As a lubricating oil is heated its viscosity decreases, but the rate at which the viscosity falls off with rise in temperature of the oil varies with the nature of the oil. Highly paraffinic oils, such as Pennsylvania oils, do not decrease in viscosity with rising temperature as rapidly as do naphthenic oils. In the manufacture of lubricating oils, it is customary to rate the quality of oils by referring to their viscosity index. High grade oils which show a small change of viscosity with temperature are arbitrarily assigned a 100 V. I. (viscosity index) and oils having a large viscosity-temperature coefficient are given a value of 0 (zero) V. I. Viscosities are usually determined at 100° F. and 210° F. A mathematical relationship between the respective viscosities in Saybolt seconds at these two temperatures has been found to exist which is characteristic of each type of oil, and which expressed as "viscosity index" indicates the suitability of a lubricating oil for various purposes. In automobile engines oils of high viscosity index are desirable so that when the engine is cold, it can be more easily started, and when the engine is hot the oil does not lose too much of its body or lubricating qualities.

The object of this invention is to provide a method by which the viscosity index of an oil can be raised to a relatively high value without detracting from its color, odor, stability towards oxidation or its lubricating properties, and by which an oil of better quality can be obtained.

The above object is accomplished by incorporating with the lubricating oil a relatively small amount of a synthetic, oil-soluble, polymerized ester of the acrylic acid or vinyl ester series. This can be done by either thoroughly mixing the preformed oil-soluble polymerized ester with the oil, or else by mixing the oil with the unpolymerized ester, and then polymerizing said ester in the oil. The amount of the polymerized ester which should be present in the oil varies somewhat with the nature of the lubricating oil used, the degree of viscosity index rise which is desired, and to a certain extent with the individual polymerized ester which is used. Since these oil-soluble polymerized esters are very powerful increasers of the viscosity index, only

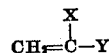
small amounts are required; quantities as low as 0.1% on the weight of the oil being effective, and, as an upper limit, 6% on the weight of the oil being extremely powerful in this respect. In general 0.6-2% on the weight of the lubricating oil gives satisfactory results.

It is known that the viscosity index of oils can be increased by adding thereto certain hydrocarbons, such as rubber, hydrogenated rubber, and hydrogenation products of polymers of olefine hydrocarbons, or certain salts, such as aluminum or zinc stearates. These compounds are either readily oxidizable (rubber) and rapidly deteriorate in the oil even when anti-oxidants are present, or else they are non-uniform compositions whose power of increasing the viscosity index is variable and in many cases relatively low compared to the substances used in the present process. Salts such as the zinc or aluminum stearates also give variable results and tend to become grainy and separate from the oil on storage or at low temperatures.

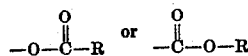
In contrast thereto the polymers used in the present invention are colorless, non-odorous, non-oxidizable materials the viscosity of which can be accurately and uniformly controlled.

Moreover, when added to lubricating oils they also have the advantage of acting as pour point depressors.

For the purpose of this invention, the oil-soluble polymerization products of esters having the vinyl or substituted vinyl group, according to the following general formula, are used; namely, esters of the formula



wherein "X" is a hydrogen atom, an alkyl or aromatic hydrocarbon group, and "Y" is



in which R is a monovalent hydrocarbon radical containing more than four carbon atoms or an ether derivative of said hydrocarbon radical. These polymers are colorless, odorless and stable toward oxidation or storage.

Compounds of the above type whose oil-soluble polymers are particularly useful for the present purpose are the esters of acrylic acid or of its alpha-alkyl or alpha-aryl substitution products and monohydric alcohols containing more than four carbon atoms such as the amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, myricyl, cetyl, or octadecyl esters of acrylic acid, alpha-metha-

acrylic acid, alpha-phenylacrylic acid, and other alpha-substituted homologues of acrylic acid. These esters are preferably those of the normal, primary saturated aliphatic alcohols, but the analogous esters of the corresponding secondary or of the branched-chain alcohols can also be used. The esters of the above acids of the acrylic series with monohydric aromatic, hydroaromatic, or ether alcohols may also be used, such as the benzyl, cyclohexyl, amylphenyl, n-butyloxyethyl esters. Also the vinyl esters of valeric, heptolic, lauric, palmitic, stearic, n-amyl-benzoic, naphthenic, hexahydrobenzoic, or of β -n-butyloxybutyric acid can be used.

