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**(54) Title:** A METHOD TO OLIGOMERIZE $C_4$ OLEFINS TOGETHER WITH LONG CHAIN OLEFINS

**(57) Abstract**

The invention concerns a process for producing synthetic oils and an olefinic polymer product which is useful as a synthetic oil or a part thereof. According to the process, olefinic hydrocarbons are polymerized in order to form an oil product having a high viscosity index and low pour point. According to the invention, the olefinic hydrocarbons used comprise $C_{8-24}$ olefins with an internal double bond, which are subjected to a polymerization reaction with lower olefins, in particular 1- and 2-butenes. The reaction is carried out in the presence of an initiator system, which contains a compound of general formula (I) $R_2AlCl$, wherein R represents halogen or an alkyl group containing 1 to 6 carbon atoms, in order to produce a polymerization product, and the polymerization product is separated from the reaction mixture in order to form a synthetic oil.

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# A method to oligomerize $C_4$ olefins together with long chain olefins

The present invention concerns a process according to the preamble of claim 1 for producing synthetic oils.

According to such a process olefinic hydrocarbons are polymerized in order to produce an oil product having a high viscosity index and low pour point.

Within the scope of the present invention, the term "to polymerize" designates the forming of large molecules by chemical reactions from single monomers (i.e. repeating units) independently of the number of monomers contained in the product. Thus, in the present application, the expression "polymerization" also includes "oligomerization", i.e. the forming of molecules with 2 to 10 monomers.

The invention also concerns a process in accordance with the preamble of claim 17 for preparing synthetic oils and functional liquids and it also concerns the copolymers according to the preamble of claim 18, which are suitable for use as synthetic oils. The present invention also relates to a process according to the preable of claim 22 for preparing the copolymers.

Presently used polyolefin-based synthetic oils are manufactured on an industrial scale from higher linear alfa-olefins, predominantly, from 1-octene and 1-decene. Polymerization carried out using Friedel-Crafts catalysts gives rise to a mixture of oligomers, which after the separation of unreacted monomers and dimers yields oily products, consisting mainly of trimers and hexamers of the respective olefins. The oils thus prepared typically have a high viscosity index (above 120), a low pour point and low volatility. The properties of the oils depend on the concentration of the individual oligomers in the product and on their chemical structure. The last-mentioned feature is affected, e.g., by the extent of isomerization reactions accompanying the acid catalyzed polymerizations. Hence, the final quality of the product is dependent not only on the polymerization conditions, but also, and to a great extent, on the catalyst used, i.e. boron fluoride, aluminium chloride or the Ziegler Natta catalytic system in most cases. Boron fluoride is the catalyst most frequently used because in the presence of protogenic cocatalysts it gives rise to oils possessing the best properties. The disadvantage of boron fluoride is its relatively high price and toxicity, which puts considerable requirements on the industrial safety of production.

Oils industrially produced from higher linear olefins belong to the most expensive oil products on the market, which limits their large-scale use.

Lower olefins, such as propene and n-butenes, can also be polymerized to synthetic oils. However, their properties are from the tribological viewpoint considerably poorer than those of products achieved by the oligomerization of higher alfa-olefins. In particular their viscosity indexes are relatively low, typically lower than 80.

Further, it is known in the art that butenes can be advantageously directly polymerized in a mixture of $C_4$-hydrocarbons, obtained as Raffinate II after the separation of 1,3-butadiene and isobutylene from pyrolytic $C_4$-fractions. A mixture of this kind, suitable for the production of poly-n-butene oils, is formed for example in connection with the production of low-molecular weight polyisobutylene and, in particular, during the production of methyl tert-butyl ether (MTBE) used as an antiknocking agent in particular for gasoline. Raffinate II contains up to 75 % of n-butenes (a mixture of 1-butene, 2-butene-cis and trans), along with isobutane, n-butane and a small quantity of isobutylene present in concentrations below 5 wt.-%.

Raffinate II is a cheap raw material, so far employed in the industrial production to a limited extent only. The viscosity index of poly-n-butene-based oils prepared from Raffinate II is, however, usually below 75, which is lower than required of engine lubrication oils. Thus, these poly-n-butene-based oils are primarily used for other applications, for example as cutting liquids.

