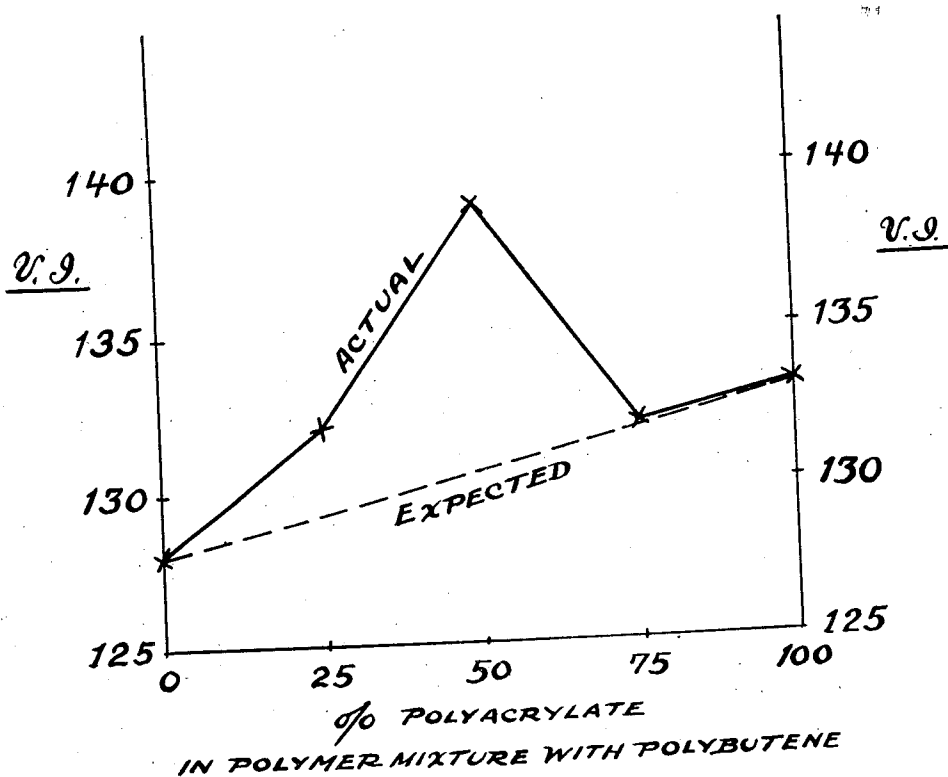


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LUBRICATING OIL COMPOSITION

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LUBRICATING OIL COMPOSITION

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1 Claim. (Cl. 252—57)

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This invention relates to hydrocarbon oil blends with a combination of additives for more effectively improving viscosity-temperature relationships of the blends with restricted thickening.

A major requirement of motor lubricating oils and other industrial petroleum oil products is a satisfactory viscosity-temperature characteristic, i. e., as little variation of viscosity over a wide temperature range as possible. Petroleum lubricating oils with high viscosities at low temperatures have poor flow characteristics in a cold engine, while with proper low viscosities at low temperatures, many of them lack sufficient viscosity at operating temperatures for proper lubrication. Although, certain thickening agents are capable of giving these oils more satisfactory viscosity-temperature characteristics, in serving this purpose, they thicken the oils to unduly high viscosities, which increase power consumption and make the oils unfit for low temperature use. Accordingly, it is desirable to improve many petroleum oil products by lowering the rate of change of viscosity with temperature, with preferably a reduction in viscosity, or at least, only a small change in viscosity, at low temperatures.

In evaluating lubricating oils on their ability to maintain a more uniform viscosity with change in temperature, the well known viscosity index classification of Dean and Davis is widely used by the oil industry. This classification comparatively rates the oils by their relative variations in viscosities accurately determined at the temperature limits of 100° F. and 210° F. in seconds Saybolt Universal (S. S. U.). Using this method of classifying and rating lubricating oils, the best petroleum lubricating oils economically obtainable by refining of crude petroleum oils have a viscosity index (V. I.) of the order of 100 and, with special solvent extraction, up to 110 or 115. But, at the same time, the lubricating oils must meet grade requirements with respect to viscosity ranges determined, for example, by S. A. E. numbers which indicate whether the oil is too heavy, too light, or suitable for a certain use.

A variety of thickening V. I. improvers have been developed. These have been characterized largely by linear chain or two dimensional polymeric compounds having molecular weights above 800, derived mainly by simple polymerization, condensation, or copolymerization of low molecular weight monomeric reactants. In order to

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be useful as V. I. improvers, these synthetic polymeric compounds must meet with certain requirements of oil-solubility, effectiveness in low concentrations, and stability under operating conditions to which the oil blends are subjected.

