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VISCOSITY INDEX IMPROVERS

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ABSTRACT OF THE DISCLOSURE

Viscosity index improver for lubricating oils in the form of pure oil-soluble hydrocarbon polymers having a molecular weight between about 50,000 and 2,000,000 composed of a hydrocarbon chain having a number of alternate stereoregular and amorphous segments, the amorphous segments contributing at least 50% of the molecular weight of the polymer giving it its oil-solubility characteristics and the stereoregular segments being present in sufficient quantity to give the polymer a viscosity index improving efficiency of at least 1.0 without destroying the oil-solubility characteristics. The stereoregular segments are preferably of the group of polybutene-1, polypropylene, poly-4-methyl, pentene-1, poly-3-methyl butene-1, polystyrene, polypropylene-butene-1 copolymers, polypropylene-styrene copolymers, polyethylene-ethylene copolymers, ethylene-butene-1 copolymers and polybuten-1. The amorphous segments are alpha olefin polymers. Preferably the polymer is a ter-polymer additionally containing up to 25 mol percent of a higher alpha olefin. Most preferably the polymer is a ter-polymer having isotactic polypropylene segments and amorphous segments of a polymer of a lower alpha olefin and additionally containing 1–20 mol percent of a higher alpha olefin. The improver is generally dissolved in petroleum lubricating oil in amount from 1 to 20%.

This invention relates to viscosity index improvers for lubricating oils and is a continuation-in-part of my copending applications Ser. No. 283,672, filed May 28, 1963, now abandoned, and Ser. No. 357,294, filed Apr. 3, 1964. The invention more particularly relates to certain hydrocarbon block copolymers which are useful as viscosity index improvers for lubricating oils; lubricating oils of improved viscosity index containing these polymers, and to a process for improving viscosity characteristics of such oils with the use of these polymers.

Ordinary lubricating oils, and particularly petroleum oils as are conventionally used in internal combustion engines generally show a decrease in viscosity with increasing temperatures. If the internal combustion engine or the machinery containing the oil is to be initially started and operated, at a low temperature, as for example in the colder climates or in the winter, it is necessary to use a thinner, lighter weight oil if the oil is to have initial fluidity at the low temperature for starting an initial lubrication. Such oils are commonly available for example, as winter-grade oil, such as SAE 10 weight or lower. As the engine operates and heats up the oil, these oils become thinner, and at higher operating temperatures the thinner, lighter weight oil may not have sufficient viscosity for optimum lubrication. Furthermore, in warmer weather, such as in summer, the lighter weight is not suitable, and it is necessary to change to a heavier weight oil, as for example a 20 or 30 weight oil. This characteristic of the oil to change its viscosity with temperature is measured by a value referred to as "viscosity index."

In order to improve the viscosity index of conventional

petroleum lubricating oils, and thus obtain an oil, such as the present commercially available multi-grade, as for example the 10–30 weight oils, it has been proposed to add to the oil certain oil soluble polymers which act as viscosity index improvers. The efficiency (referred to as "E") of the viscosity index improver is measured as the ratio of the specific viscosity of the oil containing the improver at 210° F., to specific viscosity at 100° F. An "E" value higher than 1 is generally desirable as an oil which has a reduced tendency to thin out with increase in temperature is necessary to meet the engine lubrication needs at higher operating temperatures. The viscosity improving efficiency, "E" of commercial products generally ranges from 1.0 to 1.5.

The thickening power or ability to increase the viscosity of an oil as a function of concentration is also an important factor of the viscosity index improvers. Generally, the small amount of the viscosity index improver which is required to achieve a desired specification in the finished oil, the more desirable the improver. For commercially attractive products 0.4 to 2, and preferably 0.8 to 1.5 weight percent of the improver should be able to achieve 11 to 12 centistokes viscosity at 210° F. with 10W–30 base oils.

It is additionally often necessary to depress the pour point of oils, such as lubricating oils, so that the same may function properly at low temperatures. Various pour point depressants are known and widely used, and some viscosity index improvers additionally act as pour point depressants.

The methacrylate polymers, such as polymethacrylate esters are presently most commonly commercially used as viscosity index improvers for lubricating oils. Additionally, polyisobutylene and polyfumarate esters are used.