Summarizing it can be stated that the conventional oils are too expensive to be used on a greater scale, while the properties of the cheaper poly-n-butene oils do not fulfil the standards set for engine lubrication oils.

It is an object of the invention to eliminate the problems related to the known synthetic lubrication oils and to provide entirely novel advantageous oils which have acceptable properties and which can be prepared from inexpensive starting materials.

It is another object of the invention to provide novel olefinic copolymers which can be used as lubrication oils or parts of synthetic oils.

It is still a further object of the invention to provide a process for preparing the novel oils and copolymers.

Comparatively high volumes of hydrocarbon fractions containing a considerable amount of olefins with internal double bond appear as wastes of pyrolytic processes during the processing of higher olefins in the petrochemical industry. In principle, these fractions therefore form an important raw material basis which could be utilized in new products. Nevertheless, said olefins have not to any larger extent been used in petrochemical processes, and their use as basic monomers in the preparation of high-quality synthetic oils has not even been suggested. This is obviously due to the fact that reactivity of the internal double bond of the longer molecule is much weaker than that of the terminal double bond, and said olefins have not been expected to react at the conditions of the oligomerization.

It has now surprisingly been found that higher olefins with internal double bond, and mixtures thereof, can be adequately both polymerized and copolymerized with lower olefins, in particular unsaturated $C_4$ hydrocarbons. The reaction is preferably carried out in the presence of initiator systems, which contain a compound of the general formula I

$$R_2AlCl$$

wherein

R represents halogen or an alkyl group with 1 to 6 carbon atoms,

By the polymerization and copolymerization reactions products are obtained which can be used as high-quality oils with an increased viscosity index.

More specifically, the process according to the invention is characterized by what is stated in the characterizing part of claim 1.

The process according to the invention for preparing synthetic oils and functional liquids is, again, characterized by what is stated in the characterizing part of claim 17.

The copolymerate according to the invention is characterized by what is stated in the characterizing part of claim 18, and the process for the preparation thereof is characterized by what is stated in the characterizing part of claim 22.

The term "olefin with internal double bond" denotes an olefin, which contains at least one double bond which is not in alfa-position. These olefins comprise linear and branched long chained olefins with 8 to 24 carbon atoms, preferably 12 to 18, in particular 14 to 18 carbon atoms.

Within the scope of the present invention, cyclic olefins (cycloalkenes) are also considered olefins with internal double bond. Particularly preferred cycloalkenes are those, which contain a vinyl group attached to the ring, the internal double bond of the cycloalkenes being isolated (unconjugated) from said group. As examples of suitable cycloalkenes, vinyl cyclohexene and cyclopentadiene-butadiene may be mentioned.

"Halogen" as used in the present context means fluorine, chlorine, bromine or iodine. Preferably the halogen is chlorine.

The terms "initiator" and "catalyst" and "initiator system" and "catalyst system", respectively, are synonymously used in connection with the present invention.

By means of the invention, a solution is provided for the preparation of synthetic oils and functional liquids, said products having improved utility properties and being constituted by polymers of higher linear and branched olefins and vinyl cyclooalkenes and copolymerates of these and lower olefins, such as propylene and n-butenes. The products according to the invention are prepared at a temperature in the range of -10 °C to +120 °C by using selected initiation systems, products having a number average molecular weight in the range of 300 to 1200 being obtained.

The lower olefins preferably used in the copolymerization are propylene, 1-butene, 2-butene-cis and trans, or advantageeously, the residue of the $C_4$-fraction obtained as the waste product Raffinate II. Also, it has been found that vinyl-cycloolefins can be used as comonomers in the production of functional liquids and synthetic oils. Their copolymerization with $C_4$-olefins in the Raffinate II gives rise not only to oils with a reactive double bond for further use, but, following their hydrogenation, oils belonging to the category of cycloalkanes can also be obtained, possessing the typical properties of oils suitable as lubricants.

