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OIL COMPOSITION

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This invention relates to novel oil compositions and to methods of preparing and using same, and more particularly it relates to lubricating oil compositions containing a paraffinic mineral oil base stock together with small amounts of two different addition agents which have viscosity index improving and pour depressing properties and which cooperate to give improved characteristics in regard to pour point stability and lowering of the cloud point.

The mineral oil base stocks which may be used according to this invention may be any of the paraffinic hydrocarbon oil fractions such as those derived from petroleum, or synthetic oils made by polymerization of olefins or other unsaturated aliphatic hydrocarbons, 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 as Diesel fuel, or even solid petroleum fractions such as paraffin wax and petrolatum.

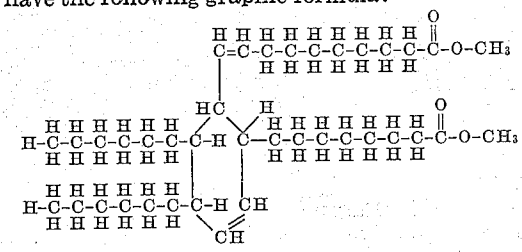
Of the two addition agents required to be used according to this invention, the one will for simplicity be referred to as a polyester, although by this term it is intended to mean only the polyester of a particular type, namely one having a molecular weight of at least 2000 formed by polymeric condensation of a dicarboxylic acid, or lower aliphatic ester thereof, with a glycol, there being at least 10 carbon atoms in at least one of two said reactants. It is essential for the present invention that this polyester be soluble at low temperatures in highly paraffinic oils, for instance having a viscosity index of at least 90, and preferably at least 100. Suitable polyesters for this purpose may be made in several ways such as either by using suitable reactants which will combine to form a polyester which per se has

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satisfactory solubility in highly paraffinic mineral oils, or by first making a polyester product, only some of the constituents of which are soluble in a paraffinic oil and then separating the desirable soluble constituents from the undesirable insoluble constituents by some suitable process such as selective solvent extraction or solvent precipitation, etc.

In preparing these polyesters by either of the above two suggested methods, it is preferable that either the dicarboxylic acid or the glycol has an even larger number of carbon atoms than suggested above, such as at least 15 to 30 or even 50 carbon atoms or more per molecule. The total number of carbon atoms in one molecule of the dicarboxylic acid, together with one molecule of the glycol should be at least 30, and preferably at least 40. Thus either the acid or the glycol may have from 2 to 50 or more carbon atoms, provided the total is at least 30 or 40 for one molecule of each. However, preferably the dicarboxylic acid to be used should be one having at least 30 carbon atoms, such as one made by the polymerization to the dimer stage of fatty acids derived from vegetable oils such as soybean oil, linseed oil, corn oil, castor oil, or other oils having in general an iodine number between the approximate limits to 20 to 155. Such dimer acids or lower alkyl esters thereof may readily be prepared by known methods such as that described by Bradley and Johnston in Industrial and Engineering Chemistry, volume 33, page 86 (1941), this reference showing the preparation of methyl dilinoleate from dehydrated or dimerized castor oil. For instance, soybean oil may be converted by methanolysis to methyl esters, as by heating to 70° C. with a liberal excess of methanol in the presence of a substantial portion of sodium methylate for several hours, and then the distilled methyl esters are polymerized chiefly to the dimer stage by heating to 300° C. with a suitable catalyst such as 0.3% of anthraquinone, for a suitable period such as about 10 to 30 hours. Unpolymerized or monomeric esters are then removed by distillation under a reduced pressure of about 1 to 5 mm. mercury, and the residual methyl dilinoleate is carefully fractionated in a short path pot still (a modified alembic flask) at 2 to 50 microns, or in a cyclic molecular still at 2 to 5 microns. The resultant distilled dimer methyl esters of soybean oil, i. e. substantially pure methyl dilinoleate, have an index of refraction of N 30/D 1.4766, (for published information on purity of product against index of refraction see Ind. and Eng. Chem., vol. 16, No. 2, Feb., 1944,

Analytical edition, page 91), and is believed to have the following graphic formula:



The color of the product was light yellow and had the following viscosity characteristics:

Temperature	Viscosity
	Centistokes
100° F.	60.0
140° F.	25.4
160° F.	17.8
210° F.	8.7

The —40° F. viscosity of the pure methyl dilinoleate is 42,464 centistokes by the Baldeschwieler and Wilcox method (see Ind. and Eng. Chem., vol. 11, page 221, April 15, 1939).

