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(54) Title: A METHOD TO OLIGOMERIZE C_4 OLEFINS TOGETHER WITH LINEAR ALPHA OLEFINS

(57) Abstract

The invention concerns a process for producing synthetic oils, wherein olefinic hydrocarbons are polymerized to form an oily product having a high viscosity index and a low pour point. According to the invention, higher linear alpha-olefins containing 6 to 24 carbon atoms are reacted with a hydrocarbon composition containing 15 to 80 % by weight of 1-butene, 5 to 50 % by weight of 2-butenes, and about 10 % by weight or less of isobutylene in the presence of an initiator system to produce a copolymer-containing reaction mixture, and the copolymer is separated from the reaction mixture. By means of the invention it is possible to prepare high-quality synthetic oils from an inexpensive raw material such as Raffinate II emanating from the production of MTBE or polyisobutylene.

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A method to oligomerize C_4 olefins together with linear alpha olefins

The invention concerns a process in accordance with the preamble of claim 1 for producing synthetic oils.

According to a process of the present kind, olefinic hydrocarbons are polymerized in order to prepare oily products whose number average molecular weights typically lie in the range from 300 to 1200.

The invention also relates to copolymers in accordance with the preamble of claim 17 useful as synthetic oils. A process for preparing such copolymers is also disclosed.

In the petrochemical industry, a mixture of hydrocarbons known as Raffinate II remains after the isolation of 1,3-butadiene and isobutylene from pyrolytic C_4 fractions. This kind of a mixture emanates, for instance, from the production of polyisobutylene and, in particular, from the production of methyl tert-butyl ether (MTBE) used as an anti-knock in petrols. The Raffinate II contains, besides n-butane and isobutane, large amounts of n-butenes. Thus, a conventional Raffinate composition comprises some 30 to 55 % by weight of 1-butene and 15 to 30 % by weight of 2-butenes (i.e. cis- and trans-butene). In addition there are minor amounts, typically less than about 3 % by weight, of isobutylene and some methanol, for instance less than about 3 % by weight, in the Raffinate.

Normally large volumes of the Raffinate II are produced and used in low value applications during processing of polyisobutylene and MTBE. Here it has been suggested in the prior art to use said Raffinate II and similar secondary raw materials for preparing synthetic oils. Thus, EP Published Patent Applications Nos. 0 337 737 and 0 367 386 teach a process for preparing poly(n-butene) oils, which comprises oligomerizing the olefinic C_4 hydrocarbons of the Raffinate II in a reaction carried out in the presence of an initiator,

such as $AlCl_3$ or alkylaluminium chlorides, and a coinitiator, typically HCl. Because Raffinate II does not contain isobutylene, or contains it in concentrations below 3 % by weight, the produced oils are predominantly the copolymers of 1-butene with cis- and trans-2-butenes.

Although poly(n-butene) oils are not yet industrially produced on a large scale, their broad application in practice is expected because they can be produced from an inexpensive secondary raw material, such as Raffinate II. However, the viscosity of these oils is strongly dependent on temperature, which today limits a broader utilization of the poly(n-butene) oils in the field of engine lubricating oils and for similar purposes.

The quality of lubricating oils is usually characterized by the pour point and the viscosity index. The latter reflects the temperature-dependency of the viscosity of the oil. In the case of high-quality synthetic oils intended for use as engine lubricating oils, it is generally required that the value of the viscosity index be about 120 or higher. Such values are obtained with conventional polyolefinic oils produced by oligomerization of higher linear alpha-olefins using Friedel-Crafts catalysts or Ziegler-Natta catalytic systems. These oils are primarily produced by oligomerization (i.e. trimerization to pentamerization) of 1-octene or 1-decene, giving oligomers with optimal properties from the point of view of both viscosity index and pour point. In comparison, it should be mentioned that the viscosity index of poly(n-butene) based oils is below 75, which — although too low for engine lubrication — still is sufficient for many other applications.

The industrially produced oils from higher linear olefins belong to the expensive oils on the market and therefore their broader use is limited.

Thus, in summary, the conventional synthetic oils are too expensive to be used on a larger scale, whereas the properties of the much more inexpensive poly(n-butene) oils do not meet the standards for engine lubricants.

One aim of the present invention is to eliminate the problems related to the prior art in the field of synthetic lubricating oils and to provide inexpensive new oils with acceptable properties.

Another aim is to provide novel olefinic copolymers which can be used as lubricating oils or as part of synthetic oil compositions.

Still a third aim is to provide processes for preparing the novel oils and copolymers.