According to an embodiment of the process according to the present invention, the higher olefins used comprise linear or branched alkenes, or mixtures thereof, containing from 12 to 18 carbon atoms in the molecule, predominantly represented by olefins with internal double bonds.

According to a second preferred embodiment of the present invention, higher olefins and 4-vinylcycloalkenes, such as 4-vinylcyclohexene, are polymerized with n-butenes in a mixture of $C_4$-hydrocarbons obtained as the waste Raffinate II in the production of methyl tert-butyl ether or polyisobutylene, as long as the total contents of n-butenes in the raffinate is above 30 wt-%. According to the invention there is added to a mixture of $C_4$-hydrocarbons higher olefins in an amount of 1 to 99 wt-%, preferably 10 to 80 %, or 4-vinylcyclo-hexene in an amount of 5 to 50 %, preferably 10 to 30 wt-%, related to the total amount of n-butenes present in the mixture.

According to a third preferred embodiment the synthetic oils are prepared by polymerizing higher olefins with internal double bond in hydrocarbon compositions, containing about 15 to 80 wt-% 1-butene, 5 to 50 wt-% 2-butenes aand about 10 wt-% or less isobutylene. The hydrocarbon compositions preferably contain about 30 to 70 wt-%, in particular 30 to 60 wt-% 1-butene, and 10 to 40 wt-%, in particular 15 to 30 wt-% 2-butenes. In addition to these components small amounts of, e.g., n-butane, isobutane, propane and other alkanes, isobutylene, methyl tert-butyl ether and other etherification products, as well as some other lower olefinic oligomers can be included in the composition.

The polymerization or copolymerization is advantageously carried out at temperatures between +20 and +100 °C when the catalyst consumption for achieving the highest conversion is lowest, while the properties of the resulting products are optimal.

The catalytic systems used in the present invention can 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. Another advantage resides 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 $R_2AlCl$ (IIa) or $RAlCl_2$ (IIb) is employed as an initiator and an anhydrous hydrogen halide as a polymerization initiator. In the above general formulas R stands for a lower alkyl having 1 to 6 carbon atoms. Preferably, alkylaluminium dichloride compounds of formula $RAlCl_2$ (IIb) are used and, in particular, the compounds are selected from the group comprising methylaluminium dichloride, ehtylaluminium dichloride, propylaluminium dichloride and butylaluminium dichloride. The hydrogen halides may comprise hydrogen chloride or hydrogen fluoride, hydrogen chloride being preferred.

The catalyst systems used in the present invention are described in more detail in the European Published Patent Applications Nos. 0 337 737 and 0 367 387.

Gradual addition of the initiator into the reaction mixture will assist in governing the rate of copolymerization by providing practically isthermal 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 aadded 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 connversions are hardly attained. Therefore, as mentioned above, the reaction is preferably carried out at temperatures above -10 °C. Typically, the initiator consumption (calculated from the obtained product) amounts to 0.3 to 0.7 % by weight at temperatures in the preferred range from -10 °C to +70 °C at olefin conversion rates in excess of 90 %.

The molecular weight of the copolymers increases with decreasing polymerization temperature and with increasing content of the higher olefin added to the initial mixture. At temperatures between +20 and +80 °C, the polymerization of higher $C_{12}$ to $C_{18}$ olefins with the double bond inside the molecule, and their mixtures, gives rise to oily products with a high viscosity index. Thus, e.g., the polymerization of a mixture of $C_{16}$ and $C_{18}$ olefins yields oils having a viscosity index above 160. The copolymerization of these olefins with $C_4$-olefins leads to a decrease in the viscosity index of the oils, depending on the composition of the initial mixture and on the polymerization conditions. For example, the copolymerization with n-butenes performed in the Raffinate II, to which a mixture of $C_{16}$ and $C_{18}$ olefins at the total weight ratio to the n-butenes present in the mixture 4:1 was added, yields oils with a viscosity index about 130, at the number-average molar weight 860 and a polydispersity $M_w/M_n$ of about 1.2. At a 1:1 ratio the viscosity index is about 110 and decreases further with the decrease in the higher olefin content.

