

HYDROCARBON OIL COMPOSITIONS

The invention relates to novel hydrocarbon oil compositions comprising a hydrocarbon oil and a polymeric additive.

Hydrocarbon oils such as gas oils, diesel oils, lubricating oils and crude oils can contain considerable amounts of paraffins. When these oils are stored, transported and used at low temperature, problems can occur as a result of crystallization of these paraffins. In order to meet these problems, it is customary to add certain polymers to the paraffinic hydrocarbon oils. Very customary for this purpose are high-molecular copolymers of ethylene and vinyl acetate, which are commercially available under various names. Though these are generally quite satisfactory, they are open to improvement as far as their activity is concerned.

In an investigation by the Applicant concerning the use of polymers as additives in paraffinic hydrocarbon oils for improving the low temperature properties of these oils, a class of polymers has now been found which appears to be outstandingly suitable for lowering the pour point (PP), the cloud point (CP) and/or the cold filter plugging point (CFPP) of these oils. Comparison of the performance of these polymers with that of the above-mentioned ethylene/vinyl acetate copolymers shows that the former polymers possess a higher activity than the commercial additives. This means that, in comparison with the commercial additives, the polymers investigated by the Applicant for this purpose give - at equal concentration - a stronger PP, CP and/or CFPP reduction, or, alternatively, that an equal PP, CP and/or CFPP reduction can be obtained at a lower concentration. These polymers

are linear polymers of carbon monoxide with one or more α -olefins having at least 10 carbon atoms per molecule (hereinafter referred to as C_{10+} α -olefins) and optionally in addition with one or more olefins having fewer than 10 carbon atoms per molecule (below referred to as C_9- olefins), in which polymers on the one hand the units originating from carbon monoxide and on the other hand the units originating from the olefins occur in a substantially alternating way. Though some of these polymers are known per se, the use of these polymers as an additive in a paraffinic hydrocarbon oil is novel. A number of the polymers found by the Applicant to be suitable as additives for paraffinic hydrocarbon oils were especially synthesized for this purpose and are novel compounds. These are polymers of carbon monoxide with one or more C_{10+} α -olefins, which polymers possess a weight average molecular weight ($\bar{M}_w$), of more than 10^4 . These polymers can be prepared by contacting the monomers, at elevated temperature and pressure and in the presence of a diluent consisting for more than 90 %v of an aprotic liquid, with a catalyst composition containing a Group VIII metal and a phosphorus bidentate ligand having the general formula $(R^1R^2P)_2R$, where R^1 and R^2 represent identical or different optionally polar substituted aliphatic hydrocarbyl groups and R a bivalent organic bridging group containing at least two hydrocarbon atoms in the bridge linking the two phosphorus atoms.

The present patent application therefore relates to novel hydrocarbon oil compositions comprising a paraffinic hydrocarbon oil and as additive linear polymers of carbon monoxide with one or more C_{10+} α -olefins and optionally moreover with one or more C_9- olefins in which polymers the units originating from carbon monoxide and the units originating from the

olefins occur in a substantially alternating way. The patent application further relates to novel polymers of carbon monoxide with one or more C_{10+} α -olefins possessing an $\bar{M}_w$ of more than 10^4 , in which polymers on the one hand the units originating from carbon monoxide and on the other hand the units originating from the olefins occur in a substantially alternating way. Finally the application relates to novel copolymers of one or more olefins intended for use as an additive in a paraffinic hydrocarbon oil, characterized in that the copolymer is a linear copolymer of carbon monoxide with one or more C_{10+} α -olefins and optionally moreover with one or more C_9- olefins in which polymers the units originating from carbon monoxide and the units originating from the olefins occur in a substantially alternating way, and also to a process for the preparation of these novel polymers by contacting the monomers at elevated temperature and pressure and in the presence of a diluent which consists for more than 90 %v of an aprotic liquid with a catalyst composition containing a Group VIII metal and a phosphorus bidentate ligand having the general formula $(R^1R^2P)_2R$.

As paraffinic hydrocarbon oils the low-temperature properties of which can be improved according to the invention, mention may be made inter alia of gas oils, diesel oils, lubricating oils and crude oils. Very favourable results were achieved inter alia with the use of the present polymers in paraffinic gas oils. The molecular weight of the polymers which are eligible to be used in the hydrocarbon oil compositions according to the invention may vary between wide limits. By preference, polymers are used having a weight average molecular weight ($\bar{M}_w$), between 10^3 and 10^6 and in particular between 10^4 and 10^5 . The C_{10+} α -olefins which are used as monomers in the preparation of the polymers are