Notable examples of satisfactory V. I. improving thickeners are the highly saturated aliphatic hydrocarbon polymers typified by the polybutenes, preferably having a molecular weight of at least 5,000 which are derived by low temperature catalytic polymerization of pure isobutene or isobutene in mixtures with other olefins. Methods for the preparation of these polymers are described in the prior art. Other analogous aliphatic hydrocarbon V. I. improvers include soluble linear type polyethylene of about 2,000 to 3,000 mol. wt., hydrogenated diolefin polymers and copolymers of olefins with diolefins.

In addition to the aliphatic hydrocarbon polymer V. I. improvers, there have been developed aliphatic-aromatic types of polymers, represented by condensation polymers of alkyl halides with aromatic hydrocarbons, e. g. chlorinated wax with naphthalene, also, various oxygen-containing condensation polymers represented by polymerized acrylates, preferably having a molecular weight of at least 5,000 e. g. polymerized laurylmethacrylate, polymerized vinyl esters, glycol-dicarboxylic acid polyesters, e. g. decamethylene glycol methyl dilinoleate polyesters, polymerized 12-hydroxy stearic acid, and the like.

In accordance with the present invention, the V. I. improving effectiveness of the thickening polymers is greatly improved with a beneficial restriction in thickening of the oil blend by an added blending agent which is substantially immiscible with the thickening additive at temperatures below about 100° F., but which, nevertheless, in suitable proportions forms a homogeneous blend with the thickened oil and substantially lowers the viscosity of the blend at these temperatures. The agents which act in this capacity will be referred to as non-solvent modifiers of the thickening V. I. improvers.

Another desirable property of the modifying agents used for controlling the thickening action of the thickening V. I. improvers in a lubricating oil is a suitably high flash point and low volatility to avoid impairment in the flash point value of the petroleum oil base and avoid loss by vaporization.

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From a study of a large number of compounds for their effects on the thickening of oil blends, it was noted that modifiers of the thickeners which behave satisfactorily in desired low concentrations for the present purposes, in general, are polar organic compounds having dielectric constants substantially higher than those of the thickeners and hydrocarbon oils, e. g. substantially above 4 at 20° C. Although, such polar compounds are non-solvents for the thickening polymers at 0° F. to 100° F., they tend to have solvency for the polymers at above 100° F. in a hydrocarbon oil.

A test procedure which may be used to predetermine whether a polar organic compound has adequate non-solvent action on the polymer consists simply in dissolving a quantity of the polymer in a clear, colorless, light hydrocarbon solvent, such as naphtha, or kerosene, e. g. 10% by weight of the polymer in 25 cc. of the liquid solvent, then adding slowly, with slight agitation, to the resulting solution, the polar organic compound to be tested. If the polar organic compound added in an amount of about 5 to 75 cc. causes precipitation of the polymer from the solution, observed by the formation of turbidity, or separation of the polymer, then the polar organic compound is indicated to have the desired non-solvent property. However, while the polar compounds having lowest miscibility with the polymer prove to be the most effective modifiers, it is also important that effective amounts of such polar compounds be capable of being blended with or homogeneously dispersed in the thickened oils containing the polymer.

Among polar organic compounds tested and found to give favorable results in restricting the thickening action of polybutene and increasing the V. I. improving effectiveness of this polymer in hydrocarbon oil blends are high boiling oxyesters, such as dibutoxy ethyl phthalate, butylacetyl ricinoleate and triethylene glycol di-2-ethyl butyrate. The potency of these compounds for controlling the thickening effect of the polymer with added V. I. improvement depends upon a number of factors, hence all polar organic compounds, including those represented by high boiling oxygen-containing compounds, do not give exactly the same effects. For example, although castor oil is a non-solvent for the hydrocarbon polymer at ordinary temperatures, it was found ineffective by itself, because it could not be homogeneously blended with the thickened oil. However, castor oil could be used together with a more oil-soluble modifier, e. g., dibutoxy ethyl phthalate. Lower alkyl phthalate esters, such as methyl and ethyl phthalates, behave somewhat like castor oil. Thus, it is important to use a non-solvent modifier which blends homogeneously with the thickened oil despite its non-solvency for the thickener at ordinary temperatures.

The hydrocarbon oils to be used in the oil blends may be of any preferred type, such as those derived from the ordinary paraffinic, naphthenic, asphaltic, or mixed base crude petroleum stocks by suitable refining practices, or by synthesis. The hydrocarbon oil component is not limited to any specific viscosity or boiling range, other than by the specification for the purpose they are to be employed, but generally those ranging from the gas oil to heavy lube oil boiling range are preferred. In making improved industrial oils, the hydrocarbon oil may have to meet certain high flash point and volatility re-

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quirements; in making lubricating oils, the hydrocarbon oil component should be substantially non-volatile and meet minimum flash point requirements.