It has now unexpectedly been found that 1-butene along with the cis- and trans-2-butenes or their mixtures contained in the Raffinate II can readily be copolymerized with higher linear alpha-olefins in the presence of suitable initiators to provide an oily product with high viscosity index and low pour point. Thus, the invention is based on the idea of polymerizing higher linear alpha-olefins in hydrocarbon compositions containing essential amounts of olefinic C_4 hydrocarbons, in particular compositions, which are comprised of the residues of the pyrolytic C_4 fractions, such as the above-mentioned Raffinate II.

In particular the process in accordance with the invention is characterized by what is stated in the characterizing part of claim 1.

The copolymers according to the invention are mainly characterized by what is stated in the characterizing part of claim 17.

The process for preparing copolymer useful as synthetic oils is characterized by what is stated in the characterizing part of claim 20.

Within the scope of the present application the term "to polymerize" denotes the formation by chemical reactions of large molecules built up by single monomers (or repeating units) irrespective of the number of such monomers in the product. Thus, for the purposes of this application "polymerizing" also includes "oligomerizing", i.e. formation of large molecules containing 2 to 10 monomers.

According to one preferred embodiment, synthetic oils are prepared by polymerizing higher linear alpha-olefines (LAO) in hydrocarbon compositions containing some 15 to 80 % by weight of 1-butene, 5 to 50 % by weight of 2-butenes, and about 10 % by weight or less of isobutylene. Preferably, the olefinic hydrocarbon compositions contain about 25 to 70 % by weight, in particular 30 to 60 % by weight of 1-butene and 10 to 40 % by weight, in particular 15 to 30 % by weight of 2-butenes. In addition to these components the composition may contain minor amounts of, for instance, n-butane, isobutane, propane and other alkanes, isobutylene, methyl tert-butyl ether and other etherification products, as well as various other lower olefinic oligomers.

In particular, the olefinic hydrocarbon compositions comprise mixtures of hydrocarbons remaining in a pyrolytic C_4 fraction after isolation of 1,3-butadiene and isobutylene. These kinds of hydrocarbon mixtures may consist of Raffinate II which is obtained from the production of methyl tert-butyl ether or from the selective polymerization of isobutylene.

To the C_4 hydrocarbon compositions there are added 1 to 99 % by weight, preferably 5 to 90 % by weight and in particular 10 to 70 % by weight of higher LAO's. The amount of the added LAO's is calculated on basis of the total amount of olefins

in the composition after the addition. The added LAO's are selected from the group comprising higher alpha-olefins containing 6 to 24 carbon atoms, preferably the LAO's may be selected from the group comprising higher linear alpha-olefins containing 6 to 18 carbon atoms, and in particular the LAO's are selected from the group comprising higher linear alpha-olefins containing 8 to 16 carbon atoms. Exemplifying LAO species are 1-octene, 1-decene, 1-dodecene, 1-tetradecene and 1-hexadecene.

The molecular weights of the produced copolymers depend on the composition of the initial mixture, on the polymerization temperature, and to some extent on the initiator system used. Typically, the number average molecular weight, $\overline{M}_n$, ranges from 300 to 1200, preferably from about 350 to about 1000.

The polymerization is preferably carried out at -10 °C to +70 °C. Without altering the composition of the reaction mixture, the number average molecular weight of the copolymers can be varied in the range from 300 to 1000 by changing the temperature of the polymerization.

The initiator systems used for the polymerization are similar to those previously employed for preparing poly(n-butenes). Reference is made, in particular, to the above-mentioned European Published Patent Applications Nos. 0 337 737 and 0 367 386, the disclosures of which are herewith incorporated by reference.

Thus, the initiator system may be based on $AlCl_3$. However, the copolymerization does not proceed solely with $AlCl_3$ and, according to one preferred embodiment, $AlCl_3$ is therefore added in an ethyl chloride solution or as a liquid complex formed from $AlCl_3$, toluene or an equivalent aromatic solvent, and hydrogen chloride. The advantage of these forms of $AlCl_3$ consists in easy dosing of the initiator into the reaction system and also in the fact that $AlCl_3$ does not need any

additional coinitiator if added in this form. Since the aluminium trichloride liquid complex is not soluble in Raffinate II, vigorous stirring of the reaction medium is required to avoid deposition of the catalyst system on the bottom of the reaction vessel.

According to another preferred embodiment, an alkylaluminium chloride of the general formulas R_2AlCl or $RAlCl_2$ is employed as an initiator and an anhydrous hydrogen halide as a polymerization coinitiator. In the above general formulas R stands for a lower alkyl having 1 to 6 carbon atoms. Preferably alkylaluminium dichloride compounds of the general formula $RAlCl_2$ are used and, in particular, the compounds are selected from the group comprising methylaluminium dichloride, ethylaluminium dichloride, propylaluminium dichloride and butylaluminium dichloride. The hydrogen halides may comprise hydrogen chloride or hydrogen fluoride, hydrogen chloride being preferred.