These esters are employed in the form of their oil-soluble polymers which should be as free as possible of unpolymerized monomeric esters, since the presence of unsaturated or volatile compounds in the lubricating oils is objectionable. Unpolymerized esters can be removed by heating the polymer or the mixture of lubricating oil and polymer in vacuo to a temperature sufficiently high to volatilize the monomeric ester, but preferably the polymerization should be carried out as completely as possible and the latter operation dispensed with.

The most effective polymers for the present purpose, from the point of view of availability, cost, and power of increasing the viscosity index of oils, are the polymerized esters of acrylic acid or alpha-methacrylic acid and monohydric, saturated, primary aliphatic alcohols containing from 5 to 18 carbon atoms in the molecule. The esters possessing the highest solubility and stability in oils and giving the highest viscosity index are those derived from the straight chain, monohydric primary, saturated aliphatic alcohols containing 8 to 18 carbon atoms such as the normal octyl, lauryl, cetyl, or octadecyl esters. These esters need not be pure, but may be prepared from technical mixtures of the higher aliphatic alcohols such as are obtained commercially from the catalytic high pressure hydrogenation of fatty acids or their esters.

Any mixture of two or more polymers of the esters set forth herein can also be used. These may be simple mixtures of such polymers, or they may be co-polymers which can be prepared by polymerizing a mixture of two or more of the monomeric esters.

The polymers are prepared for use in the present process, preferably by heating the monomeric esters at 70°-100° C. in the presence of small amounts of polymerization-inducing catalysts such as peroxides or ozonides. These are referred to as "heat polymerization products". Other catalysts may, however, be used, such as anhydrous halides of polyvalent or amphoteric metals, according to the known art of polymerizing vinyl compounds.

In the following examples the polymers used were prepared by heating the monomeric esters at 100° C. for 15 hours in the presence of 0.5% by weight of benzoyl peroxide and, if necessary, removing any unchanged monomeric ester by carefully heating the product in high vacuo (0.5-1 mm.) to a temperature just above the boiling point of the monomer. The polymers obtained were colorless or faintly yellow. They were each dissolved in the oil in the concentrations shown by warming to about 100° C. and stirring until a homogeneous clear solution was obtained.

By using 0.1% of benzoyl peroxide on the weight of the monomeric ester and polymerizing at 75° C. for 24-48 hours, the polymers are more

rubbery and viscous than those made at the higher temperature (100° C.) with 1% of benzoylperoxide and give slightly higher rises in viscosity index than the latter.

Viscosities were determined at 100° F. and 210° F. and the viscosity index calculated according to standard methods, (see The Oil and Gas Journal, March 31, 1932, pp. 92, 93, 169). The following table shows the effect of various polymerized esters of acrylic acid, etc., on the viscosity and viscosity index of lubricating oils.

Oil A was a Mid-Continent oil showing the following inspection:

Gravity °A. P. I.	25.0	15
Saybolt vis./100° F.	219	
Saybolt vis./210° F.	45.	
Viscosity index	63	
Flash point	°F.	400
Fire point	do.	460
Pour point	do.	0

Example 1

Polymerized ester added	% added	Viscosity**		Viscosity index
		At 100° F.	At 210° F.	
Original oil (A) (Mid-Continent type)	0.00	219	45.5	63
Cetyl-alpha-methacrylate	1.00	282	51	95
Do.	1.32	330	54.9	104
Do.	2.00	357	57.9	111
n-Amyl-alpha-methacrylate	1.20	249	49.4	100
Do.	0.60	233	47.1	80
n-Hexyl-alpha-methacrylate	0.60	253	48.2	78
Do.	1.20	261	49.5	87
n-Octyl-alpha-methacrylate	2.00	279	51.1	98
Do.	0.60	246	48.1	85
n-Lauryl-alpha-methacrylate	1.20	281	51.5	100
Vinyl laurate	0.60	258	48.9	85
Co-polymer of equal weights cetyl-alpha-methacrylate and lauryl-alpha-methacrylate	0.50	270	49.5	85
n-Cetyl-acrylate	1.20	260	50	98
n-Lauryl acrylate	1.33	311.1	54.6	107
Do.	2.00	339	56	110
Iso-amyl acrylate	0.50	252	48.5	81

* % is calculated on the weight of the oil.

** Viscosity is measured in Saybolt seconds.

Example 2

The oil used was a Pennsylvania oil and possessed the following constants:

Saybolt viscosity	Viscosity index
100° F., 210° F. 270 sec., 60.9 sec.	100

(a) Upon adding 1.3% by weight of n-octadecyl-alpha-methacrylate polymer, the oil showed the following properties:

Saybolt vis. at 100° F.	sec.	355.7
Saybolt vis. at 210° F.	do.	60.5
Viscosity index		122

(b) The addition of 0.7% by weight of polymerized lauryl acrylate to the above oil gave an oil having a viscosity index of 113.