The particular type of thickening V. I. improver to be used may vary with the type of hydrocarbon oil and the purpose of the blend. This component may amount to about 1% to 15%, or higher, by weight of the finished blend, but is generally used in motor oils in a proportion of about 1% to 5% by weight.

The nature and quantity of the thickener modifying agent also depends upon the particular hydrocarbon oils, the particular V. I. improving thickening agent, and the proportions of these components in the finished blend. With common types of petroleum lubricating oils and preferred aliphatic hydrocarbon polymers of the polybutene type as the V. I. improving thickener, the non-solvent modifier is preferably used in a proportion of about 1% to 50% by weight of the total blend, and for the sake of economy, in as small a proportion as possible, e. g., about 5 to 40%. The effects of various thickening and modifying blending agents in the oil blends will be apparent from the test results reproduced hereinafter.

One procedure used in formulating blends of the thickeners with petroleum oils and the added non-solvent modifier to control the action of the polymer was to blend the non-solvent modifier with a petroleum base oil together with a small proportion of more viscous oil until the viscosity of this blend corresponded closely to the original viscosity of the base oil at 210° F. for reference purposes, after which the thickening V. I. improver was added to the oil blend, slightly warmed and with agitation. The viscosities of the resulting blends were then determined accurately at 100° F. and 210° F. in order to observe the effects of the non-solvent modifier.

The amount of the thickening V. I. improver added to the oil in the blends was completely soluble in the hydrocarbon oil and was completely soluble in the blends with the non-solvent modifiers used in proper proportions, so that the heating and agitation of the blend is simply to facilitate solution. The procedure of the blending may be varied as desired. The non-solvent modifier for the thickening V. I. improver may be added subsequent to the thickening of the hydrocarbon oil, simultaneously with the thickener, and in practice be used without the added small proportion of more viscous hydrocarbon oil.

In a specific investigation of how a satisfactory non-solvent for the thickener acts, use was made of the Staudinger method for determining viscosity characteristics of the thickening polymer, as explained in Staudinger's articles, *Trans. Faraday Soc.* 29, 30 (1933). It was observed that a non-solvent modifier for the thickening polymer tends to reduce the specific viscosity of the polymer at lower temperatures, below about 100° F., with less reduction or even some increase at higher temperatures, thereby decreases the differential of the specific viscosities with respect to increase in temperature, and thus makes the desired modification in the thickening action of the polymers. This effect is illustrated by the following data, in which N_{sp} denotes the specific viscosity (ratio of viscosity coefficient of thickened oil to that of the oil minus 1) and C denotes the concentration of the polymers having varying molecular weights which were tested in samples of the same petroleum lubricating oil.

TABLE 1

Viscosity characteristics of polybutenes in hydrocarbon oil blends

Approx. M. W. of Polybutene	20° C. $N_{sp}/C.$	45° C. $N_{sp}/C.$	65° C. $N_{sp}/C.$	Differential of Specific Viscosities Unit Change in $N_{sp}/C.$ 20° to 65° C.
20,000	0.24	0.20	0.15	0.09
45,000	0.28	0.24	0.18	0.10
98,000	0.42	0.35	0.26	0.16

TABLE 2

Viscosity characteristics of polybutenes in hydrocarbon oil blends with 10% non-solvent (dibutoxy ethyl phthalate)

Approx. M. W. of Polybutene	20° C. $N_{sp}/C.$	45° C. $N_{sp}/C.$	65° C. $N_{sp}/C.$	Differential of Specific Viscosities Unit Change in $N_{sp}/C.$ 20° to 65° C.
20,000	0.19	0.18	0.16	0.03
45,000	0.23	0.22	0.20	0.03
98,000	0.40	0.36	0.33	0.07

To illustrate how the non-solvent modifier acts to beneficially decrease thickening and at the same time improve viscosity-temperature characteristics of the polymer thickened oil on the V. I. scale, the following data are presented:

TABLE 3

	S. S. U. Vis. at—		V. I.
	100° F.	210° F.	
Hydrocarbon reference oil (S. A. E. 10 W)-----	93.8	37.32	8.9
Blends with Thickener and Modifier used Separately			
36% Dibutoxy ethyl phthalate (+4% Oil of 65 S. S. U. at 210° F.)-----	89.64	36.74	9.7
2% Polybutene 13,000 M. W.-----	227.7	51.63	128.0
Blends with thickener and Modifier used Together			
2% Polybutene+36% Dibutoxy ethyl phthalate (+4% Oil of 65 S. S. U. at 210° F.)-----	121.5	46.04	171.7

The data in Table 3 illustrate how the modifier itself has little effect on the V. I. of a base oil, but when used in conjunction with the thickening V. I. improver, considerably increases in V. I. and beneficially lowers the thickening at the lower temperature level (100° F.), so that the resulting blend is more useful as a lighter grade, lower power-consuming lubricating oil of highly improved V. I. value.