While these viscosity index improvers effectively improve the viscosity index of the lubricating oil, and thus overcome the above-mentioned problem and allow the marketing of a multi-grade oil, which is suitable for all-season uses, having an initial low enough viscosity for starting in cold weather use and yet has sufficient viscosity at higher temperatures, the same have a number of disadvantages, such as high initial cost and tendency to undergo thermal depolymerization with a resultant limited life and poor shear stability.

One object of this invention is the provision of viscosity improvers for lubricating oils without the above-mentioned disadvantages.

A further object of this invention is viscosity index improvers having high efficiency, excellent compatibility to the oil and its additives and high thermal stability.

A further object of this invention is a superior oil viscosity index improver which may be produced at a relatively lower cost.

These and still further objects will become apparent from the following description:

In accordance with the invention I have discovered that certain substantially pure oil-soluble hydrocarbon polymers of a molecular weight of between about 50,000 and 2,000,000 composed of a hydrocarbon chain having a number of alternate stereo-regular and amorphous segments constitute highly efficient viscosity index improvers for lubricating oil, which overcome many of the disadvantages of the prior known improvers. The viscosity improvers in accordance with the invention are completely compatible to the lubricating oil and its conventional additives in its normal use environment; are highly stable under the rigors of temperature and use, and may be readily produced.

The molecular weight of the polymer is the molecular weight as measured by intrinsic viscosity. The stereo-

regular segments constitute polymer blocks composed of linear polymer chains consisting substantially solely of methylene and branched chains of methylene units or hydrocarbon rings which are arranged in an orderly spatial distribution to give the polymer its stereoregular characteristics. The molecular arrangement of hydrocarbon polymers which render the same stereoregular in nature is well known in the art, as are the methods for polymerizing a hydrocarbon into such an arrangement.

The amorphous segments are simply amorphous hydrocarbon blocks or chains and must contribute at least 50% of the molecular weight of the hydrocarbon polymer. The stereoregular segments must be present in sufficient quantity to give the polymer a viscosity index improving efficiency of at least 1.0 as measured in the conventional manner, as for example in connection with an SAE 20/30 weight petroleum oil.

The stereoregular segments or blocks must have a molecular configuration which would give the same certain oil solubility characteristics if they collectively existed apart per se as a polymer, i.e. if all the amorphous segments were removed from the polymer chain in accordance with the invention and if the stereoregular segments were rejoined together as a polymer. Under these assumed conditions the stereoregular blocks or segments would have to form a polymer which would be insoluble in oil at a temperature below 0° C., and preferably insoluble at a temperature below 20° C. As the chain of the polymer in accordance with the invention is composed of the stereoregular and amorphous segments which may also be referred to as blocks, the polymer may be considered as a block copolymer and is sometimes referred to herein as such.

As used herein, the term "oil insolubility" is intended to designate solubility of less than .1% by weight in an SAE 5W-paraffinic stock and complete oil solubility is intended to designate solubility of at least 10% by weight in an SAE 5W-paraffinic stock.

Most preferably the stereoregular polymer blocks or segments are isotactic polypropylene and/or polybutene-1 blocks. Additionally other stereoregular polymer blocks having the above-set forth characteristics are applicable. Examples of such stereoregular polymer blocks include stereo-specifically polymerized polymers alpha olefins having from 3 to 8 carbon atoms per molecule such as: of 4 methylpentene-1,3 methyl butene-1, and styrene; copolymers of propylene and butene-1 containing, for example, from 5–30 mol percent of butene-1, and preferably from 5–20 mol percent of butene-1; stereo-specifically polymerized copolymers of propylene and styrene containing, for example 10–40 mol percent of styrene and preferably from 15–30 mol percent of styrene; stereo-specifically polymerized copolymers of propylene and ethylene containing from 5–25% of ethylene and preferably from 10–20 mol percent of ethylene; stereo-specifically polymerized copolymers of ethylene and butene-1 containing, for example, 5–30 mol percent of butene-1 and preferably 15–25 mol percent butene-1 and isotactic polypentene.

The amorphous blocks as mentioned must contribute at least 50% of the total molecular weight of the polymer in accordance with the invention and must be of such a nature that if collectively joined together as a polymer per se without the stereoregular blocks or segments, it would form a polymer soluble in oil at a temperature of —20° C. and above, and preferably at a temperature of —30° C. and above.

As used herein, the designation of the amorphous blocks as being soluble in oil and oil soluble designates a solubility of at least 10% by weight in an SAE 5W paraffinic oil.

