

[54] **MINERAL OILS CONTAINING
COPOLYMERS OF AZIRIDINEETHYL
ACRYLATES AND METHACRYLATES:
ALKYL ACRYLATES AND
METHACRYLATES**

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252/51.5 A

[56] **References Cited**

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[57] **ABSTRACT**

Crude oils having high pour points, mineral lubricating oils and fuel oils are improved in one or more of their characteristics such as their dispersancy, pour point, viscosity and viscosity index characteristics by the addition of a copolymer of (a) a monomeric aziridineethyl acrylate or methacrylate and (b) a monomeric alkyl ester of acrylic or methacrylic acid whose alkyl substituent contains 8 to 18 carbon atoms, said copolymer having a molecular weight of at least about 20,000 and a mole ratio of (a):(b) within the range of about 1:2 to about 1:99, respectively, e.g., aziridineethyl methacrylate:lauryl methacrylate (1:19).

13 Claims, No Drawings

MINERAL OILS CONTAINING COPOLYMERS OF AZIRIDINEETHYL ACRYLATES AND METHACRYLATES: ALKYL ACRYLATES AND METHACRYLATES

This invention relates to mineral oil compositions and more particularly to mineral oil compositions improved in one or more of the following characteristics: dispersancy, pour point, viscosity and viscosity index.

Mineral oils, both crude and refined, frequently require modification to improve one or more of their characteristics such as their dispersancy, pour point, viscosity and viscosity index characteristics.

The term "dispersancy" is used in connection with the ability of an oil to keep oil-insoluble products dispersed or suspended in the oil. Dispersant additives were initially used in oils to prevent heavy deposits from forming in the ring belt area at the high temperature of diesel-engine operation. The ability to keep carbonaceous and other deposits dispersed in the oil also is important in gasoline engines. For example, in engines which contain hydraulic valve lifters, the dispersancy characteristic of an oil is extremely important. Hydraulic valve lifters can tolerate very little varnish or sludge before they begin to stick. A dispersant-type additive thus contributes to engine cleanliness, since the products of oil oxidation and contaminants from combustion are held in suspension until the oil is drained from the engine crankcase.

In order to improve the ability of oils to maintain an engine in clean condition, a wide variety of metal-organic compounds (principally alkaline earth metal salts), such as salts of substituted phenols and petroleum sulfonic acids, salicylates, thiophosphoric acids and carboxylic acids have been proposed. Unfortunately, metal organic detergents themselves tend to form still other deposits, that is, combustion ash deposits, in the combustion chambers of internal combustion engines upon combustion of oils containing such metal-organic addition agents.

The term "pour point" is used to denote the lowest temperature at which an oil will pour or flow when chilled without disturbance under specified conditions. The pour point of a crude oil or a refined oil is of great practical importance. In order to avoid problems, such as the blocking of transport lines and the clogging of filters, the pour point of the oil should be below the minimum temperature to which the oil will be subjected in use or storage. If an oil encounters a temperature below its pour point, solid or semisolid waxy particles appear in the oil. When solid or semisolid waxy particles are formed in an oil, its distribution and filtration is rendered difficult or impossible. Pour point problems associated with the transportation, storage and use of crude oils and heavy oils such as lubricating oils has long been recognized. While similar problems associated with the pour point of middle distillate fuel oils have also existed, the prior rather limited use of such oils has not given rise to great concern in this respect. More recently, with increased use of middle distillate fuel oils at temperatures approximating their pour points, the problems and difficulties encountered in their use have become more acute. In the transportation, distribution and storage of furnace oils or diesel oils, temperatures in the order of -15°F. (-26.1°C.) and lower may be encountered. Jet fuels may encounter much lower temperatures, for example, -40°F. (-40°C.) to -50°F. (-45.6°C.) because of the alti-

tudes at which jet aircraft are capable of operating. At such low temperatures, crystallization and solidification of wax in the oil often occurs. When solidification of the wax is encountered, the flow of oil is decreased and in some instances, completely stopped which results in equipment failure.

In the past, the low temperature flow characteristics of a lubricating oil have been improved by incorporating special types of polymers in the oil. To this end, polymers of acrylic and methacrylic acid have been widely used. In many instances compounds which are effective in lowering the pour point of lubricating and other heavy oils, i.e., crude oils, are ineffective in lowering the pour point of middle distillate fuel oils and vice versa. The term "middle distillate fuel oils" as used herein is intended to refer to distillate petroleum fractions boiling within the range of about 300°F. (148.9°C.) to about 750°F. (398.9°C.) and includes furnace oil, diesel oil, kerosene and aviation jet fuel.

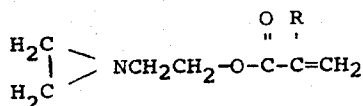
The difficulty encountered in the low temperature flow characteristics of middle distillate fuel oils has been overcome in some instances by using lighter fractions as fuel oils, i.e., by lowering the maximum distillation temperature at which the distillate fraction is collected. However, a lowering of the maximum distillation temperature results in a loss of valuable distillate product. In the face of energy crises, it is highly undesirable to operate in any manner which results in lower yields of fuel. It has also been suggested that the pour point of distillate fuel oil fractions may be improved by urea dewaxing. Separately or in combination lowering the end points of distillate fuel oils and dewaxing are unattractive.