Pronounced beneficial effects were also obtained with polybutene in a high V. I. petroleum lubricating oil base having a V. I. of 102, and also in hydrocarbon oils of extremely low V. I., e. g. a naphthenic lube oil phenol extract having a V. I. of -77, and with other polymers, e. g., an aliphatic-aromatic hydrocarbon V. I.-improving polymer made from chlorwax (of about 20 to 25% Cl) and naphthalene according to U. S. Patent 2,339,493, and a polylauryl methacrylate.

Additional specific types of compounds found to act effectively as soluble non-solvent modifiers for obtaining blends of improved V. I. with lower viscosity at temperatures below about 100° F.

in clear, thickened hydrocarbon oil blends are represented by:

Butyl-acetyl ricinoleate
Diethylene glycol (mono) laurate
Triethylene glycol di-2-ethyl butyrate
Triethylene glycol di-2-ethyl hexate
Glyceryl oleate
Diglycol oleate
Butoxy ethyl stearate
Methoxy ethyl oleate
Butyl stearate
Tributyl acomitate

Mixtures of two or more soluble non-solvents may be used. The number and variety of effective modifiers is much larger than shown by the illustrative specific examples and can be further extended by the use of the guiding explanations given.

For the sake of brevity, some of the other types of polar compounds that satisfy the requirement of being non-solvents for the thickening polymers and useful for modifying the polymers in the thickened oil blends are included in the following classes: halogenated hydrocarbons, alcohols, ethers, ketones, phenols; also nitrogen-containing and sulfur-containing organic compounds, e. g. nitro compounds, amines, thioethers and the like.

While in lubricating oils the non-solvent modifier preferably should have no substantially greater volatility than the lightest component of the hydrocarbon oil and no lower flash point than the hydrocarbon components, in some instances, e. g., in some light industrial oils, which are less viscous than lube oils, it may be desirable to have the modifier as completely volatile as the hydrocarbon oil or solvent component. Examples of effective volatile modifiers are ethylene dichloride, isopropyl alcohol, mesityl oxide, ethyl ether, nitroethane and acetonitrile.

Some of the modifiers are more effective than others on account of their greater non-solvent action on the thickeners. It is apparent that a number of the preferred modifiers for use in lubricating oils are high boiling oxy-esters, i. e. hydroxy or alkoxy esters. Some of the modifiers are more effective with one kind of thickener than another. For example, methoxy ethyl oleate appears to be more effective than triethylene glycol di-2-ethyl butyrate with a polyacrylate thickener.

The non-solvent modifiers may be only partially miscible with the hydrocarbon oils, which occurs often in the case of highly potent modifiers. Those having too low solubility in the hydrocarbon oil for making a homogeneous blend may be used beneficially together with a more oil-soluble modifier.

Copending application Serial No. 695,560, filed September 7, 1946, is particularly directed to the use of several non-solvents, at least one of which is substantially insoluble in the mineral oil base-stock being used, and at least one of which is soluble therein and serves to solubilize the insoluble one.

The use of castor oil as an insoluble non-solvent modifier illustrates the importance of homogeneously blending the modifier with the thickened oil to secure a further improvement in V. I. and at the same time restrict thickening. Castor oil is found to restrict thickening to some extent in low concentrations with a polybutene thickened oil, but it also lowered the V. I. and made the solution cloudy. When the castor oil was

jointly used in small concentrations with a more oil-soluble modifier, dibutoxy ethyl phthalate, in the polybutene thickened oil, the blend was clear, the thickening was reduced, and the V. I. of the thickened oil was increased considerably, the test results being as follows:

amount of solubility and insolubility of the non-solvents in the hydrocarbon oil base stock, according to the particular V. I.-improving polymer being used. In general the amount of insoluble non-solvent to be used should be about 0.5 to 10%, preferably about 1 to 5%.

TABLE 4

Per Cent Comp.			Per Cent Polybutene ¹	Vis./210° F.			V. I.		
Oil	Castor Oil	D. e. p. (90% +10% oil)		0	1	2	0	1	2
100				36.3		50.6	13.0		124.4
73		27		37.1		47.4	11.2		132.9
64		36		36.7	(39.9)	46.0	9.7	(105)	171.7
90	1	9		37.7		48.3	20.5		122.1
80	2	16		37.5		46.4	14.2		126.0
64	3.6	32.4			44.6			157	

¹ Added as 20% solution of polybutene, about 13,000 mol. wt., in a light blend oil.