(The physical properties of dilinoleic acid are: Unsaturation, two double bonds; molecular weight, 560; neutral equivalent, 280; conjugation, negligible; melting point, non-crystalline at —60° C.)

Approximately 40 parts by weight of purified methyl dilinoleate are obtained from 100 parts by weight of raw soybean oil.

The dimer acid thus obtained is then subjected to polymeric condensation with a glycol such as ethylene glycol, propylene glycol, butylene glycol, various pentadiols such as 2-methyl-2-4-pentadiol, or preferably even higher glycols such as decamethylene glycol or commercial glycols such as 12-hydroxy stearol which may be made by hydrogenation of castor oil acids, and may be obtained commercially under the tradename of Hydrofol Glycerides 200. Such condensation or esterification of the dicarboxylic acid with the glycol is conveniently accomplished at temperatures ranging from about 150° C. to 260° C., preferably at about 193 to 210° C., and preferably when the dimer acid is used and not the methyl ester of the acid in the presence of a small amount of condensation catalyst such as para-toluene sulfonic acid. It is desirable to pass a stream of nitrogen or other suitable inert gas through the reaction mass to stir and to facilitate removal of methanol (when methyl ester is used) and water (when acid is used) formed during the reaction. The resultant condensation products or polyesters have a high molecular weight ranging from 2,000 up to 50,000 or more depending upon specific detailed operating conditions, polyesters having an average molecular weight in the range of 5,000 to 30,000 or so being usually obtained.

Although under some conditions it is possible, as suggested above to prepare such polyesters which per se are soluble in paraffinic mineral oils at low temperatures such as 15° F. (about —8 to —9° C.), the preparation of such soluble polyesters is quite difficult and expensive, and accordingly if preferred one may subject the crude polyesters formed as described above to a suitable solvent precipitation in order to separate the insoluble constituents from the desired ones which are soluble in a highly paraffinic oil. This separation may be accomplished for instance by dissolving a crude polyester having an average molecular weight of 20,000 or so and derived from methyl dilinoleate and decamethylene glycol, in a highly paraffinic mineral oil base stock such as a Barosa mineral lubricating oil base stock having a viscosity of about 43 seconds Saybolt at 210° F. and a viscosity index of about 110 or 112, by mixing the polyester into the oil with stirring at elevated temperatures such as 140° C. and then cooling the resultant solution to a temperature of about 15° F. or so for 10 to 20 hours or more. During such cooling, the least soluble constituents of the crude polyester mixture precipitate out of solution and may be separated by filtration, preferably in the presence of a filter aid such as a 10 mm. layer of a calcined diatomaceous earth, e. g. Hy-Flow, and preferably using vacuum to assist in the filtration.

The resultant solution of soluble polyester in heavy mineral oil may, if desired, be used as such by merely diluting it with an additional suitable amount of paraffinic mineral oil to produce a solution having the desired concentration of polyester, or if preferred, may be treated to separate the soluble polyester from the heavy mineral oil by suitable methods such as by the addition of an alcohol to the oil in order to precipitate the polyester out of the oil. If desired, a small amount of a suitable material such as dibutoxy ethyl phthalate may be added with the alcohol to solubilize the alcohol in the polyester-oil blend. The thus precipitated soluble polyester may be separated by decantation, filtration or other suitable means and after washing, as with alcohol, or other suitable liquids such as ethyl ether or ethylene, or ethane, may be added in desired proportion to any suitable paraffinic oil base stock. Such soluble polyesters made as described above should in general have an oxygen content between the approximate limits of about 4 to 13%, preferably about 8 to 12%.