preferably unbranched. They preferably contain fewer than 40 and in particular fewer than 30 carbon atoms per molecule. The preference for a given molecular weight of the polymers and for a given number of carbon atoms in the C_{10+} α -olefins which are used as monomers in their preparation is substantially determined by the nature of the paraffins present in the hydrocarbon oil. Besides C_{10+} α -olefins, in the preparation of the polymers C_9 -olefins such as ethene, propene, butene-1 and cyclopentene can also be used. By preference, in the preparation of the polymers exclusively C_{10+} α -olefins are used as olefins. The monomer mixture from which the polymers are prepared may contain both one and more C_{10+} α -olefins in addition to carbon monoxide. As examples of copolymers with which very favourable results were achieved in paraffinic hydrocarbon oils, mention can be made of a carbon monoxide/n-tetradecene-1 copolymer and a carbon monoxide/n-hexadecene-1 copolymer. As an example of a very suitable terpolymer for the present purpose, mention can be made of a carbon monoxide/n-tetradecene-1/n-octadecene-1 terpolymer. In addition to separate polymers, mixtures of polymers can also be used in the hydrocarbon oil compositions according to the invention. Thus, for example, very favourable results were achieved by using mixtures of a carbon monoxide/n-tetradecene-1 copolymer with a carbon monoxide/n-hexadecene-1 copolymer in paraffinic hydrocarbon oils. The quantity of polymer which according to the invention is taken up in the paraffinic hydrocarbon oils can vary between wide limits. For preference, 1-10,000 and in particular 10-1,000 mg of polymer is taken up per kg of hydrocarbon oil. In addition to the present polymers, the hydrocarbon oil compositions according to the invention can also contain other additives such as antioxidants, corrosion inhibitors and metal deactivators.

Linear polymers of carbon monoxide with ethylene and with one or more α -olefins having at least three carbon atoms per molecule (below referred to as C_{3+} α -olefins) in which polymers on the one hand the units originating from carbon monoxide and on the other hand the units originating from the olefins occur in a substantially alternating way and which polymers possess an $\bar{M}_w$ of more than 10^4 can be prepared at a high reaction rate by contacting the monomers, at elevated temperature and pressure and in the presence of a protic diluent, with a catalyst composition containing a Group VIII metal and a phosphorus bidentate ligand having the general formula $(R^3R^4P)_2R$, where R^3 and R^4 represent identical or different optionally polar substituted aromatic hydrocarbyl groups and R has the meaning previously indicated. The above-mentioned preparation method has proved to be less suitable for the preparation of polymers of carbon monoxide with one or more C_{3+} α -olefins (that is to say, in the absence of ethylene) in which polymers on the one hand the units originating from carbon monoxide and on the other hand the units originating from the olefins occur in a substantially alternating way. Although in this manner polymers of this type such as copolymers of carbon monoxide with propene or with butene-1 can be prepared, this is only possible at a comparatively low reaction rate and with formation of polymers having a comparatively low $\bar{M}_w$. It has meanwhile been found that in the above-mentioned polymerization of carbon monoxide with one or more C_{3+} α -olefins considerably higher reaction rates can be achieved and polymers having a considerably higher $\bar{M}_w$ can be obtained by replacing in the catalyst composition the phosphorus bidentate ligand having the general formula $(R^3R^4P)_2R$ by a phosphorus bidentate ligand having

the general formula $(R^1R^2P)_2R$ where R, R^1 and R^2 have the previously indicated meanings.

As has been elucidated above, as regards application as additives in paraffinic hydrocarbon oils to improve the properties of these oils at low temperature, there is above all interest in polymers of the present type based on carbon monoxide with one or more C_{10+} α -olefins which polymers possess an $\bar{M}_w$ of more than 10^4 . The Applicant has performed an investigation into the preparation of these polymers. This investigation showed that in the polymerization of carbon monoxide with a C_{3+} α -olefin using a catalyst composition containing a phosphorus bidentate ligand having the general formula $(R^1R^2P)_2R$ and in the presence of a protic diluent, a strong decline in the reaction rate and a strong decline in the $\bar{M}_w$ of the resultant polymers occurs, according as the C_{3+} α -olefin applied as comonomer contains more carbon atoms per molecule. Although copolymers having a comparatively high $\bar{M}_w$ can be prepared in this way at acceptable reaction rates with the use of propylene and butene-1 as comonomer, if for example octene-1 is used as comonomer it becomes nevertheless extremely difficult to prepare polymers having a high $\bar{M}_w$ at an acceptable reaction rate. On the basis of the results of the investigation performed by the Applicant, it can be stated that until recently it has not been found possible to prepare polymers of carbon monoxide with one or more C_{10+} α -olefins having an $\bar{M}_w$ above 10^4 in this manner and at an acceptable reaction rate.

Continued investigation by the Applicant on this subject, however, has disclosed that with the application of a catalyst composition containing a Group VIII metal and a phosphorus bidentate ligand having the general formula $(R^1R^2P)_2R$, polymers of carbon monoxide with one or more C_{10+} α -olefins can be prepared at an acceptable

reaction rate, in which polymers on the one hand the units originating from carbon monoxide and on the other hand the units originating from the applied olefins occur in a substantially alternating way and which polymers possess an $\bar{M}_w$ above 10^4 , by performing the polymerization in the presence of a diluent which consists for more than 90 %v of an aprotic liquid.

Polymers of carbon monoxide with one or more C_{10+} α -olefins in which polymers on the one hand the units originating from carbon monoxide and on the other hand the units originating from the olefins occur in a substantially alternating way and which polymers possess an $\bar{M}_w$ of more than 10^4 are novel per se.

As examples of the novel polymers which were prepared by the Applicant, mention may be made of carbon monoxide/n-tetradecene-1 copolymers, carbon monoxide/n-hexadecene-1 copolymers, carbon monoxide/n-octadecene-1 copolymers, carbon monoxide/n-tetradecene-1/n-octadecene-1 terpolymers, carbon monoxide/n-tetradecene-1/n-hexadecene-1/n-octadecene-1 quaterpolymers, carbon monoxide/n-dodecene-1/n-tetradecene-1/n-hexadecene-1/n-octadecene-1 polymers and polymers of carbon monoxide with a mixture of unbranched α -olefins having 20-24 carbon atoms per molecule.