The "viscosity" and "viscosity index" of an oil is an indication of its ability to function under a given set of conditions. While low-viscosity oils give low friction and easy flow, too low a viscosity at higher temperatures will allow metal-to-metal contact and rupture of the oil film which separates adjacent moving parts. In order for a lubricating oil to be effective at low temperatures and yet be viscous enough to lubricate at high temperatures, the oil should have a fairly flat viscosity-temperature relationship. The relative change of viscosity with temperatures is referred to as viscosity index. A low viscosity index signifies a relatively large change in viscosity with temperature. Viscosity index values are calculated by standard ASTM D 567, formulas and tables, based on the relationship of the oil in question to certain reference oils. It is desirable for the viscosity index of a lubricating oil to be above 100.

It has been proposed to overcome viscosity deficiencies in uncompounded lubricating oils at high temperatures by incorporating therein small proportions of viscosity index improvers comprising oil-soluble, nonmetallic organic polymeric materials. By means of these materials the viscosity of lubricating oils can be maintained relatively constant notwithstanding increases in temperature. However, typical commercial viscosity index improvement agents exhibit little or no cleansing ability in lubricating oils.

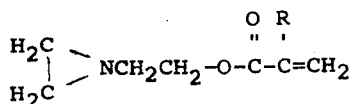
I have found that the detergent-dispersant properties of a mineral lubricating oil, as well as the viscosity and viscosity index properties of such an oil and the pour point characteristics of a high pour point crude oil, a lubricating oil and a fuel oil can be improved by incorporating in the oil a small amount of an oil-soluble co-

polymer of (a) a monomeric aziridinyl ethyl carboxylic acid ester having the formula



where R is selected from the group consisting of the hydrogen atom and the methyl group and (b) a monomeric alkyl ester of acrylic or methacrylic acid whose alkyl substituent contains 8 to 18, preferably 10 to 18 carbon atoms. The average molecular weight of the copolymer is normally greater than about 20,000 and preferably greater than about 100,000 as determined by conventional methods. Usually the average molecular weight of the copolymer will be in the range of about 60,000 to about 600,000 but the molecular weight can be as much as 2,000,000 or more, provided, the molecular weight is not so large as to render the copolymer insoluble in the oil to which it is added. The copolymer is formed by copolymerizing the monomeric aziridinyl ethyl carboxylic acid ester and the monomeric alkyl ester of acrylic or methacrylic acid in mole ratios of about 1:2 to 1:99, aziridinyl monomer:alkyl acrylate or methacrylate monomer, respectively.

Accordingly, the present invention is directed to an oil composition which comprises a major amount of a mineral oil selected from the group consisting of crude oils, lubricating oils and fuel oils and a small amount, sufficient to improve the oil in at least one of its characteristics selected from the group consisting of dispersancy, pour point, viscosity and viscosity index characteristics, of an oil-soluble copolymer of (a) a monomeric aziridinyl ethyl carboxylic acid ester having the formula



where R is selected from the group consisting of the hydrogen atom and the methyl group and (b) a monomeric alkyl ester having the formula



where R is selected from the group consisting of the hydrogen atom and the methyl group and R₁ is selected from the group consisting of straight- and branched-chain alkyl groups containing 8 to 18 carbon atoms, said copolymer having a molecular weight of at least about 20,000 and a ratio of the constituent monomers (a) and (b) in the range of about 1:2 to about 1:99, (a):(b), respectively.

Specific examples of copolymers which can be used according to the invention are the 1:2, 1:4, 1:9, 1:19 and 1:20 mole ratio copolymers of monomeric aziridineethyl methacrylate and monomeric lauryl methacrylate, respectively. Examples of other copolymers which can be used in compositions of the invention are the 1:4, 1:9 and 1:19 to 1:99 mole ratio copolymers of aziridineethyl acrylate and lauryl methacrylate and the 1:2 to 1:99 mole ratio copolymers of (a) monomeric aziridineethyl acrylate and methacrylate and (b) monomeric n-octyl, oxo-octyl, 2-ethylhexyl, isodecyl, un-

decyl, tridecyl, myristyl, pentadecyl, palmityl and stearyl acrylates and methacrylates.