As an optional procedure one may hydrogenate either the dimer acid (or lower alkyl ester thereof) to be used or the resultant polyester, in order to stabilize them against oxidation and against further condensation or other undesirable chemical reactions.

These various above described polyesters which are soluble in highly paraffinic mineral oils, e. g. having a viscosity index of at least 90 and preferably at least 100, have several interesting inherent properties, one of which is that of being a viscosity index improver, by which is meant that when dissolved in a mineral oil base stock it will raise the viscosity index of the oil for instance from 100 up to about 150 or slightly more, depending upon the amount used. This soluble polyester also has substantial pour depressing properties, particularly when used in small amounts, e. g. less than 5%, the effect being greatest in still smaller concentrations such as about 1% or so. In certain types of base stocks this soluble polyester also has the additional interesting characteristic of reducing the cloud point, as for instance in the case of the highly paraffinic Diesel fuel base stock having a cetane number of about 60, in which case the cloud point was reduced from —4.2° C. to —7.3° C. by 0.5% of the soluble polyester, larger amounts thereof ranging up to 6% producing a cloud point approaching back up to the —4.2° C. pour point of the plain base stock. However, in other base stocks such as a blend of 90% of Pennsylvania neutral spindle oil and 10% of paraffinic brightstock, it had little, if any, effect in lowering the cloud point.

The other primary addition agent to be used according to this invention in preparing mineral oil compositions, and which apparently cooperates in some unknown manner with the above described polyester, is a substance which for the sake of simplicity will be referred to as a pour depressor since materials of this class have been known heretofore primary due to that characteristic. The chief requirement of this pour depressor for purposes of the present invention is that it be of a substantially different chemical structure than the dicarboxylic-glycol polyester. It is believed preferable that such pour depressors should either be free of oxygen or have a lower oxygen content than the polyesters, and should preferably have less than 5% oxygen. These materials may be selected from a fairly wide variety of known pour depressors such as high molecular weight hydrocarbon compounds made for instance by Friedel-Crafts condensation of chlorinated wax with aromatic hydrocarbons such as naphthalene, benzene, anthracene, or various lower alkylated aromatic compounds, or they may be derivatives of high molecular weight hydrocarbons containing one or more groups containing or consisting of only one oxygen atom, where such oxygen atom serves as a necessary link in building up a high molecular weight molecule; on the other hand, ester groups may be present as side chains without interfering with the operation of the invention. Examples of suitable pour depressors are the wax-aromatic condensation products such as those produced by Friedel-Crafts condensation of chlorinated wax with naphthalene and which have a molecular weight generally in the range of about 500 to 10,000, condensation products made by Friedel-Crafts condensation of chlorinated paraffin wax with phenol, with or without subsequent acylation with acid such as phthalic acid, adipic acid or benzoic acid, as well as the more essentially aliphatic but oxygen-containing pour depressors of the polyvinyl ether type such as polyvinyl oleyl ether of sperm oil alcohols.

Other types of pour depressors may be used such as:

Paraffin wax-aromatic hydrocarbon condensation products.

Other paraffin wax-aromatic compound condensation products and their derivatives including the metal derivatives.

Paraffin wax heterocyclic condensation products, e. g., paraffin wax condensed with diphenylene oxide, and their modifications.

Fatty acid derivatives. These may comprise the metallic soaps, the fatty acid amides, the so-called mixed ketones, the polymerized fatty acids, the reaction products of unsaturated fatty acids with aromatic compounds, and the fatty acid derivatives of the coumarone and indene type resins.

Pour depressants obtained as by-products of petroleum refining, for example, cracking coil tar and extracted components of pitch.

Vinyl ether derivatives for example, the polymerized vinyl ethers of fatty alcohol.

Pour depressants derived from paraffin wax itself, for example, oxidized paraffin wax, polymerized chlorinated wax.