In the preparation of the novel polymers according to the invention, suitably use is made of a catalyst composition which contains a Group VIII metal and a phosphorus bidentate ligand having the general formula $(R^1R^2P)_2R$. In the present patent application, Group VIII metals are understood as being the noble metals ruthenium, rhodium, palladium, osmium, iridium and platinum, and the iron group metals iron, cobalt and nickel. In the catalyst compositions, the Group VIII metal is preferentially chosen from palladium, nickel and cobalt. Special preference is given to palladium as Group



VIII metal. Incorporation of the Group VIII metal in the catalyst compositions is preferably effected in the form of a carboxylate, particularly an acetate. In addition to a Group VIII metal and a phosphorus bidentate ligand, the catalyst compositions furthermore preferably contain an anion of an acid having a pKa below 6 and in particular an anion of an acid having having a pKa below 2. Examples of acids having a pKa below 2 are mineral acids such as perchloric acid, sulphonic acids such as para-toluene sulphonic acid, and halogen carboxylic acids such as trifluoro acetic acid. The anion can be introduced into the catalyst compositions either in the form of a compound from which the desired anion splits off, or in the form of a mixture of compounds from which the desired anion is formed by inter-reaction. As a rule, the anion is taken up in the catalyst compositions in the form of an acid. If desired, the anion can also be incorporated in the catalyst compositions in the form of a main group metal salt or a non-noble transition metal salt of the relevant acid. Nickel perchlorate is very suitable as salt of an acid having a pKa below 2. If the choice falls on an anion of a carboxylic acid, it may be incorporated in the catalyst compositions in the form of an acid or in the form of a derivative thereof such as an alkyl or aryl ester, an amide, an imide, an anhydride, an orthoester, a lactone, a lactam or an alkylidene dicarboxylate. The anion is preferably present in the catalyst compositions in a quantity of 1-100 and in particular 2-50 mol per gram atom of Group VIII metal. Besides resulting from use as a separate component, the anion of an acid having a pKa below 6 can also be present in the catalyst compositions as a result of the application of, for example, palladium trifluoro acetate or palladium para-tosylate as Group VIII metal compound.

Besides a Group VIII metal, a phosphorus bidentate ligand and optionally an anion of an acid having a pKa below 6, the catalyst compositions preferably contain an organic oxidant as well. Examples of suitable organic oxidants are 1,2- and 1,4-quinones, aliphatic nitrites such as butyl nitrite, and aromatic nitro-compounds such as nitrobenzene and 2,4-dinitrotoluene. Preference is given to 1,4-quinones such as 1,4-benzoquinone and 1,4-naphthoquinone. The quantity of organic oxidant used is preferably 5 to 5,000 and in particular 10 to 1,000 mol per gram atom of Group VIII metal.

The phosphorus bidentate ligand is preferably present in the catalyst compositions in a quantity of 0.5-2 and in particular of 0.75-1.5 mol per gram atom of Group VIII metal. In the phosphorus bidentate ligand having the general formula $(R^1R^2P)_2R$, the groups R^1 and R^2 preferably each contain not more than 10 and in particular not more than six carbon atoms. Furthermore preference is given to phosphorus bidentate ligands in which the groups R^1 and R^2 are identical alkyl groups. With regard to the bridging group R present in the phosphorus bidentate ligands, preference is given to bridging groups containing three atoms in the bridge of which at least two are carbon atoms. Examples of suitable bridging groups R are the $-CH_2-CH_2-CH_2-$ group, the $-CH_2-C(CH_3)_2-CH_2-$ group, the $-CH_2-Si(CH_3)_2-CH_2-$ group and the $-CH_2-O-CH_2-$ group. A very suitable phosphorus bidentate ligand for use in the present catalyst compositions is 1,3-bis(di-n-butyl phosphino)propane.

The quantity of catalyst composition used in the preparation of the polymer can vary between wide limits. For each mol of olefin to be polymerized it is preferred to use a quantity of catalyst composition which contains 10^{-7} - 10^{-3} and in particular 10^{-6} - 10^{-4} gram atom of Group VIII metal.

In the illustrated preparation of the polymers, the contacting of the monomers with the catalyst composition should take place in the presence of a diluent which consists for more than 90 %v of an aprotic liquid. Both polar and apolar liquids are eligible as aprotic liquids. As examples of polar aprotic liquids, mention may be made of aliphatic ketones such as acetone and methyl ethyl ketone, aliphatic carboxylic acid esters such as methyl acetate, ethyl acetate and methyl propionate, cyclic ethers such as tetrahydrofuran and dioxane, alkyl ethers of glycols such as the dimethyl ether of di-ethylene glycol, lactones such as γ -butyrolactone, lactams such as N-methylpyrrolidone and cyclic sulphones such as sulpholane. As examples of apolar liquids, mention may be made of hydrocarbons such as n-hexane, n-heptane, cyclohexane and toluene. The diluent in which the polymerization is performed preferably contains a small quantity of a protic liquid. Lower aliphatic alcohols and in particular methanol are very suitable for this purpose. Very favourable results were obtained by performing the polymerization in a mixture of tetrahydrofuran and methanol. If desired, the C₁₀₊ α -olefin used as monomer can also fulfil the function of aprotic liquid, so that the polymerization can be performed in the absence of an additional aprotic liquid such as tetrahydrofuran. An example of such a polymerization is the preparation of a carbon monoxide/n-hexadecene-1 copolymer which was performed by contacting carbon monoxide and n-hexadecene-1 with a methanolic solution of the catalyst composition.