Gradual addition of the initiator into the reaction mixture will assist in governing the rate of copolymerization by providing practically isothermal reaction control of the strongly exothermic copolymerization. In this way it is possible to ensure that a product of even quality will be obtained.

In the case of an initiator system comprising an initiator and a coinitiator, it is preferred to add the coinitiator at the beginning of polymerization. If anhydrous hydrogen chloride is used, the total amount of initially added coinitiator ranges from 0.1 % by weight to 0.3 % by weight. The coinitiator can be added dissolved in the reaction mixture. Alkylaluminium dichloride can be then added in small portions, preferably in an inert solvent, and thus an almost isothermal course of polymerization can be secured at the required temperature. At an inverse addition order of components, there is a danger that the exothermal reaction

cannot be controlled and proceeds extremely fast. In such a case, an undesirable overheating of the reaction mixture may take place.

The initiator and the coinitiator are consumed by the polymerization reaction. At polymerization temperatures below -10 °C, the relative consumption of the initiator increases and high conversions are hardly attained. Therefore, as mentioned above, the reaction is preferably carried out at temperatures above -10 °C. Typically, the initiator consumption (calculated on basis of the obtained product) amounts to 0.3 - 0.7 % by weight at temperatures in the preferred range from -10 °C to +70 °C at olefin conversion rates in excess of 90 %.

According to one particularly preferred embodiment of the invention, to an olefinic hydrocarbon composition, which contains n-butenes in a total concentration of at least 30 % by weight, there are added alpha-olefins containing 6 to 18 carbon atoms in the molecule. The alpha-olefins are reacted with the butenes of the hydrocarbon composition in the presence of an initiator system comprising a solution of $AlCl_3$ in ethyl chloride or a liquid complex formed from $AlCl_3$, toluene and HCl to provide oils with viscosity indeces from 100 to 150 and pour points from +5 °C to -65 °C, the molar ratio of alpha-olefins to n-butenes being in the range from 1:1 to 1:5.

According to another particularly preferred embodiment of the invention, to an olefinic hydrocarbon composition, which contains n-butenes in a total concentration of at least 30 % by weight, there are added alpha-olefins containing 8 to 16 carbon atoms in the molecule. The alpha-olefins are reacted with the butenes of the hydrocarbon composition in the presence of an initiator system comprising an alkylalumium dichloride together with hydrogen chloride to provide an oil with viscosity index from 100 to 140 and pour points from

0 °C to -65 °C, the molar ratio of alpha-olefins to n-butenes being in the range from 1:1 to 1:5.

The copolymers according to the invention essentially consist of repeating units of n-butene, cis- and trans-2-butenes and higher linear alpha-olefins with 6 to 18 carbon atoms. The polydispersity of these copolymers defined as the ratio $\overline{M}_w/\overline{M}_n$ is lower than 1.4.

As mentioned above, the invention also concerns a process for producing a copolymer product useful as a synthetic oil or part thereof. The process may be summarized as comprising the steps of

- mixing higher linear alpha-olefins having 6 to 18 carbon atoms with a C_4 hydrocarbon composition derived from the production of methyl tert-butyl ether or from the selective polymerization of isobutylene and containing at least 15 % by weight of 1-butene and at least 5 % by weight of 2-butenes to form a reaction mixture,
- adding an initiator system to the reaction mixture,
- keeping the temperature of the reaction mixture in the range from -10 °C to +70 °C,
- allowing the higher linear alpha-olefins to react with the 1-butenes and 2-butenes to form a reaction product, and
- separating volatile components and any initiator system residues to form a oily product consisting essentially of copolymers having a number average molecular weight in the range from 300 to 1200.

The oily products of the invention are characterized by having higher viscosity index than have the poly(n-butene) oils as such. Also the pour point is improved by the copolymerization of n-butenes with higher linear alpha--olefins. The pour point of the present oils is lower than that of poly(n-butene) oils and it is, in fact, even lower

that the pour points of oligomers of higher linear alpha--olefins of comparable molecular weights.

According to a preferred embodiment of the present invention, the hydrocarbon composition should contain only trace amounts, if any, of methanol, since the methanol may interfere with the polymerization reaction by consuming the initiator and causing inhibition of the polymerization. Therefore, if Raffinate II obtained from the production of methyl tert-butyl ether is used, which sometime may contain up to a couple of per cent per weight of methanol, the residual methanol is removed or its concentration lowered to below 3000 ppm before the polymerization reaction.

