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(54) Middle distillate compositions with improved low temperature flow properties

Zwischendestillatzubereitungen mit verbessertem Fliessverhalten bei niedriger Temperatur

Compositions distillées intermédiaires avec propriété d'écoulement à basse température améloirée

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EP-A- 0 061 894	**DE-A- 2 102 469**
DE-A- 2 206 719	**DE-C- 2 102 469**
GB-A- 1 593 672	**US-A- 3 048 479**
US-A- 3 961 916	

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Description

Description

Mineral oils containing paraffin wax have the characteristic of becoming less fluid as the temperature of the oil decreases. This loss of fluidity is due to the crystallization of the wax into plate-like crystals which eventually form a spongy mass entrapping the oil therein.

It has long been known that various compositions act as wax crystal modifiers when blended with waxy mineral oils. These compositions modify the size and shape of wax crystals and reduce the adhesive forces between the wax and oil in such a manner as to permit the oil to remain fluid at a lower temperature.

Various pour point depressants have been described in the literature and several of these are in commercial use. For example, U.S. Pat. No. 3,048,479 teaches the use of copolymers of ethylene and C_3-C_5 vinyl esters, e.g. vinyl acetate, as pour depressants for fuels, specifically heating oils, diesel and jet fuels. Hydrocarbon polymeric pour depressants based on ethylene and higher alpha-olefins, e.g. propylene, are also known. U.S. Patent 3.961,916 teaches the use of a mixture of copolymers. one of which is a wax crystal nucleator and the other a growth arrestor to control the size of the wax crystals.

Similarly United Kingdom Patent 1253152 suggests that the size of the wax crystals may be controlled by using a copolymer having a lower degree of side chain branching.

With the increasing diversity in distillate fuels. types of fuel have emerged which cannot be treated by the existing additives or which require an uneconomically high level of additive. One particular group of fuels that present such problems are those which have a relatively narrow boiling range. Fuels are frequently characterised by their Initial Boiling Point. Final Boiling Point and the interim temperatures at which certain volume percentages of the initial fuel have distilled. Fuels whose 20% to 90% distillation point differ within the range from 70 to 100°C (ASTM 086) and 90% boiling temperature is generally from 10 to 30°C especially 10 to 25°C of the final boiling point have been found particularly difficult to treat sometimes being virtually unaffected by additives or otherwise requiring very high levels of additive. All distillations referred to herein are according to ASTM D86.

Furthermore with the increase in the cost of crude oil it has also become important for a refiner to increase his producticn of distillate fuels and to optimise his operations using what is known as sharp fractionation again resulting in distillate fuels that are difficult to treat with conventional additives or that require a treat level that is unacceptably high for the economic standpoint. Typical sharply fractionated fuels have a 90% to final boiling point of 10 to 20°C usually with a 20 to 90% boiling range of 90 to 110°C. Both types of fuel have final boiling points above 350°C generally a final boiling point in the range 350°C to 375°C especially 350°C to 370°C.

The copolymers of ethylene and vinyl acetate which have found widespread use for improving the flow of the previously widely available distillate fuels generally contained up to 30 wt % vinyl acetate where the additive was used to control the size of wax crystals forming in the fuel or they contained around 36 wt % or more vinyl acetate where their prime function was to lower the pour point of the distillate fuel. We have not found either of these types of additive to be effective in the treatment of the narrow boiling and/or sharply fractionated fuels described above.

EP-A-61 894 describes inter alia, the improvement of the flow properties of a distillate fuel whose 20% and 90% distillation points differ by 106°C and whose 90% boiling point temperature is 31°C below its final boiling temperature of 375°C, said fuel being described as "Fuel 3" on page 14 thereof.

The document describes providing the improvement by adding "Polymer 15" to the fuel, which polymer being a mixture of about 75 wt % of a wax growth arrestor consisting of a copolymer of ethylene and about 38 wt % of vinyl acetate and having a number average molecular weight of about 1800 and about 25 wt % of a wax crystal nucleator consisting of a copolymer of ethylene and about 16 wt % of vinyl acetate and having a number average molecular weight of about 3000.

Polymer 15 is described in the above-mentioned US-A-3 961 916, the arrestor being referred to as Copolymer B and the nucleator as Copolymer H. and is considered to be one of the most preferred additives disclosed in that document.

We have found that the above-mentioned known additives are not sufficiently effective in improving the flow properties of the narrower boiling distillate fuel oils referred to above. We have, however, found that specific mixtures of copolymers of ethylene and vinyl esters of carboxylic acids are particularly effective in the treatment of these fuels.