Examples of the amorphous hydrocarbon polymer blocks include copolymers of propylene and butene-1 containing from 30–70 mol percent of butene-1; atactic polybutene-1; copolymers of ethylene and butene-1 containing from 40–70 mol percent of butene-1; copolymers of propylene and C_5–C_{20} alpha olefins containing from 30–90 mol percent of the higher alpha-olefins; copolymers of propylene and ethylene containing from 25–70 mol percent ethylene and preferably from 30–60 mol percent of ethylene; interpolymers of C_5–C_{20} alpha olefins; terpolymers of C_2–C_{20} alpha olefins; copolymers of ethylene, and C_5–C_{20} alpha olefins containing from 30–90 mol percent of higher olefins, and C_5–C_{20} alpha-olefin homopolymers.

Most conveniently, the amorphous hydrocarbon polymer blocks are formed by the co- or interpolymerization of the monomer or monomers used to form the stereoregular block with one or more differing alpha-olefins, as for example having a molecular weight between C_2–C_{20}. Alternately, the amorphous hydrocarbon polymer block may be formed from the same monomer used to form the stereoregular block under polymerization conditions, however, which will not produce a stereoregular polymer, but which will produce the required amorphous oil soluble block.

The molecular weights and oil solubility characteristics of the steroregular and amorphous blocks specified herein and in the claims are, as mentioned, those that the blocks per se would have as independent unattached polymers.

The oil soluble hydrocarbon polymers containing the number of alternate stereoregular and amorphous segments are produced by the well known polymerization techniques, and preferably from monomer mixtures which will form the stereoregular and amorphous blocks or segments, and the polymerization may be achieved utilizing batch or continuous techniques. Polymerization may be effected using highly dispersed stereo-specific catalysts, as for example, the well known Ziegler catalyst formed, for example, from organo-metallic compounds such as aluminum trialkyls or alkyl aluminum halides, and transition metal salts, as for example halides or alcoholates. Examples of such catalyst systems include aluminum triethyl with titanium or vandium tetra- or trichloride; diethylaluminum chloride with titanium or vanadium tetra- or trichloride; butyl lithium with titanium tetra- or trichloride, or vanadium tetra- or trichloride, or the like. The polymerization is effected in an inert hydrocarbon solvent, as for example, normal heptane or pentane under an inert atmosphere, as for example nitrogen at moderate temperatures, as for example between about 30 and 150° C., and preferably between about 80 and 120° C. at normal or slightly elevated pressure. The polymerization should be effected so that both the amorphous and stereospecific segments are formed. Preferably the hydrocarbon polymers forming the viscosity index improvers in accordance with the invention are formed from monomer mixtures which will form the stereoregular and amorphous segments or blocks. The polymerization may be effected as a continuous process or as a batch process.

It is possible to produce the viscosity index improver polymer in accordance with the invention by, for example, first effecting the polymerization under conditions which will favor formation of the stereoregular blocks or segments, which conditions are, of course, known per se in the art, and to continue the polymerization under the known conditions which will favor the formation of the amorphous segments or blocks. For this purpose the polymerization may be effected in the same reaction zone using, for example the batch method, or may be effected in two separate reaction zones with the stereoregular chain passing into the second reaction zone for continuation of the polymerization with the formation of the amorphous segments. As mentioned, however, it is preferable to form the polymers from monomer mixtures which form both stereoregular and amorphous blocks.

Utilization may be made of the different reactivities of different monomers of the mixture to form the stereoregular and amorphous segments. Thus, for example,

when using propylene and butene-1 as the monomers the reactivity of the propylene will generally initially favor the formation of isotactic polypropylene segments. Polymerization of the amorphous blocks or segments will also occur in increasing amounts without any requirement for temperature, or any other adjustments.

The polymerization reaction may be discontinued and the polymer recovered and isolated in the conventional manner, as for example by washing with ethylene glycol to remove the catalyst residue and precipitating the polymer with methanol, or distilling off the solvent leaving the polymer residue.

For continuous operation the polymerization may be basically effected in the same manner and under the same conditions with, for example, a continuous pumping of the catalyst system. It is possible, for instance, to continuously pump the catalyst solution in series through two reactor stages with the necessary residence time in each stage and with each stage being effected under conditions to form the stereoregular blocks or segments.

The polymers obtained in accordance with the invention are admixed with the conventional lubricating oils in the conventional manner as viscosity index improvers. Thus the polymers may be added to the lubricating oils in amounts of 0.1 to 30, and preferably 0.3 to 10, and most preferably 0.5–5% by weight.