The amount of the copolymer added to the mineral oil composition in accordance with the present invention is that amount which is sufficient to improve the oil in one or more of its characteristics selected from the group consisting of dispersancy, pour point, viscosity and viscosity index characteristics. The amount is usually within the range of about 0.001 to about 10 percent by weight of the oil. The minimum and optimum effective proportions can vary somewhat according to the nature of the particular copolymer and the base oil to which the copolymer is added. In general, the copolymer is included in a petroleum middle distillate in an amount of about 0.001 to about 5 percent by weight of the petroleum distillate, preferably about 0.01 to about 0.5 percent by weight of the distillate. Good pour point improvement in distillate oils has been obtained with copolymers of the class disclosed herein when used in amounts of about 0.02 to about 0.1 percent by weight of the distillate. When the copolymer is added to a lubricating oil, the copolymer is generally employed in amounts greater than that employed in a fuel oil. Thus, in a mineral lubricating oil, the copolymer is employed in amounts of about 0.5 to about 10 percent by weight of the lubricating oil, preferably about 1 to about 5 percent by weight of the oil. Lubricating oils which contain copolymers of the class disclosed herein in addition to having improved pour point characteristics also have good dispersancy, viscosity and viscosity index characteristics. Marked pour point depressant, viscosity index improvement and dispersancy characteristics in lubricating oils have been obtained with copolymers of the class disclosed herein when used in amounts of about 2 to about 4 percent by weight of the oil. When the copolymer is added to a high pour point crude oil to improve its pour point, the copolymer is generally employed in amounts of about 0.001 to about 5 percent by weight of the oil, preferably about 0.01 to about 0.1 percent by weight of the crude oil. The exact amount, of course, will depend upon the particular copolymer employed and upon the characteristics of the crude oil to which the copolymer is added.

The monomeric aziridinyl ethyl carboxylic acid esters from which the copolymers used in the present invention are prepared are known. The preparation of aziridineethyl methacrylate and aziridineethyl acrylate, for example, is described in U.S. Pat. No. 3,338,885 which issued to William P. Coker et al on Aug. 29, 1967. As disclosed in said patent 2-(1-aziridinyl) ethyl methacrylate is prepared by heating dried methyl methacrylate with N-(2-hydroxyethyl)aziridine in the presence of N,N'-diphenyl-p-phenylenediamine as a polymerization inhibitor. After bringing the mixture to a boil, the heat is removed after which small pieces of sodium are added. Heating is then continued to effect conversion. The product is then cooled, filtered and distilled. A cut obtained at 44° to 50° C. at 0.1 mm of Hg comprises 2-(1-aziridinyl)ethyl methacrylate. As further disclosed in U.S. Pat. No. 3,338,885, 2-(1-aziridinyl)ethyl acrylate is similarly prepared by heating ethyl acrylate and N-(2-hydroxyethyl)aziridine. Upon distillation, a product distilling at 37° C. and 0.75 mm of Hg comprises 99+ purity 2-(1-aziridinyl)ethyl acrylate.

The monomeric C₈₋₁₈ alkyl esters of acrylic and methacrylic acid are known materials. The monomeric alkyl

esters of acrylic or methacrylic acid from which the copolymers used in the present invention are prepared can be represented by the general formula: $\text{CH}_2=\text{CRCOOR}_1$, where R is a hydrogen atom or a methyl group and R_1 is a straight- or branched-chain alkyl group containing 8 to 18, preferably 10 to 18 carbon atoms such as capryl, lauryl, myristyl, palmityl or stearyl. The alkyl ester substituent of the acrylate or methacrylate can comprise mixtures of radicals derived from commercially available materials. For example, the alkyl ester substituents of the monomeric alkyl ester of acrylic or methacrylic acid can be derived from a mixture of synthetically produced, isomeric, branched-chain alcohols such as are produced by the well-known oxo synthesis process. Alternatively, the ester substituents can be derived from coconut oil fatty acids or tallow fatty acids or other acids derived from naturally occurring fats or oils.

The copolymers utilized by this invention can be prepared in any suitable way. Thus, the copolymers can be prepared from the corresponding monomers with a diluent such as water in a heterogeneous system (usually referred to as emulsion or suspension polymerization), or with a diluent such as toluene, benzene, ethyl acetate, butyl acetate, ethylene dichloride, or methyl isobutyl ketone in a homogeneous system (usually referred to as solution polymerization). Solution polymerization in benzene or toluene or a solvent having similar chain transfer activity is the preferred method used in forming the copolymers disclosed herein, as this method and solvent produce a preferred class of copolymers characterized by a relatively high molecular weight.

Copolymerization of the herein described monomers takes place readily under the influence of heat, light and/or catalysts. Peroxide-type free radical catalysts, such as benzoyl peroxide, lauroyl peroxide, or t-butyl hydroperoxide; azo-type, free radical catalysts such as alpha, alpha'-azodiisobutyronitrile; and anionic catalysts such as metallic sodium in liquid ammonia, are examples of catalysts that can be used. The catalysts are normally employed in catalytic proportions, that is, from a few hundredths percent up to one or two percent by weight of the monomers. Preferably, the catalyst is employed in proportions of about 0.2-1.0 percent.

Copolymerization of the herein disclosed monomers can be effected over a wide range of temperatures, depending upon the particular catalyst and monomers chosen. For example, when using metallic sodium in liquid ammonia as a catalyst, copolymerization can take place at temperatures as low as -75°C . or lower. On the other hand, when alpha, alpha'-azodiisobutyronitrile is used as a catalyst, as is preferred, temperatures ranging from ambient atmospheric temperature (approximately 25°C .) to about 150°C . can be used. Temperatures in the lower part of this range are preferred as such temperatures tend to favor formation of higher molecular weight copolymers.