The present invention therefore provides the use as an additive for improving the flow properties of a distillate petroleum fuel oil whose 20% and 90% distillation points differ within the range of from 70 to 100°C and whose 90% boiling-temperature is from 10 to 30°C of the final boiling point, and whose final boiling point is above 350°C of an additive comprising

a mixture of two copolymers of ethylene and a vinyl ester of a carboxylic acid containing 1 to 4 carbon atoms, one of which copolymers is a growth arrester while the other one is a wax crystal nucleator, said mixture containing at least 10 parts by weight of said growth arrester for each part by weight of said wax crystal nucleator and an average of 32 to 35 wt. % of the vinyl ester and having a number average molecular weight of 1000 to 6000.

The present invention further provides a distillate fuel whose 20% and 90% distillation points differ by 70°C to 100°C, whose 90% boiling-temperature is from 10 to 30°C of the final boiling point, and whose final boiling point is above 350°C containing from 50 to 500 ppm of a mixture of two copolymers of ethylene and a vinyl ester of a carboxylic acid containing 1 to 4 carbon atoms, one of which copolymers is a growth arrester while the other one is a wax crystal nucleator, said mixture containing at least 10 parts by weight of said growth arrester for each part by weight of said wax crystal nucleator and an average of 32 to 35 wt. % of the vinyl ester and having a number average molecular weight of 1000 to 6000.

The additive is a mixture of two copolymers which may or may not contain the same vinyl ester. Such an additive mixture is particularly useful for treating the above type of fuel since it allows added flexibility.

In a preferred embodiment of the present invention therefore the additive comprises from 10 to 15 parts by weight of a synthetic polymeric material having the property of a wax growth arrestor in said fuel for each part of a synthetic polymeric material having the properties of a wax growth stimulator, said wax growth arrestor and growth stimulator being copolymers of ethylene and vinyl esters of carboxylic acids containing from 1 to 4 carbon atoms the average ester content of said copolymers being in the range 32 to 35 wt. % and the number average molecular weight thereof being in the range 1000 to 6000.

In a further embodiment of the present invention the fuel contains from 50 to 500 ppm (parts per million) of the additive mixture of the above-mentioned preferred embodiment.

The fuels used in the present invention may have final boiling points between 350°C and 375°C more usually between 350°C and 370°C.

The wax growth stimulator or nucleator is a synthetic polymeric material which is soluble in the distillate at temperatures substantially above the saturation temperature but on cooling of the distillate progressively separates out in the form of small particles as the temperature of the distillate approaches the saturation point, e.g. is cooled from a point slightly above (e.g. 10°C above; preferably about 5°C above) said saturation temperature. The term "saturation temperature" is defined as the lowest temperature at which solute, e.g. wax, cannot be crystallized out of the solution even if known crystallization inducement methods are used. Whilst not known certainly it is believed that as cooling continues, additional nucleator particles separate out in a more or less continuous manner. These additional particles act as nucleators for continued wax crystallization, which in effect, would prevent substantial supercooling of the distillate. The advantages of having fresh nucleator particles formed continuously is that the supersaturation of the distillate with n-paraffins is kept at the lowest possible level thus facilitating a molecule of growth arrestor to build itself into the growth center of growing crystals and by so doing to stop the further growth.

The inhibitory effect of a growth arrester is believed to result from the presence of bulky groups in its molecule. Additional nucleator should separate out to replace the deactivated growth centers. The wax growth arrester is more soluble in said distillate than said nucleator and it acts as a growth arrester as the wax crystal forms.

The nucleator should not be insoluble in the distillate at elevated temperatures nor should it start to separate out at a temperature substantially above that at which wax crystallization can occur. If nucleators separate out at a temperature substantially above the temperature at which crystallization can occur, then they tend to settle at the bottom of the vessel holding the distillate, instead of remaining dispersed within the distillate. This factor is especially important when the distillate is subjected to repeated warming and cooling as during the warm and cool parts of a day since it does not result in adequate redispersion of the nucleant particles in the distillate. The synthetic polymeric materials used as wax growth stimulators and wax growth arresters may contain the same or different vinyl esters.

For the purpose of this invention, wax crystal growth stimulators, wax nucleators and nucleants for wax are all considered equivalent terms and are used interchangeably.

