

UNITED STATES PATENT OFFICE

2,344,912

LUBRICATING OIL BLEND

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No Drawing. Application April 15, 1942,
Serial No. 439,082

6 Claims. (Cl. 252—59)

This invention relates to hydrocarbon lubricat-
ing oil blends with additives that effect improve-
ment in viscosity characteristics. More particu-
larly, it relates to novel additives characterized
by highly aromatic type polymers of tri-aryl- 5
methyl radicals.

An object of this invention is to provide lubri-
cating oil compositions of enhanced viscosity
index characteristics.

Another object is to provide homogeneous lu- 10
bricating oil blends with a viscosity index im-
prover which is highly effective in paraffinic oils
and proper mixtures of paraffinic oils with
naphthenic type or lower viscosity index oils.

A further object of this invention is to provide 15
oil blends with a viscosity index improving
additive that has a distinctively high stability
against mechanical breakdown.

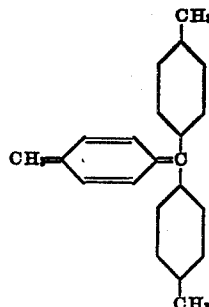
Other objects and advantages will appear from
the following description.

Unlike polymers of olefinic substances which
have thus far been found most practical as vis-
cosity index improvers, highly aromatic type
polymers of the present invention have a rela-
tively low solubility in paraffinic petroleum lubri-
cating oils. They have a greater resistance to
mechanical breakdown. Also they exhibit better
ability to improve the viscosity index of lubricat-
ing oils with less thickening.

In a specific embodiment of this invention it
was found that polymer products resulting from
disproportionation of tri-arylmethyl radicals are
useful blending agents or additives for accom-
plishing the object set forth. While there is still
more to be learned about the structure and com-
position of these polymers, investigations have
indicated that they contain a quinoid type unit
which is unsaturated and thus readily absorbs
oxygen or similar reactive substances. Basically,
these polymers are formed by the coupling of
free tri-arylmethyl radicals which might be de-
rived by several types of reactions, such as (1)
dissociation of hexa-aryl ethanes, (2) dispropor-
tionation of tri-arylmethane resulting from the
removal of hydrogen from a free tri-arylmethyl
radical, and (3) by electrolysis of aromatic
Grignard reagents.

The tri-arylmethyl molecules which give the
desired polymerization products have been rep- 50

resented as having the following type of struc-
ture:



This structure is subject to variation with re-
spect to the alkyl substituents in the aryl groups
as, for example, some of the aryl groups may be
phenyl radicals, or some of the aryl groups may
contain higher alkyl substituents, but so far it
has been found preferable to have in the unit a
para-methyl-phenyl or tolyl group.

In studying the properties of these polymers,
it was observed that their effectiveness as viscosity
index (V. I.) improvers is very high when they
are used in small concentrations coming within
the low limits of their solubilities in any lubri-
cating oil with which they are to be blended, and
preferably these concentrations are in the range
of about 0.1% to about 1%.

To illustrate the invention, the following typi-
cal example is given:

EXAMPLE 1

The polymer tested as a petroleum lubricating oil
additive was the polymeric product derived from
the disproportionation of tri-p-tolylmethyl. This
polymeric material consisted of a brownish-yel-
low powder which was fairly soluble in hexane,
in benzene, and in tetrahydronaphthalene but al-
most insoluble in ether. Descriptions of methods
for preparing these polymers are given in the
Journal of the American Chemical Society, vol.
61; October 1939, pages 2769 to 2775; vol. 63,
September 1941, pages 2316 to 2320; and October
1941, pages 2574 to 2576. In accordance with
these articles, a convenient method of prepara-
tion consists in heating tri-p-tolylmethyl chlo-
ride under reflux conditions with dry pyridine in

an atmosphere of nitrogen. Under these conditions, the chloride is considered to be decomposed to the free tri-p-tolylmethyl radical, which in turn undergoes a rearrangement known as disproportionation to yield tri-p-tolylmethane and the free radical having a high degree of unsaturation which may assume a quinoid structure that finally results in a polymeric residue.

