

Description

The invention relates to novel hydrocarbon oil compositions containing a hydrocarbon oil and polymeric additives.

Hydrocarbon oils such as gas oils, diesel oils, lubricating oils and crude oils can contain considerable amounts of paraffins. When such 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. A class of polymers which is very suitable for this purpose is formed by linear polymers of carbon monoxide with one or more olefins consisting at least in part of α -olefins having at least 10 carbon atoms per molecule (hereinafter referred to as 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. A second class of polymers which is very suitable for this purpose is formed by polymers of one or more olefinically unsaturated compounds consisting at least in part of alkyl acrylates or alkyl methacrylates having at least eight carbon atoms in the alkyl group (hereinafter referred to as C_{8+} alkyl esters). A third class of polymers which is likewise suitable for this purpose is formed by polymers of ethene with one or more vinyl esters of saturated aliphatic monocarboxylic acids.

GB-A-1272614 relates to additives for hydrocarbon oil compositions being olefin/carbon monoxide copolymers obtainable by free radical catalyzed polymerization. Such polymers are branched copolymers having a relatively modest carbon monoxide content, e.g. up to 20% mol as illustrated in the working examples.

CH-A 572969 relates to paraffinic crude oil compositions comprising as additive polymers or copolymers comprising heterocyclic rings mixtures and aliphatic substituents having at least 10 carbon atoms.

US-A 4175926 relates to mineral oil compositions comprising as pour point depressing additives copolymers of ethylene and vinyl esters of saturated carboxylic acids.

An investigation performed by the Applicant into the use of polymers as additives in paraffinic hydrocarbon oils for improving the properties of these oils at low temperature has disclosed that mixtures of polymers of the first class with polymers of the second and/or third class, which polymers each possess activity per se to reduce the pour point (PP), the cloud point (CP) and/or the cold filter plugging point (CFPP) of these oils, display a synergistic activity. This means that when the mixture is used in a given concentration a stronger PP, CP and/or CFPP reduction is obtained than when each of the polymers is used individually in the same concentration, or that the mixture can produce the same PP, CP and/or CFPP reduction at a lower concentration.

The present patent application therefore relates to novel hydrocarbon oil compositions characterized in that they contain a paraffinic hydrocarbon oil and as additives:

- a) linear polymers of carbon monoxide with one or more olefins consisting at least in part of 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 moreover one or more polymers selected from
- b) polymers of olefinically unsaturated compounds consisting at least in part of C_{8+} alkyl esters, and
- c) polymers of ethene with one or more vinyl esters of saturated aliphatic monocarboxylic acids.

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 are achieved inter alia with the use of the present polymer mixtures in paraffinic gas oils and crude oils. The molecular weight of the polymers which are eligible for use in the hydrocarbon oil compositions according to the invention can vary within wide limits. For preference, additives are used having a weight average molecular weight ($\overline{M}_w$) between 10^3 and 10^6 and in particular between 10^4 and 10^5 . Both the C_{10+} α -olefins which are used as monomers in the preparation of the polymers mentioned in a) and the alkyl groups present in the C_{8+} alkyl esters which are used as monomers in the preparation of the polymers mentioned in b) should preferably be unbranched. Both the C_{10+} α -olefins and the alkyl groups present in the C_{8+} alkyl esters, if present, preferably contain fewer than 40 and in particular fewer than 30 carbon atoms. The preference for a given molecular weight of the polymers and for a given number of carbon atoms in the C_{10+} α -olefins and in the alkyl groups of the C_{8+} alkyl esters which are used as monomers in the preparation of the polymers is largely determined by the nature of the paraffins present in the hydrocarbon oil.

In the preparation of the polymers mentioned in a), besides C_{10+} α -olefins, olefins with fewer than 10 carbon atoms can also be used such as ethylene, propylene, butene-1 and cyclopentene. Preferably, in the preparation of the polymers mentioned in a), exclusively C_{10+} α -olefins are used as olefins. The monomer mixture from which the polymers mentioned in a) are prepared may contain in addition to carbon monoxide both one and more C_{10+} α -olefins. As an example of a copolymer with which very favourable results were achieved according to the invention, mention may be made of a carbon monoxide/1-octadecene copolymer. As an example

of a terpolymer which is very suitable for the present purpose, mention may be made of a carbon monoxide/1-tetradecene/1-octadecene terpolymer. Polymers of carbon monoxide with a mixture of unbranched α -olefins having 20-24 carbon atoms per molecule were also found to be very suitable for use in the present polymer mixtures.

As has been noted hereinbefore, as regards the polymers mentioned in a) there is a preference for polymers based on carbon monoxide with one or more C_{10+} α -olefins which polymers possess an $\bar{M}_w$ above 10^4 . An investigation into these polymers recently performed by the Applicant disclosed an attractive method of preparation. This preparation method consists basically of 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 carbon atoms in the bridge linking the two phosphorus atoms. There is a preference for the use of catalyst compositions which contain 0.75-1.5 mol of a phosphorus bidentate ligand per gram atom of Group VIII metal where the groups R^1 and R^2 are identical alkyl groups having not more than six carbon atoms and which moreover per gram atom of Group VIII metal contain 2-50 mol of an anion of an acid having a pKa below 2 and optionally 10-1,000 mol of an organic oxidant. Special preference exists for catalyst compositions based on palladium acetate, 1,3-bis(di-n-butylphosphino)propane, 1,4-naphthoquinone and trifluoroacetic acid or nickel perchlorate. The preparation of the polymers is preferably performed at a temperature of 30-130°C, a pressure of 5-100 bar and a molar ratio of the olefins relative to carbon monoxide of 5:1 to 1:5 and with the use of such a quantity of catalyst composition as to contain 10^{-8} to 10^{-3} gram atom of Group VIII metal per mol of olefin to be polymerized. The polymerization is preferably performed in a diluent which contains a small quantity of a protic liquid. A very suitable diluent for the present polymerization is a mixture of tetrahydrofuran and methanol.