Wax growth arresters (hereinafter sometimes referred to as wax arresters), generally include in their molecular structure wax-like polymethylene segments which are capable of building themselves into the lattice of the wax crystals at the point of lattice dislocation. and also contain bulky groups which prevent incorporation of further molecules of n-paraffins at the point of lattice dislocation and by so doing stop further growth of crystal.

A good synthetic polymeric wax nucleator, can be chosen by visually comparing a transparent container containing a 0.1 to 3.0 wt.% solution of the potential nucleator in a distillate to an identical container with the same distillate having no additive, as the temperature of the two materials is lowered. The onset of the wax crystallization from the distillate containing a polymeric material which has nucleator characteristics will occur at a higher temperature than that at which the crystallization will start in the absence of said nucleator. Similarly, a wax arrester usually is characterized by the ability to delay onset of crystallization.

The synthetic polymers used as nucleating agents and as wax growth arresters are copolymers of ethylene and vinyl ester and may contain the same or different ester monomer.

The vinyl ester content and molecular weight are the average over the mixture.

Typical vinyl esters include vinyl acetate, vinyl propionate, and vinyl butyrate.

The flow improvers when incorporated into the distillate fuels preferably are effective in:

1. maintaining these fuels fluid at the operating temperatures,
2. arresting the growth of separating wax crystals when the oils are submitted to slow cooling, i.e. 0.2°F to 2°F./hr, which are typical of the rates encountered when "oil in bulk" is exposed to atmospheric cooling.
3. arresting the growth of separating wax crystals when the oils are submitted to fast cooling, i.e. 10° F. to 100°F./hr/. which are typical of the rates encountered when relatively warm oil enters transfer lines and is there suddenly exposed to low temperatures.

All three above-quoted criteria are desired in order to assure that a fuel is pumpable and filterable under the conditions of its distribution and it use.

As mentioned the molecular weight is the average of the two polymers and in general, the preferred number average molecular weight (VPO) for the nucleator will be within the range of 500-6000, more preferably 1200-6000. Specifically, for example, a relatively low molecular weight ethylenevinyl ester copolymer with a relatively high vinyl ester content has been found to act as a wax growth arrester. On the other hand, a relatively high molecular weight copolymer of ethylene with a vinyl ester which copolymer has a relatively low content of vinyl ester acts as a nucleating agent. Even more specifically, blends containing ethylene/vinyl acetate copolymers of number average molecular weights from 1200-6000 (VPO) with vinyl acetate contents of about 32-50 wt.% (e.g. about 11 to 25 mole % ester) as the wax arresters and ethylene/vinyl acetate copolymers of about 500-10,000 (VPO) number average molecular weight with vinyl acetate comonomer proportions by weight of 1-30 wt.% (e.g. about 0.3 to 12 mole % ester) as the wax growth stimulators have been found to be highly effective. Where the nucleant is an ethylene/vinyl acetate copolymer its number average molecular weight is preferably at least 500, preferably 1000, higher and/or the ester content at least 5% lower than the corresponding property of the wax growth arrester.

All molecular weights specified herein are "number average molecular weights", which are molecular weights as measured by Vapor Phase Osmometry (VPO), e.g. using Mechrolab Vapor Phase Osmometer 301A. The vinyl acetate contents are determined by saponification. Thus, relative to the growth arrester, the nucleator can comprise an ethylene-vinyl acetate copolymer of a higher molecular weight if the vinyl acetate content of both polymeric materials is about equal. The two synthetic polymers may be made separately or they can be made consecutively in one batch by varying the reaction conditions. Thus, the reaction conditions can be selected so that the initial polymerization reaction produces a polymer having primarily nucleator characteristics and the reaction conditions can be changed to produce a polymer having primarily wax growth arresting properties or vice versa. In this manner, a mixture of polymers can be produced having both types of functions.

In the specific embodiment of the invention which employs two different copolymers of ethylene and vinyl acetate the relationships between the concentration of vinyl acetate in the copolymer and molecular weight of the copolymers are important since they are factors which determine the role of the particular copolymer in the fuel. That is, they determine, given the other polymer properties are similar whether or not the copolymer as a whole will be performing within the composition as a wax arrester or as a wax nucleating agent. Thus, very generally as a rule of thumb, the nucleating agents should have relatively long polymethylene segments, and so as these synthetic polymers approach low molecular weight ranges, the proportion of vinyl acetate should also decrease. On the other hand, as the molecular weight increases, the proportion of vinyl acetate should also increase. Thus, the specific wax nucleating agents will comprise a copolymer of ethylene and a relatively low proportion of vinyl acetate with a relatively high molecular weight.