The yield of the product in the copolymerization of n-butenes with 4-vinyl cyclohexene depends on the content of 4-vinyl cyclohexene in the starting mixture: with its increasing content the yield decreases, if recalculated to the total content of the components present. The copolymerization can also be advantageously carried out in a mixture of hydrocarbons present in Raffinate II. The products are viscous oils, light yellow in coloyr, readily soluble in both nonpolar and polar solvents, such as e.g. paraffinic and aromatic hydrocarbons, halogenated solvents, ethers, and ketones. The viscosity indexes of these copolymers are comparativeley low. For oils obtained by the copolymerization of n-butenes in Raffinate II the viscosity indexes are below 30. On the other hand, however, the copolymers contain a reactive double bond in the molecule, due to the incorporated 4-vinylcyclohexene, and can therefore be employed in the preparation of other products of technical interest.

If Raffinate II used comes from the production of methyl tert-butyl ether, it should be beforehand freed of methanol to its conocentration below 3000 ppm.

The copolymers according to the present invention essentially comprise repeating units derived from lower alkenes and $C_{6-24}$ olefins with internal double bond and its number average molecular weight is from 300 to 1200 and polydispersity, $M_w/M_n$, is less than 1.4.

As explained above, the repeating units derived from olefins are preferably derived from olefins which contain 12 to 18 carbon atoms in the molecule, or vinylcycloalkenes, such as vinylcyclohexene. The lower olefin-derived repeating units are derived from 1-butene and cis- and trans-2-butenes. The molar ratio between the olefin units and the 1-butene units in the copolymers according to the invention is from 1:1 to 1:5.

The present invention also relates to a process for preparing a polymer product useful as a synthetic oil or a part thereof. Summarizing, it should be mentioned that the process comprises the following steps:

- forming a reaction mixture by mixing together internal bond-containing $C_{6-24}$-olefins with a $C_4$ hydrocarbon mixture, which comes from the production of methyl tert.butyl ether or the selective polymerization of isobutylene and which contains at least 15 wt-% 1-butene and at least 5 wt-% 2-butenes,
- adding to the reaction mixture an initiator system, which contains a compound having the general formula

$$R_2AlCl$$

wherein

R represents halogen or an alkyl group with 1 to 6 carbon atoms,

- maintaining the temperature of the reaction mixture at -10 to +120 °C,
- subjecting the olefins to a reaction with the 1-butene and 2-butenes in order to form a reaction product, and
- separating the volatile components and initiator residues, if any, in order to form an oily product, which primarily consists of copolymers having a number average molar mass of 300 to 1200.

The oil products of the invention typically have higher viscosity index than the poly-n-butene oils as such. Copolymerization of n-butenes with higher linear alfa-olefins also improves the pour point of the products. The pour point of the present oils is lower than that of poly-n-butene oils, and it is even lower than the pour point of oligomers of higher linear alfa-olefin with comparable molecular weight.

According to a preferred embodiment of the present invention the hydrocarbon composition should contain at the most a small amount of methanol, because methanol can 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 few per cent by weight of methanol, the residual methanol is removed or its concentration is lowered to below 3000 ppm before the polymerization reaction.

The reaction mixture after polymerization is processed in the common way. It is washed preferably with about 5 % aqueous solution of soda and then with water. Alternatively sorption clay is added into the mixture in the amount of approx. 0.5 to 10 %, preferably about 2 %, related to the initial content of olefins to remove the catalyst. The low-boiling portions are distilled off by heating up to 120 °C at 13 Pa and colourless or slightly yellowish oils are obtained.

The obtained copolymers are characterized by a relatively narrow distribution of molecular weight corresponding to polydispersity defined as the ratio $M_w/M_n$ lower than 1.4.

The invention provides significant advantages. Thus, a particularly important advantage of the invention consists in the possibility of using as raw materials of the process higher olefins with internal double bond, which form a particularly advantageous raw material. The copolymerization of n-butenes can be carried out in Raffinate II a cheap secondary raw material which normally is discarded, without having to isolate and purify the n-butenes.