Pour depressants derived from aromatic compounds themselves, for example, aromatic hydrocarbons are polymerized with aluminum chlorine. This is particularly applicable to the polynuclear hydrocarbons, for example, naphthaline anthracene, etc.

Reaction product of olefins, for example, cracked paraffin wax reacted with aromatics, vapor phase cracked gasoline polymerized with aluminum chloride.

Pour depressants produced by ultra violet radiation by subjecting hydrocarbon oils in form of a thin film to ultra violet radiation of several lengths, predominantly less than 2800 angstrom units.

Rubber derivatives which may comprise hydrogenated rubber, rubber modified by amphoteric metal halides, unvulcanized rubber, plasticized with peptizing agents for example phenyl hydrazine, rubber condensed with various types of organic compounds, for example chlorinated hydrocarbons, aromatic compounds, etc.

Pour depressants derived from fatty alcohols.

Pour depressants formed by action of silent electric discharge on hydrocarbon oils or products of low-oxygen content (voltolized products).

Chlorinated polymers, for example, chlorinated polybutene or other high molecular weight hydrocarbon materials or products of low-oxygen content condensed with aromatic compounds.

Pour depressors of the types described above all have the characteristic of making substantially large reductions in the pour point of paraffinic mineral oils in which they are dissolved. Some of them also have the additional property of increasing to some extent the viscosity index of the oil in which they are dissolved, but this improvement in viscosity index is not nearly as great in proportion as is obtained with materials of the polyester type referred to above which are outstandingly effective as viscosity index improvers. Another interesting fact about the pour depressors is that even though they reduce the pour point of a mineral oil they generally have little or no effect on the cloud point of the oil.

It is also interesting to note that the pour point as measured by the standard A. S. T. M. method is usually much lower than the so-called stable pour point which is determined by subjecting the oil solution to cycles of alternate heating and cooling and using as the "stable pour point" the highest pour point attained in any of the six cycles. The procedure used to obtain "stable pour point" is given in an article by C. E. Hodges and A. B. Boehm in a paper entitled "Pour point stability of pour depressant treated oils under winter storage" (Oil and Gas Journal, June 24, 1943). The determination of the stable pour point is of interest because it has been known for some years that pour depressant treated motor oils under winter storage conditions sometimes become solid at temperatures higher than those indicated as their A. S. T. M. pour points, even though oils that are actually in service do not show this difficulty, or at least not to any serious extent. In the laboratory test procedure for determining stable pour point the oil samples are alternately heated and cooled, the temperatures to which the samples are heated being controlled successively from 50° F. in the first cycle to 0° F. in the sixth cycle, but the temperature to which the samples are cooled being in each case —28° F., and the samples being tilted every 5° drop in temperature during cooling to determine when they become solid. The pour point is reported as 5° F. above the solid point.

One of the primary features of this invention is that it has been found that a soluble dicarboxylic-glycol polyester type of material cooperates with a pour depressor type of material in some un-

known manner as to accomplish at least to highly unexpected results, one being a lowering of the stable pour point of the pour depressor, and the other is the production of a lower cloud point than is obtained with either addition agent separately.

These and other objects and advantages of the invention will appear more fully from a consideration of the following experimental data which are given for the sake of illustration but without intention that the invention be limited to the particular materials which have been given merely for the sake of illustration.

In order to show the effect of a polyester per se on the pour point, cloud point and viscosity characteristics on an oil, a series of tests was made, the results of which are shown in Table 1, in which the oil base stock used consisted of 90% by volume of a Pennsylvania neutral light lubricating oil "A" and 10% by volume of a paraffinic brightstock. This oil base stock was tested alone and together with three different concentrations ranging from 1 to 5% of a soluble polyester having an average molecular weight of about 9,000 which was made by condensation of methyl dilinoleate with decamethylene glycol to a crude polyester having an average molecular weight of about 22,000, with subsequent removal of the less soluble constituents, in the manner described above.