The copolymerization reaction is preferably carried out to substantial completion, that is, until the rate of formation of larger polymers has declined substantially. Substantial completion of the reaction can be judged by periodic sampling of the reaction mixture and by determination of the viscosity of the samples, the viscosity being an index of molecular weight. Although for best

results it is preferred to carry out the reaction to substantial completion, this is not absolutely necessary. It is sufficient merely to allow copolymerization to proceed until the viscosity of a hydrocarbon oil containing the reaction mixture will be appreciably increased. The time required to reach any given stage of polymerization can differ somewhat depending on the particular reaction conditions and upon the monomers employed. By way of example, good results have been obtained with times of polymerization in the range of about 3 to 72 hours.

Although copolymerization can be effected in contact with the atmosphere, a more desirable group of copolymers, having relatively higher viscosities and molecular weights, can be obtained by carrying out the polymerization in the absence of oxygen. This can be achieved, for example, by blanketing the reaction mixture with an inert gas, such as nitrogen.

The average molecular weight of the copolymers disclosed herein will normally be greater than about 20,000, and is preferably greater than about 100,000, as determined by conventional test methods. Usually, the molecular weights will not exceed about 2,000,000 but in some instances the molecular weights of the copolymers can be greater. In fact, copolymers having molecular weights of any upper limit can be used, provided such molecular weight is not so great as to render the copolymers insoluble in hydrocarbon oils. The molecular size of the copolymers described herein is affected to some extent by the type of diluent, the monomer:diluent ratio, the type of catalyst, the catalyst:monomer ratio, and the reaction temperature employed during copolymerization. The desired molecular size and copolymer yields can usually be adjusted within the limits indicated above to produce the desired results. Thus, excellent results for the purposes of the present invention can be obtained by copolymerization of the herein disclosed monomers in about twice the weight of solvent using about 0.15 to about 0.6 percent alpha, alpha'-azodiisobutyronitrile as catalyst at temperatures in the range of 60° to 85°C . over a period in the range of 5 to 66 hours.

It is important for the purposes of this invention that the copolymers be prepared directly from the monomers rather than by indirect methods, as the copolymers obtained by direct copolymerization of monomers are chemically and functionally distinct and different from copolymers prepared by indirect methods, at least partly by reason of their more uniform and more controlled composition.

The copolymers described herein can be incorporated in a wide variety of mineral lubricating and fuel oils and crude oils. For example, the copolymers can be added to lubricating oils that have been derived from paraffinic, naphthenic or mixed base crude petroleum oils, and that have been subjected to solvent and/or sulfuric-acid treatment, aluminum chloride treatment, hydrogenation and/or other refining treatments. Also, the copolymer described herein can be incorporated in petroleum distillates, such as for example, diesel fuels, jet fuels, furnace oils, heater oil fractions, kerosene, gas oils and other light oils. The fuel oil may be of virgin or cracked petroleum stock, or mixtures thereof, boiling in the range of about 300°F . (148.9°C .) to about 750°F . (398.9°C .) and preferably in the range of about 350°F . (176.7°C .) to about 650°F . (343.3°C .). The fuel oil may contain cracked components, such as for

example, those derived from cycle oils or cycle oil cuts boiling above gasoline, usually in the range of about 450° F. (232.2° C.) to about 750° F. (398.9° C.) and may be derived by catalytic or thermal cracking. Oils of high or low sulfur content such as diesel oils may be used.

Preferred distillate fuel oils which are improved in accordance with the invention have an initial boiling point within the range of about 350° F. (176.7° C.) to about 475° F. (246.1° C.), and end point in the range of about 500° F. (260° C.) to about 650° F. (343.3° C.), an API gravity of at least about 30 and a flash point (P-M) not lower than about 110° F. (43.3° C.).

The herein described copolymers can be incorporated in the mineral oils in any convenient way. Thus, the copolymers can be added directly to the oil by dissolving the desired copolymer in the oil at the desired level of concentration. Alternatively, the copolymer may be blended with suitable solvents to form concentrates that can be readily dissolved in the appropriate oil at the desired concentration. If a concentrate is employed, it ordinarily will contain at least 10 percent by weight of the copolymer and preferably about 25 to about 65 percent by weight of the copolymer. The solvent in such a concentrate may be present in amounts of about 35 to about 90 percent by weight. When the concentrate is added to a fuel oil, the solvent preferably boils within the range of about 100° F. (37.8° C.) to about 700° F. (371.1° C.). Suitable solvents which can be used for this purpose are naphtha, kerosene, benzene, xylene, toluene, hexane, light mineral oil and mixtures thereof. The particular solvent selected should, of course, be selected so as not to adversely affect the other desired properties of the ultimate oil composition. Thus, the solvent for use in incorporating the copolymer in a fuel oil should preferably burn without leaving a residue and should be noncorrosive with respect to metal, specifically ferrous metals.

If desired, the copolymers described herein can be employed in conjunction with other additives commonly used in petroleum products. Thus, there can be added to the oil compositions of this invention rust and corrosion inhibitors, anti-emulsifying agents, antioxidants, dyes, haze inhibitors, anti-static agents and other detergent-dispersant inhibitors, viscosity index improvement agents and pour point reducing agents. Soaps or other thickening agents may be added to the lubricating oil compositions to form compositions having the consistency of a grease. When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions of the hereindescribed copolymer together with said other additives whereby the several additives are added simultaneously. Dissolution of the copolymer or additive concentrate into the mineral oil may be facilitated by mixing accompanied with mild heating, but this is not absolutely essential.