Further advantage of the production of synthetic oils according to the invention consists in obtaining high quality synthetic oils with viscosity indexes which are of the same magnitude as the corresponding indexes of expensive synthetic oils prepared from pure higher linear alpha-olefins.

The oils produced by polymerization and copolymerization according to this invention have a broad technical application. Because of their very convenient values of viscosity index they can be used as high quality engine lubricating oils. The lubrication properties, in particular the stability, can be enhanced by hydrogenation of the product.

Their expected use is as lubricating oils for two-stroke combustion engines, oils applicable in metallurgy for rolling and drawing of metallic materials, transformer, electro, insulation and cable oils, oils for energy transfer in cooling and heating systems and many others. The oils are non-toxic and can be utilized as additives for plastics and rubbers. Furthermore, the non-hydrogenated oil can be used as raw material for the preparation of different products based on the reactivity of the double bonds (e.g., dispersion media, additives for paper, oils and plastics).

The invention is further illustrated in several examples of performace of the polymerization and copolymerization in Raffinate II. However, it should be understood that the scope of invention is by no means restricted to these examples. In particular, it should be noticed that in the present invention it is possible to use other hydrocarbon compositions which contain essential amounts of olefinic $C_4$ hydrocarbons.

**Apparatus 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 initator and with outside cooling. The temperature of the reaction mixture was monitored with a thermocouple connected to a recorder. Hydrogen chloride in the gaseous state was added to the initial reaction mixture and then the polymerization course was controlled by gradual dosing of the initiator so that the temperature of the reaction mixture was kept in the region of 30 °C around the required temperature.

In the preparation of oils, a hydrocarbon compositin (Raffinate II) comprising the residue of a $C_4$-fraction from the production of MTBE was used, which was three times washed with water in order to remove methanol and dried in the liquid state over KOH in a pressure vessel.

The hydrocarbon product 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 content of methanol 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 wt-% 1-olefin.

Molecular weights $M_n$ and $M_w$ and polydispersity $M_w/M_n$ of the products were evaluated from GPC and VPO measurements.

**Example 1**

A glass reactor with a volume of 150 ml was charged with 75 g $C_{14}$-olefins, which contained more than 90 % molecules with internal double bonds. After the addition of 0.5 g anhydrous hydrogen chloride (HCl) in gaseous state, the polymerization was carried out by gradual addition of ethylaluminium dichloride in heptane solution at +80 °C. The polymerization was stopped after 50 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. The volatile fraction was removed by heating the reaction mixture up to 170 °C at 13 Pa. A colourless oil obtained had number average molecular weight, $M_n$, of 521 and viscosity index 152. The consumption of $EtAlCl_2$ related to the final product was 1.9 wt-% at a conversion of the present olefins amounting to 65 wt-%. Kinematic viscosity (cSt): 3.85/100 °C, 152.1/40 °C, pour point -53 °C, polydisperisity $M_w/M_n$ = 1.3.

**Example 2**

The polymerization of $C_{14}$-internal olefins was carried out in an analogous way as in Example 1, with the exception that the catalyst was changed and liquid complex $AlCl_3$-toluene-HCl was used. The product prepared at a polymerization temperature of +20 °C had a molecular weight, $M_n$, of 610, the viscosity index being 129, kinematic viscosity (cSt) 6.8/100 °C, 40.0/40 °C, pour point -50 °C, and polydispersity $M_w/M_n$ 1.28. The consumption of $AlCl_3$ was 1.8 wt-% at a conversion of 56 wt-%.

**Example 3**

The polymerization of $C_{16}$, $C_{18}$ mixture internal olefins was carried out as described in in Example 2, but the polymerization temperature was 100 °C. The product isolated had a molecular weight $M_n$ of 580, the viscosity index being 161, pour point -57 °C and polydispersity $M_w/M_n = 1.25$. The consumption of $AlCl_3$ was 1.5 wt-% at a conversion of 61 wt-%.