The polymer thus obtained was used to formulate blends with a naphthenic mineral lubricating oil having a V. I. of 65.8 and with a paraffinic lubricating oil having an original V. I. of 110.8. The effects of the added polymer on the viscosity characteristics of these oils are shown in the following table:

TABLE I

Base lubricating oil	Percent tri-p-tolylmethyl polymer added	Saybolt seconds Universal viscosity at—		V. I.
		100° F.	210° F.	
Naphthene base.....	0	92.32	38.10	65.8
Do.....	1	107.7	41.20	136.0
Paraffin base.....	0	158.2	44.37	110.8
Do.....	1	173.0	47.00	129.0

The results shown in the foregoing table demonstrated that the tri-arylmethyl polymer has exceptionally high V. I. improving potency combined with a desirably restricted thickening action as compared to polymerized olefins which have considerably higher solubility in paraffinic petroleum oils. For example, a comparison may be made with a representative isobutylene polymer thickener blend with the same type of paraffinic base oil. The effects of this thickener are shown in the following table:

TABLE II

Base lubricating oil	Percent isobutylene polymer added	Saybolt seconds Universal viscosity at—		V. I.
		100° F.	210° F.	
Paraffin base.....	None	158.2	44.37	110.8
Do.....	0.6	197.4	48.68	128.1
Do.....	1.2	248.0	54.18	132.2

By comparing the effects of the two types of polymer in the paraffin base lubricating oil, it can be seen that the tri-p-tolylmethyl polymer raises the viscosity of the oil at 100° F. only by about 10% in giving substantially the same V. I. improvement as obtained in thickening the same base oil with the isobutylene polymer at 100° F. to the considerably greater degree of more than 20%. Thus, the highly aromatic polymer is much more effective for increasing the V. I. of the paraffinic oils with restricted thickening, which is an important factor in maintaining the grade of the lubricating oil.

Breakdown tests on the highly aromatic polymer very clearly demonstrated its high resistance to mechanical breakdown as is shown in the following results obtained when the paraffin base oil containing 1% of the tri-tolylmethyl polymer was forced through the capillary tube 4.55 cm. in length and 0.0109 cm. in radius. After each passage through the capillary tube, the viscosity characteristics of the polymer blend were determined and these showed no appreciable change in the viscosities and therefore no appreciable breakdown of the polymer.

TABLE III

Pressure viscosimeter breakdown test

Pressure lbs./sq. in. 1440
 Rate of flow g./minute 17.2
 Temperature ° F. 92

Pass number	Saybolt seconds Univ. viscosity at—	
	100° F.	210° F.
0.....	173.0	47.00
1.....	173.0	47.02
2.....	173.1	47.00

In contrast to the above results, in general, the linear aliphatic polymer V. I. improves with molecular weights above 10,000 undergo a substantial breakdown in the initial passes through the pressure viscosimeter capillary tube at 92° F. as is exhibited by substantial decreases in the viscosities of the oil blends containing them.

As already mentioned, the described highly aromatic polymers contain a certain amount of unsaturation which makes them readily add on oxygen, but in place of oxygen, other substances which react with double bonds may be incorporated into the polymers as, for example, hydrogen, halogens, sulfur, or similar metalloids, organic groups, or metal-containing groups.

One may take fuller advantage of the high V. I. improving effectiveness of these highly aromatic polymers and their restricted solubility in paraffinic oils by using the polymers in a ternary lubricating composition in which the polymers are homogeneously blended with a naphthenic or aromatic oil and with a highly paraffinic oil as an anti-solvent to obtain optimum polymer solubility and superior V. I. improving properties. In such ternary compositions, the highly naphthenic or aromatic oil may have a relatively low viscosity as compared to the paraffinic oil. Such compositions are indicated to be very satisfactory in their low pour points, high V. I., and high stability properties for use as hydraulic fluids.