The oils may be of any of the known or conventional lubricating oils as for example, petroleum lubricating oils of the conventional weights used in internal combustion, such as automotive engines. The oil, for example, may have a viscosity so that after the addition of the polymer in accordance with the invention, the oil will have an SAE rating of 10W–30.

The oil may, of course, contain all the known and conventional additives, such as the conventional detergents, dispersing aids, pour point depressants, anti-oxidants, viscosity improvers, or the like.

In addition, to use with conventional petroleum lubricating oils, which, for example, consist of conventional base stocks or base stock blends with or without conventional additives, the polymers in accordance with the invention, may be added to any other liquid, hydrocarbons for viscosity index improvement, as for example synthetic lubricating oils, such as the Fischer-Tropsch produced oils, or the like.

Viscosity index improvers are often marketed as concentrated solutions in a base oil, as for example in concentrations between 10–30, and preferably 20–30% by weight, which is blended with the lubricating oil. The base oil of the concentrate may, for example, be a 100 S.U.S. paraffinic oil. In connection with polymers in accordance with the invention containing amorphous hydrocarbon polymer blocks formed from lower alpha olefins, i.e. alpha olefins containing up to 4 carbon atoms, the same may tend to unduly thicken the base oil rendering handling of the concentrate difficult.

In accordance with a preferred embodiment of the invention, it has been found that this tendency to unduly thicken the base oil of the concentrate may be avoided if the polymer is formed as a terpolymer additionally containing components formed from 0.5 to 25 mol percent and preferably from 1 to 20 mol percent based on the total monomer charged of a higher alpha olefin containing 5–25, and preferably 7–15 carbon atoms. The higher alpha olefin should be present in the polymerization mixture before complete formation of the polymer and should be preferably present during the formation of the isotatic blocks. Examples of higher alpha olefins which may be used include n-pentene-1, n-hexene-1, n-heptene-1, n-octene-1, n-nonene-1, n-decene-1, n-dodecene-1, n-octadecene-1, and mixtures of alpha olefins available as fractions, as for example C_5–C_7 alpha olefin fractions, C_7–C_9 alpha olefin fractions, C_9–C_{11} alpha olefin fractions, and C_{11}–C_{16} alpha olefin fractions. Branched alpha olefins, such as 3-methylbutene-1, 4-methylpentene-1, isobutylethylene, neopentylethylene, and isoamylethylene may also be used.

It is believed that the alpha olefin in the formation of the terpolymer randomyl distributes in or adjacent the isotactic polymer blocks, or in or adjacent both the isotatic and amorphous polymer blocks. The terpolymer, having the higher alpha olefin component, however, enables the preparation of pourable concentrated oil solutions of the polymer without unduly affecting the efficiency of the polymer as a viscosity index improver.

It is believed that the polymers in accordance with the invention perform their viscosity index improving function by the initial dissolution of the amorphous block in the oil at a lower temperature which holds the entire polymer in solution while actually the stereoregular block remains substantially unsolvated but progressively is solvated in the oil with a temperature increase causing the desired compensation for the natural decrease in viscosity with increasing temperatures. It is thus believed that the unique oil-solubility characteristics of polypropylene make it preferable as the stereoregular polymer block in accordance with the invention. Other usable stereoregular polymer blocks, are for example, isotactic polybutene-1, or isotactic polypentene-1, which latter dissolves in oil at about 20° C. and is completely soluble at 30° C. so that the same is not as desirable as isotactic polybutene-1 for normal lubricating oil use, but is a highly desirable component of a polymer useful as a viscosity index improver for low temperature applications.

In view of the fact that the polymers in accordance with the invention are substantially pure hydrocarbon products, they are completely compatible with the oils and any additive which, in turn, is compatible with the oil itself. Furthermore, the products may be considered ashless as they by conventional catalyst removal techniques, such as alcohol washing, may be reduced to an ash content below 0.1% which is preferable for the use herein. As compared with the conventional viscosity index improvers, as for example, the methacrylate polymers, the polymers in accordance with the invention are highly stable in their environmental use, do not undergo thermal depolymerization and have high shear stability. Furthermore, the polymers may be easily, readily, and inexpensively produced by the known polymerization techniques.