The viscosity index of the copolymerisate depends on the content and the kind of the higher linear alpha-olefins used and tends to increase with increasing content and length of the linear alpha-olefin. Pour point of the obtained copolymer also depends on the higher linear alpha-olefin used and increases with increasing length of the copolymer molecule and with increasing molar content of n-butenes.

After polymerization, the reaction mixture is processed by methods known *per se*. According to a preferred embodiment, it is washed, in particular, with an about 5 % aqueous solution of soda and then with water. Alternatively, sorption clay is added to the mixture in an amount of approx. 0,5 to 10 %, in particular about 2 %, calculated on basis of the initial content of olefins, to remove the catalyst. The low-boiling portions are distilled off by heating to at least 140 °C at 13 Pa. A colourless or slightly yellowish oil is obtained with a kinematic viscosity in the range from 4 to 15 cSt at +100 °C and in the range from 27 to 160 cSt at +40 °C. The obtained copolymers are characterized by a relatively narrow distribution of molecular weight corresponding to a polydispersity defined as the ratio $\overline{M}_w/\overline{M}_n$ lower than 1.4.

The invention provides considerable benefits. A particularly important advantage of the present process resides in the fact that the copolymerization of n-butenes can be carried out in Raffinate II, which is a cheap secondary raw material normally discarded, without having to isolate and purify the n-butenes.

A further advantage of the invention consists in producing high quality synthetic oils with viscosity indeces on the same level as those of expensive synthetic oils prepared from pure higher linear alpha-olefins.

The oils produced by copolymerization of n-butenes with higher linear alpha-olefins according to this invention can be used for a number of different applications. In particular, because of their very convenient values of viscosity index and pour point, they can be employed as high-quality engine lubricating oils in applications where the viscosity changes with temperature should be as small as possible. The low polydispersity of their molecular weights is important as it indicates that the oil viscosity will not change too much during long-term mechanical stress. The obtained properties are similar to these of multigrade oils with long-term service lives.

Another important feature of the present oils consists in the fact that they do not release any carbonization residue after heating to high temperature or combustion. This is why their expected use is as lubricating oils for two-stroke combustion engines, as oils useful in metallurgy for rolling and drawing of metallic materials, as oils for transformers, electrical insulations and cables, as oils for energy transfer in cooling and heating systems, and as oils for many other similar applications. The oils are non-toxic and can be utilized as additives in plastics and rubbers.

In the following, the invention will be further examined in

detail with the aid of working examples illustrating the copolymerization of n-butenes with higher linear alpha-olefins in a Raffinate II. It should, however, be understood that the scope of the invention is not limited to these examples. In particular it should be noted that other hydrocarbon compositions containing essential amounts of olefinic C_4 hydrocarbons can be used for the purposes of the present invention.

Equipment and materials

The copolymerizations were carried out in a glass reactor with a volume of 150 ml or, alternatively, in a stainless steel reactor with a volume of 1000 ml. Both reactors were equipped with a magnetic stirrer, valve for charging and dosing the initiator and with outside cooling. The temperature of the reaction mixture was monitored with a thermocouple connected to a recorder. The polymerization course was controlled by gradual dosing of the initiator so as to keep the temperature of the reaction mixture in the region of +3 °C around the required temperature.

For the purpose of preparing the oils, a hydrocarbon composition (Raffinate II) comprising the residue of a C_4 fraction from the production of MTBE was used. It was washed three times with water in order to remove methanol and dried in the liquid state over KOH in a pressure vessel.

The hydrocarbon composition refined in this way had the following composition: 49.2 % 1-butene, 15.1 % trans--2-butene, 9.7 % cis-2-butene, 2.2 % isobutylene, 15.6 % n-butane, 7.2 % isobutane and 0.6 % propane. The methanol content was always less than 3000 ppm and the content of methyl tert-butyl ether was less than 0.2 %. The linear alpha-olefins were of commercial purity and contained more than 99 % by weight 1-olefin.

Molecular weights $\overline{M}_n$ and $\overline{M}_w$ and polydispersity $\overline{M}_w/\overline{M}_n$ of the products were evaluated by GPC and VPO.