Procedures by which the copolymers utilized in the present invention can be prepared are illustrated in the following specific examples.

EXAMPLE 1

A mixture of 62.1 grams (0.4 mole) of aziridineethyl methacrylate, 419.2 grams (1.6 moles) of lauryl methacrylate, 962.6 grams of benzene and 2.89 grams of alpha, alpha'-azodiisobutyronitrile is heated at 65° C. with stirring in a nitrogen atmosphere for 12 hours. To

450 grams of the resulting polymer solution is added 300 grams of a hydrofinished light neutral petroleum oil (32.4° API). The mixture is then subjected to evaporation in vacuum until all of the benzene is removed leaving a residue of 451 grams of a clear light-yellow viscous liquid containing approximately 33 percent of a copolymer comprising 20 mole percent aziridineethyl methacrylate and 80 mole percent lauryl methacrylate (1:4 mole ratio). The 1:4 mole ratio copolymer prepared in this example has an intrinsic viscosity of 0.45 deciliter per gram determined in toluene solution at 25° C., from which an average molecular weight of 500,000 may be estimated by the Mark-Houwink equation.

EXAMPLE 2

A concentrate comprising a 33 percent solution in a light mineral oil of a 1:9 mole ratio copolymer of aziridineethyl methacrylate and lauryl methacrylate is prepared by heating 31.0 grams of aziridineethyl methacrylate, 471 grams of lauryl methacrylate and 2.12 grams of alpha, alpha'-azodiisobutyronitrile in 1004 grams of toluene according to the procedure of Example 1 except the heating and stirring is continued for 66 hours. The toluene is then removed by vacuum evaporation. The mixture is then diluted with 1010 grams of hydrofinished light neutral petroleum oil (32.4° API). The product thus obtained comprises a 33 percent oil solution of the copolymer of aziridineethyl methacrylate and lauryl methacrylate (1:9 mole ratio). The copolymer is very viscous and has an average molecular weight in excess of 100,000.

EXAMPLE 3

A concentrate comprising a 33 percent solution in a light mineral oil of 1:19 mole ratio copolymer of aziridineethyl methacrylate and lauryl methacrylate is prepared by heating 31.0 grams of aziridineethyl methacrylate, 995.6 grams of lauryl methacrylate and 6.2 grams of alpha, alpha'-azodiisobutyronitrile in 2054 grams of benzene according to the procedure of Example 1. The benzene is then removed by vacuum evaporation. The mixture is then diluted with 2095 grams of hydrofinished light neutral petroleum oil (32.4° API). The product thus obtained comprises a 33 percent oil solution of the copolymer of aziridineethyl methacrylate and lauryl methacrylate (1:19 mole ratio). The average molecular weight of the copolymer comprises about 60,000.

EXAMPLE 4

A concentrate comprising a 33 percent solution in a light mineral oil of a 1:19 mole ratio copolymer of aziridineethyl methacrylate and lauryl methacrylate is prepared by heating 15.5 grams of aziridineethyl methacrylate, 498 grams of lauryl methacrylate and 3.08 grams of alpha, alpha'-azodiisobutyronitrile in 1026 grams of hydrofinished light neutral petroleum oil (32.4° API) according to the procedure of Example 1, except that evaporation of a solvent is not necessary. The product thus obtained comprises a 33 percent oil solution of the copolymer of aziridineethyl methacrylate and lauryl methacrylate (1:19 mole ratio).

EXAMPLE 5

A concentrate comprising a 33 percent solution in a light mineral oil of a 1:12 mole ratio copolymer of aziridineethyl methacrylate and lauryl methacrylate is

prepared by heating 102.1 grams of aziridineethyl methacrylate, 1991 grams of lauryl methacrylate and 12.6 grams of alpha, alpha'-azodiisobutyronitrile in 6292 grams of hydrofinished light neutral petroleum oil (32.4° API) according to the procedure of Example 1 except that evaporation of solvent is not necessary. The product thus obtained comprises a 33 percent oil solution of the copolymer of aziridineethyl methacrylate and lauryl methacrylate (1:12 mole ratio).

EXAMPLE 6

A concentrate comprising a 33 percent solution in a light mineral oil of a 1:4 mole ratio copolymer of aziridineethyl methacrylate and lauryl methacrylate is prepared by heating 31.0 grams of aziridineethyl methacrylate, 209.6 grams of lauryl methacrylate and 4.8 grams of alpha, alpha'-azodiisobutyronitrile in 481.3 grams of toluene according to the procedure of Exam-

teristics of a middle distillate fuel oil when compounded in accordance with the invention, pour points (ASTM D97-66) were obtained on the fuel oil with and without the addition of the 1:9 and 1:19 aziridineethyl methacrylate:lauryl methacrylate copolymers of Examples 2 and 3. The fuel oil used in this illustration has the following typical characteristics.