(c) 1% by weight of polymerized cetyl-alpha-methacrylate was added to a Pennsylvania oil having a pour point of +35° F. The pour point of the mixture was +15° F.

It will be seen from the above table that the addition of about 1% of the polymers on the weight of the oil raises the viscosity index about 30 points. The addition of 4% of any of the above polymers on the weight of the above oil approximately doubles the original viscosity index.

Instead of the above tabulated esters, any of the other polymerized esters enumerated herein can similarly be used, the above tabulated results being simply typical of the whole group of compounds.

If an oil of higher viscosity index than that shown in Example 1 is used, for instance, a Pennsylvania oil having a viscosity index of 80, smaller quantities of the polymerized ester are required to give an oil with a viscosity index of more than 100.

It is understood that the term "lubricating oil" as used herein is to be interpreted broadly as referring to natural or synthetic oils, essentially hydrocarbons, possessing lubricating properties regardless of their actual viscosity, and includes crude or refined petroleum, hydrogenated petroleum oils or hydrogenated cracked petroleum oils, high molecular oily hydrocarbons, such as are obtained by the polymerization of olefines or by the condensation of olefines with aromatic hydrocarbons. These lubricating oils can also contain other materials in solution or in suspension which are not necessarily hydrocarbons but which serve to give certain desirable properties in such oils, such as anti-oxidants, pour point depressors, or graphite. These oils may also be used for the manufacture of other lubricants such as greases by incorporating in them the soaps of lime, soda, potash, etc., as is customary in the preparation of lubricating greases. Oils treated by the hereindescribed process are particularly useful as gear oils, bearing oils, and cylinder oils in automotive engines. They may also be used as oils for hydraulic brakes, artillery recoil systems and similar equipment where rapid changes of viscosity with temperature are undesirable.

What I claim is:

1. An oil of improved viscosity-temperature coefficient comprising a lubricating oil of relatively low viscosity index to which has been added a small quantity of an oil-soluble, viscous, heat polymerization product of an ester of alpha-methacrylic acid and a monohydric saturated alcohol containing more than four carbon atoms.

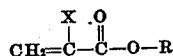
2. An oil of improved viscosity-temperature coefficient and increased viscosity index comprising a lubricating oil of relatively low viscosity index to which has been added from 0.1 to 6% by weight of an oil-soluble, viscous, heat polymerization product which is a member of the group consisting of the amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, myricyl, cetyl and octadecyl esters of alpha-methacrylic acid.

3. A lubricating oil of relatively high viscosity

index consisting of an oil of relatively low viscosity index and a small amount of an oil-soluble joint polymer of at least two different esters of alpha-methacrylic acid the alcohol radicals of which are saturated and contain more than 4 carbon atoms.

4. An oil of improved viscosity-temperature coefficient comprising a lubricating oil of relatively low viscosity index to which has been added a small quantity of an oil-soluble, viscous, polymerization product of an ester of alpha-methacrylic acid and a monohydric saturated alcohol containing more than four carbon atoms.

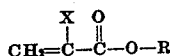
5. An oil, comprising a lubricating oil to which has been added as a material for increasing the viscosity index, a small amount of a viscous, oil-soluble polymerization product of an ester having the formula



wherein "X" is an alkyl group and R is the radical of a monohydric saturated alcohol having more than 4 carbon atoms.

6. A lubricating oil, containing as a material for increasing its viscosity index, a small amount of an oil-soluble polymer of an ester of alpha-methacrylic acid and a primary, aliphatic, monohydric alcohol containing from 8 to 18 carbon atoms inclusive.

7. A lubricating oil containing as a material for increasing its viscosity index, a small amount of an oil-soluble joint polymer of at least two different esters having the formula



wherein "X" is an alkyl group and R is the radical of an aliphatic monohydric saturated alcohol having more than 4 carbon atoms.

8. An oil having lubricating properties containing, as a material for increasing its viscosity index, a small amount of an oil-soluble, viscous polymerization product of an ester of alpha-methacrylic acid and lauryl alcohol.

9. An oil having lubricating properties containing, as a material for increasing its viscosity index, a small amount of an oil-soluble, viscous polymerization product of an ester of alpha-methacrylic acid and cetyl alcohol.

10. An oil having lubricating properties containing, as a material for increasing its viscosity index, a small amount of an oil-soluble, viscous polymerization product of an ester of alpha-methacrylic acid and octadecyl alcohol.

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