In the preparation of the polymers mentioned in b), besides C_{8+} alkyl esters other olefinically unsaturated compounds can also be used such as alkyl acrylates and alkyl methacrylates having fewer than eight carbon atoms in the alkyl group, olefinically unsaturated aromatic compounds such as styrene and olefinically unsaturated heterocyclic compounds such as vinyl pyridines. The monomer mixture from which the polymers mentioned in b) are prepared can contain both one and more C_{8+} alkyl esters. As examples of terpolymers with which very favourable results can be achieved according to the invention, mention may be made of a 1-dodecyl methacrylate/1-octadecyl methacrylate/2-vinylpyridine terpolymer and a 1-octadecyl acrylate/1-eicosyl acrylate/1-docosyl acrylate terpolymer. As examples of polymers with which likewise very favourable results were achieved according to the invention, mention may be made of polymers of 4-vinylpyridine with a mixture of n-alkyl acrylates having 18-22 carbon atoms in the alkyl groups, polymers of mixtures of n-alkyl acrylates having 12-15 carbon atoms in the alkyl groups, and polymers of methylacrylate with a mixture of n-alkyl acrylates having 12-15 carbon atoms in the alkyl groups.

Examples of polymers mentioned in c) with which advantageous results are obtained are copolymers of ethene with vinyl propionate or acetate, especially the latter give good results. They are obtainable commercially in a variety of molecular weights and weight distributions, specially formulated for ready addition to hydrocarbon oils.

In the hydrocarbon oil compositions according to the invention, both one or more of the polymers mentioned in a) and one or more of the polymers mentioned in b) and c) may be present. Preference exists for hydrocarbon oil compositions which contain only two additives: only one of the polymers mentioned in a) and only one of the polymers mentioned in b) and c). Besides the present polymer mixtures, the hydrocarbon oil compositions may also contain other additives such as antioxidants, corrosion inhibitors and metal deactivators.

The quantity of polymer mixture which is taken up in the paraffinic hydrocarbon oils according to the invention and the relative ratio of the polymers in the polymer mixture can vary between wide limits. For preference, 0.1-10,000 and in particular 1-1,000 mg of the polymer mixture is taken up per kg of hydrocarbon oil. The polymer mixture used preferably contains 1-90 %w and in particular 10-75 %w of the polymers mentioned in a), and thus preferably 10-99, in particular 25-90 %w, of the polymers mentioned in b) and c) together.

The invention will now be illustrated with reference to the following examples:

Example 1

A carbon monoxide/1-octadecene copolymer was prepared as follows. In a stirred autoclave with a capacity of 250 ml which contained 100 ml of tetrahydrofuran and 40 g of 1-octadecene in a nitrogen atmosphere, a catalyst solution was introduced, containing:

5 ml methanol,

0.1 mmol palladium acetate,
 0.5 mmol nickel perchlorate,
 0.12 mmol 1,3-bis(di-n-butylphosphino)propane, and
 5 6 mmol 1,4-naphthoquinone.

After injection of carbon monoxide to a pressure of 40 bar, the contents of the autoclave were heated to 50 °C. After 30 h, 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 copolymer having an $\overline{M}_w$ of 20,300.

10 Example 2

A carbon monoxide/1-tetradecene/1-octadecene terpolymer was prepared in substantially the same manner as the carbon monoxide/1-octadecene copolymer in Example 1, but with the following differences:

- 15 a) the autoclave contained 30 g of 1-octadecene instead of 40 g and moreover 30 g of 1-tetradecene,
 b) the reaction temperature was 35 °C instead of 50 °C, and
 c) the reaction time was 20 instead of 30 h.

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

20 Example 3

A polymer of carbon monoxide with a mixture of linear α -olefins having 20-24 carbon atoms per molecule was prepared in substantially the same manner as the carbon monoxide/1-octadecene copolymer in Example 1, but with the following differences:

- 25 a) the autoclave contained 40 g of a mixture of linear α -olefins having 20-24 carbon atoms per molecule instead of 1-octadecene,
 b) carbon monoxide was injected into the autoclave to a pressure of 70 instead of 40 bar, and
 c) the reaction time was 15 instead of 30 h.

The yield was 38 g of polymer having an $\overline{M}_w$ of 22,700.

30 Example 4:

A carbon monoxide/1-hexadecene copolymer was prepared in substantially the same manner as the carbon monoxide/1-octadecene copolymer in Example 1, but with the following differences:

- 35 a) the autoclave contained 38 g of 1-hexadecene instead of 40 g of 1-octadecene,
 b) carbon monoxide was injected into the autoclave to a pressure of 70 instead of 40 bar, and
 c) the reaction time was 15 instead of 30 h.

The yield was 40 g of copolymer having an $\overline{M}_w$ of 35,000.

40 Example 5

A carbon monoxide/1-tetradecene/1-hexadecene/1-octadecene quaterpolymer was prepared in substantially the same manner as the carbon monoxide/1-octadecene copolymer in Example 1, but with the following differences:

- 45 a) the autoclave contained 38 g of an n-C₁₄/n-C₁₆/n-C₁₈ α -olefin mixture having a molar ratio of 1:2:1 instead of 40 g of 1-octadecene,
 b) carbon monoxide was injected into the autoclave to a pressure of 70 instead of 40 bar, and
 c) the reaction time was 15 instead of 30 h.

The yield was 42 g of quaterpolymer having an $\overline{M}_w$ of 22,000.

50 Example 6

The following polymers were tested as additives in two crude oils (A and B) and in two gas oils (C and D) to reduce the PP of these oils.

- 55 Additive 1: The copolymer prepared according to Example 1.
 Additive 2: The terpolymer prepared according to Example 2.
 Additive 3: The polymer prepared according to Example 3.
 Additive 4: A 1-dodecyl methacrylate/1-octadecyl methacrylate/2-vinylpyridine terpolymer having an $\overline{M}_w$ of 66,000.