The wax arrester on the other hand will, in general, be a relatively low molecular weight copolymer of a relatively high vinyl acetate content since the function of wax arresting depends more on the presence of bulky groups, such as ester groups, attached to the backbone of the molecule of the copolymer.

Although the separate copolymers may be blended directly in the fuel, it will normally be found desirable to prepare a concentrate. This may be effected by first associating each with a separate solvent, but most preferably by dissolving each in a common solvent. Thus, both the preferred relatively lower molecular weight high vinyl acetate (second) copolymer and the preferred first, the relatively high molecular weight low vinyl acetate copolymer, may be dissolved in a kerosene or heavy aromatic naphtha. Preferred concentrates will contain 5-60%, preferably 10-50% total copolymer with the balance being a hydrocarbon oil solvent.

The arrester copolymers may be prepared by known procedures employing free-radical initiators, preferably organic peroxide compounds. Suitable procedures are high temperature and high pressure processes or the solution processes described in U.S. specifications, such as U.S. Pat. Nos. 3,048,479 or 3,093,623, and in United Kingdom Patent Specification 1263152.

In one aspect the fuels to which the present invention relates are difficult to treat with conventional additives because of the relatively narrow boiling range of the 20% to 90% degree fraction of the fuel, the 90% fraction boiling from 70 to 100°C above that of the 20% fraction and because of the relatively small gap between the 90% boiling point and the final boiling point of from 10 to 30°C, such as to 25°C and even, in some instances to 20°C.

Suitably there is present a total of 0.001% to 0.5% by weight of additive, based on the weight of fuel; preferably 0.005 to 0.1%, most preferably 0.01 to 0.04%, all percents being weight percents. The polymeric materials may be used in ratios of 10 to 15 parts by weight of growth arrester, per part of the nucleator.

The present invention is illustrated by the following Examples in which an additive of the present invention (additive A) was an oil solution containing 63 wt.% of a combination of polymers comprising 13 parts by weight of a wax crystal growth arrestor comprising an ethylene vinyl acetate copolymer of number average molecular weight 2500 and vinyl acetate content of 36 wt.% and 1 part by weight of wax crystal simulator of number average molecular weight 3500 and a vinyl acetate content of about 13 wt.% Additive B was an oil solution containing 45 wt.% of an additive combination of 3 parts by weight of the abovementioned wax crystal growth arrestor and 1 part of the wax crystal simulator according to United States Patent 3961916. Additive C is 50 wt.% solution in oil of an ethylene acetate copolymer of number average molecular weight 2000 and vinyl acetate content 30 wt.%.

The fuels used in the Examples were as follows:

	Initial B.P. °C	20% B.P. °C	90% B.P. °C	Final B.P. °C
Fuel 1	200	248	334	360
Fuel 2	228	280	351	374
Fuel 3	220	266	346	367
Fuel 4	224	268	341	359
Fuel 5	221	259	331	361
Fuel 6	244	264	336	360
Fuel 7	163	240	344	362
Fuel 8	160	234	344	358
Fuel 9	200	257	336	362
Fuel 10	213	264	338	360

In the Examples the Wax Crystal Size at Fast Cooling Rates is measured by the Cold Filter Plugging Point test (CFPP). This test is carried out by the procedure described in "Journal of the Institute of Petroleum", Volume 52, No. 510, June 1966, pp. 173-185. In brief, the CFPP test is carried out with a 45 ml sample of the oil to be tested. The oil placed in the ASTM cloud point jar is cooled in a bath maintained at about -30°F. Every two degrees drop in temperature, starting from 4°F. above the cloud point, the oil is forced at a suction of 8 inches of water through a filter element provided with a 350 mesh screen into a pipette to a mark indicating a volume of 20 ml., at which time the oil is allowed to return by gravity flow to the cooling chamber. The test is repeated with each 2°C drop in oil temperature until the oil fails to fill the pipette in a period of 60 seconds to the aforesaid mark. The results of the test are reported as the Cold Filter Plugging Point which is the highest temperature at which the oil fails to fill the pipette.

