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LUBRICATING COMPOSITION CONTAINING A SULFURIZED HYDROCARBON VISCOSITY INDEX IMPROVER

Franklin I. L. Lawrence and Michael J. Pohorilla, % Kendall Refining Co., Bradford, Pa.

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5 Claims. (Cl. 252—45)

This invention relates to the improvement of the viscosity index, detergency, stability against oxidation, and depression of the pour point of oleaginous compositions. More particularly, the invention embraces lubricating oils, greases, power transmission fluids, and shock absorber fluids, of the aforementioned type, which contain viscosity index improving amounts of substantially oil compatible hydrocarbonaceous condensation products formed by contacting specific hydrocarbon starting materials with elemental sulfur at a temperature of at least about 400° F., for example, about 400° F. to about 600° F.

The wide use of automobiles, aircraft and other types of machines and apparatus which are operated through widely varying temperature ranges, requires lubricating oils, greases, power transmission fluids, and shock absorber fluids which are attended by superior viscosity-temperature characteristics. Materials known to the art to have the necessary boiling and flash points, such as mineral oil fractions, demonstrate excessive variations in viscosity with temperature. Ideally, the viscosity of lubricating oils, power transmission fluids, and shock absorber fluids, would be substantially constant throughout wide ranges of temperature. The art, therefore, has sought to combine appropriate additives with lubricating oils, greases, power transmission fluids, and shock absorber fluids, to improve the viscosity index thereof. Additionally, the art has sought to combine appropriate additives with lubricating compositions to improve such qualities as detergency, stability against oxidation and pour point depression.

In its quest for improved products, the prior art has admixed certain sulfurized petroleum fractions with lubricating compositions. Thus, for example, U.S. Patent 2,732,346 to Jones discloses that acid contacted or clay-treated bright stocks, bright stock extracts and lubricant distillate extracts produce suitable lubricating oil additives when sulfurized. These petroleum fractions, described as containing substantial proportions of alkyl aromatics and no more than minor amounts of olefinic hydrocarbons, are exemplified by materials having a molecular weight ranging from about 380 to about 400 and a viscosity of from about 75 to about 220 SUS at 210° F., although petroleum hydrocarbons having a viscosity of up to 500 SUS at 210° F. are said to be appropriate starting materials. These petroleum fractions, which themselves have a molecular weight approximating the molecular weight of lubricating oils, when sulfurized at temperatures of from 375° to 500° F., produce additives designed to enhance the detergency, antioxidant and pour stability characteristics and to inhibit the corrosivity of lubricating compositions. These particular additives, however, are not disclosed to effect improvement in the viscosity index of the lubricating composition. On the contrary, Jones teaches that other viscosity index improving agents be incorporated into lubricating compositions containing the disclosed sulfurized additives. Moreover, while motor oils containing the additives disclosed in U.S. 2,732,346 are taught to be substantially noncorrosive, the exemplified compositions still exhibit an undesirable measure of corrosivity in the copper strip test.

It is a primary object of this invention to provide compounded lubricating oils, greases, power transmission fluids, and shock absorber fluids of improved viscosity index.

It is an additional object of the invention to provide compositions which are effective simultaneously to improve the viscosity index, detergency, stability against oxidation and pour point depression of oleaginous compositions, such as lubricating oils, greases, power transmission fluids, and the like.

A further object of the invention is an oxidation resistant lubricating composition having a high viscosity index, low pour point, and greatly reduced corrosivity.

In accordance with the present invention, it has been found that certain high molecular weight, viscous, resin-like petroleum hydrocarbons when reacted with sulfur produce hydrocarbon condensation products which not only enhance the detergency, stability against oxidation and pour point characteristics of lubricants but also are excellent viscosity index improving agents. Moreover, the condensation products of the invention when blended with a motor oil exhibit no tarnish or corrosion when evaluated by the ASTM Copper Strip Corrosion Test D–130.

The resin-like hydrocarbon starting materials employed in the present invention are characterized by an average ebullioscopic molecular weight of at least about 1000. An optimum average ebullioscopic molecular weight range is from about 1200 to about 1700. Additionally, the starting materials are characterized by a viscosity of at least about 900 SUS at 210° F. The resin-like starting materials exhibit a degree of unsaturation and are characterized by a bromine number within the range of about 1 to about 10.