Additive 5: A 1-octadecyl acrylate/1-eicosyl acrylate/1-docosyl acrylate terpolymer having an $\overline{M}_w$ of 220,000.

Additive 6: A polymer of 4-vinylpyridine with a mixture of n-alkyl acrylates having 18-22 carbon atoms in the alkyl groups and having an $\overline{M}_w$ of 135,000.

Additive 7: A polymer of a mixture of n-alkyl acrylates having 12 to 15 carbon atoms in the alkyl groups and having an $\overline{M}_w$ of 160,000.

Additive 8: A polymer of methyl acrylate with a mixture of n-alkyl acrylates having 12-15 carbon atoms in the alkyl groups and having an $\overline{M}_w$ of 224,000.

The polymers were introduced into the oil in the form of a solution of 50 %w of solid matter in toluene. The results of the experiments are given below in Table I, in which the PP is reported after preheating to the stated temperature (50 or 90 °C) and, if applicable, adding at 50 °C the stated amount of polymer solution expressed as mg of polymer solution per kg of paraffinic oil. All mixtures of additives had a weight ratio of 1:1, except the mixture of test 5, which had a weight ratio of 1:2. The PPs were determined in accordance with standard method ASTM D97.

TABLE I - POUR POINTS

Test	Oil	Additive	Solution	Preheating	PP
No.		Nos.	mg/kg	°C	°C
*1	A	-	-	50	30
2	A	1+6	2000	50	21
3	A	1+6	4000	50	15
4	A	1+6	6000	50	12
*5	A	1+6	6000	50	12
*6	A	-	-	90	30
7	A	3+6	400	90	21
8	A	3+6	600	90	18
9	A	3+6	1000	90	12
10	A	3+6	2000	90	12
*11	B	-	-	90	27
12	B	3+5	400	90	3
13	B	3+5	600	90	0
14	B	3+5	800	90	0
*15	C	-	-	50	-12
16	C	2+7	200	50	-21
*17	C	1	100	50	-15
*18	C	1	2000	50	-18
*19	C	1	4000	50	-18
*20	C	4	100	50	-15
*21	C	4	2000	50	-21
*22	C	4	4000	50	-21
23	C	1+4	100	50	-21
24	C	1+4	2000	50	-33
25	C	1+4	4000	50	-36
*26	D	-	-	50	-18
*27	D	1	200	50	-21
*28	D	8	200	50	-24
29	D	1+8	200	50	-27

* - Not according to the invention, for comparison

" - Weight ratio additive 1 : additive 6 = 1:2

The sixteen polymer mixture-containing hydrocarbon oil compositions as described above and tested for their PP are compositions according to the invention. The synergism which occurs when a mixture of a polymer listed under a) with a polymer listed under b) is used, is readily apparent from a comparison of the results of the experiments performed with either additive 1 (tests 17-19) or additive 4 (tests 20-22) with a 1:1 mixture

of additives 1 and 4 (tests 23-25). This synergism also emerges clearly upon comparison of the results of tests 26-29 performed with gas oil D.

5 Example 7

The following polymers were tested as additives in a gas oil (E) to reduce the CFPP of this oil.

Additive 9: the copolymer prepared according to Example 4.

Additive 10: the copolymer prepared according to Example 5.

10 Additive 11: a copolymer of ethene and vinyl acetate, commercially available as a solution under the trademark PARAMIN ECA 5920.

Additive 12: a copolymer of ethene and vinyl acetate, commercially available as a solution under the trademark PARAMIN PARAFLOW 214.

15 Additive 13: a copolymer of ethene and vinyl acetate, commercially available as a solution under the trademark PARAMIN ECA 8182.

Additives 9 and 10 were introduced into the oil in the form of a solution of 50 %w of solid matter in toluene. Additives 11-13 were introduced into the oil in the form of their commercial solutions. The results of the experiments are given below in Table II, in which the CFPP is reported after preheating to 50 °C and, if applicable, adding at 50 °C the stated quantity of polymer solution expressed as mg of solution per kg of gas oil. All mix-
20 tures of additives had a weight ratio of 1:1. The CFPPs were determined according to standard method IP 309.

TABLE II - COLD FILTER PLUGGING POINTS

25	Test	Additive	Solution	CFPP
	No.	Nos.	mg/kg	°C
	*30	-	-	-6
	*31	9	40	-9
30	*32	12	40	-12
	33	9+12	40	-19
	*34	9	75	-12
35	*35	12	75	-14
	*36	12	300	-19
	37	9+12	75	-20
	*38	11	40	-12
40	*39	11	75	-16
	*40	11	300	-21
	41	9+11	75	-24
45	*42	13	40	-15
	43	9+13	40	-20
	44	10+12	75	-19
50	*45	10	75	-13
	*46	13	75	-16
	47	10+13	75	-19

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* - Not according to the invention, for comparison

The six polymer mixture-containing hydrocarbon oil compositions as described above and tested for their

CFPP are compositions according to the invention. The synergism which occurs when a polymer listed under a) is mixed with a polymer listed under c), is readily apparent from mutual comparison of the results of tests 31-33, of tests 34, 35 and 37, of tests 34, 39 and 41, of tests 31, 42 and 43, of tests 35, 44 and 45, or of tests 45-47.

Examples 1-5, in which the preparation is described of the polymers used as additives in Examples 6 and 7, fall outside the scope of the invention. By means of ^{13}C -NMR analysis, it was determined that these polymers were constructed 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 prepared from monomer mixtures containing two or more C_{10+} α -olefins, the units originating from the various C_{10+} α -olefins occurred in random sequence relative to one another.