The polymerization is preferably performed at a temperature of 25-150°C and a pressure of 2-150 bar and in particular at a temperature of 30-130°C and a pressure of 5-100 bar. The molar ratio of the olefins to carbon

monoxide is preferably between 10:1 and 1:10 and in particular between 5:1 and 1:5.

The invention will now be elucidated with reference to the following examples.

In the examples, the abbreviations used have the following meanings.

CO	carbon monoxide
$\text{C}_{12}^{\equiv}$	n-dodecene-1
$\text{C}_{14}^{\equiv}$	n-tetradecene-1
$\text{C}_{16}^{\equiv}$	n-hexadecene-1
$\text{C}_{18}^{\equiv}$	n-octadecene-1
$\text{C}_{20}^{\equiv} - \text{C}_{24}^{\equiv}$	mixture of linear α -olefins having 20-24 carbon atoms per molecule

Example 1

A CO/ $\text{C}_{14}^{\equiv}$ copolymer was prepared as follows. In a stirred autoclave with a capacity of 250 ml which contained 100 ml of tetrahydrofuran and 40 ml of $\text{C}_{14}^{\equiv}$ in a nitrogen atmosphere, a catalyst solution was placed which contained:

5 ml methanol,
0.1 mmol palladium acetate,
0.5 mmol nickel perchlorate,
0.12 mmol 1,3-bis(di-n-butylphosphino)propane, and
6 mmol naphthoquinone.

After injecting CO to a pressure of 40 bar, the contents of the autoclave were heated to 35°C. After 20 hours, the polymerization was terminated by cooling the reaction mixture to ambient temperature and depressuring. After the addition of acetone to the reaction mixture, the polymer was filtered off, washed with acetone and dried. The yield was 40 g of CO/ $\text{C}_{14}^{\equiv}$ copolymer having an $\overline{M}_w$ of 103,000.

Example 2

A CO/C₁₆ copolymer was prepared in substantially the same manner as the CO/C₁₄ copolymer in Example 1, but with the following differences:

- a) the autoclave contained 40 ml of C₁₆ instead of C₁₄, and
 - b) the reaction temperature was 50°C instead of 35°C.
- The yield was 35 g of CO/C₁₆ copolymer having an $\overline{M}_w$ of 20,000.

Example 3

A CO/C₁₈ copolymer was prepared in substantially the same manner as the CO/C₁₄ copolymer in Example 1, but with the following differences:

- a) the autoclave contained 40 ml of C₁₈ instead of C₁₄,
 - b) the reaction temperature was 50°C instead of 35°C, and
 - c) the reaction time was 30 hours instead of 20 hours.
- The yield was 40 g of CO/C₁₈ copolymer having an $\overline{M}_w$ of 20,300.

Example 4

A CO/C₁₄/C₁₈ terpolymer was prepared in substantially the same manner as the CO/C₁₄ copolymer in Example 1, but with the difference that the autoclave contained 30 ml of C₁₄ instead of 40 ml, and contained additionally 30 ml of C₁₈.

The yield was 41 g of CO/C₁₄/C₁₈ terpolymer having an $\overline{M}_w$ of 78,000.

Example 5

A CO/C₁₄/C₁₆/C₁₈ quaterpolymer was prepared in substantially the same manner as the CO/C₁₄ copolymer in Example 1, but with the following differences:

- a) the autoclave contained 40 ml of a C₁₄/C₁₆/C₁₈ mixture in a molar ratio of 1:2:1 instead of neat C₁₄
- b) CO was injected into the autoclave to a pressure of 70 bar instead of 40 bar,

- c) the reaction temperature was 50°C instead of 35°C, and)
- d) the reaction time was 15 hours instead of 20 hours. The yield was 42 g of $\text{CO}/\text{C}_{14}^{\overline{\overline{}}}/\text{C}_{16}^{\overline{\overline{}}}/\text{C}_{18}^{\overline{\overline{}}}$ tetrapolymer having an $\overline{M}_w$ of 22,150.

Example 6

A $\text{CO}/\text{C}_{20}^{\overline{\overline{}}}-\text{C}_{24}^{\overline{\overline{}}}$ polymer was prepared in substantially the same manner as the $\text{CO}/\text{C}_{14}^{\overline{\overline{}}}$ copolymer in Example 1, but with the following differences:

- a) the autoclave contained 40 g of $\text{C}_{20}^{\overline{\overline{}}}-\text{C}_{24}^{\overline{\overline{}}}$ instead of $\text{C}_{14}^{\overline{\overline{}}}$,
- b) CO was injected into the autoclave to a pressure of 70 bar instead of 40 bar,
- c) the reaction temperature was 50°C instead of 35°C, and
- d) the reaction time was 15 hours instead of 20 hours. The yield was 38 g of $\text{CO}/\text{C}_{20}^{\overline{\overline{}}}-\text{C}_{24}^{\overline{\overline{}}}$ polymer with an $\overline{M}_w$ of 22,700.