TABLE 1

Properties of polyester

	Pour	Cloud	Saybolt viscosity [1] at—		V. I.
			100	210	
Test oil	+30	+34	185.2	45.82	103
Test oil +1% polyester	−20	+32	216.7	50.47	126.5
Test oil +2.5% polyester	−15	+32	280.6	58.84	138
Test oil +5.0% polyester	0	+32	408.9	78.92	145

Test oil: 90% Penn neutral+10% brightstock.
[1] Converted from kinematic viscosities.

The data in Table 1 show that 1% of the polyester effected a very great lowering or depressing of the pour point from +30° F. to −20° F. but that further addition of the polyester permitted the pour point to rise gradually back up to 0 with a 5% concentration of polyester. They also show that the polyester per se had little effect on the cloud point even in a concentration as high as 5%. They also show that the polyester is a very potent V. I. (viscosity index) improver since 1% raised the V. I. from 103 to 126 and 5% raised it on up to 145.

Now another series of tests was made with identical concentrations of polyester, but in each case also adding 1% of pour depressor A which is a commercially available pour depressor made by Friedel-Crafts condensation of chlorinated paraffin wax having a chlorine content of about 12 to 15% with naphthalene, with subsequent hydrolysis and removal of the catalyst and distillation of the reaction products under fire and steam up to about 600° F. to remove unreacted materials or low boiling products. The oil base stock used in this series of tests was the same as that used in the previous test except for the omission of the brightstock.

TABLE 2

Properties of polyester+1% pour depressor A

Test oil	A. S. T. M.		Saybolt viscosity at—		V. I.
	Pour	Cloud	100	210	
Oil "A"	+30	+32	140	42.57	101
1% pour depressor A	−25	+30	143.5	42.73	99
1% pour depressor A+1% polyester	−30	+28	171.8	46.72	127
1% pour depressor A+2.5% polyester	−15	+26	218.5	53.66	142
1% pour depressor A+5.0% polyester	[1] 0	+22	319.3	68.94	148

[1] Slight.

The data in Table 2 show that 1% of pour depressor A lowered the pour point of the oil from +30 to −25 and that the further addition of 1% of polyester lowered it still further to −30° F. but that further additions of polyester permitted the pour point to rise again up to 0° F. for the blend containing 1% of pour depressor A and 5% of polyester. There is thus little or no advantage in regard to A. S. T. M. pour point in using more than 2% of polyester in conjunction with the 1% of pour depressor A, but the use of only 1% of polyester appears to obtain an unexpected further lowering of the pour point. However, a point of outstanding importance is that the cloud point was lowered to a very surprising extent by the addition of further amounts of the polyester ranging from the 1% up to the 5% when used in conjunction with 1% of pour depressor A. This in spite of the fact that as shown in Table 1 the polyester per se had little or no effect on the cloud point even in 5% concentration; it could also be shown, but is well known, that materials of the type of pour depressor A have little or no effect on the cloud point. The viscosity data in Table 2 show that the use of 1% of pour depressor A had no deleterious effect on the V. I. improving properties of the polyester.

Another series of tests was made to study the effect of the polyester on the stable pour point of a blend containing a pour depressor. In this series of tests the oil base stock used consisted of Pennsylvania neutral light lubricating oil A to which had been added 2.5% of Pennsylvania panhandle brightstock, which is a paraffinic residual oil. The A. S. T. M. pour point, cloud point and viscosity characteristics of this oil base stock were studied alone and together with 1% of pour depressor A, and also together with 1% of that pour depressor and also 1% polyester, and stable pour points were also obtained for these blends but not for the plain base stock. The data obtained in this series of tests are shown in Table 3.

TABLE 3

Stable pour point of blends with and without polyester and pour depressor A

Oil [1]	Pour depressor "A"	Polyester	A. S. T. M.		Saybolt viscosity at—		V. I.	Stable pour point, ° F.
			Pour, ° F.	Cloud, ° F.	100° F.	210° F.		
100			+30	+34	149.3	43.37	102	+30
99	1		−15		152.0	43.50	103	+5
98	1	1	−20	+32	179.0	47.49	128.5	[2] −6

[1] Pennsylvania neutral oil A+2.5 Panhandle brightstock.
[2] Average of two tests −5 and −8, respectively.