Example 1

Copolymerization of n-butenes was carried out in a mixture of hydrocarbons known as Raffinate II which had been separated from the C_4 fraction in the production of MTBE . To this mixture 30 mol % of 1-decene was added, the amount of 1 decene added being calculated on basis of amounts of olefins in the new mixture formed. The copolymerization was performed at a mean temperature of +20 °C by gradual addition of small amounts of a 10 % $AlCl_3$ solution in ethyl chloride in such a way that the reaction mixture was not overheated by more than 3 °C. The polymerization was stopped after 40 min by addition of alcohol, the reaction mixture was washed with a 5 % solution of soda and then with water. The hydrocarbon layer was separated, mixed with filtration clay and filtered under pressure. Volatile fraction was removed by heating the reaction mixture up to 120 °C at 13 Pa. The colourless oil obtained had a number average molecular weight $\overline{M}_n$ = 810 and a viscosity index of 107. The consumption of $AlCl_3$ related to the final product was 0.6 % by weight at an olefin conversion rate of 97 % by weight

Example 2

Copolymerization of n-butenes with 1-dodecene was carried out in Raffinate II in an analogous way as in Example 1. The copolymer prepared with 30 mol.% 1-dodecene at polymerization temperature +20 °C had a molecular weight $\overline{M}_n$ of 850, a viscosity index of 122 and a pour point of -43 °C. The consumption of $AlCl_3$ was 0.7 % by weight at a conversion rate of 95 % .

Example 3

Copolymerization of n-butenes present in Raffinate II was carried out with the addition of 30 mol.% 1-tetradecene analogously as in Example 1. The molecular weight $\overline{M}_n$ of the oil obtained at a polymerization temperature of +20 °C was 810, whereas the polydispersity $\overline{M}_w/\overline{M}_n$ was 1.3 and the viscosity index was 141.

Example 4

Copolymerization of n-butenes was carried out in the residue of a C_4 fraction (Raffinate II) with the addition of 30 mol.% 1-hexadecene (the added amount related to the total amount of olefins in the same way as in Example 1). The copolymerization was conducted at +20 °C, the conversion rate, as calculated on basis of the olefins present in the mixture, being 92 %. The prepared oil had a number average molecular weight $\overline{M}_n$ of 910, a polydispersity $\overline{M}_w/\overline{M}_n$ of 1.1, a viscosity index of 148 and a pour point of -3 °C. The consumption of $AlCl_3$ was 0.65 % by weight at a 92 % conversion rate.

Example 5

Copolymerization of n-butenes present in the residue of a C_4 fraction was carried out with the addition of 30 % by weight of 1-hexadecene at +20 °C under initiation with a liquid complex of $AlCl_3$, toluene and anhydrous HCl. The liquid complex was prepared by introducing gaseous HCl into a suspension of 5.0 g $AlCl_3$ in 6.0 ml toluene at 0 °C until all $AlCl_3$ was transferred into the solution. A conversion rate of 94 % was attained by gradual dosing of the initiator into the reaction mixture for 30 min.

The obtained oil had a molecular weight $\overline{M}_n$ of 700, a polydispersity $\overline{M}_w/\overline{M}_n$ of 1.31, a viscosity index of 130 and a pour

point of -15 °C. The consumption of $AlCl_3$ related to the product was 0.6 % by weight.

Example 6

Copolymerization of n-butenes was carried out in the residue of a C_4 fraction with 50 % by weight of 1-decene at +70 °C under initiation with a liquid $AlCl_3$ complex prepared according to Example 5. The polymerization was stopped after 30 min by addition of alcohol at a 93.5 % conversion rate. The oily product had a molecular weight $\overline{M}_n$ = 560, a viscosity index of 117 and a pour point of -38 °C.

Example 7

Copolymerization of n-butenes was carried out in Raffinate II by the addition of 30 % by weight of 1-dodecene related to the total content of olefins in the resulting mixture using a liquid $AlCl_3$ complex prepared according to the disclosure of Example 5 as an initiator. The copolymerization proceeded at -10 °C during 50 min under gradual dosing of the initiator up to a conversion rate of 85 % related to the total content of olefins. The obtained copolymer had a molecular weight $\overline{M}_n$ of 860, a viscosity index of 105 and a pour point of -31 °C. The consumption of $AlCl_3$ related to the product was 0.83 % by weight.

Example 8

Copolymerization of n-butene in Raffinate II was carried out with linear alpha-olefins C_6 to C_{16} added into the reaction mixture in an amount of 37 % by weight related to the total amount of olefins in the new resulting mixture. The polymerizations were carried out at +20 °C under initiation with an $AlCl_3$ solution in ethyl chloride. The consumption of $AlCl_3$ related to the product ranged from 0.45 to 0.75 % by weight. The results are given in Table I.