The following examples are given to demonstrate the viscosity producing property of an aromatic type polymer in a ternary lubricating composition:

EXAMPLE 2

A copolymer was formulated by an emulsion polymerization reaction of 32% isoprene with 68% styrene. The copolymer was hard and brittle. This copolymer was almost colorless, and it had a molecular weight of about 16,700. The product was insoluble in a paraffinic mineral oil that had a viscosity at 210° F. of 5.5 centistokes and a V. I. of 112.9.

The copolymer was found to be soluble in a mineral oil that had a viscosity at 210° F. of 5.47 centistokes and a V. I. of 6.5. One gram of the copolymer was dissolved in 99 grams of the 6.5 V. I. oil at about 150° F. and viscosity results on the resulting blend are listed:

TABLE IV

Temperature	Viscosity in centistokes	Age of solution
° F.		Hours
60	250.1	29
68	196.3	29
100	60.76	29
150	17.45	29
210	6.63	29

Calculated A. S. T. M. slope over 60° F. to 210° F. = 0.795.

To the polymer solution with a viscosity of 6.63 centistokes at 210° F., 10% by weight of the 112.9 V. I. paraffinic mineral oil was added. After the ternary mixture had been agitated at room temperature, the viscosity of the product was determined and the checked results are listed:

TABLE V

Temperature	Viscosity in centistokes	Approx. age of solution	Viscosity in centistokes	Approx. age of solution
° F.		Hours		Hours
60	199.1	18	198.7	177
68	168.7	18	168.8	177
100	54.6	18	54.7	177
130	24.7	18	24.7	177
150	16.2	18	16.3	177
210	6.3	18	6.3	177

Calculated A. S. T. M. slope over 60° F. to 210° F. = 0.775

These data illustrate how the ternary lubrication mixture has a determined Ubbelohde viscosity at 60° F. that is calculated to be about 31 centistokes lower than would be expected from plotted data obtained on the A. S. T. M.—Chart C—A. S. A. No. Z11.39—1937. Also, these data prove that the ternary mixture has a better A. S. T. M. slope over the range of 60° F. to 210° F. than would be expected or predicted from the viscosity blending law—

$$\log \phi = n_1 \log \phi_1 + n_2 \log \phi_2$$

where

ϕ = viscosity

n_1 = mol. fraction of solution 1

n_2 = mol. fraction of solution 2

EXAMPLE 3

To the 1% copolymer-oil blend (that had a viscosity at 210° F. of 6.63 centistokes and an A. S. T. M. slope of .795 over the temperature range of 60° F. to 210° F.) were added 40% by weight of the polymer non-solvent oil that had a V. I. of 112.9. Viscosity results on the resulting solution are listed:

TABLE VI

Temperature	Viscosity in centistokes	Age of solution	Viscosity in centistokes	Age of solution
° F.		Hours		Hours
68	136.02	8	136.05	227
100	50.69	8	50.71	227
150	15.77	8	15.77	227
210	5.87	8	5.88	277

Calculated A. S. T. M. slope over 68° F. to 210° F. = 0.796.

These data indicate that the ternary lubrication mixture has a determined Ubbelohde viscosity at 68° F. that is calculated to be about 15 centistokes lower than would be expected from plotted data obtained on the same chart as used in Example 1. The calculated theoretical A. S. T. M. slope for this oil over the temperature range of 68° F. to 210° F. is 0.814.

The results in Examples 2 and 3 indicate that normal blending laws do not hold for these ternary solutions at temperatures below about 70° F. These data also indicate that as the temperature is raised, a larger amount of non-solvent oil is used to obtain the desired reduction in viscosity at the lower temperature. For example, in the temperature range of 60° F. to 210° F., 10% non-solvent oil decreased the A. S. T. M. slope by 0.020, but over the temperature range of 68° F. to 210° F. it required 40% non-solvent oil to decrease the A. S. T. M. slope by 0.018.