The figures for "stable pour point" in the above table were derived from six-cycle laboratory tests determined by the method referred to previously, the detailed test results being shown in the following table:

TABLE 4

Stable pour point tests of blends of oil with and without polyester and pour depressor A

Per cent composition			Pour point (° F.) in cycle of test				
Oil	Pour depressor A	Polyester	Cycle II	Cycle III	Cycle IV	Cycle V	Cycle VI
99	1	-------	+3	[1]+5	+2	+2	−4
98	1	1	−17	−13	[1]−8	−12	−17
			−21	−17	−19	[1]−5	−7

[1] Means the "stable" pour point (highest in the six cycles).

The most remarkable feature of the data in Table 3 is the great lowering of the stable pour point from +5° F. in the blend of the oil with 1% pour depressor A, down to −6° F. by the further addition of 1% of polyester. This will be especially appreciated by those skilled in the art who realize that it is extremely difficult to lower the stable pour point to such a low temperature, and that such a result could not be obtained by the use of either the pour depressor A alone or the polyester alone. In fact when using pour depressor A alone in similar base stocks, 2% of the pour depressor generally produces a higher stable pour point than when only 1% is used; and judging from the data in Table 1 it would appear likely that when the polyester is used alone, 2% of it would produce a higher stable pour point than when only 1% is used.

As a further checkup on the pour point stability of such blends, some actual field observations were made over a period of 47 days from January 5 to February 19 in two different relatively cold locations in the United States, namely, one in Minnesota and one in Warren, Pa., the samples being stored in protected outdoor racks where they were exposed to the daily normal atmospheric temperature fluctuations. The samples used were the same blends as tested in Tables 3 and 4, but in the field test the samples did not have to be heated and cooled artificially and merely were examined daily to see whether they were fluid or solid. The following table shows the number of observations, how many times the samples were found to be solid, and the highest solid point temperature observed for each of the two blends containing pour depressant A, with and without polyester.

TABLE 5

Field observation data (47 days)[1] pour stability properties of polyester

	Oil [2]+% depressant A		Oil [2]+1% depressant A+1% polyester	
	Warren, Pa.	Minnesota	Warren, Pa.	Minnesota
Number of observations	47	42	47	42
Number of times solid	6	11	None	
Highest solid point in field ° F.	+11	+16	Below −1	Below −9

[1] From Jan. 5 to Feb. 19, 1944.
[2] Penn neutral oil A+2.5% Panhandle brightstock.

This Table 5 shows that whereas the oil containing 1% of pour depressant A but no polyester was found to be solid 6 days and 11 days, respectively, at Warren, Pa., and in Minnesota, the same blend containing 1% of polyester was not found solid any day during the entire test period. It is also interesting to note that for the blend not containing polyester the highest temperatures at which the samples were found solid were +11° F. and +16° F. at Warren, Pa. and Minnesota, respectively, whereas the similar blend containing polyester had remained fluid even at the lowest atmospheric temperatures observed, namely −1° F. and −9° F. at Warren, Pa. and in Minnesota, respectively.

The polyester used in the above-described tests was made by the method described previously in a general way but was specifically as follows:

The following is given as a specific example of the preparation of a suitable dimer acid and subsequent condensation with a glycol to produce the preferred type of polyester. Soybean oil is converted by methanolysis to methyl esters, as by heating to 70° C. with a liberal excess of methanol in the presence of a substantial portion of sodium methylate for several hours, and then the distilled methyl esters are polymerized by heating to 300° C. with a suitable catalyst such as 0.3% of anthraquinone, for a suitable period such as about 10–30 hours. Unpolymerized esters are then removed by distillation under reduced pressure of 1–5 mm., and the residual methyl dilinoleate is care fully fractionated in a short path pot still (a modified alembic flask) at 2 to 50 microns, or in a cyclic molecular still at 2 to 5 microns. The several distilled dimer methyl esters of soybean oil, i. e., methyl dilinoleate, had an index of refraction of N 30/D 1.4766. This dimer acid ester is then used as raw material in the following experimental work.