The data in Table 4 show that 3.6% of castor oil (insoluble non-solvent) with 32.4% of dibutoxy ethyl phthalate (soluble non-solvent) produce a V. I. of 157 compared to only about 105 without the castor oil, in a mineral oil containing 1% of polybutene.

Hydrogenated castor oil considered to have more oil solubility than castor oil, also increased the thickening action of the polymer and adversely affected the viscosity index of the oil when used alone as a modifier and further demonstrated the need of having the modifier homogeneously blended with the thickened oil.

Another set of tests, in which castor oil was used as insoluble non-solvent in a paraffinic mineral lubricating oil base stock having a V. I. of about 102, the soluble non-solvent used being a mixture of two different soluble esters, namely, diglycol laurate S and diglycol oleate, with and without polybutene showed that when 3% of castor oil is used along with 27% of the soluble non-solvent mixture, which has the effect of solubilizing the castor oil in the mineral oil, the mixed non-solvents are then very potent in improving the V. I. when polybutene is used (149 V. I. with the non-solvent, compared to 124 without the non-solvent).

Some compositions of a substantially different nature, and intended for use as hydraulic oils, were made by using as mineral oil base stock, a Columbian gas oil, which has a viscosity so far below of the ordinary lubricating oil viscosity range and using rapeseed oil as insoluble type non-solvent for the polybutene, and triethylene glycol di-2-ethyl hexoate as soluble non-solvent. The blend containing the polymer and non-solvent has substantially better viscosity-temperature relationships than the base stock alone.

As an insoluble non-solvent, one may use a number of other materials than the castor oil, hydrogenated castor oil and rapeseed oil mentioned above, for instance, other hydroxy fatty oils, various esters and other organic compounds containing a relatively high proportion of oxygen compared to carbon and hydrogen, and which preferably have less than 3 carbon atoms for each oxygen atom in the molecule, such as the lower alkyl phthalates, e. g., methyl phthalate and ethyl phthalate. But butyl phthalate and other higher alkyl phthalates are sufficiently soluble in hydrocarbon lubricating oils that they act as soluble non-solvents for the polymer instead of as insoluble non-solvents. Thus one may use a mixture of higher and lower alkyl phthalates in controlled proportions to obtain exactly the desired

By "substantially insoluble non-solvent" is intended to mean one insoluble, or having a solubility of less than 3% by weight, in mineral oil at room temperature. The polymer used should normally not swell or get tacky if immersed in such a non-solvent.

The modified thickened oil blends, prepared in accordance with this invention, may contain two or more different types of thickeners and two or more different types of modifiers. They may also contain small amounts of other kinds of oil additives used for stabilizing, dyeing, inhibiting oxidation, imparting oiliness, lowering the pour point, etc.

It has now been found that unexpected advantages are obtained by using in a single oil composition two or more polymers which supplement each other's V. I.-improving characteristics in such a way as to obtain better results with the combination than would be expected from the sum of the several separate constituents. Although there is some evidence that two different V. I.-improving polymers supplement each other with unexpected advantages even in the absence of a non-solvent, the unexpectedly superior results are greatest and more surprising when a non-solvent is used. Even two or more non-solvents may be used to advantage, particularly by selecting ones which are separately most effective for each of the different polymers used.

One theory as to the reason for obtaining the unexpected advantages with a plurality of polymers, is that the solubility characteristics of any one particular polymer are likely to be quite different from the solubility characteristics of almost any other type of polymer not belonging to the same homologous series. Thus each polymer may be considered to have its own characteristic critical complete solution or thickening temperature, i. e. the temperature at which maximum thickening occurs when being heated, or at which the degree of thickening starts to lessen when being cooled, and it is believed that the unexpected advantages of this invention may accrue from the fact that when a hot solution containing two or more polymers and a non-solvent is cooled gradually, one of the polymers first has its solubility reduced to such an extent as to reduce its thickening action, and then as the solution is cooled further, the other polymer in turn has its solubility and thickening action reduced.

The following experimental data will illustrate the use of a plurality of polymers in a lubricating oil composition with a non-solvent.