Table 1 Characteristics of copolymers of n-butenes in Raffinate II with various 1-olefins (about 37 % by weight 1-olefin, 20 °C)

1-Olefin	Conversion %	Molecular weight $\bar{M}_n$	$\bar{M}_w$	Kinematic viscosity [cSt] 40	100	Viscosity index	Pour point °C
C_4	83.3	620	740	156.0	12.9	66	
C_6	92.5	690	820	155.1	13.8	82	
C_8	-	750	840	147.6	13.7	87	
	89.4	680	800	131.3	12.8	88	
C_{10}	94.0	660	810	98.5	10.9	94	
C_{12}	93.8	760	910	109.0	12.2	102	-38
C_{14}	96.4	680	860	64.9	9.3	122	-33
C_{16}	95.4	680	860	56.5	8.6	127	-16

Polymerization conditions: initiator - aluminium chloride in ethyl chloride, polymerization temperature +20 °C

The content of 1-olefins (C_4-C_{16}) relates to the olefins present in the Raffinate II only

Example 9

Copolymerization of n-butenes was carried out in a mixture of C_4 hydrocarbons (Raffinate II) obtained from the production of MTBE. To this mixture 37 % by weight of 1-decene was added, the added amount being calculated on basis of the total amount of olefins in the new mixture formed. Before the polymerization, 0.3 % by weight of gaseous hydrogen chloride was introduced into the reaction mixture. The copolymerization was performed at a mean temperature of +20 °C by gradual addition of small amounts of a 10-% $EtAlCl_2$ solution in heptane in such a way that the reaction mixture

was not overheated by more than 3 °C. The polymerization was stopped after 40 min by adding alcohol, the reaction mixture was washed with a 5 % solution of soda and then with water. The hydrocarbon layer was separated, mixed with filtration clay and filtered under pressure. Volatile fraction was removed by heating the reaction mixture up to 120 °C at 13 Pa. The colour-less oil obtained had a number average molecular weight $\overline{M}_n$ of 640 and a viscosity index of 97. The consumption of $EtAlCl_2$ related to the final product was 0.5 % by weight at a 92 % conversion rate of the olefins.

Example 10

Copolymerization of n-butenes with 1-dodecene was carried out in Raffinate II in an analogous way as in Example 9. The copolymer prepared with 37 % by weight of 1-dodecene at a polymerisation temperature of +20 °C had a molecular weight $\overline{M}_n$ of 111 and a pour point of -38 °C. The consumption of $EtAlCl_2$ was 0.7 % by weight at a conversion rate of 93 %.

Example 11

Copolymerization of n-butenes present in Raffinate II was carried out with the addition of 37 % by weight of 1-tetradecene analogously as in Example 9. The oil obtained at a polymerization temperature of +20 °C had a molecular weight $\overline{M}_n$ of 630, a polydispersity $\overline{M}_w/\overline{M}_n$ of 1.2, a viscosity index of 109 and a pour point of -33 °C.

Example 12

Copolymerization of n-butenes was carried out in a residue of a C_4 fraction (Raffinate II) with the addition of 37 % by weight of 1-hexadecene related to the total amount of olefins in the same way as in Example 9 at +20 °C. The prepared oil had a number average molecular weight $\overline{M}_w$ of 820, a poly-dispersity $\overline{M}_w/\overline{M}_n$ of 1.25, a viscosity index of 110 and pour

point of -16°C. The consumption of $EtAlCl_2$ was 0.65 % by weight at a conversion rate of 91 %. Anhydrous hydrogen chloride was added at the beginning into the initial reaction mixture in the amount of 0.25 % by weight.

Example 13

Copolymerization of n-butenes present in a residue of a C_4 fraction was carried out with the addition of 13 % by weight of 1-hexadecene at +20 °C under initiation with anhydrous HCl and $EtAlCl_2$. A 89 % conversion rated was attained by gradual dosing of the initiator into the reaction mixture for 30 min. The obtained oil had a molecular weight $\overline{M}_n$ of 680, a polydispersity $\overline{M}_w/\overline{M}_n$ of 1.15, a viscosity index of 83 and a pour point of -45 °C. The consumption of $EtAlCl_2$ related to the product was 0.6 % by weight.

Example 14

Copolymerization of n-butenes was carried out in a C_4 fraction residue with 50 % by weight of 1-decene at +70 °C under initiation with HCl and $EtAlCl_2$. The polymerization was stopped after 30 min by the addition of alcohol at a conversion rate of 93.5 % by weight. The oily product had a molecular weight $\overline{M}_n$ of 560, a viscosity index of 119 and a pour point of -63 °C.

Example 15

Copolymerization of n-butenes was carried out in Raffinate II with the addition of 30 % by weight of 1-octene related to the total content of olefins in the resulting mixture using $EtAlCl_2$ as an initiator. The copolymerization proceeded at -10 °C during 50 min under gradual dosing of the initiator up to a conversion of 85 % by weight related to the total content of olefins. The obtained copolymer had a molecular weight $\overline{M}_n$ of 860, a viscosity index of 105 and a pour point

of -21 °C. The consumption of $EtAlCl_2$ related to the product was 0.83 % by weight. Anhydrous hydrogen chloride was added at the beginning into the reaction mixture in an amount of 0.35 % by weight.