It is preferred that resin-like petroleum hydrocarbons which are utilized as starting materials for the production of the viscosity index improving agents of the invention contain more than about 2 naphthenic rings per molecule, which rings can be individually integrated with the paraffinic chain portion of the hydrocarbon molecules or condensed with aromatic rings and/or with other naphthenic ring systems. It is also preferred that the hydrocarbon starting materials contain an average of not more than about 50% aromatic carbon atoms.

Additionally, it is preferred that the resin-like petroleum fractions from which the viscosity index improving agents of the invention are produced contain not more than about 10% of wax type materials. The wax content herein referred to is determinable by a procedure similar to that described under ASTM designation D–721–51T with the exception that methyl isobutyl ketone is employed to precipitate the wax, the sample size is reduced to 0.5 grams, and the determination is conducted at 0° F. While the starting materials which contain substantially more than 10% by weight of wax, as determined by this test, e.g., petrolatum which may reflect a wax content on the order of 40% by weight, can be employed in the production of the viscosity index improving agents of the invention, such materials are not preferred. Such materials best can be used as blending with more desirable starting materials, such as the preferred petroleum fractions above described, in proportions up to about 25% by weight of the total blend.

Resin-like hydrocarbons operable as starting materials in the invention can be obtained by conventional liquefied normally gaseous hydrocarbon precipitation processes from normal or vacuum distillation or residual stocks and analogous fractions of paraffin or mixed base crude oils. Pennsylvania crude oils are a particularly desired source for resin-like oils. Further refinement of such precipitated, high molecular weight hydrocarbons, which include both light and heavy resin fractions, by extraction with furfural, phenol, SO_2 or the like in conventional manner, yields a raffinate from which viscosity index im-

proving agents of maximum effectiveness are produced. Conventional solvent extraction processes are utilized to obtain such raffinates. Such processes are well known to the prior art and are described in detail, inter alia, in Industrial and Engineering Chemistry, 40, pages 220–227 (1948), and at pages 335–336 of "Chemical Refining of Petroleum" by V. A. Kalichevsky and B. A. Stagner, Reinhold Publishing Co., 1942. Generally, the degree of extraction should be such as to yield about a 70% to 85% raffinate. More drastic extraction, for example, to yield 50% to 60% raffinates, may be practiced to obtain still more desirable starting materials for the production of the viscosity index improving agents of the invention.

The condensation products of the present invention are produced by contacting the above described resin-like hydrocarbon starting material while at a temperature of at least about 400° F., preferably about 425° F. to about 575° F., with at least about 5% by weight of elemental sulfur for a time period requisite to produce a final condensation product effective in a concentration of about 10% by weight to increase the viscosity index of a 60 at 100 SUS standard base oil derived from a paraffinic crude source at least ten viscosity index units more than a like amount of hydrocarbon starting material from which said condensation product is produced.

The viscosity index improving agents of this invention are characterized by a ring and ball softening point, as measured by ASTM Method E28–42T, of more than about 80° F. Some viscosity index improving agents comprehended by the invention have a ring and ball softening point or viscosity too low to be effectively measured in accordance with the aforementioned procedure. Such materials are characterized by a viscosity of at least 1150 SUS at 210° F. and, in any event, a viscosity of at least about 250 SUS at 210° F. greater than the hydrocarbon starting materials from which the viscosity index improving agents are produced.

The substantially oil compatible hydrocarbonaceous condensation products which constitute the viscosity index improving agents of this invention appear to result from the chain reaction of free radical intermediates which are formed thermally or by the reaction of at least some of the molecules of the hydrocarbon starting materials with sulfur.

The rate of supply of elemental sulfur to the reaction mixture is not critical to the production of the condensation products. Two suitable methods of sulfur addition are hereinafter described.

A first method is to add most of the sulfur, or about 20 to 25 parts by weight of sulfur per 100 parts of hydrocarbon, at room temperature or some temperature below that at which sulfur will readily react with the hydrocarbon, i.e., about 350° F. The temperature is then slowly raised at a rate so that the foam caused by the hydrogen sulfide generated in the reaction will not overflow the reaction vessel. This generally takes about two to four hours to reach 500° F. A small amount of sulfur is then added to bring the condensate up to the desired ring and ball softening point.