Claims

Claims for the following Contracting States : BE, DE, FR, GB, IT, NL

1. Hydrocarbon oil compositions, characterized in that they contain a paraffinic hydrocarbon oil and as additives:
 - a) one or more linear polymers of carbon monoxide with one or more olefins consisting at least in part of α -olefins having at least 10 carbon atoms per molecule (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 moreover one or more polymers selected from:
 - b) polymers of one or more olefinically unsaturated compounds consisting at least in part of alkyl acrylates or alkyl methacrylates having at least eight carbon atoms in the alkyl group (C_8+ alkyl esters), and
 - c) polymers of ethene with one or more vinyl esters of saturated aliphatic monocarboxylic acids.
2. Hydrocarbon oil compositions as claimed in claim 1, characterized in that the additives possess a weight average molecular weight ($\bar{M}_w$), between 10^3 and 10^6 .
3. Hydrocarbon oil compositions as claimed in claim 1 or 2, characterized in that both the C_{10+} α -olefins and the alkyl groups present in the C_8+ alkyl esters, if present, contain fewer than 40 carbon atoms.
4. Hydrocarbon oil compositions as claimed in any one or more of claims 1-3, characterized in that exclusively C_{10+} α -olefins are used as olefins in the preparation of the polymers mentioned in a).
5. Hydrocarbon oil compositions as claimed in any one or more of claims 1-4, characterized in that they contain polymers mentioned in a) based on carbon monoxide with one or more C_{10+} α -olefins which polymers possess an $\bar{M}_w$ above 10^4 and which polymers are obtainable 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 $(\text{R}^1\text{R}^2\text{P})_2\text{R}$, 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 carbon atoms in the bridge linking the two phosphorus atoms.
6. Hydrocarbon oil compositions as claimed in any one or more of claims 1-5, characterized in that they contain polymers mentioned in b) selected from n-dodecyl methacrylate/n-octadecyl methacrylate/2-vinyl pyridine terpolymers, n-octadecyl acrylate/n-eicosyl acrylate/n-docosyl acrylate terpolymers, polymers of 4-vinyl pyridine with a mixture of n-alkyl acrylates having 18-22 carbon atoms in the alkyl groups, polymers of mixtures of n-alkyl acrylates having 12-15 carbon atoms in the alkyl groups, and polymers of methylacrylate with a mixture of n-alkyl acrylates having 12-15 carbon atoms in the alkyl groups.
7. Hydrocarbon oil compositions as claimed in any one or more of claims 1-6, characterized in that they contain polymers mentioned in c) selected from copolymers of ethene with vinyl propionate or acetate.
8. Hydrocarbon oil compositions as claimed in any one or more of claims 1-7, characterized in that they contain only one of the polymers mentioned in a) and only one of the polymers mentioned in b) and c).

CFPP are compositions according to the invention. The synergism which occurs when a polymer listed under a) is mixed with a polymer listed under c), is readily apparent from mutual comparison of the results of tests 31-33, of tests 34, 35 and 37, of tests 34, 39 and 41, of tests 31, 42 and 43, of tests 35, 44 and 45, or of tests 45-47.

Examples 1-5, in which the preparation is described of the polymers used as additives in Examples 6 and 7, fall outside the scope of the invention. By means of ^{13}C -NMR analysis, it was determined that these polymers were constructed 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 prepared from monomer mixtures containing two or more C_{10+} α -olefins, the units originating from the various C_{10+} α -olefins occurred in random sequence relative to one another.

Claims

Claims for the following Contracting States : BE, DE, FR, GB, IT, NL

1. Hydrocarbon oil compositions, characterized in that they contain a paraffinic hydrocarbon oil and as additives:
 - a) one or more linear polymers of carbon monoxide with one or more olefins consisting at least in part of α -olefins having at least 10 carbon atoms per molecule (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 moreover one or more polymers selected from:
 - b) polymers of one or more olefinically unsaturated compounds consisting at least in part of alkyl acrylates or alkyl methacrylates having at least eight carbon atoms in the alkyl group (C_8+ alkyl esters), and
 - c) polymers of ethene with one or more vinyl esters of saturated aliphatic monocarboxylic acids.
2. Hydrocarbon oil compositions as claimed in claim 1, characterized in that the additives possess a weight average molecular weight ($\bar{M}_w$), between 10^3 and 10^6 .
3. Hydrocarbon oil compositions as claimed in claim 1 or 2, characterized in that both the C_{10+} α -olefins and the alkyl groups present in the C_8+ alkyl esters, if present, contain fewer than 40 carbon atoms.
4. Hydrocarbon oil compositions as claimed in any one or more of claims 1-3, characterized in that exclusively C_{10+} α -olefins are used as olefins in the preparation of the polymers mentioned in a).
5. Hydrocarbon oil compositions as claimed in any one or more of claims 1-4, characterized in that they contain polymers mentioned in a) based on carbon monoxide with one or more C_{10+} α -olefins which polymers possess an $\bar{M}_w$ above 10^4 and which polymers are obtainable 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 $(\text{R}^1\text{R}^2\text{P})_2\text{R}$, 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 carbon atoms in the bridge linking the two phosphorus atoms.
6. Hydrocarbon oil compositions as claimed in any one or more of claims 1-5, characterized in that they contain polymers mentioned in b) selected from n-dodecyl methacrylate/n-octadecyl methacrylate/2-vinyl pyridine terpolymers, n-octadecyl acrylate/n-eicosyl acrylate/n-docosyl acrylate terpolymers, polymers of 4-vinyl pyridine with a mixture of n-alkyl acrylates having 18-22 carbon atoms in the alkyl groups, polymers of mixtures of n-alkyl acrylates having 12-15 carbon atoms in the alkyl groups, and polymers of methylacrylate with a mixture of n-alkyl acrylates having 12-15 carbon atoms in the alkyl groups.
7. Hydrocarbon oil compositions as claimed in any one or more of claims 1-6, characterized in that they contain polymers mentioned in c) selected from copolymers of ethene with vinyl propionate or acetate.
8. Hydrocarbon oil compositions as claimed in any one or more of claims 1-7, characterized in that they contain only one of the polymers mentioned in a) and only one of the polymers mentioned in b) and c).