The amounts of Additive A, Additive B and Additive C required to achieve a 6°C, 8°C and 10°C reduction in the temperature at which these fuels would pass the CFPP test were determined to be as follows:

Fuel	6°C			8°C			10°C		
	Additive	Additive	Additive	Reduction			Reduction		
	A	B*	C*	A	B*	C*	A	B*	C*
1	410	760	700	560	1050	not possible	700	1360	not possible
2	130	400	440	190	540	620	250	650	not possible
3	420	700	-	500	850	-	520	820	-
4	700	not possible		800	not possible		900	not possible	
5	780	not possible		840	not possible		not possible	not possible	
6	250	-	1000	330	-	1000	410	-	1000
7*	570	-	900	620	-	950	710	-	1100
8*	500	-	900	600	-	1000	700	-	1100
9	260	-	not possible	370	-	not possible	450	-	not possible

* Comparative

(continued)

Fuel	6°C			8°C			10°C		
	Additive	Additive	Additive	Reduction			Reduction		
	A	B*	C*	A	B*	C*	A	B*	C*
10	530	-	not possible	570	-	not possible	600	-	not possible

* Comparative

In a further series of experiments the amount of additive required to give a reduction of 6, 8 and 10°C in the CFPP value of various fuels was tested and compared with the amounts required for additives outside of the present invention.

The fuels used were:

Fuel No.	IBP	20%	90%	FBP
11	107	244	351	381
12	113	242	355	375
13	200	248	334	360
14	220	263	350	373
15	220	266	346	367
16	221	259	331	361
17	222	260	328	354
18	228	280	351	374

and the additives used were A, B and C as used in the previous example together with Additives D to H as follows:

Additives	Wt. % Vinyl Acetate	Molecular Weight
D	34.8	2650
E	27.1	3170
F	28.9	2590
G	28.2	2940
H	29.9	2300

The results are given in the following table.

Fuel No.	CFPP Depression °C	Amount of Additive Required p.p.m. A	B*	C*	D*	E*	F*	G*	H*
11 *	6	45	90	35	50	100	26	40	80
	8	70	110	40	75	220	35	75	105
	10	90	140	70	90	>500	85	120	135
12 *	6	100	250	195	155	>500	130	145	210
	8	160	320	200	195	>500	200	210	270
	10	180	380	350	270	>500	275	300	350
13	6	500	750	550	650	>2000	650	200	1050
	8	650	800	1000	1000	>2000	800	300	1020
	10	730	900	1080	1090	>2000	1000	500	1300
14	6	280	340	300	300	>800	320	440	420
	8	350	380	400	350	>800	420	460	450
	10	370	440	470	380	>800	500	480	480
15	6	370	460	600	500	>1500	550	600	650
	8	450	560	710	600	>1500	750	650	700
	10	470	760	860	1060	>1500	800	750	800
16	6	580	550	750	500	1850	600	1100	1000
	8	800	750	110	680	>2000	700	1350	1150
	10	880	880	1330	870	>2000	850	1400	1200
17 *	6	600	850	1000	580	>2000	1350	1500	1600
	8	790	980	1300	750	>2000	1850	2000	2000
	10	890	1160	1500	920	>2000	2200	>2000	>2000
18	6	140	400	370	140	>750	700	>750	>750
	8	160	470	500	160	>750	>750	>750	>750
	10	180	540	650	175	>750	>750	>750	>750
Average	6	327	461	474	359	High	541	>596	>720
	8	429	546	656	476	High	>688	>718	>828
	10	474	650	789	607	High	>848	>788	>874

* Comparative

Claims

1. The use as an additive for improving the flow properties of a distillate petroleum fuel oil whose 20% and 90% distillation points differ within the range of from 70 to 100°C and whose 90% boiling-temperature is from 10 to 30°C of the final boiling point, and whose final boiling point is above 350°C of an additive comprising

   a mixture of two copolymers of ethylene and a vinyl ester of a carboxylic acid containing 1 to 4 carbon atoms, one of which copolymers is a growth arrester while the other one is a wax crystal nucleator, said mixture containing at least 10 parts by weight of said growth arrester for each part by weight of said wax crystal nucleator and an average of 32 to 35 wt. % of the vinyl ester and having a number average molecular weight of 1000 to 6000.

2. The use according to claim 1 wherein the vinyl ester is vinyl acetate.

3. A distillate fuel whose 20% and 90% distillation points differ by 70°C to 100°C, whose 90% boiling-temperature is from 10 to 30°C of the final boiling point, and whose final boiling point is above 350°C containing from 50 to 500 ppm of

a mixture of two copolymers of ethylene and a vinyl ester of a carboxylic acid containing 1 to 4 carbon atoms, one of which copolymers is a growth arrester while the other one is a wax crystal nucleator, said mixture containing at least 10 parts by weight of said growth arrester for each part by weight of said wax crystal nucleator and an average of 32 to 35 wt. % of the vinyl ester and having a number average molecular weight of 1000 to 6000.