Example 7

A $\text{CO}/\text{C}_{12}^{\overline{\overline{}}}/\text{C}_{14}^{\overline{\overline{}}}/\text{C}_{16}^{\overline{\overline{}}}/\text{C}_{18}^{\overline{\overline{}}}$ polymer was prepared in substantially the same manner as the $\text{CO}/\text{C}_{14}^{\overline{\overline{}}}$ copolymer in Example 1, but with the following differences:

- a) the autoclave contained 50 ml of a $\text{C}_{12}^{\overline{\overline{}}}/\text{C}_{14}^{\overline{\overline{}}}/\text{C}_{16}^{\overline{\overline{}}}/\text{C}_{18}^{\overline{\overline{}}}$ mixture in a molar ratio of 1:2:2:1 instead of $\text{C}_{14}^{\overline{\overline{}}}$ alone,
- b) the reaction temperature was 50°C instead of 35°C, and
- c) the reaction time was 15 hours instead of 20 hours. The yield was 40 g of $\text{CO}/\text{C}_{12}^{\overline{\overline{}}}/\text{C}_{14}^{\overline{\overline{}}}/\text{C}_{16}^{\overline{\overline{}}}/\text{C}_{18}^{\overline{\overline{}}}$ polymer having an $\overline{M}_w$ of 28,600.

Example 8

A $\text{CO}/\text{C}_{12}^{\overline{\overline{}}}/\text{C}_{14}^{\overline{\overline{}}}/\text{C}_{16}^{\overline{\overline{}}}/\text{C}_{18}^{\overline{\overline{}}}$ polymer was prepared in substantially the same manner as the $\text{CO}/\text{C}_{14}^{\overline{\overline{}}}$ copolymer in Example 1, but with the following differences:

- a) the autoclave contained 50 ml of a $\overline{\text{C}}_{12}/\overline{\text{C}}_{14}/\overline{\text{C}}_{16}/\overline{\text{C}}_{18}$ mixture in a molar ratio of 2:1:1:2 instead of $\overline{\text{C}}_{14}$ alone,
- b) the reaction temperature was 50°C instead of 35°C, and
- c) the reaction time was 15 hours instead of 20 hours. The yield was 42 g of $\text{CO}/\overline{\text{C}}_{12}/\overline{\text{C}}_{14}/\overline{\text{C}}_{16}/\overline{\text{C}}_{18}$ polymer having an $\overline{\text{M}}_{\text{w}}$ of 26,100.

Example 9

A $\text{CO}/\overline{\text{C}}_{16}$ copolymer was prepared in substantially the same manner as the $\text{CO}/\overline{\text{C}}_{14}$ copolymer in Example 1, but with the following differences:

- a) the autoclave contained 100 ml of $\overline{\text{C}}_{16}$ instead of tetrahydrofuran and $\overline{\text{C}}_{14}$,
- b) CO was injected into the autoclave to a pressure of 70 bar instead of 40 bar,
- c) the reaction temperature was 50°C instead of 35°C, and
- d) the reaction time was 15 hours instead of 20 hours. The yield was 45 g of $\text{CO}/\overline{\text{C}}_{16}$ copolymer having an $\overline{\text{M}}_{\text{w}}$ of 35,400.

Example 10

The following polymers and polymer mixtures were tested as additives in three gas oils (A, B and C) in order to lower the PP, the CP and/or the CFPP of these oils.

Additive 1: $\text{CO}/\overline{\text{C}}_{14}$ copolymer prepared according to Example 1

Additive 2: $\text{CO}/\overline{\text{C}}_{16}$ copolymer prepared according to Example 2

Additive 3: $\text{CO}/\overline{\text{C}}_{14}/\overline{\text{C}}_{18}$ terpolymer prepared according to Example 4

Additive 4: mixture of $\text{CO}/\overline{\text{C}}_{14}$ copolymer prepared according to Example 1 and $\text{CO}/\overline{\text{C}}_{16}$ copolymer

prepared according to Example 2, in a weight ratio of 1:1

Additive 5: mixture of CO/C₁₄ copolymer prepared according to Example 1 and CO/C₁₆ copolymer prepared according to Example 2, in a weight ratio of 1:3

For the sake of comparison, in addition the following four additives, which are commercially available for the present purpose, were tested.

Additive 6: PARAMIN ECA 5920 (PARAMIN is a trademark)

Additive 7: PARAMIN ECA 8182

Additive 8: PARAMIN ECA 8400

Additive 9: PARAFLOW 214 (PARAFLOW is a trademark)

The additives were introduced into the gas oils in the form of a 50 %w solution in an organic solvent. The result of the experiments is embodied in Tables 1-3, where for each of the gas oils the PP, CP and/or CFPP is reported after addition of the indicated quantity of polymer solution (containing 50 %w of active material) stated as mg of polymer solution per kg of gas oil.