EXAMPLE I

A series of tests was made in which a highly paraffinic solvent extracted mineral lubricating oil base stock, having a viscosity of 43 seconds Saybolt at 210° F., was blended with various concentrations of a polybutene of about 12,000 molecular weight and a polyoctadecyl methacrylate of about 17,000 molecular weight, both with and without 12% of dibutyloxyethyl phthalate as non-solvent. The viscosity and V. I. of each blend were determined, and the results are summarized in the following table:

TABLE 5

Polybutene and polyacrylate

Blend No.	Polymer Blend Ratio		Per cent Total Polymer	Without Non-Solvent		With 12% Non-Solvent	
	Polybutene	Polyacrylate		Cs. Visc. at 210° F.	V. I.	Cs. Visc. at 210° F.	V. I.
1	0	all	6	12.16	148	12.0	153
2	0	all	3	8.34	143	8.14	147
3	0	all	1	6.37	131	6.14	133
4	1	3	6	13.72	144	13.42	145
5	1	3	3	8.83	140	8.41	141
6	1	3	1	6.55	130	6.22	132
7	3	3	6	19.19	141	18.84	149
8	3	3	3	9.93	138	9.16	148
9	3	3	1	6.71	135	6.22	139
10	3	1	6	20.62	138	20.81	138
11	3	1	3	10.62	135	10.42	135
12	3	1	1	6.88	130	6.21	132
13	all	0	6	22.91	135	21.84	136
14	all	0	3	11.22	132	10.98	133
15	all	0	1	7.03	126	6.92	128

The above data show in (blends 1-3) that when the polyacrylate is used without any polybutene the V. I. obtained is 148 without non-solvent and 153 with non-solvent, in the case of a 6% polymer concentration, whereas when only 1% of polymer was used the non-solvent only effected an increase in V. I. from 131 to 133. On the other hand, if a mixture of polybutene and polyacrylate is used in which the polybutene represents 25% and the polyacrylate 75% of the polymer mixture (blends 4-6), the use of a non-solvent effected likewise only a relatively minor increase in V. I. from 144 to 145 in the case of 6% polymer concentration and from 130 to 132 in the case of 1% polymer concentration. However, if the polybutene and polyacrylate are used in equal proportions (as in blends 7-9) then the non-solvent effects a surprisingly great increase in V. I. from 141 to 149 in the case of 6% polymer and from 131 to 139 in the case of 1% of polymer.

To further emphasize how unexpectedly superior the results are that were obtained with mixtures of the two polymers, particularly when used in equal proportions, the V. I. data obtained in 5 blends, namely blends Nos. 3, 6, 9, 12, and 15, representing in all cases a lubricating oil composition containing 1% of total polymer and 12% of non-solvent, and the polymer representing various mixtures of polybutene and polyacrylate, were plotted graphically on a chart shown in the accompanying drawing. In this chart the V. I. is plotted vertically on the scale ranging from 125 up to 140, against the per cent of polyacrylate in the polymer mixture with polybutene, on the horizontal axis, ranging from 0 to 100% of polyacrylate in the polymer mixture.

As shown in Table 1 and in the drawing, if the 1% of polymer used is all polybutene (blend No. 15), the V. I. obtained (with the non-solvent) is 128 as shown at the left side of the chart. On the other hand, as shown at the right side of

the chart, if the 1% of polymer used is all polyacrylate (blend No. 3), the V. I. obtained is 133. It would therefore be expected that mixtures of the two polymers, when used in a total concentration of 1%, would have V. I. blend values following along the dotted line on the chart, as could readily be calculated arithmetically according to the proportionate V. I. effect of each polymer. However, the V. I. blend data obtained, particularly in the case of equal proportions of the two polymers (blend No. 9) and shown at the upper and middle portion of the chart, were surprisingly higher than what would be expected.

From a consideration of these data on the 1% total polymer blends, and also those for the 3% and 6% total polymer blends, it is apparent that the outstandingly superior and unexpected results are obtained chiefly in mixtures containing about 30 to 70% of the one polymer with the balance of 70 to 30% of the other polymer.

EXAMPLE II

In another series of tests polybutene having an average molecular weight of about 12,000 and a soluble polyethylene having a molecular weight of about 2,000 to 3,000 were used in admixtures of several different proportions as V. I. improvers in the same highly paraffinic lubricating oil base stock as used in the above Example I. The viscosity and V. I. data obtained are as follows:

TABLE 6

Polybutene and polyethylene

Polymer Blend Ratio		Without Non-Solvent		With 15% Non-Solvent		Increase in to Non-Solvent
		S. S. U. at 210° F.	V. I.	S. S. U. at 210° F.	V. I.	
0	0	43.1	112	39.6	108	-4
2.0	2.0	73.74	139	68.4	148	9
2.0	6.0	80.20	144	78.3	155	11

The above data show that the use of 15% of dibutyloxyethyl phthalate as non-solvent produced increases in V. I. of 9 and 11, respectively, in the blend containing 2% of polybutene and 2% of polyethylene, and in the blend containing 2% of polybutene and 6% of polyethylene.