4. A distillate fuel according to claim 3 wherein the vinyl ester is vinyl acetate.

Patentansprüche

1. Verwendug als Zusatz zur Verbesserung der Fließeigenschaften eines Destillaterdölbrennstofföls, dessen 20% und 90% Destillationspunkte sich im Bereich von 70°C bis 100°C unterscheiden, dessen 90% Siedetemperatur um 10 bis 30° C unter dem Endsiedepunkt liegt und dessen Endsiedepunkt über 350° C liegt, wobei der Zusatz

eine Mischung zweir Copolymere aus Ethylen und einem Vinylester einer Carbonsäure, die 1 bis 4 Kohlienstoffatome enthält, von denen das eine Copolymer ein Wachstumshemmer ist, während das andere ein Paraffinkristallkeimbildner ist, wobei die Mischung mindestens 10 Gewichtsteile des Wachstumshemmers auf jedes Teil des Paraffinkristallkeimbildners und durchschnittlich 32 bis 35 Gew.% des Vinylesters enthält und ein durchschnittliches Molekulargewicht (Zahlenmittel) von 1000 bis 6000 aufweist, umfaßt.

2. Verwendung nach Anspruch 1, wobei der Vinylester Vinylacetat ist.

3. Destillatbrennstoff, dessen 20% und 90% Destillationspunkte sich um 70°C bis 100°C unterscheiden, dessen 90% Siedetemperatur 10°C bis 30°C unter dem Endsiedepunkt liegt und dessen Endsiedepunkt über 350°C liegt, das 50 bis 500 ppm

einer Mischung zweier Copolymere aus Ethylen und einem Vinylester einer Carbonsäure, die 1 bis 4 Kohlenstoffatome enthält, von denen das eine Copolymer ein Wachstumshemmer ist, während das andere ein Paraffinkristallkeimbildner ist, wobei die Mischung mindestens 10 Gewichtsteile des Wachstumshemmers auf jedes Teil des Paraffinkristallkeimbildners und durchschnittlich 32 bis 35 Gew.% des Vinylesters enthält und ein durchschnittliches Molekulargewicht (Zahlenmittel) von 1000 bis 6000 aufweist. enthält

4. Destillatbrennstoff nach Anspruch 3, bei dem der Vinylester Vinylacetat ist.

Revendications

1. Utilisation comme additif pour améliorer les propriétés d'écoulement d'une huile combustible de distillation de pétrole dont les points d'ébullition à 20 % et à 90 % différent des valeurs comprises dans la plage de 70 à 100° C et dont la température d'ébullition à 90 % diffère de 10 à 30° C du point d'ébullition final, et dont le point d'ébullition final dépasse 350° C, d'un additif comprenant :

un mélange de deux copolymères méthylène et d'un ester de vinyle d'un acide carboxylique contenant 1 à 4 atomes de carbone, l'un des copolymères étant un inhibiteur de croissance tandis que l'autre est un agent de nucléation des cristaux de cire, ledit mélange contenant au moins 10 parties en poids dudit inhibiteur de croissance pour chaque partie en poids dudit agent de nucléation ces cristaux de cire et une moyenne de 32 à 35 % en poids de l'ester de vinyle et ayant une moyenne numérique au poids moléculaire de 1000 à 6000.

2. Utilisation suivant la revendication 1, dans laquelle l'ester de vinyle est l'acétate de vinyle.

3. Combustible distillé dont les points de distillation à 20 % et à 90 % diffèrent de 70 à 100°C, dont la température d'ébullition à 90 % s'écarte de 10 à 30°C du point d'ébullition final, et dont le point d'ébullition final est au-dessus de 350° C, contenant 50 à 500 ppm

un mélange de deux copolymères d'éthylène et d'un ester de vinyle d'un acide carboxylique contenant 1 à 4 atomes de carbone, l'un des copolymères étant un inhibiteur de croissance tandis que l'autre est un agent de nucléation des cristaux de cire, ledit mélange contenant au moins 10 parties en poids dudit inhibiteur de croissance pour chaque partie en poids dudit agent de nucléation des cristaux de cire et une moyenne de 32 à 35 % en poids de l'ester de vinyle et ayant une moyenne numérique du poids moléculaire de 1000 à 6000.

4. Combustible distillé suivant la revendication 3, dans lequel l'ester de vinyle est l'acétate de vinyle.