Table 1

GAS OIL A				
Added quantity of polymer solution, mg/kg	Polymer No.	Cloud point according to ASTM D2500 °C	Pour point according to ASTM D97 °C	Cold filter plugging point according to IP 309 °C
Gas oil A as such		2	-12	-9
100	6			-15
200	6			-16
300	6			-16

Table 1 (Cont'd)

GAS OIL A				
Added quantity of polymer solution, mg/kg	Polymer No.	Cloud point according to ASTM D2500 °C	Pour point according to ASTM D97 °C	Cold filter plugging point according to IP 309 °C
400	6			-18
600	6	0		
1000	6	-1		
100	2		-18	-19
200	2		-24	
600	2	-0.5	-24	
1000	2	-1.5		
40	3			-19
400	3			-24
100	4			-17
150	4			-20
300	4			-22
2000	5		-42	
2000	6		-39	
100	7	2	-12	
200	7	2	-15	
600	7	2	-18	
1000	7	1	-24	
100	8	1.5		
200	8	1.5		
600	8	1		
1000	8	0.5		
100	9		-12	-13
200	9		-15	-18

Table 2

GAS OIL B				
Added quantity of polymer solution, mg/kg	Polymer No.	Cloud point according to ASTM D2500 °C	Pour point according to ASTM D97 °C	Cold filter plugging point according to IP 309 °C
Gas oil B as such		1	-15	-9
100	6		-21	-17
400	6		-27	
600	6		-30	-18
4000	6		-30	-6
100	2		-24	-17
400	2		-30	
4000	2		-36	
100	4		-24	
4000	4		-51	-13
200	3			-20
400	3			-22

Table 3

GAS OIL C				
Added quantity of polymer solution, mg/kg	Polymer No.	Cloud point according to ASTM D2500 °C	Pour point according to ASTM D97 °C	Cold filter plugging point according to IP 309 °C
Gas oil C as such		0	-18	-5
75	6			-5
300	6			-6
150	2			-11
150	1			-15
300	1			-17
150	4			-18
75	3			-13
600	3		-27	

The results reported in Tables 1 to 3 clearly demonstrate the superiority of the polymers according to the invention in terms of their capability for PP, CP and/or CFPP reduction of paraffinic hydrocarbon oils in comparison to commercially available additives for this purpose.

The $\bar{M}_w$ of the new polymers prepared according to Examples 1-9 was determined by means of GPC analysis. Using ^{13}C -NMR analysis, it was found that these polymers were built of linear chains in which on the one hand the units originating from carbon monoxide and on the other hand the units originating from the C_{10+} α -olefins occurred in an alternating way. In the polymers which were prepared from monomer mixtures containing two or more C_{10+} α -olefins, the units originating from the

various C₁₀+ α -olefins occurred in random sequence relative to one another.



C L A I M S

1. Hydrocarbon oil compositions comprising a hydrocarbon oil and a polymeric additive characterized in that they comprise a paraffinic hydrocarbon oil and as additive linear polymers of carbon monoxide with one or more α -olefins having at least 10 carbon atoms per molecule (C_{10+} α -olefins) and optionally moreover with one or more olefins having fewer than 10 carbon atoms per molecule (C_9- olefins), in which polymers the units originating from carbon monoxide and the units originating from the olefins occur in a substantially alternating way.
2. Hydrocarbon oil compositions as claimed in claim 1, characterized in that the polymers possess a weight average molecular weight ($\overline{M}_w$), between 10^3 and 10^6 .
3. Hydrocarbon oil compositions as claimed in claim 1 or 2, characterized in that the C_{10+} α -olefins used as monomers in the preparation of the polymers contain fewer than 40 carbon atoms per molecule.
4. Hydrocarbon oil compositions as claimed in any one or more of claims 1-3, characterized in that they contain as additive polymers selected from carbon monoxide/n-tetradecene-1 copolymers, carbon monoxide/n-hexadecene-1 copolymers, carbon monoxide/n-tetradecene-1/n-octadecene-1 terpolymers and mixtures of carbon monoxide/n-tetradecene-1 copolymers with carbon monoxide/n-hexadecene-1 copolymers.
5. Hydrocarbon oil compositions as claimed in any one or more of claims 1-4, characterized in that they contain 1-10,000 mg of polymer per kg of hydrocarbon oil.
6. Polymers of one or more olefins intended for use as additives in a paraffinic hydrocarbon oil, characterized in that they are linear copolymers of carbon monoxide





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with one or more α -olefins having at least 10 carbon atoms per molecule (C_{10+} α -olefins) and, optionally, moreover with one or more olefins having less than 10 carbon atoms per molecule (C_9 -olefins), in which copolymers the units originating from carbon monoxide and the units originating from the olefins occur in a substantially alternating way.

7. Polymers of carbon monoxide with one or more α -olefins, characterized in that they consist of linear chains in which on the one hand units originating from carbon monoxide and on the other hand units originating from one or more α -olefins having at least 10 carbon atoms per molecule (C_{10+} α -olefins) occur in a substantially alternating way and that they possess a weight average molecular weight ($\overline{M}_w$), of more than 10^4 .

8. Polymers as claimed in claim 7, characterized in that they belong to the group formed by carbon monoxide/*n*-tetradecene-1 copolymers, carbon monoxide/*n*-hexadecene-1 copolymers, carbon monoxide/*n*-octadecene-1 copolymers, carbon monoxide/*n*-tetradecene-1/*n*-octadecene-1 terpolymers, carbon monoxide/*n*-tetradecene-1/*n*-hexadecene-1/*n*-octadecene-1 quaterpolymers, carbon monoxide/*n*-dodecene-1/*n*-tetradecene-1/*n*-hexadecene-1/*n*-octadecene-1 pentapolymers and polymers of carbon monoxide with a mixture of unbranched α -olefins having 20 to 24 carbon atoms per molecule.