**Example 4**

The copolymerization of n-butenes in Raffinate II was carried out with the addition of 50 wt-% of $C_{14}$ internal olefin related to the total amount of olefins in formed mixture. The same liquid complex was used as in Example 2, prepared by introducing gaseous HCl into a suspension of 5.0 g $AlCl_3$ in 6.0 ml toluene at 0 °C until all $AlCl_3$ had been tranferred into solution. The conversion at polymerization temperature +20 °C was 78 wt-% attained by gradual dosing of the catalytic complex into the raction mixture for 40 min. The obtained oil had a molecular weight, $M_n$, of 720, the viscosity index being 80 and consumption of catalyst 1.8 wt-%/polymer.

**Example 5**

The polymerizations of $C_{14}$ and the mixtures $C_{16}$, $C_{18}$ internal olefins were carried out at +20 °C and +40 °C and catalyzed with the $AlCl_3$ solution in ethylchloride. The results are summarized in Table 1..

Table 1. Homopolymers prepared from $C_{14}$ and $C_{16}$,$C_{18}$ internal olefins

| Olefin | Polymerization temperature, °C | Isolated olefin | Polymer | | | Catalyst consumption, wt.%/polymer | Viscosity 40° | Viscosity 100° | Viscosity index | Pour point °C |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | % | $M_n$ | $M_w$ | | mm₂·sec⁻¹ | | | |
| $C_{14}$ | 20 | 58.0 | 41.4 | 651 | 717 | 3.6 | 35.3 | 6.4 | 135 | - |
| $C_{14}$ | 40 | 46.0 | 53.8 | 635 | 689 | 5.0 | - | - | - | - |
| $C_{16}$,$C_{18}$ | 20 | 28.9 | 70.6 | 910 | 1013 | 1.3 | - | - | - | - |
| $C_{16}$,$C_{18}$ | 40 | 23.0 | 75.9 | 953 | 1067 | 1.5 | 52.6 | 9.3 | 162 | -8 |
| $C_{16}$,$C_{18}$ | 20 | 47.5 | 52.0 | | | 1.7 | 75.4 | 12.1 | 157 | -4 |

**Example 6**

The copolymerization of $C_{14}$ and mixtures of $C_{16}$, $C_{18}$ internal olefins were carried out with the addition of 10 wt-& 4-vinylcyclohexene under the iniitiation with $AlCl_3$ in ethylchloride solution. The results are given in Table 2.

Table 2. Copolymers prepared from $C_{14}$ and $C_{16}$, $C_{18}$ internal olefins in Raffinate II

| Olefin | Olefins in monomer feed- wt-% | Polymerization temperature, °C | Isolated olefin | Copolymer | | | Catalyst consumption, wt-%/polymer | Viscosity $mm_2 \cdot sec^{-1}$ | | Viscosity index | Pour point °C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | % | $M_n$ | $M_w$ | | 40° | 100° | | |
| $C_{14}$ | 59,4 | 40 | 53,6 | 39.7 | 650 | 728 | 1.9 | 119.3 | 11.4 | 78 | - |
| $C_{16}$, $C_{18}$ | 59,0 | 40 | 37,3 | 52.9 | 781 | 877 | 1.0 | 123.4 | 13.3 | 102 | - |
| $C_{16}$, $C_{18}$ | 79,6 | 40 | 31,3 | 65.3 | 865 | 987 | 1.2 | 87.7 | 11.9 | 129 | - |
| $C_{16}$, $C_{18}$ | 91,0 | 40 | 29,1 | 70.3 | 911 | 1054 | 1.3 | 74.6 | 11.4 | 145 | -10 |

Polymerization conditions: initiator system – aluminium chloride in ethyl chloride

Example 7

The n-butenes of Raffinate II were copolymerized with 10 wt-% of 4-vinylcyclohexene. After 50 minutes the reaction was quenched by alcohol. The reaction took place at 50 °C under initiation with $AlCl_3$ solution in ethyl chloride. A yellowish viscose oil with number average molecular weight, Mn, 420 was obtained. The conversion was 65 wt-%, calculated from the total amount of monomers. Viscosity index was 22.2 and pour point -21 °C.