Generically, the highly aromatic polymers that act appropriately in the described ternary blends are polymers which have a low solubility in paraffinic petroleum lubricating oils and relatively higher solubility in naphthenic or non-paraffinic petroleum lubricating oils. They may have molecular weights ranging from about 5,000 to 25,000. From the nature of their syntheses, they contain a substantially larger number of carbon atoms in aromatic ring than in aliphatic chain structures, but nevertheless, preferably contain alkyl group branches. The aromatic polymers which have given particularly good results contained from about 2 to 6 carbon atoms in aromatic rings for each 1 carbon atom in aliphatic (alkyl or alkylene) group.

A scheme found useful for determining how variations in aromaticity of the polymers affects the behavior as viscosity index improving agents is illustrated in studies of copolymers prepared from styrene and isoprene. By these studies it was found that with increase of the aromaticity of the polymers by increasing the proportion of the aromatic reactant, styrene, so as to lower the solubility of the polymers in paraffinic oils, the polymers were made more effective as viscosity index improvers so long as they still could be dissolved in naphthenic or non-paraffinic oils. This is shown by the following data:

TABLE VII

Polymer concentration grams/100 ml. of petroleum oil	Polymer constituents		S. S. U. viscosity at—		V. I.
	Percent styrene	Percent isoprene	100° F.	210° F.	
None	—	—	234.6	44.1	6.5
1.0	64	36	282.3	46.6	25.6
1.0	66	34	280.1	47.3	33.3
1.0	68	32	287.2	47.4	39.0
1.0	70	30	289.7	47.9	46.3

It was found, accordingly, that increasing of the aromatic reactant or constituent of the polymer made the polymer less soluble but more effective for elevating the V. I. provided the aromatic polymer gave a homogeneous solution in the oil, and thus by using the aromatic polymer in a ternary composition with sufficient naphthenic oil to make the composition homogeneous and with paraffinic oil to lower the solubility of the polymer, the viscosity index improvement is enhanced.

The improved oil blends prepared in accordance with this invention may contain two or more types of viscosity index improvers. They may also contain other kinds of oil additives useful for stabilizing, dyeing, inhibiting oxidation, imparting oiliness, lowering the pour point, reducing sludging, or imparting extreme pressure properties, etc.

The present invention has been illustrated by typical 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, specific polymer composition, or blend. Any modification coming within the spirit of the invention is intended to be included within the scope thereof as defined in the following claims.

We claim:

1. A lubricating composition comprising a highly aromatic polymer containing from about 2 to 6 carbon atoms in aromatic rings for each

carbon atom in an aliphatic group which has a low solubility in a paraffin base lubricating oil dissolved in a non-paraffinic oil in a concentration above its solubility in a paraffinic oil, and said solution being homogeneously blended with a paraffinic oil restricted in amount to avoid precipitation of the polymer.

2. A ternary lubricating composition which consists in a homogeneous solution of a highly aromatic polymer containing from about 2 to 6 carbon atoms in aromatic rings for each carbon atom in an aliphatic group in a non-paraffinic hydrocarbon oil to which said polymer imparts an improved viscosity index, and a paraffinic mineral lubricating oil which is less miscible with said polymer in an amount that prevents precipitation of the polymer but increases the viscosity index improving effectiveness of the polymer.

3. A ternary lubricating oil composition which consists in a homogeneous solution of a tri-p-tolylmethyl polymer in a naphthenic hydrocarbon oil, and a paraffinic mineral lubricating oil.

4. A ternary lubricating oil composition which consists in a homogeneous solution of a styrene-isoprene copolymer dissolved in a low viscosity index mineral lubricating oil and a paraffinic mineral lubricating oil.

5. A lubricating oil composition comprising a lubricating hydrocarbon oil blended with a small amount of a polymeric product derived from the polymerization of a tri-arylmethyl radical.

6. A lubricating oil composition comprising a petroleum lubricating oil base blended with a small amount of a tri-p-tolylmethyl polymer.

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