Example 16

Copolymerization of n-butene in Raffinate II was carried out by adding linear alpha-olefins C_6 to C_{16} into the reaction mixture in an amount of 37 % by weight related to the total olefins in the new resulting mixture. The polymerizations were carried out at +40 °C under initiation with a solution of $EtAlCl_2$ and HCl as coinitiator. The consumption of $EtAlCl_2$ related to the product ranged from 0.40 to 0.70 % by weight. The results are given in Table 2.

Example 17

Copolymerization of n-butenes present in Raffinate II was carried out with the addition of 10 % by weight of 1-octene and 10 % by weight of 1-decene at +20 °C under initiation with anhydrous HCl and methyl aluminium dichloride $MeAlCl_2$. The polymerization was stopped at a coversion rate of 93 % by weight. The consumption of $MeAlCl_2$ related to the product was 0.65 % by weight, the number average molecular weight ($\overline{M}_n$) of the oily product was 610, the viscosity index 95 and the pour point -55 °C.

Example 18

Copolymerization of a n-butenes mixture in the Raffinate II was carried out with 50 % by weight of 1-decene under initiation with HCl and butyl aluminium dichloride $BuAlCl_2$ at +50 °C.

The isolated polymer had a molecular weight $\overline{M}_n$ of 550, a viscosity index of 108 and a pour point of -51 °C. The

consumption of $BuAlCl_2$ was 10.73 % by weight at a conversion rate of olefins of 92 % by weight.

Table 2 Characteristics of copolymers of n-butenes in Raffinate II with various 1-olefins (about 37 % by weight 1-olefin, 40 °C)

1-Olefin	Conversion %	Molecular weight $\overline{M}_n$	$\overline{M}_w$	Kinematic viscosity [cSt] 40	100	Viscosity index	Pour point °C
C_4	89.9	560	690	68.4	7.9	74	
C_6	90.9	490	610	40.3	5.8	78	
C_8	95.2	520	620	45.8	6.7	98	
C_{10}	100.0	570	720	48.6	7.0	99	
C_{12}	83.2	500	680	25.1	4.7	107	-61
C_{14}	92.1	530	700	26.3	5.0	115	-41
C_{16}	90.8	660	820	56.6	8.1	111	-23

Polymerization conditions: initiator system: ethylaluminium dichloride, polymerization temperature +40 °C

[a]Content of 1-olefins (C_4-C_{16}) relates to the olefins present in the Raffinate II only

Claims

1. A process for producing synthetic oils, wherein olefinic hydrocarbons are polymerized to form an oily product having a high viscosity index and a low pour point, c h a r a c t e r i z e d by

- reacting higher linear alpha-olefins containing 6 to 24 carbon atoms with a hydrocarbon composition containing essential amounts of 1-butene and 2-butenes in the presence of an initiator system to produce a copolymer-containing reaction mixture, and
- separating the copolymer from the reaction mixture.

2. The process according to claim 1, wherein the higher linear alpha-olefins are reacted with a hydrocarbon composition containing 15 to 80 % by weight of 1-butene, 5 to 50 % by weight of 2-butenes, and about 10 % by weight or less of isobutylene.

3. The process according to claim 2, wherein the higher linear alpha-olefins are reacted with a hydrocarbon composition containing about 25 to 70 % by weight, in particular 30 to 60 % by weight of 1-butene and 10 to 40 % by weight, in particular 15 to 30 % by weight of 2-butenes.

4. The process according to any one of claims 1 to 3, wherein the hydrocarbon composition comprises the residue of a C_4 fraction remaining after the separation of essentially all of the 1,3-butadiene and isobutylene compounds.

5. The process according to claim 4, wherein the hydrocarbon composition comprises a mixture of hydrocarbons known as Raffinate II obtained from a process for preparing a product selected from the group comprising methyl tert-butyl ether and poly(isobutylene).

6. The process according to any one of claims 1 to 5,

wherein 1 to 99 % by weight, preferably 5 to 90 % by weight and in particular 10 to 70 % by weight of higher linear alpha-olefins are added to the hydrocarbon composition and reacted with the 1-butene and 2-butenes fraction thereof, the amount of the added linear alpha-olefins being calculated on basis of the total amount of olefins in the composition after the addition.

7. The process according to any of the previous claims, wherein the higher linear alpha-olefins are selected from the group comprising higher alpha-olefins containing 6 to 18 carbon atoms.

8. The process according to claim 7, wherein the higher linear alpha-olefins are selected from the group comprising 1-octene, 1-decene, 1-dodecene, 1-tetradecene and 1-hexadecene.