A second method is to first heat the hydrocarbon to the reaction temperature, i.e., about 500° F., and then add sulfur slowly enough so the foam caused by the generated hydrogen sulfide does not overflow the reaction vessel. This rate is generally about one part by weight of sulfur per 100 parts by weight of hydrocarbon every 0.25 hours.

About 16 hours or more may be used to effect the condensation but this extreme length of time is not preferred. It is preferred to limit the time at the elevated temperature to less than 8 hours. The time required may be reduced down to a few minutes provided the equipment can handle the large amount of foam produced.

Reactive materials, such as chlorine, hydrogen chloride, phosphorus pentoxide, and like materials, which serve as activators can appropriately be introduced into the reaction mixture in conjunction with the elemental sulfur. Conventional catalysts known to the art can be employed, if desired. Rubber vulcanization accelerators such as diphenylguanidine, tetramethyl thiuram disulfide, and the like, however, do not catalyze the sulfurization.

In order to substantially completely minimize corrosion problems, it is often desirable further to treat the sulfur condensed product of the invention. It is generally considered that even to the very limited extent that the untreated condensation products are corrosive, such characteristic is essentially attributable to the presence of residual sulfur compounds, such as hydrogen sulfide, reacive organic sulfides and polysulfides, mercaptans, and the like. Such residual sulfur compounds can be removed or rendered innocuous in various ways, two of which are described hereinafter.

A first method is generally chemical in its approach and entails the treatment of the condensate with an oxidizing agent, such as air or elemental oxygen, hydrogen peroxide, the various other inorganic peroxides, inorganic chlorates and perchlorates, such as sodium chlorate, potassium chlorate, sodium perchlorate, potassium perchlorate, chlorine dioxide, nitrogen dioxide, organic peroxides, such as benzoyl peroxide, ditertbutyl peroxide, and the like, and organic hydroperoxides, for example, cumene hydroperoxide, and tertiary butyl hydroperoxide. A second method is essentially physical in character and entails contacting the condensation product with an inert gas, normally as a sweep gas. A representative inert gas useful for this purpose is nitrogen.

The viscosity index improving agents contemplated by this invention can be employed in wide and effective proportions in all types of mineral oils, greases, power transmission fluids, shock absorber fluids, and like materials. Specifically with respect to lubricating oils and greases, the sulfur condensed resin additives of the invention are appropriately utilized in a concentration of at least about 1.0% by weight, preferably from about 3.0% to about 15.0% by weight. However, the invention contemplates the use of the recited resinous agents in all proportions effective to improve such characteristics as viscosity index, detergency, pour point, etc. of all oleaginous compositions, including base oils, greases, power transmission fluids, shock absorber fluids, and the like, in which they are incorporated.

The viscosity index improving agents can be employed in oils, greases, and power transmission fluids derived from Pennsylvania crude oils, Mid-Continent crude oils, asphalt base oils, and all other types of mineral oils, as well as synthetic oils, including particularly the synthetic ester type oils, such as di-2-hexylethyl sebacate and di-2-ethylhexyl adipate, and phosphonate oils, such as dibutyl diphosphonate, tetrabutyl tetramethylene diphosphonate, and bis(2-ethylhexyl)2-ethylhexyl phosphonate. The base lubricating oil preferably employed is derived from a paraffinic crude source. The invention, however, contemplates oleaginous materials generically.

In addition to the viscosity improving agents of this invention, the oleaginous base may contain conventional additives. Thus, since the viscosity improving agents of this invention do not enhance film strength or extreme pressure properties, such properties appropriately may be improved utilizing additives known to the art.

Having generally described the invention, the following examples are presented to describe a process for preparation of the sulfur-condensed resin and to illustrate specific embodiments of improved oleaginous compositions in accordance with the invention.