Gravity, °API	33.7
Viscosity, cs at 100° F. (37.8°C.)	2.61
Flash point, P-M, °F. (°C.)	164 (73.3)
Pour point, °F. (°C.)	-20 (-28.9)
Distillation	
Over Point, °F. (°C.)	374 (190)
End Point, °F. (°C.)	630 (332.2)
10% at: °F. (°C.)	428 (220)
50% at: °F. (°C.)	499 (259.4)
90% at: °F. (°C.)	587 (308.3)

The comparative pour points are shown in Table I.

TABLE I

Composition, Vol %	A	B	C	D	E
Fuel Oil	100	100	100	100	100
Added, Wt. %					
33% oil solution of 1:9 mole ratio aziridineethyl methacrylate: lauryl methacrylate copolymer (Example 2)	—	0.1	0.2	—	—
33% oil solution of 1:19 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 3)	—	—	—	0.08	0.06
Pour Point, °F. (°C.)	-20(-28.9)	-55(-48.3)	-50(-45.6)	-40(-40)	-40(-40)

ple 1. The mixture is then diluted with 483.8 grams of hydrofinished light neutral petroleum oil (32.4° API). The toluene is then removed by vacuum evaporation. The product thus obtained comprises a 33 percent oil solution of the copolymer of aziridineethyl methacrylate and lauryl methacrylate (1:4 mole ratio). The average molecular weight of the copolymer comprises about 60,000.

The foregoing Examples are illustrative only. Similar copolymers can be obtained by the use of monomeric aziridineethyl acrylate and monomeric lauryl methacrylate. Other monomer mole proportions between 1:2 and 1:99 as disclosed herein can also be used. Also, there can be prepared in accordance with the methods indicated above the 1:2, 1:4, 1:6, 1:8, 1:10, 1:12, 1:14, 1:16, 1:18 and 1:20 to 1:99 mole ratio copolymers of monomeric aziridineethyl acrylate and methacrylate and monomeric n-octyl, Oxo octyl, 2-ethylhexyl, n-decyl, undecyl Oxo tridecyl, n-tetradecyl, sec-tetradecyl, n-hexadecyl and n-octadecyl acrylates and methacrylates.

In order to illustrate the improved pour point charac-

It is evident from the above that 1:9 and 1:19 copolymers of aziridineethyl methacrylate and lauryl methacrylate have excellent pour depressing characteristics on a middle distillate fuel oil.

In order to illustrate the improved pour point characteristics of lubricating oil compositions when compounded in accordance with the invention, the pour points (ASTM D97) of hydrofinished lubricating oils are compared with the pour points of the same base oils containing the aziridineethyl methacrylate-lauryl methacrylate copolymers of Examples 1 to 6. The two base mineral lubricating oils employed in the illustrations are hydrofinished oils having API gravities 30.5 and 32.4. Each base oil has a pour point of +5° F. (-15° C.). The higher gravity (32.4° API) mineral lubricating oil also contains 0.83 percent by volume of a combined antioxidant, bearing-corrosion inhibitor, pressure carrier and antiwear agent and 0.0003 percent by weight of an antifoam agent. The lower gravity (30.5° API) contains no other additives. The make-up of the test lubricants and the comparative pour points are shown in Table II.

TABLE II

Composition, Vol %	F	G	H	I	J	K	L	M
Mineral lubricating oil (32.4°API)	99.17	—	99.17	99.17	99.17	99.17	—	99.17
Mineral lubricating oil (30.5°API)	—	100	—	—	—	—	100	—
"Lubrizol 1395" (1)	0.83	—	0.83	0.83	0.83	0.83	—	0.83
Added, Wt. %								
33% oil solution of 1:4 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 1)	—	—	9.0	—	—	—	—	—
33% oil solution of 1:9 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 2)	—	—	—	9.0	—	—	—	—

TABLE II-Continued

Composition, Vol %	F	G	H	I	J	K	L	M
177								
33% oil solution of 1:19 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 3)	—	—	—	—	9.0	—	—	—
33% oil solution of 1:19 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 4)	—	—	—	—	—	9.0	—	—
33% oil solution of 1:12 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 5)	—	—	—	—	—	—	9.0	—
33% oil solution of 1:4 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 6)	—	—	—	—	—	—	—	9.0
"Silicone Polymer" (2)	0.0003	—	0.0003	0.0003	0.0003	0.0003	—	0.0003
Pour Point, °F.	+5	+5	-25	-25	-55	-45	-50	-35
°C.	-15	-15	-31.7	-31.7	-48.3	-42.8	-45.6	-37.2

(1) A commercial antioxidant, bearing corrosion inhibitor, pressure carrier and antiwear agent.

(2) A commercial antifoam agent.

It is evident from the data in Table II that aziridineethyl methacrylate:lauryl methacrylate copolymers have excellent pour depressing characteristics in mineral lubricating oils.