For the highest V.I. improving efficiency, the relative length of the oil-soluble block should be the minimum required to hold the polymer in solution at a lower temperature, as for example at 0° F. This is dependent, to a degree, on the type of the oil stock in connection with which the improver is being used. In general, the molecular weight of the amorphous hydrocarbon polymer block should be at least 50% of the molecular weight of the stereoregular block with stereoregular and amorphous segments of approximate equal length being satisfactory for most purposes.

The following examples are given by way of illustration and not limitation:

EXAMPLE 1

To a one-liter autoclave under a dry nitrogen atmosphere was added a solution of 1.9 ml. (15 mmols) of diethyl aluminum chloride in 350 ml. of n-heptene. A titanium trichloride catalyst (1.5 g.) containing ⅓ mol of aluminum trichloride per mol to titanium trichloride was then added to the autoclave, and the temperature was adjusted to 50° C. 50 grams of butene-1 was charged to the autoclave, and polymerization was allowed to continue at that temperature for 45 minutes. 100 grams of a mixture containing 53 mol percent propylene and 47 mol percent butene-1 was then charged, the reactor was heated to 110° C. over a 30-minute period, and was held at that temperature an additional 30 minutes. The autoclave was then cooled and vented. The viscous solution in the autoclave was removed, washed with etyhelne glycol and water to remove catalyst residue and the polymer was isolated by precipitation with methanol. After drying in a vacuum oven, 98 g. of polymer was obtained. The poly-

mer was completely soluble in warm heptane and showed a melt index (190° C., 2160 g. load) of 4.0. The specific viscosity of a 0.5% solution of the polymer dissolved in an SAE 20 weight Mid-Continent stock was 1.4 at 100° F. and 1.75 at 210° F. Calculation of the ratio gives a V.I. improving efficiency of 1.25. In shear stability tests conducted on 1.0% solutions of the polymer in a naphthenic base stock, the polymer was greatly superior to commercial methacrylate V.I. improvers.

EXAMPLE 2

The catalyst was the same as that used in Example 1. A mixture containing 18 g. of styrene and 40 g. of propylene was added to the autoclave at 60° C. Polymerization was allowed to proceed one hour. A small sample of polymer was removed at this point. Infra-red analysis indicated that the polymer contained 16 mol percent styrene. 100 grams of an equimolar mixture of propylene and butene-1 was then charged and the temperature was varied to 100° C. over a 30-minute period, and was kept at that temperature for an additional 30 minutes. The polymer was worked up as in Example 1. 84 grams of polymer having a melt index of 11.9, was obtained. A 1% solution of this polymer in a solvent refined SAE 30 weight Mid-Continent stock showed a V.I. improving efficiency of 1.2.

EXAMPLE 3

To a 1 liter autoclave under a dry nitrogen atmosphere was added a solution of 2.2 ml. (20 mmols) of titanium tetrachloride in 250 ml. of a straight mineral oil (Texaco Regal Oil B) previously treated with molecular sieves. A solution of 1 ml. (7.5 mmols) of triethyl aluminum in 100 ml. n-heptane was added and the mixture was warmed to 180° C. over an hour. The autoclave was then cooled to 50° C. and 7.0 ml. (52.5 mmols) of triethyl aluminum in 50 ml. of mineral oil was added. Butene-1 (50 g.) was charged and polymerization was allowed to proceed 30 minutes, at which time the pressure dropped from 50 lbs. gauge to atmospheric pressure. A mixture (100 g.) containing equal molar amounts of propylene and butene-1 was charged, and polymerization was allowed to continue as the temperature was increased to 100° C. over 45 minutes. The autoclave was then cooled and vented. The viscous solution was washed with ethylene glycol and water. The heptane was stripped in vacuo. A viscous residue weighing 368 g. and containing 128 g. of polymer was obtained. Dilution of a sample to 1% concentration in a typical Mid-Continent SAE 10 weight stock gave a solution which showed a viscosity improving efficiency of 1.22.

EXAMPLE 4

Example 1 is repeated and the temperature of the polymerization raised to 110° C. and the propylene-butene-1 charged after the initial butene-1 had polymerized to isotactic butene-1 with a molecular weight of about 100,000. The polymerization at the higher temperature was discontinued when the amorphous copolymer block of propylene and butene-1 had reached a molecular weight between about 200,000–300,000. A 1% solution of the polymer formed acted as a viscosity index improver when used as a 1% solution in a conventional lubricating oil (Texaco Regal Oil B).