9. Hydrocarbon oil compositions as claimed in any one or more of claims 1-8, characterized in that they contain 0.1-10,000 mg of polymer mixture per kg of hydrocarbon oil.
- 5 10. Hydrocarbon oil compositions as claimed in any one or more of claims 1-9, characterized in that the polymer mixture used contains from 1-90 %w of the polymers mentioned in a).

Claims for the following contracting State : ES

- 10 1. A process for preparing hydrocarbon oil compositions, characterized in that a paraffinic hydrocarbon oil is admixed with the following additives:
- a) one or more linear polymers of carbon monoxide with one or more olefins consisting at least in part of α -olefins having at least 10 carbon atoms per molecule (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
- 15 b) polymers of one or more olefinically unsaturated compounds consisting at least in part of alkyl acrylates or alkyl methacrylates having at least eight carbon atoms in the alkyl group (C_{8+} alkyl esters), and.
- c) polymers of ethene with one or more vinyl esters of saturated aliphatic monocarboxylic acids.
- 20 2. Process as claimed in claim 1, characterized in that the additives possess a weight average molecular weight ($\overline{M}_w$), between 10^3 and 10^6 .
3. Process as claimed in claim 1 or 2, characterized in that both the C_{10+} α -olefins and the alkyl groups present in the C_{8+} alkyl esters, if present, contain fewer than 40 carbon atoms.
- 25 4. Process as claimed in any one or more of claims 1-3, characterized in that exclusively C_{10+} α -olefins are used as olefins in the preparation of the polymers mentioned in a).
5. Process as claimed in any one or more of claims 1-4, characterized in that they contain polymers mentioned in a) based on carbon monoxide with one or more C_{10+} α -olefins which polymers possess an $\overline{M}_w$ above 10^4 and which polymers are obtainable 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 hydro-
- 30 carbonyl groups and R a bivalent organic bridging group containing at least two carbon atoms in the bridge linking the two phosphorus atoms.
6. Process as claimed in any one or more of claims 1-5, characterized in that they contain polymers mentioned in b) selected from n-dodecyl methacrylate/n-octadecyl methacrylate/2-vinyl pyridine terpolymers, n-octadecyl acrylate/n-eicosyl acrylate/n-docosyl acrylate terpolymers, polymers of 4-vinyl pyridine with a mixture of n-alkyl acrylates having 18-22 carbon atoms in the alkyl groups, polymers of mixtures of n-alkyl acrylates having 12-15 carbon atoms in the alkyl groups, and polymers of methylacrylate with a mixture of n-alkyl acrylates having 12-15 carbon atoms in the alkyl groups.
- 45 7. Process as claimed in any one or more of claims 1-6, characterized in that they contain polymers mentioned in c) selected from copolymers of ethene with vinyl propionate or acetate.
8. Process as claimed in any one or more of claims 1-7, characterized in that they contain only one of the polymers mentioned in a) and only one of the polymers mentioned in b) and c).
- 50 9. Process as claimed in any one or more of claims 1-8, characterized in that they contain 0.1-10,000 mg of polymer mixture per kg of hydrocarbon oil.
10. Process as claimed in any one or more of claims 1-9, characterized in that the polymer mixture used contains from 1-90 %w of the polymers mentioned in a).
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Patentansprüche