The copolymers of aziridineethyl methacrylate and lauryl methacrylate in addition to improving the pour point characteristics of a mineral lubricating oil also improve its viscosity and viscosity index properties. To illustrate the viscosity improving characteristics of the copolymers of aziridineethyl:lauryl methacrylate, vis-

cosity measurements were made on hydrofinished mineral oils (30.5° and 32.4° API) with and without aziridineethyl methacrylate:lauryl methacrylate copolymers. The higher gravity (32.4° API) mineral lubricating oil also contains 0.83 percent by volume of a combined antioxidant, bearing corrosion inhibitor, pressure carrier and antiwear agent and 0.0003 percent by weight of an antifoam agent. The lower gravity oil (30.5° API) contains no other additives. The make-up of the test lubricants and the results obtained are set forth in Table III.

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TABLE III

Composition, Vol %	F	G	H	I	J	K	L	M
Mineral lubricating oil (32.4°API)	99.17	—	99.17	99.17	99.17	99.17	—	99.17
Mineral lubricating oil (30.5°API)	—	100	—	—	—	—	100	—
"Lubrizol 1395" (1)	0.83	—	0.83	0.83	0.83	0.83	—	0.83
Added, Wt. %								
33% oil solution of 1:4 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 1)	—	—	9.0	—	—	—	—	—
33% oil solution of 1:9 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 2)	—	—	—	9.0	—	—	—	—
33% oil solution of 1:19 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 3)	—	—	—	—	9.0	—	—	—
33% oil solution of 1:19 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 4)	—	—	—	—	—	9.0	—	—
33% oil solution of 1:12 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 5)	—	—	—	—	—	—	9.0	—
33% oil solution of 1:4 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 6)	—	—	—	—	—	—	—	9.0
"Silicone Polymer" (2)	0.0003	—	0.0003	0.0003	0.0003	0.0003	—	0.0003
viscosity, ASTM D445								
cs at 100°F. (37.8°C.)	21.8	50.6	32.7	34.54	33.23	53.00	99.8	31.30
cs at 210°F. (98.9°C.)	4.12	7.0	6.44	6.62	6.36	10.58	15.06	6.00
Viscosity Index, ASTM D2270	97	104	149	146	145	153	137	143

(1) A commercial antioxidant, bearing corrosion inhibitor, pressure carrier and antiwear agent.

(2) A commercial antifoam agent.

It is evident from the data in Table III that aziridineethyl methacrylate:lauryl methacrylate copolymers

results of the dispersancy tests are summarized in Table IV.

TABLE IV

Composition, Vol %	H	I	J	K	M	N
Mineral lubricating oil (32.4°API)	99.17	99.17	99.17	99.17	99.17	93.67
"Lubrizol 1395" (1)	0.83	0.83	0.83	0.83	0.83	0.83
"Acryloid 917" (2)	—	—	—	—	—	5.50
<u>Added, Wt. %</u>						
33% oil solution of 1:4 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 1)	9.0	—	—	—	—	—
33% oil solution of 1:9 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 2)	—	9.0	—	—	—	—
33% oil solution of 1:19 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 3)	—	—	9.0	—	—	—
33% oil solution of 1:19 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 4)	—	—	—	9.0	—	—
33% solution of 1:4 mole ratio aziridineethyl methacrylate:lauryl methacrylate copolymer (Example 6)	—	—	—	—	9.0	—
"Silicone Polymer" (3)	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
<u>Dispersancy Evaluation</u>						
Piston varnish (10 Perfect)	7.5	6.5	7.0	7.0	7.0	5.5
Total varnish (50 Perfect)	45.0	42.0	43.0	39.5	42.0	42.0
Total Sludge (50 Perfect)	48.5	47.7	47.5	47.0	46.0	43.2
Total Engine Rating (100 Perfect)	93.5	89.7	90.5	86.5	88.0	85.2

(1) A commercial antioxidant, bearing-corrosion inhibitor, pressure carrier and antiwear agent.

(2) A commercial dispersant, pour depressant and viscosity index improver.

(3) A commercial antifoam agent.

have excellent viscosity and viscosity index improving characteristics on mineral lubricating oils.

In addition to improved pour point, viscosity and viscosity index characteristics, lubricating oil compositions of the present invention have good dispersancy characteristics. To illustrate the dispersancy characteristics of lubricating compositions of the invention, the compounded oils were subjected to a low temperature dispersancy evaluation. The compounded oils were also compared with the same base oil containing a commercially available dispersant, pour depressant and viscosity index improver "Acryloid 917". Briefly, the evaluation comprises operating a single cylinder engine with the test oil as the crankcase lubricant for 180 hours at a constant speed of 1800 r.p.m. under a load of 21 lb/ft (31.25 Kgs./meter) with a cooling jacket outlet temperature cycled for 3 hours at 120° F. (48.9° C.) and one hour at 200° F. (93.3° C.). In testing lubricating oils by this procedure, a fuel that tends to promote engine deposits is used. At the conclusion of the test period, the engine is disassembled and the piston and other engine parts are rated on the basis of deposits. The internal engine parts are given a total varnish and a total sludge rating. Each of the above-indicated ratings is then combined in a weighted average to form a total engine cleanliness rating, a rating of 100 being considered perfect. The lubricating oil also contains 0.83 percent by volume of a combined antioxidant, bearing corrosion inhibitor, pressure carrier and antiwear agent and 0.0003 percent by weight of an antifoam agent. The make-up of the test lubricants and the

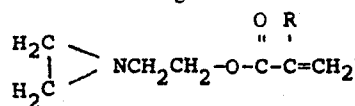
Comparison of the results obtained with a reference oil (Composition N) and with compounded test oils indicates that the lubricating oil compositions of the invention have good dispersancy characteristics and a better total engine rating than the reference oil. While Composition K was slightly inferior in its total varnish rating in comparison with the other compositions, nevertheless the total engine rating was better than the total engine rating of the reference oil (Composition N).