9. A process for the preparation of the polymers as claimed in any one or more of claims 6 to 8, characterized in that it comprises contacting the monomers, at elevated temperature and pressure and in the presence of a diluent consisting for more than 90 %v of an aprotic liquid, with a catalyst composition containing a Group VIII metal, in particular palladium, and a phosphorus bidentate ligand having the general formula $(R^1R^2P)_2R$ where R^1 and R^2 represent identical or

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different optionally polar substituted aliphatic hydrocarbyl groups and R a bivalent organic bridging group containing at least two carbon atoms in the bridge linking the two phosphorus atoms.

10. A process as claimed in claim 9, characterized in that it is performed at a temperature of 25-150°C, a pressure of 2-150 bar and a molar ratio of the olefins relative to carbon monoxide between 10:1 and 1:10, and that per mol of olefin to be polymerized a quantity of catalyst composition is used which contains between 10^{-7} and 10^{-3} gram atom of Group VIII metal.

11. A process as claimed claim 9 or 10, characterized in that the C_{10+} α -olefin used as monomer also performs the function of aprotic liquid.

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A B S T R A C T

HYDROCARBON OIL COMPOSITIONS

Hydrocarbon oil compositions which contain as additive a polymer of carbon monoxide and one or more C₁₀₊ α -olefins in which the units originating from carbon monoxide and the units originating from the olefin(s), occur in a substantially alternating way, show an improved pour point, cold filter plugging point and/or cloud point.

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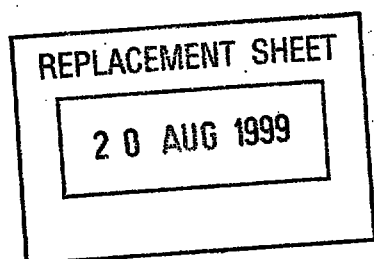
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olefines occur in an alternating way. The patent application further relates to polymers of carbon monoxide with one or more α -olefins, characterised in that they consist of linear chains in which on the one hand units originating from carbon monoxide and on the other hand units originating from one or more α -olefins having at least 10 carbon atoms per molecule (C_{10+} α -olefins) occur in an alternating way and that they possess a weight average molecular weight ($\bar{M}_w$), of more than 10^4 in that they belong to the group formed by carbon monoxide/n-tetradecene-1 copolymers, carbon monoxide/n-hexadecene-1 copolymers, carbon monoxide/n-octadecene-1 copolymers, carbon monoxide/n-tetradecene-1/n-octadecene-1 terpolymers, carbon monoxide/n-tetradecene-1/n-hexadecene-1/n-octadecene-1 quaterpolymers, carbon monoxide/n-dodecene-1/n-tetradecene-1/n-hexadecene-1/n-octadecene-1 pentapolymers and polymers of carbon monoxide with a mixture of unbranched α -olefins having 20-24 carbon atoms per molecule. Polymers based on each one of the latter α -olefin have been mentioned in EP-A-393753 and US-A-4761453 in the context of their use as engineering plastics. The application further relates to a process for the preparation of polymers of carbon monoxide with one or more C_{10+} α -olefins possessing an $\bar{M}_w$ of more than 10^4 , in which polymers on the one hand the units originating from carbon monoxide and on the other hand the units originating from the olefins occur in an alternating way, which process comprises contacting the monomers at elevated temperature and pressure and in the presence of a diluent which consists for more than 90 %v of an aprotic liquid with a catalyst composition containing a Group VIII metal and a phosphorous bidentate ligand having the general formula $(R^1R^2P)_2R$.

Finally, the application relates to the polymers which are obtainable by this process.

As paraffinic hydrocarbon oils the low-temperature properties of which can be improved according to the invention, mention may be made inter alia of gas oils, diesel oils, lubricating oils and crude oils. Very favourable results were achieved inter alia with the use of the present polymers in paraffinic gas oils. The molecular weight of the polymer which are eligible to be used in the hydrocarbon oil compositions according to the invention may vary between wide limits. By preference, polymers are used having a

weight average molecular weight ($\bar{M}_w$), between 10^3 and 10^6 and in particular between 10^4 and 10^5 . The C_{10+} α -olefins which are used as monomers in the preparation of the polymers are



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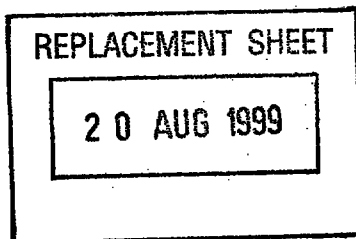
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reaction rate, in which polymers on the one hand the units originating from carbon monoxide and on the other hand the units originating from the applied olefins occur in an alternating way and which polymers possess an $\bar{M}_w$ above 10^4 , by performing the polymerization in the presence of a diluent which consists for more than 90 %v of an
5 aprotic liquid.

Polymers of carbon monoxide with one or more C_{10+} α -olefins in which polymers on the one hand the units originating from carbon monoxide and on the other hand the units originating from the olefins occur in a substantially alternating way and which polymers possess an $\bar{M}_w$ of more than 10^4 are novel per se.