Patentansprüche für folgende Vertragsstaaten : BE, DE, FR, GB, IT, NL,

1. Kohlenwasserstofföl-Zusammensetzungen, dadurch gekennzeichnet, daß sie ein paraffinisches Kohlenwasserstofföl enthalten, sowie als Zusatzstoffe:
 - a) ein oder mehrere lineare Polymere aus Kohlenmonoxid mit einem oder mehreren Olefinen, bestehend zumindest zum Teil aus α -Olefinen mit mindestens 10 Kohlenstoffatomen pro Molekül (C_{10+} - α -Olefine), in welchen Polymeren einerseits die von Kohlenmonoxid ausgehenden Einheiten und andererseits die von den Olefinen ausgehenden Einheiten auf eine im wesentlichen alternierende Art vorkommen, und außerdem ein oder mehrere Polymere, ausgewählt aus:
 - b) Polymeren aus einer oder mehreren olefinisch ungesättigten Verbindung(en), bestehend zumindest zum Teil aus Alkylacrylaten oder Alkylmethacrylaten mit mindestens acht Kohlenstoffatomen in der Alkylgruppe (C_{8+} -Alkylester), und
 - c) Polymeren aus Ethen mit einem oder mehreren Vinylestern von gesättigten aliphatischen Monocarbonsäuren.
2. Kohlenwasserstofföl-Zusammensetzungen, wie in Anspruch 1 beansprucht, dadurch gekennzeichnet, daß die Zusatzstoffe ein durchschnittliches Molekulargewicht ($\bar{M}_w$) zwischen 10^3 und 10^6 aufweisen.
3. Kohlenwasserstofföl-Zusammensetzungen, wie in Anspruch 1 oder 2 beansprucht, dadurch gekennzeichnet, daß die C_{10+} - α -Olefine sowie die Alkylgruppen, die in den C_{8+} -Alkylestern vorliegen können, weniger als 40 Kohlenstoffatome enthalten.
4. Kohlenwasserstofföl-Zusammensetzungen, wie in irgendeinem oder mehreren der Ansprüche 1 bis 3 beansprucht, dadurch gekennzeichnet, daß ausschließlich C_{10+} - α -Olefine als Olefine bei der Herstellung der unter a) erwähnten Polymere verwendet werden.
5. Kohlenwasserstofföl-Zusammensetzungen, wie in irgendeinem oder mehreren der Ansprüche 1 bis 4 beansprucht, dadurch gekennzeichnet, daß sie unter a) erwähnte Polymere enthalten, basierend auf Kohlenmonoxid mit einem oder mehreren C_{10+} - α -Olefinen, welche Polymere ein $\bar{M}_w$ über 10^4 besitzen und welche Polymere erhältlich sind durch das in-Berührung-bringen der Monomeren bei erhöhter Temperatur und erhöhtem Druck und in Gegenwart eines Verdünnungsmittels, bestehend zu mehr als 90 Vol% aus einer protogenen Flüssigkeit, mit einer Katalysator-Zusammensetzung, enthaltend ein Metall der Gruppe VIII und einen Phosphorbidentatligand der allgemeinen Formel $(R^1R^2P)_2R$, in der R^1 und R^2 identische oder unterschiedliche, gegebenenfalls polarsubstituierte aliphatische Kohlenwasserstoffgruppen und R ein zweiwertiges organisches Brückenglied, enthaltend mindestens zwei Kohlenstoffatome in der Brücke, die die beiden Phosphoratome verbindet, enthält.
6. Kohlenwasserstofföl-Zusammensetzungen, wie in irgendeinem oder mehreren der Ansprüche 1 bis 5 beansprucht, dadurch gekennzeichnet, daß sie unter b) erwähnte Polymere enthalten, ausgewählt aus Methacrylsäure-n-dodecylester/Methacrylsäure-n-octadecylester/2-Vinylpyridin-Terpolymeren, Acrylsäure-n-octadecylester/Acrylsäure-n-eicosylester/Acrylsäure-n-docosylester-Terpolymeren, Polymeren von 4-Vinylpyridin mit einem Gemisch von Acrylsäure-n-alkylestern mit 18 bis 22 Kohlenstoffatomen in den Alkylgruppen, Polymeren von Gemischen von Acrylsäure-n-alkylestern mit 12 bis 15 Kohlenstoffatomen in den Alkylgruppen, und Polymeren von Acrylsäure-methylester mit einem Gemisch von Acrylsäure-n-alkylestern mit 12 bis 15 Kohlenstoffatomen in den Alkylgruppen.
7. Kohlenwasserstofföl-Zusammensetzungen, wie in irgendeinem oder mehreren der Ansprüche 1 bis 6 beansprucht, dadurch gekennzeichnet, daß sie unter c) genannte Polymere enthalten, ausgewählt aus Copolymeren von Ethen mit Vinylpropionat oder -acetat.
8. Kohlenwasserstofföl-Zusammensetzungen, wie in irgendeinem oder mehreren der Ansprüche 1 bis 7 beansprucht, dadurch gekennzeichnet, daß sie nur eines der unter a) genannten Polymere und nur eines der unter b) und c) genannten Polymere enthalten.
9. Kohlenwasserstofföl-Zusammensetzungen, wie in irgendeinem oder mehreren der Ansprüche 1 bis 8 beansprucht, dadurch gekennzeichnet, daß sie 0,1 bis 10.000 mg Polymergemisch pro kg Kohlenwasserstofföl enthalten.



10. Kohlenwasserstofföl-Zusammensetzungen, wie in irgendeinem oder mehreren der Ansprüche 1 bis 9 beansprucht, dadurch gekennzeichnet, daß das verwendete Polymergemisch 1 bis 90 Gew% der unter a) genannten Polymere enthält.

Patentansprüche für folgenden Vertragsstaat : ES

1. Ein Verfahren zur Herstellung von Kohlenwasserstofföl-Zusammensetzungen, dadurch gekennzeichnet, daß ein paraffinisches Kohlenwasserstofföl mit den folgenden Zusatzstoffen vermischt wird:
 - a) ein oder mehrere lineare Polymere von Kohlenmonoxid mit einem oder mehreren Olefinen, bestehend zumindest zum Teil aus α -Olefinen mit mindestens 10 Kohlenstoffatomen pro Molekül (C_{10+} - α -Olefine), in welchen Polymeren einerseits die von Kohlenmonoxid ausgehenden Einheiten und andererseits die von den Olefinen ausgehenden Einheiten auf eine im wesentlichen alternierende Art vorkommen, und außerdem ein oder mehrere Polymere, ausgewählt aus:
 - b) Polymeren von einer oder mehreren olefinisch ungesättigten Verbindung(en), bestehend zumindest zum Teil aus Alkylacrylaten oder Alkylmethacrylaten mit mindestens acht Kohlenstoffatomen in der Alkylgruppe (C_8+ -Alkylester), und
 - c) Polymeren aus Ethen mit einem oder mehreren Vinylester(n) von gesättigten aliphatischen Monocarbonsäuren.
2. Ein Verfahren, wie in Anspruch 1 beansprucht, dadurch gekennzeichnet, daß die Zusatzstoffe ein durchschnittliches Molekulargewicht ($\bar{M}_w$) zwischen 10^3 und 10^6 aufweisen.
3. Ein Verfahren, wie in Anspruch 1 oder 2 beansprucht, dadurch gekennzeichnet, daß die C_{10+} - α -Olefine sowie die Alkylgruppen, die in den C_8+ -Alkylestern vorliegen können, weniger als 40 Kohlenstoffatome enthalten.
4. Ein Verfahren, wie in irgendeinem oder mehreren der Ansprüche 1 bis 3 beansprucht, dadurch gekennzeichnet, daß ausschließlich C_{10+} - α -Olefine als Olefine bei der Herstellung der unter a) erwähnten Polymere verwendet werden.
5. Ein Verfahren, wie in irgendeinem oder mehreren der Ansprüche 1 bis 4 beansprucht, dadurch gekennzeichnet, daß sie unter a) erwähnte Polymere enthalten, basierend auf Kohlenmonoxid mit einem oder mehreren C_{10+} - α -Olefinen, welche Polymere ein $\bar{M}_w$ über 10^4 besitzen und welche Polymere erhältlich sind durch das in-Berührung-bringen der Monomeren bei erhöhter Temperatur und erhöhtem Druck und in Gegenwart eines Verdünnungsmittels, bestehend zu mehr als 90 Vol% aus einer protogenen Flüssigkeit, mit einer Katalysator-Zusammensetzung, enthaltend ein Metall der Gruppe VIII und einen Phosphorbidentatligand der allgemeinen Formel $(R^1R^2P)_2R$, in der R^1 und R^2 identische oder unterschiedliche, gegebenenfalls polarsubstituierte aliphatische Kohlenwasserstoffgruppen und R ein zweiwertiges organisches Brückenglied, enthaltend mindestens zwei Kohlenstoffatome in der Brücke, die die beiden Phosphoratome verbindet, enthält.
6. Ein Verfahren, wie in irgendeinem oder mehreren der Ansprüche 1 bis 5 beansprucht, dadurch gekennzeichnet, daß sie unter b) erwähnte Polymere enthalten, ausgewählt aus Methacrylsäure-n-dodecylester/Methacrylsäure-n-octadecylester/2-Vinylpyridin-Terpolymeren, Acrylsäure-n-octadecylester/Acrylsäure-n-eicosylester/Acrylsäure-n-docosylester-Terpolymeren, Polymeren von 4-Vinylpyridin mit einem Gemisch von Acrylsäure-n-alkyl-estern mit 18 bis 22 Kohlenstoffatomen in den Alkylgruppen, Polymeren von Gemischen von Acrylsäure-n-alkylestern mit 12 bis 15 Kohlenstoffatomen in den Alkylgruppen, und Polymeren von Acrylsäure-methylester mit einem Gemisch von Acrylsäure-n-alkylestern mit 12 bis 15 Kohlenstoffatomen in den Alkylgruppen.
7. Ein Verfahren, wie in irgendeinem oder mehreren der Ansprüche 1 bis 6 beansprucht, dadurch gekennzeichnet, daß sie unter c) erwähnte Polymere enthalten, ausgewählt aus Copolymeren von Ethen mit Vinylpropionat oder -acetat.
8. Ein Verfahren, wie in irgendeinem oder mehreren der Ansprüche 1 bis 7 beansprucht, dadurch gekennzeichnet, daß sie nur eines der unter a) genannten Polymere und nur eines der unter b) und c) genannten Polymere enthalten.