EXAMPLE I

Preparation of Resinous Starting Materials

About 75,000 grams of a cylinder stock derived by distillation from paraffin base Pennsylvania crude oil and characterized by a boiling point in excess of about 850° F., a molecular weight of about 750, a viscosity at

210° F. of 225 SUS, an A.P.I. gravity of about 24.8, and a flat point (Cleveland Open Cup) of about 600° F. are mixed with propane heated to a temperature of about 190° F. and then cooled to a temperature of about 65° F. The cylinder stock-propane solution is thereafter transferred into a chilling tank wherein the presure is reduced to an extent requisite to volatilize sufficient propane to lower the temperature of the solution to about —20° F. to about —50° F. Makeup propane is added during the chilling operation, such that the ratio of propane to cylinder stock is about 3 to 1 at the end of the chilling cycle. During the chilling cycle, petrolatum is precipitated from the solution. The chilled cylinder stock-propane solution containing precipitated petrolatum is transferred to a filter feed tank and thence passed through an appropriate filter to effect removal of the petrolatum from the chilled solution.

Propane is added to the filtrate in an amount sufficient to raise the propane-cylinder stock ratio to about 10 to 1 and the temperature of the solution so obtained is elevated to about 150° F. to 180° F. whereupon about 15,000 grams of high molecular weight viscous materials are precipitated. These viscous materials still contain some propane.

The material so obtained is then mixed at a temperature of about 130° F. to 135° F. with additional propane to increase the propane-oil ratio to about 20 to 1. The temperature of the resulting solution is lowered to about 100° F. whereupon about 6,000 grams of viscous hydrocarbons are precipitated. These materials, after removal of all residual propane, are designated as heavy resins and are characterized by a molecular weight of about 1400, a viscosity of about 4100 SUS at 210° F., and a bromine number of 3.7.

The remaining oil-propane solution is heated to about 150° F. whereupon 9,000 grams of additional viscous hydrocarbons which are designated as light resins are precipitated. Any residual propane is removed in a flash chamber. These light resins are characterized by a molecular weight of about 1300, a viscosity of about 1150 SUS at 210° F., and a bromine number of about 4.0.

EXAMPLE II

About 5,000 grams of the viscous material separated from the cylinder stock in the manner described in Example I and designated as light resin is heated to about 425° F. Elemental sulfur is added in 1% by weight increments every fifteen minutes for a total of about 23.5% sulfur. Nitrogen gas is passed through the reacting mixture continuously at the rate of about one meter per minute. The final product is characterized by a ring and ball softening point of about 182° F. A blend of about 10% by weight of this product in a medium neutral 95% raffinate lubricating oil exhibits no tarnish or corrosion when evaluated by the ASTM Copper Strip Corrosion Test D–130.

The viscosity index improving effectiveness of this product is demonstrated when blended into a mixture of Pennsylvania base neutrals illustrated in Table 1.

TABLE 1

Weight percent of condensed resin	Vis. at 210° F. (SUS)	Vis. at 100° F. (SUS)	V.I.
0	38.0	84.7	91.5
4	40.0	101.1	119.5
7	42.5	122.3	131.6
10	45.3	150.4	132.8

EXAMPLE III

A viscosity index improving agent is prepared from a fraction of Pennsylvania paraffin base crude oil designated as heavy resin described in Example I, which has been further processed by solvent extracting with phenol to a 65% raffinate yield.

The raffinate is characterized by an average molecular weight of about 1680, a viscosity of about 1550 SUS at 210° F., a bromine number of 1.2, and is substantially wax and asphalt free. This material is heated to a temperature of about 475° F. and condensed with about 21% by weight of sulfur while the reaction mixture is maintained within a temperature range of 450–500° F. for a time requisite to produce a product having a ring and ball softening point of about 154° F. The final product is blown with air to render it non-corrosive to a copper strip when tested in accordance with ASTM Procedure D–130.

The condensed resin so obtained was blended with a nuetral oil having a viscosity of about 60 SUS at 100° F. derived from Pennsylvania paraffin base crude oil by redistillation of a dewaxed wide boiling primary distillate. The effectiveness of the condensed resin as a V.I. improver is reflected in Table 2.

TABLE 2

Weight percent of condensed resin	Vis. at 100° F.	Vis. at 210° F.	V.I.
0.0	60.7	35.1	88.7
4.0	73.3	37.5	132.1
7.0	90.6	40.1	156.5

EXAMPLE IV

Example III is repeated with the exception that the condensation reaction is continued to produced a product having a ring and ball softening point of about 250° F.