10 As examples of the novel polymers which were prepared by the Applicant, mention may be made of carbon monoxide/n-tetradecene-1 copolymers, carbon monoxide/n-hexadecene-1 copolymers, carbon monoxide/n-octadecene-1 copolymers, carbon monoxide/n-tetradecene-1/n-octadecene-1 terpolymers, carbon monoxide/n-tetradecene-1/n-hexadecene-1/n-octadecene-1 quaterpolymers, carbon monoxide/n-
15 dodecene-1/n-tetradecene-1/n-hexadecene-1/n-octadecene-1 polymers and polymers of carbon monoxide with a mixture of unbranched α -olefins having 20-24 carbon atoms per molecule.

In the preparation of the novel polymers according to the invention, suitably use is made of a catalyst composition which contains a Group VIII metal and a phosphorus
20 bidentate ligand having the general formula $(R^1R^2P)_2R$. In the present application, Group VIII metals are understood as being the noble metals ruthenium, rhodium, palladium, osmium, iridium and platinum, and the iron group metals iron, cobalt and nickel. In the catalyst compositions, the Group VIII metal is preferentially chosen from palladium, nickel and cobalt. Special preference is given to palladium as Group



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C L A I M S

1. Hydrocarbon oil compositions comprising a hydrocarbon oil and a polymeric additive characterized in that they comprise a paraffinic hydrocarbon oil and as additive linear polymers of carbon monoxide with one or more α -olefins having at least 10 carbon atoms per molecule (C_{10+} α -olefins) and optionally moreover with one or more olefins having fewer than 10 carbon atoms per molecule (C_9- olefins), in which polymers the units originating from carbon monoxide and the units originating from the olefins occur in a substantially alternating way.
2. Hydrocarbon oil compositions as claimed in claim 1, characterized in that the polymers possess a weight average molecular weight ($\overline{M}_w$), between 10^3 and 10^6 .
3. Hydrocarbon oil compositions as claimed in claim 1 or 2, characterized in that the C_{10+} α -olefins used as monomers in the preparation of the polymers contain fewer than 40 carbon atoms per molecule.
4. Hydrocarbon oil compositions as claimed in any one or more of claims 1-3, characterized in that they contain as additive polymers selected from carbon monoxide/n-tetradecene-1 copolymers, carbon monoxide/n-hexadecene-1 copolymers, carbon monoxide/n-tetradecene-1/n-octadecene-1 terpolymers and mixtures of carbon monoxide/n-tetradecene-1 copolymers with carbon monoxide/n-hexadecene-1 copolymers.
5. Hydrocarbon oil compositions as claimed in any one or more of claims 1-4, characterized in that they contain 1-10,000 mg of polymer per kg of hydrocarbon oil.

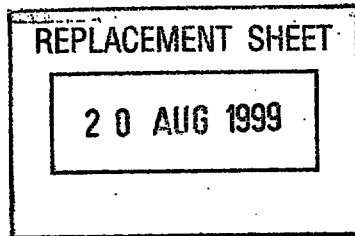
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6. Polymers of carbon monoxide with one or more α -olefins, characterised in that they consist of linear chains in which on the one hand units originating from carbon monoxide and on the other hand units originating from one or more α -olefins having at least 10 carbon atoms per molecule (C_{10+} α -olefins) occur in an alternating way and that
- 5 they possess a weight average molecular weight ($\bar{M}_w$), of more than 10^4 in that they belong to the group formed by carbon monoxide/n-tetradecene-1 copolymers, carbon monoxide/n-hexadecene-1 copolymers, carbon monoxide/n-octadecene-1 copolymers, carbon monoxide/n-tetradecene-1/n-octadecene-1 terpolymers, carbon monoxide/n-tetradecene-1/n-hexadecene-1/n-octadecene-1 quaterpolymers, carbon monoxide/n-
- 10 dodecene-1/n-tetradecene-1/n-hexadecene-1/n-octadecene-1 pentapolymers and polymers of carbon monoxide with a mixture of unbranched α -olefins having 20-24 carbon atoms per molecule.
7. A process for the preparation of polymers of carbon monoxide with one or more α -olefins, characterised in that they consist of linear chains in which on the one hand units
- 15 originating from carbon monoxide and on the other hand units originating from one or more α -olefins having at least 10 carbon atoms per molecule (C_{10+} α -olefins) occur in an alternating way and that they possess a weight average molecular weight ($\bar{M}_w$), of more than 10^4 which process comprises contacting the monomers, at elevated temperature and pressure and in the presence of a diluent consisting for more than 90 %v of an aprotic
- 20 liquid, with a catalyst composition containing a Group VIII metal, in particular palladium, and a phosphorus bidentate ligand having the general formula $(R^1R^2P)_2R$ where R^1 and R^2 represents identical or different optionally polar substituted aliphatic hydrocarbyl groups and R a bivalent organic bridging group containing at least two carbon atoms in the bridge linking the two phosphorus atoms.
- 25 8. A process as claimed in claim 7, characterised in that it is performed at a temperature of 25-150°C, a pressure of 2-150 bar and a molar ratio of the olefins relative to carbon monoxide between 10:1 and 1:10, and that per mol of olefin to be polymerized a quantity of catalyst composition is used which contains between 10^{-7} and 10^{-3} gram atom of Group VIII metal.



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9. A process as claimed in claim 7 or 8, characterised in that the C_{10+} α -olefin used as monomer also performs the function of aprotic liquid.
10. Polymers of carbon monoxide and one or more α -olefins, characterised in that they are obtainable by a process as claimed in any one or more of claims 7 to 9.