Example 1

A mixture of 37 grams of the methyl dilinoleate described above and 11.2 grams of decamethylene glycol was heated with about 0.25 gram of paratoluene sulfonic acid as catalyst, under nitrogen, for about 98 hours. A general stream of nitrogen through the reaction mass served to stir the mixture and to facilitate removal of alcohol formed in the reaction. No air or oxygen was present in the reaction at any time. The resulting polyester had a molecular weight of about 22,500 by viscosity test: it was soluble in chloroform at room temperature and insoluble in Barosa 43 mineral oil (a highly paraffinic lubricating oil having a viscosity of 43 seconds Saybolt at 210° F. and a viscosity index of about 110 or 112). However, a 6% solution of such polyester in such paraffinic oil, which gadually cooled, showed a cloud point of 15° C.

The primary object of the present invention is to subject such a polyester to solvent separation in order to obtain therefrom a fraction completely soluble in highly paraffinic oil even at extremely low temperatures.

Thirty grams of the polyester thus obtained was dissolved in 200 grams of Barosa 43 mineral oil at 140° C. The mineral oil had been saturated with nitrogen at room temperature, and nitrogen was added to the oil solution as the temperature was increased to 140° C. This was for the purpose of avoiding any possibility of oxidation of the polyesters during the solvent separation. The polymer-oil mixture was then placed in a 1-liter flask under an atmosphere of

nitrogen and then placed in an ice-box at about 15–20° F. for 17 hours, during which time some of the polyesters separated out of solution and settled to the bottom of the flask while other particles of precipitated polyesters remained suspended in the oil. The cold mixture was filtered through paper and a layer about 10 mm. thick of Hy-Flow, which is a calcined diatomaceous earth, at about 15–20° C., using vacuum to assist in the filtration. The filtrate which was then only slightly turbid was treated with about 15% by volume of dibutoxy ethyl phthlate and about 50% by volume of 99% isopropyl alcohol, in order to precipitate the rest of the polyester which was substantially completely dissolved in the Barosa mineral oil. The dibutoxy ethyl phthalate was merely used to solubilize the alcohol into the polymer-oil blend. The amount of soluble polyester thus recovered was about 17 grams and it had an average molecular weight of about 9,000.

Another sample of polyester was prepared by reacting 37 gm. of pure methyl ester of dilinoleic acid and 11.23 gm. of C. P. (chemically pure) decamethylene glycol. The temperature was held at 193° C. and time of run was 48 hours. Reaction was conducted in an atmosphere of pure nitrogen. The nitrogen in gas form was used to stir the mixture and facilitate removal of alcohol formed in the reaction. No air or oxygen was present in the reaction as a mercury trap was used on the vapor exit line. The final sample had a molecular weight of about 12,000. An oil leach was made on the polymer, as described in the previous example. Results indicated that 65% of the polymer was soluble in Barosa 43 oil (a highly paraffinic oil of 43 sec. viscosity at 210° F.).

1% of pour depressor B which is a commercial pour depressor consisting essentially of phthalic esters of wax alkylated phenol, was added to a paraffinic oil base stock consisting of Pennsylvania neutral oil A to which was added 2.5% of Panhandle brightstock, and it was found that the A. S. T. M. pour point was lowered from +30° F. to −15° F. The further addition of 1% of the soluble polyester just described above lowered the pour point still further to −20° F., although it did not reduce the cloud point. On the other hand, a pour depressor C which was a polyvinyl oleyl ether of sperm oil alcohols, which is not only a good pour depressor but also has fair viscosity index improving properties, lowered the pour point to −20° F. in 1% concentration and had no effect on the cloud point of the oil base stock which was +34° F. When 1% of the polyester just referred to above was added to such a blend containing pour depressor C, it reduced the cloud point to +30° F., thereby indicating that there is some unexplained cooperation between the pour depressor C and the polyester.