The specific embodiments set forth hereinabove are illustrative only and similar improvements in dispersancy viscosity index and/or pour point can be obtained by the use in the base oils of the preceding embodiments or other base oils disclosed herein of the same or equivalent proportions of other copolymers of the class disclosed herein.

Numerous modifications and variations of the invention as herein set forth can be resorted to without departing from the spirit or scope of the invention. Accordingly, only such limitations should be imposed as are indicated in the claims appended hereto.

I claim:

1. An oil composition which comprises a major amount of a mineral oil and a small amount of an oil-soluble copolymer of (a) a monomeric aziridinyl ethyl carboxylic acid ester having the formula



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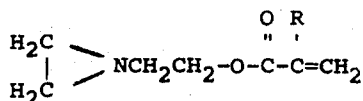
where R is selected from the group consisting of the hydrogen atom and the methyl group and (b) a monomeric alkyl ester having the formula



where R is selected from the group consisting of the hydrogen atom and the methyl group and R₁ is selected from the group consisting of straight- and branched-chain alkyl groups containing 8 to 18 carbon atoms, said copolymer having a molecular weight of at least 20,000 and a ratio of the constituent monomers (a) and (b) in the range of about 1:2 to about 1:99, (a):(b), respectively.

2. The oil composition of claim 1 wherein said small amount is about 0.001 to about 10 percent by weight of the composition.

3. A distillate fuel oil composition which comprises a major amount of a petroleum distillate boiling in the range of about 300° F. (148.9° C.) to about 750° F. (398.9° C.) and about 0.001 to about 5 percent by weight of a copolymer of (a) a monomeric aziridinyl ethyl carboxylic acid ester having the formula



where R is selected from the group consisting of the hydrogen atom and the methyl group and (b) a monomeric alkyl ester having the formula



where R is selected from the group consisting of the hydrogen atom and the methyl group and R₁ is selected from the group consisting of straight- and branched-chain alkyl groups containing 8 to 18 carbon atoms, said copolymer having a molecular weight of at least about 20,000 and a ratio of the constituent monomers (a) and (b) in the range of about 1:2 to about 1:19, (a):(b), respectively.

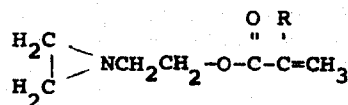
4. The distillate fuel oil composition of claim 3 wherein constituent monomer (a) is aziridineethyl methacrylate and constituent monomer (b) is lauryl methacrylate.

5. The distillate fuel oil composition of claim 4 wherein the mole ratio of (a):(b) is 1:9.

6. The distillate fuel oil composition of claim 4 wherein the mole ratio of (a):(b) is 1:19.

7. A lubricating oil composition which comprises a major amount of a mineral lubricating oil and about 0.5 to about 10 percent by weight of a copolymer of (a) a monomeric aziridinyl ethyl carboxylic acid ester having the formula

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where R is selected from the group consisting of the hydrogen atom and the methyl group and (b) a monomeric alkyl ester having the formula



where R is selected from the group consisting of the hydrogen atom and the methyl group and R₁ is selected from the group consisting of straight- and branched-chain alkyl groups containing 8 to 18 carbon atoms, said copolymer having a molecular weight of at least about 20,000 and a ratio of the constituent monomers (a) and (b) in the range of about 1:2 to about 1:99, (a):(b), respectively.

8. The lubricating oil composition of claim 7 wherein constituent monomer (a) is aziridineethyl methacrylate and constituent monomer (b) is lauryl methacrylate.

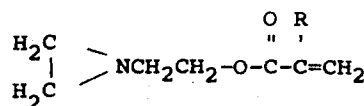
9. The lubricating oil composition of claim 8 wherein the mole ratio of (a):(b) is 1:4.

10. The lubricating oil composition of claim 8 wherein the mole ratio of (a):(b) is 1:9.

11. The lubricating oil composition of claim 8 wherein the mole ratio of (a):(b) is 1:12.

12. The lubricating oil composition of claim 8 wherein the mole ratio of (a):(b) is 1:19.

13. A crude oil composition which comprises a major amount of a mineral crude oil and about 0.001 to about 5 percent by weight of a copolymer of (a) a monomeric aziridinyl ethyl carboxylic acid ester having the formula



where R is selected from the group consisting of the hydrogen atom and the methyl group and (b) a monomeric alkyl ester having the formula



where R is selected from the group consisting of the hydrogen atom and the methyl group and R₁ is selected from the group consisting of straight- and branched-chain alkyl groups containing 8 to 18 carbon atoms, said copolymer having a molecular weight of at least 20,000 and a ratio of the constituent monomers (a) and (b) in the range of about 1:2 to about 1:99, (a):(b), respectively.

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