Example 8

The copolymerization of n-butenes was carried out in Raffinate II with the addition of 30 wt-% 4-vinylcyclohexene related to the total content of olefinns in the resulting mixture. The copolymerization proceeded at 20 °C under initiation with ethyl aluminium dichloride and HCl as co-catalyst. The obtained oil had a molecular weight, $M_n$, of 497, $M_w$, of 676, the polydispersity $M_w/M_n$ being 1.360, viscosity index 8.5 and pour point -2 °C. Consumption of the catalyst at a conversion of 45 wt-% was about 3 wt-%.

Claims:

1. A process for producing synthetic oils with high viscosity index and low pour point, according to which method
   - olefinic hydrocarbons are polymerized in order to form an oil product,

characterized in that
   - the olefinic hydrocarbons used comprise $C_{8-24}$ olefins with internal double bond,
   - the $C_{8-24}$ olefins are subjected to a polymerization reaction in the presence of lower olefins in order to form a reaction product which contains polymers of olefins with internal double bond and copolymers of olefins with internal double bond and lower olefins, and
   - the reaction product is separated from the reaction mixture.

2. A process according to claim 1, characterized in that the polymerization reaction is carried out in the presence of an initiator system containing a compound of the general formula (I)

$$R_2AlCl \qquad (I)$$

wherein
R represents halogen or an alkyl group with 1 to 6 carbon atoms.

3. A process according to claim 2, characterized by using an initiator system, which contains a compound of the general formula (I), wherein R represents chlorine as halogen.

4. A process according to any one of claims 1 to 3, characterized in that the olefins are subjected to polymerization and copolymerization reactions in a hydro-

carbon mixture containing substantial amounts of 1-butene ja 2-butenes.

5. A process according to claim 4, characterized in that the olefins with internal double bond are subjected to polymerization and copolymerization reactions in a hydrocarbon composition, which contains 30 to 80 wt-% 1-butene, 5 to 50 wt-% 2-butenes and a maximum of about 10 wt-% isobutylene.

6. A process according to claim 4 or 5, characterized in that the olefins with internal double bond are subjected to polymerization and copolymerization reactions in a hydrocarbon composition, which contains about 30 to 70 wt-%, in particular 35 to 60 wt-% 1-butene, and 10 to 40 wt-%, in particular 15 to 30 wt-% 2-butenes.

7. A process according to claim 4, characterized in that the hydrocarbon composition comprises a $C_4$ fraction residue remaining after substantially all 1,3-butadiene and isobutylene compounds have been removed.

8. A process according to claim 7, characterized by using as hydrocarbon mixture Raffinate II, which is obtained from the preparation of methyl tert.-butyl ether or polyisobutylene.

9. A process according to claim 7, characterized in that the polymerization reaction is carried out by adding to a mixture of lower olefins 1 to 99 wt-%, preferably 5 to 90 wt-%, and in particular 10 to 70 wt-% olefins with internal double bond, which are reacted with the 1-butene and 2-butene fraction, the amount of added olefins being calculated on basis of the total amount of olefins contained in the mixture after the addition.

10. A process according to claim 1, character-

ized by using as olefins with internal double bond linear or branched olefins and/or vinylcycloalkenes containing 8 to 24 carbon atoms.

11. A process according to claim 10, characterized in that the olefins used comprise an internal olefin containing 12 to 18 carbon atoms or 4-vinylcyclohexene.

12. A process according to any of the preceeding claims, characterized by using as an initiator system $AlCl_3$ together with HCl, $AlCl_3$ in a solution of ethyl chloride, a liquid complex formed from $AlCl_3$, an aromatic solvent and hydrogen chloride, or alkyl aluminium chlorides of general formulas $R_2AlCl$ or $RAlCl_2$, wherein R represents a lower alkyl with 1 to 6 carbon atoms, together with an anhydrous hydrogen halogenide.

13. A process according to claim 12, characterized in that the initiator system is gradually added during the reation.

14. A process according to claim 1, characterized by preparing oil products having molecular weights in the range from 300 to 1200.

15. A process according to claim 1, characterized in that the methanol concentration of the hydrocarbon composition is maintained below 3000 ppm.