Although from the point of view of cloud point reduction and V. I. improvement, it may be desirable to use amounts of dicarboxylic-glycol polyesters in concentrations as much as 5% or even 10% or more, in conjunction with a small amount of the pour depressor type of material, it is believed that the most outstanding features of the invention are attained when the polyester is used in concentrations of less than 5%, and preferably less than 2%, in conjunction with the pour depressor type of material in concentrations of less than 2% and preferably not more than 1%. For instance, the remarkable feature of producing very unexpectedly low stable pour point is obtained by the use of only 1% of the polyester with only 1% of the pour depressor.

While there are above disclosed but a limited number of embodiments of the composition of the present invention, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed and it is therefore desired that only such limitations be imposed on the appended claims as are stated therein or required by the prior art.

The invention claimed is:

1. A composition comprising a major proportion of a paraffinic hydrocarbon, and dissolved therein a small amount of a dicarboxylic-glycol polyester having a molecular weight of at least 2,000, there being at least 10 carbon atoms per molecule in at least one of said two reactants and the total number of carbon atoms in 1 molecule of the dicarboxylic acid together with 1 molecule of the glycol being at least 30, and a small amount of a pour depressor consisting essentially of a high molecular weight condensation product of a long chain aliphatic compound and an aromatic compound.

2. A composition according to claim 1 in which the polyester is soluble at temperatures as low as 15° F. in highly paraffinic mineral lubricating oil base stocks having a viscosity index of at least 90.

3. A composition according to claim 1 in which the pour depressor contains at least 91% carbon and hydrogen.

4. A lubricating oil composition comprising a major proportion of waxy mineral lubricating oil and, dissolved therein less than 5% of a polyester having an average molecular weight of at least 2,000, containing about 9 to 13% oxygen and consisting of a polymeric condensation product of a glycol with a dicarboxylic acid or ester, said polyester reactants containing a total of at least 30 aliphatic carbon atoms in one molecule of said acid or ester, together with one molecule of said glycol, said composition also containing dissolved therein less than 2% of a pour depressor consisting of a high molecular weight condensation product of a long chain aliphatic compound and an aromatic compound.

5. A composition according to claim 4 in which the pour depressor is a Friedel-Crafts wax-aromatic condensation product.

6. A composition according to claim 4 in which the pour depressor is a Friedel-Crafts wax-naphthalene condensation product substantially nonvolatile under fire and steam distillation up to about 600° F.

7. A composition according to claim 4 in which the polyester is a polymeric condensation product of a glycol with a high molecular weight organic compound consisting chiefly of carbon, hydrogen and oxygen containing at least 28 aliphatic carbon atoms and containing 2 —COOR groups in which R is either hydrogen or a lower alkyl group.

8. A composition according to claim 4 in which the polyester is a polymeric condensation product of a glycol and a substantially pure dimer of a high molecular weight fatty acid.

9. A composition according to claim 4 in which the polyester is a polymeric condensation product of methyl dilinoleate with decamethylene glycol.

10. A lubricating oil composition having a low stable pour point, comprising a major proportion of a waxy mineral lubricating oil, about 1% of a soluble polyester of methyl dilinoleate and decamethylene glycol, said polyester having an aver-

age molecular weight of at least 5,000 and being soluble at temperatures as low as 15° F. in a paraffinic hydrocarbon lubricating oil base stock having a viscosity index of at least 100, said lubricating composition also containing about 1% of a pour depressor which is a Friedel-Crafts condensation product of about 2 to 3 mols of chlorinated paraffin wax of about 10 to 15% chlorine content and about 1 mol of naphthalene, said pour depressor being substantially non-volatile under fire and steam distillation up to about 600° F.

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