EXAMPLE 5

Polymerization is effected in the manner described in Example 1 using the catalyst system described therein with, however, a mixture of propylene and butene-1 as the monomer containing amounts of propylene ranging between 25–75 mol percent propylene. In each case an excellent viscosity index improver for lubricating oil is formed.

EXAMPLE 6

Example 5 is repeated except that in place of the mixture of propylene and butene-1, a mixture of propylene and ethylene containing about 30–60 mol percent of ethylene is introduced in the second polymerization stage where the polymerization is effected at the higher temperature.

EXAMPLE 7

Example 6 is repeated, except in the second stage instead of the propylene-ethylene mixture, an alpha-olefin having an average molecular weight between C_5–C_{20} is used.

EXAMPLE 8

Example 1 is repeated but in place of the butene-1, a mixture of ethylene and butene-1 containing 40–70 mol percent of butene-1 is introduced. The polymerization is continued until the amorphous ethylene-butene-1 copolymer is built up to a molecular weight of 200,000.

EXAMPLE 9

Example 8 is repeated, except that the polymerization is continued at the higher temperature of 110° C. by introducing a mixture of propylene and C_5–C_{20} alpha olefins containing about 30–90 mol percent of the C_5–C_{20} alpha olefins. The polymerization of the propylene-higher alpha olefin amorphous block was continued to a molecular weight of 200,000–300,000.

EXAMPLE 10

Example 1 is repeated but the butene-1 initially charged is admixed with 80–95 mol percent of propylene with the polymerization of the stereo-specific copolymer continued to a molecular weight of about 100,000. The mixture containing the larger amount of butene-1, i.e. the 47 mol percent was then introduced and the polymerization continued at a higher temperature until the amorphous polymer block reached a molecular weight of 300,000.

EXAMPLE 11

Example 2 is repeated with the initial stereo-specific polymerization being effected to a molecular weight of 90,000. Thereafter the polymerization is continued at the increased temperature of 100° C. utilizing propylene and an alpha olefin of an average molecular weight of C_5–C_{20} in substantially equal parts. The polymerization of the amorphous copolymer is discontinued after a molecular weight of 150,000 is achieved.

EXAMPLE 12

A mixture of propylene and ethylene containing about 10–20 mol percent of ethylene was stereo-specifically polymerized with the catalyst system of Example 1 at a temperature of about 40° C. to a molecular weight of about 20,000. Thereafter, the quantity of ethylene in the gas mixture was raised to about 50% and the polymerization temperature to about 90° C. and the polymerization continued to a total molecular weight of the polymer formed of about 250,000 and is purified by removal of the solvent and washing in methyl alcohol.

EXAMPLE 13

Example 10 is repeated except that ethylene is used in place of the propylene.

EXAMPLE 14

Example 1 is repeated initially using, however, pentene-1 in place of the butene-1 to form an isotactic polypentene-1 block in place of the isotactic polybutene-1 block. Additionally, in place of the amorphous propylene-butene-1 copolymer block an atactic polybutene-1 block may be formed.

EXAMPLE 15

To a one-gallon autoclave, under a dry nitrogen atmosphere is added a solution of 3.7 ml. (30 mmols.) of diethyl aluminum chloride in one liter of heptane. A titanium trichloride catalyst (3.0 g.) containing ⅓ mol of aluminum trichloride per mol of titanium trichloride is added and the temperature is raised to 65° C. Sixteen grams of hexene-1 is added followed immediately by 56 g. of

butene-1. Polymerization is allowed to continue 30 minutes at 65° C. The reactor is then vented and 60 g. of a butene-propylene mixture containing 52 mol percent propylene is charged. Polymerization is allowed to proceed an additional 60 minutes at 65° C. The autoclave is then emptied and polymer is precipitated from the viscous heptane solution with isopropanol. After drying, 85 grams of polymer are obtained. This polymer, as a 1% solution in a 100 S.U.S. paraffinic oil, exhibits a viscosity index improving efficiency of 1.23, and a 10% solution of the polymer in the same base oil is readily pourable. The hexene-1 constitutes 7.9 mol percent of the monomer charge.