16. A process according to claim 1, characterized in that the olefins are reacted with 1-butene and 2-butenes of the hydrocarbon mixture at a temperature in the range of -10 °C to +120 °C, preferably about -10 °C to +70 °C.

17. A process for preparing synthetic oils and functionalized liquids having improved utility properties, characterized by polymerizing and copolymerizing

higher linear or branched $C_{12-18}$ olefins containing at least one internal double bond, and/or 4-vinylcyclohexene together with a hydrocarbon composition containing propylene or substantial amount of 1-butene and 2-butene in the presence of an initiator system in order to prepare a product having a high viscosity index or containing a reactive group.

18. An olefinic polymer product, which is useful as a synthetic oil or a part thereof, characterized in that it comprises repeating units derived from lower alkenes and from $C_{6-24}$ olefins with internal double bond and its number average molecular weight is 300 to 1200 and its polydispersity $M_w/M_n$ is less than 1.4.

19. A polymer product according to claim 18, characterized in that the reapeting units derived from olefins are derived from olefins, which contain in their molecule 8 to 24 carbon atoms.

20. A polymer product according to claim 18, characterized in that the olefin-derived repeating units are derived from a vinylcycloalkene, such as vinylcyclohexene.

21. A polymer according to claim 19, characterized in that lower olefin-derived repeating units are derived from 1-butene and cis- and trans-2-butenes.

22. A copolymer according to any of claims 18 - 21, characterized in that molar ratio between the olefinic units and the 1-butene units is 1:1 to 1:5.

23. A process for preparing a polymer product useful as a synthetic oil or a part thereof, characterized by

- forming a reaction mixture by mixing together internal bond-containing $C_{6-24}$-olefins with a $C_4$ hydrocarbon mixture, which stems from the production of methyl tert.-butyl ether or the selective polymerization of isobutylene and which contains at least 15 wt-% 1-butene and at least 5 wt-% 2-butenes,

- adding to the reaction mixture an initiator system, which contains a compound having the general formula

$$R_2AlCl$$

wherein

R represents halogen or an alkyl group with 1 to 6 carbon atoms,

- maintaining the temperature of the reaction mixture at -10 to +120 °C,
- subjecting the olefins to a reaction with the 1-butene and 2-butenes in order to form a reaction product, and
- separating the volatile components and initiator residues, if any, in order to form an oily product, which primarily consists of copolymers having a number average molecular weight of 300 to 1200.

24. A process according to claim 23, characterized in that in the general formula R as halogen represents chlorine.

25. A process according to claim 23 or 24, characterized in that the initiator system is gradually added during the reaction of the higher linear alfa-olefins and the 1- and 2-butenes.

26. Use of a product prepared according to any one of claims 1 to 17 or 22 to 25 or of a product according to any one of claims 18 to 21 as a hydrogenated lubricating oil or dispersion medium or as a raw material for paper, oil and polymer additives.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 95/00176

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 210/08, C07C 2/08, C10G 50/02
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)

IPC6: C07C, C08F, C10G

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)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| X | EP 0449453 A2 (TEXACO CHEMICAL COMPANY), 2 October 1991 (02.10.91), abstract<br>-- | 1,26 |
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| X | US 4434308 A (JOHN M. LARKIN ET AL), 28 February 1984 (28.02.84), example 27, claim 1, claim 6<br>-- | 1,26 |

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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|---|---|
| Date of the actual completion of the international search<br>18 July 1995 | Date of mailing of the international search report<br>20 -07- 1995 |
| Name and mailing address of the ISA/<br>Swedish Patent Office<br>Box 5055, S-102 42 STOCKHOLM<br>Facsimile No. +46 8 666 02 86 | Authorized officer<br>Agneta Österman Wallin<br>Telephone No. +46 8 782 25 00 |

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 95/00176

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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29/05/95

International application No.

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| US-A- | 4434308 | 28/02/84 | NONE | | |
| US-A- | 3330883 | 11/07/67 | NONE | | |
| EP-A2- | 0337737 | 18/10/89 | FI-B,C- | 93368 | 15/12/94 |