9. Ein Verfahren, wie in irgendeinem oder mehreren der Ansprüche 1 bis 8 beansprucht, dadurch gekennzeichnet, daß sie 0,1 bis 10.000 mg Polymergemisch pro kg Kohlenwasserstofföl enthalten.
10. Ein Verfahren, wie in irgendeinem oder mehreren der Ansprüche 1 bis 9 beansprucht, dadurch gekennzeichnet, daß das verwendete Polymergemisch 1 bis 90 Gew% der unter a) genannten Polymere enthält.

Revendications

Revendications pour les Etats contractants suivants : BE, DE, FR, GB, IT, NL

1. Compositions d'huile hydrocarbonurée, caractérisées en ce qu'elles contiennent une huile hydrocarbonurée paraffinique et, en tant qu'additifs:
 - a) un ou plusieurs polymères linéaires de monoxyde de carbone avec une ou plusieurs oléfines consistant au moins en partie en α -oléfines ayant au moins 10 atomes de carbone par molécule (α -oléfines en C_{10+}), polymères dans lesquels les unités provenant d'une part du monoxyde de carbone et les unités provenant d'autre part des oléfines apparaissent de façon sensiblement alternée, et de plus un ou plusieurs polymères choisis parmi:
 - b) des polymères de un ou plusieurs composés oléfiniquement insaturés consistant au moins en partie en alkyl acrylates ou en alkyl méthacrylates ayant au moins 8 atomes de carbone dans le groupe alkyle (alkyl esters en C_8+), et
 - c) des polymères d'éthène avec un ou plusieurs esters vinyliques d'acides monocarboxyliques aliphatiques saturés.
2. Compositions d'huile hydrocarbonurée telles que revendiquées dans la revendication 1, caractérisées en ce que les additifs possèdent un poids moléculaire moyen pondéré ($\bar{M}_w$) compris entre 10^3 et 10^6 .
3. Compositions d'huile hydrocarbonurée telles que revendiquées dans la revendication 1 ou 2, caractérisées en ce que aussi bien les α -oléfines en C_{10+} que les groupes alkyles présents dans les alkyl esters en C_8+ , s'ils sont présents, contiennent moins de 40 atomes de carbone.
4. Compositions d'huile hydrocarbonurée telles que revendiquées dans une ou plusieurs revendications quelconques 1 à 3, caractérisées en ce qu'on utilise exclusivement des α -oléfines en C_{10+} en tant qu'oléfines dans la préparation des polymères mentionnés en a).
5. Compositions d'huile hydrocarbonurée telles que revendiquées dans une ou plusieurs revendications quelconques 1 à 4, caractérisées en ce qu'elles contiennent des polymères mentionnés en a) à base de monoxyde de carbone avec une ou plusieurs α -oléfines en C_{10+} , lesquels polymères possèdent une valeur de $\bar{M}_w$ supérieure à 10^4 et lesquels polymères pouvant être obtenus en mettant en contact les monomères, à température élevée et sous pression élevée et en présence d'un diluant constitué à plus de 90% en volume d'un liquide aprotique, avec une composition de catalyseur contenant un métal du groupe VIII et un ligand bidenté phosphoré ayant la formule générale $(R^1R^2P)_2R$, où R^1 et R^2 représentent des groupes hydrocarbyles aliphatiques substitués optionnellement polaires, identiques ou différents, et R un groupe organique bivalent de pontage contenant au moins deux atomes de carbone dans le pont reliant les deux atomes de phosphore.
6. Compositions d'huile hydrocarbonurée telles que revendiquées dans une ou plusieurs revendications quelconques 1 à 5, caractérisées en ce qu'elles contiennent des polymères mentionnés en b) choisis parmi des terpolymères n-dodécyl méthacrylate/n-octadécyl méthacrylate/2-vinyl pyridine, des terpolymères n-octadécyl acrylate/n-eicosyl acrylate/n-docosyl acrylate, des polymères de 4-vinyl pyridine avec un mélange de n-alkyl acrylates ayant de 18 à 22 atomes de carbone dans les groupes alkyles, des polymères de mélanges de n-alkyl acrylates ayant de 12 à 15 atomes de carbone dans les groupes alkyles, et des polymères de méthylacrylate avec un mélange de n-alkyl acrylates ayant de 12 à 15 atomes de carbone dans les groupes alkyles.
7. Compositions d'huile hydrocarbonurée telles que revendiquées dans une ou plusieurs revendications quelconques 1 à 6, caractérisées en ce qu'elles contiennent des polymères mentionnés en c) choisis parmi des copolymères d'éthène avec du propionate ou de l'acétate de vinyle.