EXAMPLE 16

To a one-gallon autoclave was charged a solution of 5.1 ml. (40 mmols) of diethyl aluminum chloride in 2 l. of n-heptane. Titanium trichloride (4.0 g.) containing ⅓ mol of $AlCl_3$ per mol of $TiCl_3$ was added and the temperature was raised to 75° C. A C_7–C_9 alpha olefin fraction (50 g.) was added followed immediately by 200 g. of a butene-1-propylene mixture containing 52 mol percent propylene. Polymerization was allowed to continue two hours, whereupon the pressure in the reaction had dropped to less than 5 p.s.i. The polymer was isolated by conventional techniques. After drying, 163 grams of polymer was obtained. A 1% solution of this polymer in a 100 S.U.S. paraffinic oil showing a viscosity index improving efficiency of 1.28 and a 10% solution of the polymer in the same base stock was readily pourable. The molecular weight of the polymer was estimated to be 800,000 from dilute solution viscosity measurements. The C_7–C_9 alpha olefin fraction constituted 10 mol percent of the monomer charge.

EXAMPLE 17

To a one-gallon autoclave, under a nitrogen atmosphere, was added 2 liters of heptane containing 3.0 g. of $TiCl_3.⅓AlCl_3$ and 3.75 ml. of diethyl aluminum chloride. The reactor was closed and the temperature was raised to 60° C. 4-methyl pentene-1 was then pumped into the reactor at a rate of 5 g./minute, and butene-1 was pumped into the reactor at a rate of 2 g./minute. After 20 minutes, the addition of 4-methyl pentene-1 was terminated. The addition of butene-1 was allowed to continue for a total of 50 minutes. After an additional hour of polymerization, the reaction was terminated by the addition of methanol. After isolating and drying in the conventional manner, 71 g. of a block copolymer (4-methyl pentene-1-butene-1 copolymer) having a molecular weight of 900,000 was obtained.

A 1% solution of this polymer in a 100 S.U.S. neutral paraffinic oil after standing three days showed a viscosity index improving efficiency of 1.99.

EXAMPLE 18

Example 17 was repeated, using styrene in place of 4-methyl pentene-1. The reaction was carried out at 80° C. After 2 hours, 45 g. of a block copolymer (styrene-butene-1 copolymer) was obtained which showed a viscosity index improving efficiency of 1.4 when measured at the conventional temperatures of 100° F. and 210° F. When the viscosity index improving efficiency was calculated from measurements made at 100° F. and 250° F., the efficiency was 1.8, indicating that this copolymer is suitable for use at temperatures higher than normally encountered in automobile engines.

While the invention has been described in detail with reference to certain specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to the skilled artisan. The invention is, therefore, only intended to be limited by the appended claims or their equivalents wherein I have endeavored to claim all inherent novelty.

I claim:

1. A lubricating oil composition comprising a petroleum lubricating oil and dissolved therein in the range of 0.3 to 10 weight percent of a block polymer having a molecular weight in the range of 50,000 to 2,000,000 and composed solely of a hydrocarbon chain having a number of alternate stereo-regular and amorphous segments, said stereo-regular segments being of a poly alpha olefin having from 3 to 8 carbon atoms and being present in an amount sufficient to give said polymer a viscosity index improving efficiency of at least 1.0, said amorphous segments being polymer segments of at least one lower alpha olefin having from 2 to 20 carbon atoms and amounting to at least 50 percent of said molecular weight, said polymer being prepared in a Ziegler catalyst system and said stereo-regular segments being of such an amount and nature so that if collectively joined in a polymer chain such polymer would be oil-insoluble at a temperature below 0° C.

2. A lubricating oil composition comprising a petroleum lubricating oil and dissolved therein in the range of 0.3 to 10 weight percent of a block polymer having a molecular weight in the range of 50,000 to 2,000,000 and composed solely of a hydrocarbon chain having a number of alternate stereo-regular and amorphous segments, said stereo-regular segments being present in an amount sufficient to give said polymer a viscosity index improving efficiency of at least 1.0 and being composed of monomer units selected from the group consisting of propylene, styrene, butene-1, and hexene-1, said amorphous segments being composed of monomer units of at least one lower alpha olefin having from 2 to 20 carbon atoms, said polymer being prepared in a Ziegler catalyst system, and said stereo-regular segments being of such an amount and nature so that if collectively joined in a continuous polymer chain, such polymer would be oil-insoluble at a temperature below 0° C.

3. The composition of claim 2 wherein said block polymer is a terpolymer of propylene, styrene and butene-1.

4. The composition of claim 2 wherein said block polymer is composed of propylene and butene-1 monomer units.

5. The composition of claim 2 wherein said block polymer is composed of ethylene and propylene monomer units.

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