EXAMPLE III

Another set of tests was made like the tests in Example II except that in place of the polyethylene a polyester was used which had a

molecular weight of about 12,000 and was made by condensing decamethyleneglycol with methyl-dilinoleate. The polybutene and the non-solvent used were the same as in Example II. The viscosity and V. I. results of the blends were as follows:

TABLE 7
Polybutene and polyester

Polymer Blend Ratio		Without Non-Solvent		With 15% Non-Solvent		Increase in V. I. due to Non-Solvent
Percent Polybutene	Percent Polyester	S. S. U. at 210° F.	V. I.	S. S. U. at 210° F.	V. I.	
0	0	43.0	112	39.8	108	-4
2.0	3.0	73.79	138	74.8	153	15
2.0	6.0	80.10	149	79.6	158	9

This table also shows that the use of the non-solvent produced substantial increases in V. I., namely 15 and 9, in the two blends containing 2% of polybutene and 3% and 6% respectively of polyester. In this case the mixture containing 60% of polyester and 40% of polybutene gave the greatest increase in V. I.

Although not pertaining to the use of two different V. I.-improving polymers, the following data illustrate various other ways of applying the general principles disclosed in this application and the parent application, namely, by the cooperation of a V. I.-improving polymer and various types of non-solvents.

12 ml. of isoamylbutyrate, which is a simple or non-oxy ester, were dissolved in 50 mls. of a naphthenic base light lubricating oil base stock having a viscosity of 42.8 cs. at 78° F. The blend had a viscosity of 9.35 cs. 1% by weight of a polybutene having a molecular weight of about 104,000, was dissolved in a sample of the plain oil base stock thereby giving a polymer-oil blend having a viscosity of 192.9 cs. at 78° F., whereas a 1% solution of the same polymer in the ester-oil blend resulted in a composition having 23.8 cs. viscosity. Thus the polymer effected an increase in viscosity of the pure oil base stock from 42.8 to 192.9 cs. viscosity and this amounted to a relative viscosity of 4.50, whereas the ester solution increased in viscosity from 9.35 to 23.8 by the addition of the polymer and this amounted to a relative viscosity of 2.54. Similarly the viscosity of the plain polymer-oil blend and the ester-polymer-oil blend were tested at 100° F. and 210° F., and the results summarized as follows:

TABLE 8

	Vis. (cs.) of Solvent	Vis. (cs.) of Polymer-Solvent Blend	Relative Vis.
Oil.....	42.8	78° F. 192.9	4.50
Oil+ester.....	9.35	23.8	2.54
Oil.....	22.5	100° F. 103.2	4.60
Oil+ester.....	6.26	17.0	2.71
Oil.....	3.61	210° F. 13.1	3.61
Oil+ester.....	1.93	4.6	2.38

The per cent change in relative viscosity of the plain polymer-oil blend over the temperature range 78° F. to 210° F. was -19.55. The corresponding per cent change in relative viscosity of the ester-polymer-oil blend was -6.30, thus indicating that the ester non-solvent, name-

ly the isoamylbutyrate, greatly reduced the relative change in viscosity with temperature.

Illustrating the use of an alcohol as a non-solvent, a blend was made of 20% by volume of n-hexanol in 80% by volume of a naphthenic lubricating oil base stock having a viscosity index of 50. The resulting hexanol-oil blend had a viscosity of 158.2 S. S. U. at 100° F. and 39.98 S. S. U. at 210° F., giving a V. I. of -66.92 for the blend. When 2% by weight of polybutene having an average molecular weight of about 12,000, was dissolved in the above mentioned hexanol-oil blend, the resulting thickened oil composition had a viscosity of 293 S. S. U. at 100° F. and 50.90 S. S. U. at 210° F., thus giving a V. I. of 87.2 for the polymer-hexanol-oil blend. This is a tremendous improvement over the V. I. of -66.92 of the hexanol-oil blend per se.

A number of different ethers were blended in 10% concentration in a Columbian gas oil distillate, and 5% by weight of polybutene having a molecular weight of about 12,000 was dissolved in the blend. The resulting compositions which had properties useful for hydraulic oil purposes were subjected to viscosity tests at -40° F. and 150° F. Since this temperature range is considerably below the range of 100° F. to 210° F. over which the viscosity index is determined, it is not possible to actually determine the viscosity index of these blends. However, it is possible by comparing the viscosity at -40° F. with that of 150° F. to observe which blends show the lowest rate of change of viscosity with temperature. The data obtained in this series of tests is as follows:

TABLE 9

Type of Ether used in the Blend	Viscosity (cs.) at —	
	-40° F.	150° F.
Amyl Xylol Ether.....	1,186	10.63
Amyl Phenyl Ether.....	821	9.84
Amyl Beta Naphthyl Ether.....	793	9.42
Amyl Benzyl Ether.....	737	10.21
t-Butyl-2-Cl.-phenyl (2-Cl.-ethyl) Ether.....	1,616	10.18

The above data in Table 9 showed that amylbenzyl ether gave the best results because the blend containing it had a viscosity of only 737 cs. at -40° F. and had a viscosity of 10.21 cs. at 150° F., whereas the tert.-butyl-2-chlorophenyl (2-chloroethyl) ether produced a blend having a viscosity of 1616 cs. at -40° F. and yet only 10.18 cs. at 150° F. All of the above ether blends showed that the ether used was an effective non-solvent for improving the V. I. properties of the polybutene-oil solution.