The condensed resin so obtained is non-corrosive to a copper strip when tested in accordance with ASTM Procedure D–130 and is effective as a viscosity index improver in the Pennsylvania oil fraction having a viscosity of 60 SUS at 100° F., of the type previously described, as reflected in Table 3.

TABLE 3

Weight percent of condensed resin	Vis. at 100° F.	Vis. at 210° F.	V.I.
4.0	79.0	38.6	153.0
7.0	110.6	43.6	164.9

EXAMPLE V

Example III is repeated with the exception that the condensation reaction is continued to produce a product having a ring and ball softening point of about 270° F.

The composition so obtained is non-corrosive to a copper strip when tested in accordance with ASTM Procedure D–130 and is effective as a viscosity index improver in the Pennsylvania oil fraction having a viscosity of 60 SUS at 100° F., of the type previously described, as reflected in Table 4.

TABLE 4

Weight percent of condensed resin	Vis. at 100° F.	Vis. at 210° F.	V.I.
4.0	80.4	38.9	159.1
5.0	88.7	40.4	169.3
7.0	113.3	44.2	166.0

EXAMPLE VI

The viscosity improving agents tabulated below are prepared by charging the designated resin to a suitable apparatus and initially heating the stock to 500° F. Sulfur is introduced into the mixture every 15 minutes in incre-

ments totaling 1% of the weight of the mixture as the temperature is raised. The temperature of the mixture is maintained at approximately 500° F. with continued incremental sulfur addition until the desired ring and ball softening point is obtained. The material finally is contacted with air to insure removal of corrosive sulfur compounds. All of the sulfur-condensed materials so produced are non-corrosive in the ASTM D–130 copper strip test. The effectiveness of these condensed resins as viscosity index improving agents, when blended in the proportions indicated with the neutral oil having a viscosity of about 60 SUS at 100° F. described in Example III, is reflected by the data appearing in Table 5.

TABLE 5

Sulfur condensed materials	Percent sulfur treat.	Percent sulfur in prod.	R & B soft. pt., ° F.	SUS vis. at 210° F.	Ebull. M. weight	V.I. of 10% blend in 60/100 oil
Heavy resin [1]	0	0.26		4,100	1,400	115.7
	12	2.91	110		1,495	130.9
	21.75	4.20	253			148.8
Light Resin [2]	0	0.17		1,210	1,110	115.8
	13.5	2.94		4,600	1,250	125.5
	24.6	4.74	246			156.3
High viscosity resin [3]	0	0.27		20,564	1,480	124.5
	8.06	1.79	138		2,130	136.4
	16.52	2.75	245			148.4

[1] The heavy resin derived from Pennsylvania base crude oil and described in Example I.
[2] Light resin derived from Pennsylvania base crude as described under Example I and characterized by a viscosity at 210° F. of 1,210 SUS and an average molecular weight of about 1,110.
[3] High viscosity resin derived from Pennsylvania base crude oil by propane precipitation from cylinder stock and characterized by a viscosity at 210° F. of about 20,565 SUS, a flash point of 660° F., a fire point of about 735° F., carbon residue of 13.95%, and 0.44% naphtha insolubles.

EXAMPLE VII

A compounded engine oil is prepared, utilizing a sulfur condensed light resin raffinate having a ring and ball softening point of about 239° F. More particularly, the compounded engine oil contained about 93.6 parts by volume of a medium neutral 95% raffinate, about 0.30 parts by volume of a commercial antioxidant, the essential active ingredient of which is a zinc alkyl dithiophosphate in which the alkyl groups contain from 6 to 10 carbon atoms and about 6.1 parts by weight of the light resin raffinate sulfur condensation product.

The oil so compounded is characterized by a viscosity at 100° F. of 326.2 SUS, a viscosity at 210° F. of 59.1 SUS, and a viscosity index of 125. The oil so prepared was tested in an International Harvester Cub Tractor Engine KRC–19 Test in which the Cub engine was operated at 2500 r.p.m. at 11 brake h.p. for 40 hours, with an oil temperature of 265° F. and a water jacket outlet temperature of 250° F. The test results reflect a piston color of 9.0 (on a scale wherein a value of 10 is applied to a clean piston) and a bearing weight loss of 0.036 grams. The used oil employed in the test is characterized by a viscosity at 100° F. of 588.6 SUS, a viscosity at 210° F. of 78.0 SUS, a viscosity index of 121, and contains 0.36% by weight of pentane insolubles and 0.51% by weight of benzene insolubles.