9. The process according to any of the previous claims, wherein the initiator system is selected from the group comprising $AlCl_3$ together with HCl, $AlCl_3$ in an ethyl chloride solution; a liquid complex formed from $AlCl_3$, an aromatic solvent and hydrogen chloride; and an alkylaluminium chloride of the general formulas R_2AlCl or $RAlCl_2$, wherein R stands for a lower alkyl having 1 to 6 carbon atoms, together with an anhydrous hydrogen halide.

10. The process according to claim 9, wherein the initiator system is added gradually during the reaction.

11. The process according to claim 9, wherein the initiator system used is selected from the group comprising $AlCl_3$ in ethyl chloride solution, and a liquid complex formed from $AlCl_3$, toluene and HCl, the process comprising reacting alpha-olefins having 6 to 18 carbon atoms with a hydrocarbon composition containing at least 30 % by weight of 1-butene at a molar ratio of alpha-olefins to 1-butenes ranging from 1:1

to 1:5 to form oily products with a viscosity index in the range from 100 to 155 and pour points in the range from +5 °C to -65 °C.

12. The process according to claim 11, wherein the number average molecular weight of the oily products lies in the range from 400 to 1000.

13. The process according to claim 9, wherein the initiator system used comprises an alkylaluminium chloride together with anhydrous hydrogen chloride, the process comprising reacting alpha-olefins having 8 to 16 carbon atoms with a hydrocarbon composition containing at least 30 % by weight 1-butene at a molar ratio of alpha-olefins to 1-butenes ranging from 1:1 to 1:5 to form oily products with a viscosity index in the range from 100 to 140 and pour points in the range from 0 °C to -65 °C.

14. The process according to claim 13, wherein the number average molecular weight of the oily products lies in the range from 350 to 900.

15. The process according to any of the previous claims, wherein the methanol content of the hydrocarbon composition is less than 3000 ppm.

16. The process according to any of the previous claims, wherein the higher linear alpha-olefins are reacted with the 1-butene and 2-butenes of the hydrocarbon composition at a temperature in the range from -10 °C to +70 °C.

17. An olefinic copolymer useful as a synthetic oil or as a component of a synthetic oil, comprising repeating units of n-butene, cis- and trans-2-butenes and higher linear alpha-olefins containing 6 to 18 carbon atoms and having a number average molecular weight in the range from 300 to 1200 and a polydispersity defined as the ratio $\overline{M}_w/\overline{M}_n$ lower than 1.4.

18. The copolymer according to claim 17, wherein the higher linear alpha-olefin units are comprised of alpha-olefins having 10 to 16 carbon atoms in the molecule.

19. The copolymer according to claim 17 or 18, wherein the molar ratio between the higher linear alpha-olefin units and the n-butene units is in the range from 1:1 to 1:5.

20. A process for producing a copolymer product useful as a synthetic oil or components thereof, comprising the steps of

- mixing higher linear alpha-olefins having 6 to 18 carbon atoms with a spent C_4 hydrocarbon composition derived from the production of methyl tert-butyl ether or from the selective polymerization of isobutylene and containing at least 30 % by weight of 1-butene and at least 5 % by weight of 2-butenes to form a reaction mixture,
- adding an initiator system to the reaction mixture,
- keeping the temperature of the reaction mixture in the range from -10 °C to +70 °C,
- allowing the higher linear alpha-olefins to react with the 1-butene and 2-butenes to form a reaction product, and
- separating volatile components and any initiator system residues to form a oily product consisting essentially of copolymers having a number average molecular weight in the range from 300 to 1200.

21. The process according to claim 20, wherein the initiator system is gradually added during the reaction between the higher linear alpha-olefins and the 1-butene and 2-butenes.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C07C 2/08, C08F 210/08
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C07C, C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPOQUE, CA SEARCH

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4311864 (JOHN P. PELLEGRINI, JR.ET AL), 19 January 1982 (19.01.82), claims 4, 6	1-21
Y	EP, A2, 0337737 (CESKOSLOVENSKA AKADEMIE VED), 18 October 1989 (18.10.89), abstract	1-21
Y	EP, A2, 0367386 (EXXON CHEMICAL PATENTS INC.), 9 May 1990 (09.05.90), abstract	1-21

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3330883 (JOSEPH P. GIANNETTI ET AL), 11 July 1967 (11.07.67), column 4, line 35 - line 58, claims -- --------	1-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

26/02/94

International application No.
PCT/FI 93/00560

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4311864	19/01/82	NONE	
EP-A2- 0337737	18/10/89	NONE	
EP-A2- 0367386	09/05/90	JP-A- 2164833	25/06/90
US-A- 3330883	11/07/67	NONE	