As an illustration of the use of a halogen-containing organic compound as a non-solvent, 22 ml. of monochlorbutoxyethyl stearate was dissolved in 100 ml. of a Columbian distillate oil of the gas oil boiling range, and 2.4 gms. of an 11,000 molecular weight copolymer of isobutylene and octadecene-1 were added. This copolymer was made at -89° C. by copolymerization of 5% of octadecene-1 with 95% by volume of isobutylene with an aluminum chloride catalyst. The resulting blend had a viscosity of 81.90 S. S. U. at 100° F. and 43.89 S. S. U. at 210° F., thus giving a V. I. of 211, which is remarkably high considering the large amount of gas oil of low V. I. which is present in the blend.

In another series of tests various amounts of sebacic dinitrite were used as non-solvent in a

Columbian gas oil base stock which had been thickened with 3.2% by weight of a 12,000 molecular weight polybutene, and the resulting blends were subjected to viscosity tests at three different temperatures ranging from -40° F. to 150° F., with the following results:

TABLE 10

Percent Non-Solvent	Viscosity (cs.) at —		
	-40° F.	100° F.	150° F.
3.....	550	10.38	5.66
3.....	550	10.37	5.68
5.....	550	10.42	5.69
7.....	540	10.72	6.13
30.....	540	11.67	6.31
50.....	545	11.68	7.29

These data show that the polymer-oil-non-solvent blends have a lower rate of change of viscosity with temperature, as the amount of non-solvent used is increased from 3% up to 50%. It is noted that the viscosity of the various blends was very closely similar at -40° F. regardless of how much non-solvent was used, but that the blends showed much greater differences at 150° F., the result indicating that the greater amount of non-solvent caused the greater thickening at the higher temperature. The data indicate that at least about 10% of the non-solvent is required in this case to produce a substantial improvement in the viscosity-temperature relationship.

Several examples are now given to show how oil compositions, useful particularly as hydraulic oils, recoil oils, watch lubricants, etc., may be prepared by dissolving a high molecular weight hydrocarbon polymer in a highly aromatic extremely low V. I. oil base stock. In one example 1% of polybutene having a molecular weight of about 54,000 was dissolved in 99% by weight of paracymene which is methylisopropyl benzene, a liquid having a freezing point of -73.5° C. and a boiling point of about 176° C., the viscosity thereof being far below the range suitable for determining viscosity index. The resulting blend showed a viscosity of 41.05 S. S. U. at 100° F. and 35.96 S. S. U. at 210° F., thereby making the tremendously high V. I. of 315.4. In other words, this blend showed only a very slightly lower viscosity at 210 F., than it did at 100° F. Another blend was made by dissolving in tetrahydronaphthalene 1% of a V. I. improver made by condensing chlorinated paraffin wax

having a chlorine content of about 25% with naphthalene. The resulting blend had a viscosity of 44.57 S. S. U. at 100° F. and 37.35 S. S. U. at 210° F., thereby indicating a viscosity index of 311.2, which is also extremely and unexpectedly high. This same principle of the invention may be applied to higher boiling aromatic low V. I. oil base stocks within the lubricating oil boiling range by dissolving polybutene or other high molecular weight V. I. improving polymer in a solvent extract of a petroleum lubricating oil base stock having a V. I. below -70 and preferably below -100, as for instance a phenol extract of a lubricating oil distillate, which extract has a V. I. of about -190. These extremely low V. I. oil base stocks are such relatively poor solvents for the high molecular polymers, e. g. polybutene, that it is not necessary to use a non-solvent to obtain the desired reduced solubility or thickening action at low temperature while yet obtaining the desired thickening action at elevated temperature.

The present invention has been illustrated by numerous examples but is not intended to be limited thereby, nor is it intended to be limited by any theory on the mechanism by which the improvement is obtained, nor to any particular kind of hydrocarbon oil, polymer, modifier, or blend. Any modification which comes within the spirit of the invention is intended to be included within the scope thereof as defined in the following claim.

We claim:

A lubricating oil composition comprising a hydrocarbon lubricating oil blended with about 3% by weight of a polybutene having a molecular weight of about 12,000, a substantially equal amount of a polyacrylate having a molecular weight of about 17,000, and with about 12% by weight of dibu oxy ethyl phthalate.

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