The light resin raffinate sulfur condensation product employed is non-corrosive to a copper strip when tested in accordance with ASTM Procedure D–130, and was prepared in the same manner as the sulfurized viscosity index improving agents of Example VI, with the exception that a light resin raffinate was employed as the starting material from which the sulfurized condensation product was produced. This light resin raffinate was obtained by phenol extraction of the light resins described in Example I to an 85% raffinate and is characterized by an ebullioscopic molecular weight of about 1350, and a viscosity at 210° F. of about 916 SUS.

EXAMPLE VIII

About 10% by weight of the sulfur condensation product produced from the light resin raffinate, as described in Example VII, is blended with 60 at 100 neutral, of the type described in Example III. The viscosity index of the blend so produced is 135.8.

EXAMPLE IX

About 4% by weight of a light resin raffinate sulfur condensation product, of the type described in Example VII, is blended with a synthetic oil consisting of bis-(2-ethylhexyl)-2-ethylhexyl phosphonate to product a blend havinug a viscosity index of 140.6. The synthetic oil containing no sulfur condensed light resin raffinate is characterized by a viscosity index of about 79.9.

EXAMPLE X

In this example, the light resin raffinate sulfur condensation product of Example VII is subjected to tests of the type first described by Fenske et al. in Industrial and Engineering Chemistry (Analytical Edition) 13, 51 (1941) to determine the oxidation characteristics thereof. More specifically, a blend containing 78% by weight of an overhead distillate derived from a naphthenic base crude oil and having a viscosity of 57.7 SUS at 100° F., about 11% by weight of a neutral fraction derived as an overhead distillate from a Pennsylvania crude oil and characterized by a viscosity of 90 SUS at 100 F., and about 11% by weight of the sulfur condensation product of Example VII is prepared. The oxidation characteristics of a 150 ml. sample of this oil blend maintained at a temperature of 328° F. in the presence of copper and iron wire as catalysts are determined. For purposes of comparison, the oxidation characteristics of the base stock containing no sulfur condensation product are similarly determined. The results of these determinations are reported in Table 6.

TABLE 6

	Oxygen absorption, moles oxygen per kilogram of oil	
	Prod. of Ex. VII	Base stock
Oxidation time, hrs.:		
0.5	0.056	0.056
5	0.559	3.121
10	1.240	5.464
15	1.648	7.72
20	1.850	9.512
Lacquer formation on 1" x 3" glass slide, mg.	0.2	475.2
Oxidized oil: Neutralization number	3.0	9.9

EXAMPLE XI

This example is illustrative of a grease composition containing a viscosity index improving agent of the type contemplated by the invention. Approximately 88 parts of prime tallow and 85 parts of hydrated barium hydroxide $BaOH_2 \cdot 8H_2O$ are mixed at room temperature in a suitable steam jacketed kettle and thereafter the temperature is raised above the boiling point of water to remove

the water of crystallization of the hydrated barium hydroxide and to form barium soaps. For the purpose of solubilizing such barium soaps, there is added a suitable quantity of a naphthenic base stock having a viscosity of about 533 SUS at 100° F., 57 SUS at 210° F. and a viscosity index of about 46. During this addition, the temperature of the mixture is raised to about 350° F. to initiate gelation. Completion of the grease manufacture was effected by adding an oil mixture consisting of 10% by weight of the sulfur condensed resin described in Example VII, and comprising a light resin raffinate sulfur condensate having a ring and ball softening point of about 243° F. and 90% by weight of a neutral fraction derived from a Pennsylvania crude having a viscosity of about 68 SUS at 100° F., the total blend having a viscosity at 100° F. of 142 SUS, a viscosity at 210° F. of 45.2 SUS, and a viscosity index of 142. The resulting grease was characterized by the following properties:

Worked penetration (ASTM D217–52T)_____ 295.
Moisture content (ASTM D128–47)_____ Trace.
Dropping point (ASTM D566–42)_____ 485° F.