8. Compositions d'huile hydrocarburée telles que revendiquées dans une ou plusieurs revendications quelconques 1 à 7, caractérisées en ce qu'elles contiennent seulement un des polymères mentionnés en a) et seulement un des polymères mentionnés en b) et c).
9. Compositions d'huile hydrocarburée telles que revendiquées dans une ou plusieurs revendications quelconques 1 à 8, caractérisées en ce qu'elles contiennent de 0,1 à 10 000 mg de mélange polymère par kg d'huile hydrocarburée.
10. Compositions d'huile hydrocarburée telles que revendiquées dans une ou plusieurs revendications quelconques 1 à 9, caractérisées en ce que le mélange polymère utilisé contient de 1 à 90% en poids des polymères mentionnés en a).

Revendications pour l'Etat contractant suivant : ES

1. Procédé pour préparer des compositions d'huile hydrocarburée, caractérisé en ce qu'on mélange une huile hydrocarburée paraffinique avec les additifs suivants:
- a) un ou plusieurs polymères linéaires de monoxyde de carbone avec une ou plusieurs oléfines consistant au moins en partie de α -oléfines ayant au moins 10 atomes de carbone par molécule (α -oléfines en C_{10+}), polymères dans lesquels les unités provenant d'une part du monoxyde de carbone et les unités provenant d'autre part des oléfines apparaissent de façon sensiblement alternée, et de plus un ou plusieurs polymères choisis parmi:
 - b) des polymères de un ou plusieurs composés oléfiniquement insaturés consistant au moins en partie en alkyl acrylates ou en alkyl méthacrylates ayant au moins 8 atomes de carbone dans les groupes alkyles (alkyl esters en C_{8+}), et
 - c) des polymères d'éthène avec un ou plusieurs esters vinyliques d'acides monocarboxyliques aliphatiques.
2. Procédé tel que revendiqué dans la revendication 1, caractérisé en ce que les additifs possèdent un poids moléculaire moyen pondéré ($\overline{M}_w$) compris entre 10^3 et 10^6 .
3. Procédé tel que revendiqué dans la revendication 1 ou 2, caractérisé en ce que aussi bien les α -oléfines en C_{10+} que les groupes alkyles présents dans les alkyl esters en C_{8+} , s'ils sont présents, contiennent moins de 40 atomes de carbone.
4. Procédé tel que revendiqué dans une ou plusieurs revendications quelconques 1 à 3, caractérisé en ce qu'on utilise exclusivement des α -oléfines en C_{10+} comme oléfines dans la préparation des polymères mentionnés en a).
5. Procédé tel que revendiqué dans une ou plusieurs revendications quelconques 1 à 4, caractérisé en ce que les compositions contiennent des polymères mentionnés en a) à base de monoxyde de carbone avec une ou plusieurs α -oléfines en C_{10+} , lesquels polymères possèdent une valeur de $\overline{M}_w$ supérieure à 10^4 et lesquels polymères pouvant être obtenus en mettant en contact les monomères à température élevée et sous pression élevée en présence d'un diluant constitué à plus de 90% en volume par un liquide aprotique, avec une composition de catalyseur contenant un métal du groupe VIII et un ligand bidenté phosphoré ayant la formule générale $(R^1R^2P)_2R$, où R^1 et R^2 représentent des groupes hydrocarbyles aliphatiques substitués optionnellement polaires, identiques ou différents, et R un groupe organique bivalent de pontage contenant au moins deux atomes de carbone dans le pont reliant les deux atomes de phosphore.
6. Procédé tel que revendiqué dans une ou plusieurs revendications quelconques 1 à 5, caractérisé en ce qu'elles contiennent des polymères mentionnés en b) choisis parmi des terpolymères n-dodécyl méthacrylate/n-octadécyl méthacrylate/2-vinyl pyridine, des terpolymères n-octadécyl acrylate/n-eicosyl acrylate/n-docosyl acrylate, des polymères de 4-vinyl pyridine avec un mélange de n-alkyl acrylates ayant de 18 à 22 atomes de carbone dans les groupes alkyles, des polymères de mélanges de n-alkyl acrylates ayant de 12 à 15 atomes de carbone dans les groupes alkyles, et des polymères de méthylacrylate avec un mélange de n-alkyl acrylates ayant de 12 à 15 atomes de carbone dans les groupes alkyles.
7. Procédé tel que revendiqué dans une ou plusieurs revendications quelconques 1 à 6, caractérisé en ce qu'elles contiennent des polymères mentionnés en c) choisis parmi des copolymères d'éthène avec du propionate ou de l'acétate de vinyle.



8. Procédé tel que revendiqué dans une ou plusieurs revendications quelconques 1 à 7, caractérisé en ce qu'elles contiennent seulement un des polymères mentionnés en a) et seulement un des polymères mentionnés en b) et c).

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9. Procédé tel que revendiqué dans une ou plusieurs revendications quelconques 1 à 8, caractérisé en ce qu'elles contiennent de 0,1 à 10 000 mg de mélange polymère par kg d'huile hydrocarbonnée.

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10. Procédé tel que revendiqué dans une ou plusieurs revendications quelconques 1 à 9, caractérisé en ce que le mélange polymère utilisé contient de 1 à 90% en poids des polymères mentionnés en a).

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