EXAMPLE XII

The light resin described in Example I is sulfur condensed at a temperature of about 425° F. The condensate, non-corrosive to a copper strip when evaluated by ASTM D–130, is blended in a mixture of neutral fraction derived from Pennsylvania base crude oil and characterized by a viscosity of 84.7 SUS at 100° F., 38.0 SUS at 210° F., and a viscosity index of 91.5. The effect of the condensed resin on viscosity index is reflected in Table 7.

TABLE 7

R & B softening point	Percent condensed resin	Viscosity, SUS		V.I.
		210° F.	100° F.	
243° F.	4	40.7	105.9	127.1
	7	43.3	128.5	134.8
	10	47.1	163.7	137.5
283° F.	4	42.8	123.5	134.9
	7	47.8	167.6	140.3
	10	56.3	254.9	137.8

Similarly, there is tabulated in Table 8 data for a comparable run wherein the condensation reaction was conducted at 575° F.

TABLE 8

R & B softening point	Percent condensed resin	Viscosity, SUS		V.I.
		210° F.	100° F.	
220° F.	4	40.6	107.7	118.9
	7	43.4	131.0	132.4
	12	49.0	195.4	129.6
266° F.	4	41.1	109.9	127.4
	7	44.6	141.8	134.2
	12	52.7	229.8	132.8
310° F.	4	41.5	130.1	112.8
	7	45.3	147.3	136.6
	12	54.5	248.1	133.7

EXAMPLE XIII

This example demonstrates the pour point depressing properties of the sulfur condensed resins employed according to this invention.

The light resin referred to in Example I, which has been sulfur condensed to a ring and ball softening point of about 246° F. is blended with a neutral oil fraction derived from a naphthenic base crude characterized by the following properties: a viscosity of 200 SUS at 100° F., a viscosity index of 65, flash point of 395° F., and a pour point of −5° F. Pour point data as determined by ASTM D97–47 are as follows:

Percent Sulfur Condensate	Pour Point, ° F.
0	−5
4	−50
7	−55

The same sulfur condensate when blended in the 60 at 100 neutral fraction described in Example III has the following characteristics:

Percent Sulfur Condensate	Pour Point, ° F.
0	0
4	−35
7	−30

The foregoing examples are presented for illustrative purposes only. Since additional embodiments of the invention will be apparent to those skilled in the art, the invention is to be limited only by the scope of the appended claims.

This application is a continuation-in-part of application Serial No. 559,759 filed January 18, 1956.

We claim:

1. A composition useful for improving the viscosity index of lubricating oils, greases, transmission fluids and the like, consisting essentially of a petroleum hydrocarbon resin which is substantially free from wax and asphalt and which is produced by fractionation of heavy petroleum fractions with a liquefied normally gaseous hydrocarbon, said resin having an SUS viscosity at 210° F. of at least 900, an ebullioscopic molecular weight of at least 1000, and a bromine number of about 1 to about 10, condensed by heating said resin with at least about 5% by weight of elemental sulfur at a temperature of about 400° F. to about 600° F. for a period of time sufficient to increase the SUS viscosity at 210° F. by at least about 250 greater than that of the original resin, the thus sulfur condensed composition having the property of increasing the viscosity index of a 60 at 100 SUS standard base oil by at least ten viscosity index units more than a like amount of the original resin, when added in the proportion of 10% to said base oil.

2. A lubricating composition consisting essentially of a lubricating oil selected from the group consisting of mineral oils, synthetic ester oils and phosphonate oils and from about 1% to about 15% by weight of the composition of claim 1.

3. The composition of claim 1 wherein the hydrocarbon resin is further extracted with a selective solvent and the raffinate is subjected to sulfur condensation.

4. The composition of claim 1 wherein the sulfur condensation product has a ball and ring softening point of at least about 80° F.

5. The composition of claim 1 wherein the hydrocarbon resin is prepared by propane fractionation of a cylinder stock obtain from a Pennsylvania crude oil.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,036,004 May 22, 1962

Franklin I. L. Lawrence et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 2, for "flat" read -- flash --; column 6, line 14, for "nuetral" read -- neutral --; column 8, line 7, for "product" read -- produce --.

Signed and sealed this 4th day of September 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents