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(54) STABILISED COMPOSITIONS COMPRISING OLEFINS

(57) The present invention is a composition stabilized against premature polymerization comprising
a) a hydrocarbon stream having a diene value of at least 0.5 g I_2/100 g as measured according to UOP 326, a bromine number of at least 5 g Br_2/ 100g as measured according to ASTM D1159, and containing at least 2 wt% of plastic pyrolysis oil which is containing contaminants, wherein said contaminants comprise constituents which are not boiling below 700°C, preferably not below 600°C, such as gums in the form of plastic oligomers and residues of pyrolysis of plastic, optionally metals and optionally solids, the remaining part of said hydrocarbon stream being a diluent,
b) at least one additive capable to reduce gums formation or buildup,
c) optionally at least one additive which is a dispersant agent.

Processed by Luminess, 75001 PARIS (FR)

Description

Field of the invention

[0001] The present invention relates to stabilised compositions comprising hydrocarbon stream resulting from the pyrolysis of plastic wastes. In particular, the present invention pertains to novel compositions for inhibiting polymerization in industrial plant of hydrocarbon streams obtained from pyrolysis of plastic waste, which contain reactive hydrocarbons and potentially oxygenates, thereby preventing fouling in processing equipment and storage tanks.

Background of the invention

[0002] Common industrial methods for recycling hydrocarbons from plastic include pyrolysis of waste plastic that otherwise could have ended in landfill or incinerator, followed by purification including hydrotreatment and contaminant removal using a variety of purification processes such as distillation.

[0003] Pyrolysis transforms plastics, and most of their additives and contaminants, into gaseous chemicals while most of the non-volatile contaminants or additives end up in the solid by-product; chars or ashes. In principle, any kind of plastic waste can be converted, although some pre-sorting of non-organic waste is desired and purification of the output material is necessary as several hetero-elements (i.e. presently referred to as elements different of carbon, hydrogen or oxygen) may be volatilized.

[0004] Plastic waste is a complex and heterogeneous material, due to several factors. First, plastic as material refers to numerous different polymers with different chemical properties that need to be separated from each other prior to recycling. The main polymers found in plastic from municipal solid waste are polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP) and polystyrene (PS). Other polymers essentially include polyurethanes, polyamides (PA), polycarbonates, polyethers and polyesters other than PET. Second, many different additives are introduced during the production phase to adjust or improve the properties of the plastic or to fulfil specific requirements. These include additives such as functional additives (stabilizers, antistatic agents, flame retardants, plasticizers, lubricants, slipping agents, curing agents, foaming agents, biocides, antioxidants etc.), dyes and pigments, fillers (e.g. glass fibers, talcum, carbon fibers, carbon nanotubes), commonly used in plastic packaging as well as additives such as flame retardants, frequently used in plastic for electronics. In addition, several metal compounds are purposely added during plastic production (often as oxides, carbonates, acids, etc.). Beside additives containing hetero elements other than metals are used in making plastics, for instance halogens such as bromine in flame retardants, plasticizers, stabilizers etc.

[0005] Silicone polymers, which are silicon containing organic materials, are often used in plastic formulations. Thanks to their surface characteristics, applications for silicones range from silicone rubbers, used as sealants for joints, to silicone surfactants for cosmetic products while they are increasingly used in the plastics sector, as process enhancing additives (processing aids), and for the modification of polymers.

[0006] On top of these hetero-elements, the used plastic waste can have been contaminated during lifespan by remains of liquids with which they were in contact (beverages, personal-care products, etc.) and of food that can also introduce contamination of the plastic. Last, some plastic waste may be present in the form of partially decomposed waste, such as partly burnt plastic.

[0007] Finally, as plastics are contaminated by oxygenates, pyrolysis plastic oils may also contain oxygenates such as aldehydes or ketones.

[0008] Pyrolysis of plastic waste allows producing naphtha, ethylene, propylene and aromatics but, as previously mentioned, those products are polluted by many hetero elements originating from the waste plastic itself. In particular, significant concentration of silicon and of organic silicon can be found in pyrolysis plastic oils. Although many prior art processes were focused on the removal of chlorine compounds, other impurities in the pyrolysis plastic oil simply forbid the direct use of pyrolysis plastic oil in other processes such as steam cracking. Indeed, steam crackers are very sensitive to the presence of olefins or dienes in the feed and to the presence of silicon or of organic silicon compounds. Moreover, oxygenates present in pyrolysis plastic oil are capable to be converted to peroxides and so enhance polymer and gums formation. In particular, the presence of olefins and oxygenates may result in undesirable polymerisation during storage, transport from the production place to further treatment place as well as during purification and further processing treatments.

[0009] In particular, purification operations are often carried out at elevated temperatures which can increase the rate of undesired polymerization. Polymerization, such as thermal polymerization, during hydrocarbon processing treatments, results not only in product loss, but also in loss of production efficiency caused by the formation of fouling deposits and their deposition on process equipment, particularly on the heat transfer surfaces of the processing equipment. More specifically the processing may include, for example, preheating, hydrogenation, fractionation, extraction, hydrocracking, vapocracking, fluid catalytic cracking, and the like of hydrocarbon streams to remove, concentrate, or have added thereto the unsaturated hydrocarbons prior to storage or use. These deposits decrease the thermal efficiency of the equipment and decrease the separation efficiency of the distillation towers. In addition, operating modifications to reduce the rate of fouling can result in reduced production capacity. The excessive build-up of such deposits can cause plugging in tower plates, transfer tubes, and process lines, which could result in unplanned shutdowns.

[0010] Undesirable polymerization may also cause operational problems such as increase in fluid viscosity, temperature, restricted flow in pipelines, and blocking of filters. In heat requiring operations, such deposition adversely affects heat transfer efficiency.

[0011] The behaviour of compositions produced from pyrolysis of waste plastic is difficult to forecast due to the complexity of such compositions. For example, analysis by gas chromatography of pyrolysis plastic oil only allows identification of 25 to 45wt% of the compounds containing oxygen and azote. Moreover, such undesirable polymerisation is generally monitored by measuring the gum content.

[0012] There is therefore a need for a stabilized composition comprising pyrolysis plastic oil.

Brief summary of the invention

[0013] The present invention is a composition stabilized against premature polymerization comprising:

a) a hydrocarbon stream having a diene value of at least 0.5 g I_2/100 g as measured according to UOP 326, a bromine number of at least 5 g Br_2/ 100g as measured according to ASTM D1159, and containing at least 2 wt% of plastic pyrolysis oil which is containing contaminants, wherein said contaminants comprise constituents which are not boiling below 700°C, preferably not below 600°C, such as gums in the form of plastic oligomers and residues of pyrolysis of plastic, optionally metals and optionally solids, the remaining part of said hydrocarbon stream being a diluent,
b) at least one additive capable to reduce gums formation or buildup,
c) optionally at least one additive which is a dispersant agent.

[0014] In one embodiment, at least one additive capable to reduce gums formation or buildup and at least one dispersant agent are present.

[0015] In one embodiment, the additive capable to reduce gums formation or buildup is an antipolymerant such as a stable free radical or a precursor thereof, such as hydroxylamines. The antipolymerant can be a stable nitroxide free radical and/or a hydroxylamine substituted with at least one alkyl, aryl or alkylaryl group.

[0016] In one embodiment, the additive capable to reduce gums formation or buildup is selected among the unhindered phenols, the hindered phenols, the aminophenols, the phenylenediamines and mixtures thereof.

[0017] In one embodiment, said at least one additive which is a dispersant agent is selected from products of reaction between a phenol substituted with a C9-110 hydrocarbon chain, an aldehyde and an amine or polyamine or ammonia, from alkenyl succinimides or mixtures thereof.

[0018] The present invention also concerns a process for preparing a composition stabilized against premature polymerization, comprising :

(a) providing a hydrocarbon stream having a diene value of at least 0.5 g I_2/100 g as measured according to UOP 326, a bromine number of at least 5 g Br_2/ 100g as measured according to ASTM D1159, and containing at least 2 wt% of plastic pyrolysis oil which is containing contaminants, wherein said contaminants comprise constituents which are not boiling below 700°C, preferably not below 600°C, such as gums in the form of plastic oligomers and residues of pyrolysis of plastic, optionally metals and optionally solids, the remaining part of said hydrocarbon stream being a diluent,
(b) adding to the hydrocarbon stream provided in step (a) at least one additive capable to reduce gums formation or buildup,
(c) optionally adding to the hydrocarbon stream provided in step (a) at least one additive which is a dispersant agent.

[0019] The present invention also concerns a process for the processing of a composition stabilized against premature polymerization, comprising :

(a) providing a composition stabilized against premature polymerization as claimed in the present invention,
(b) optionally submitting the composition provided in step (a) to an evaporation step under operating conditions efficient to obtain a composition containing a reduced amount of additives,
(c) the stabilized composition provided in step (a) or the composition containing a reduced amount of additives provided in step (b) is (i) processed in a steamcracker, (ii) processed in a fluid catalytic cracker, (iii) processed in a catalytic hydrogenation unit, (iv) processed in a hydrocracking unit and/or (v) separated into usable streams for the preparation of fuels such as LPG, naphtha, gas oil, heavy fuel oil and/or for the preparation of lubricants.

[0020] The use of these novel stabilized compositions prevents fouling of equipment and product during handling, processing, purification, and storage.

[0021] In particular, the composition is stabilized against premature polymerization without being contacted with, and/or without any use of, a solid removal material that requires a further separation step. In particular, the present invention does not require the use/presence of solid material suitable for removing oxygen, metals, phosphorous, halogens and/or nitrogen contained in pyrolysis plastic oil, whatever the form of oxygen, metals, phosphorous, halogens and/or nitrogen. Such solid removal materials include silica gel, alumina, promoted alumina, inorganic materials such as clay, pillared clay, apatite, hydroxyapatite, alkaline or alkaline earth metal oxide, calcined alumina, boehmite, bayerite, hydrotalcite, spinel, acid-exchanged clay, molecular sieves (which are alkaline or alkaline earth metal containing alumino-silicate sieves 3A, 4A, 5A or 13X).

Definitions

[0022] The terms "alkane" or "alkanes" as used herein describe acyclic branched or unbranched hydrocarbons having the general formula C_nH_{2n+2}, and therefore consisting entirely of hydrogen atoms and saturated carbon atoms; see e.g. IUPAC. Compendium of Chemical Terminology, 2nd ed. (1997). The term "alkanes" accordingly describes unbranched alkanes ("normal-paraffins" or "n-paraffins" or "n-alkanes" or "paraffins") and branched alkanes ("iso-paraffins" or "iso-alkanes") but excludes naphthenes (cycloalkanes). They are sometimes referred to by the symbol "HC-".

[0023] The terms "olefin", "olefins", "alkene" or "alkenes" as used herein relate to an unsaturated hydrocarbon compound containing at least one carbon-carbon double bond. They are sometimes referred to by the symbol "HC=".

[0024] The terms "alkyne" or "alkynes" as used herein relate to an unsaturated hydrocarbon compound containing at least one carbon-carbon triple bond.

[0025] The term "hydrocarbon" or "hydrocarbons" refers to the alkanes (saturated hydrocarbons), cycloalkanes, aromatics and unsaturated hydrocarbons alone or in combination.

[0026] As used herein, the terms "$C_\#$ alcohols", "$C_\#$ alkenes", or "$C_\#$ hydrocarbons", wherein "$_\#$" is a positive integer, is meant to describe respectively all alcohols, alkenes or hydrocarbons having $_\#$ carbon atoms. Moreover, the term "$C_\#$+ alcohols", "$C_\#$+ alkenes", or "$C_\#$+ hydrocarbons", is meant to describe all alcohol molecules, alkene molecules or hydrocarbons molecules having $_\#$ or more carbon atoms. Accordingly, the expression "C_5+ alcohols" is meant to describe a mixture of alcohols having 5 or more carbon atoms.

[0027] As used herein, the terms "silicon", "metals", "phosphorous", "halogens", "nitrogen" and "oxygen" refer to their respective chemical elements contained in the stream to be purified.

[0028] Weight hourly space velocity (WHSV) is defined as the hourly weight of flow per unit weight of catalyst and liquid hourly space velocity (LHSV) is defined as the hourly volume of flow per unit of volume of catalyst.

[0029] The terms "comprising", and "comprises" as used herein are synonymous with "including", "includes" or "containing", "contains", and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps.

[0030] The recitation of numerical ranges by endpoints includes all integer numbers and, where appropriate, fractions subsumed within that range (e.g. 1 to 5 can include 1, 2, 3, 4 when referring to, for example, a number of elements, and can also include 1.5, 2, 2.75 and 3.80, when referring to, for example, measurements). The recitation of endpoints also includes the recited endpoint values themselves (e.g. from 1.0 to 5.0 includes both 1.0 and 5.0). Any numerical range recited herein is intended to include all sub-ranges subsumed therein.

[0031] The term "conversion" means the mole fraction (i.e., percent) of a reactant converted to a product or products. The term "selectivity" refers to the percent of converted reactant that went to a specified product.

[0032] The terms "wt%", "vol%", or "mol%" refers to a weight, volume, or molar percentage of a component, respectively, based on the total weight, the total volume of material, or total moles, that includes the component. In a non-limiting example, 10 grams of component within 100 grams of the material is 10 wt% of components.

[0033] Unless otherwise specified, "wtppm" or "ppm" each equally refer to "parts per million" and are given based on weight. For instance, "100 ppm" shall mean 100 ppm by weight. Similarly, the term "wtppb" or "ppb" refers to "parts per billion" and are given based on weight.

[0034] The term **"naphtha"** refers to the general definition used in the oil and gas industry. Naphtha refers to a hydrocarbon originating from crude oil distillation having a boiling range from 15 to 250°C as measured by ASTM D2887. Naphtha contains substantially no olefin as the hydrocarbons originates from crude oil. It is generally considered that a naphtha has carbon number between C3 and C11, although the carbon number can reach in some case C15. It is also generally admitted that the density of naphtha ranges from 0.65 to 0.77 g/mL.

[0035] The term **"gas oil"** refers to the general definition used in the oil and gas industry. It refers to a hydrocarbon originating from crude oil distillation having a boiling range from 210 to 360°C as measured by ASTM D86. Gas oil contains substantially no olefin as the hydrocarbons originates from crude oil. It is generally considered that a gas oil has carbon number between C12 and C20, although the carbon number can reach in some case C25. It is also generally admitted that the density of gas oil ranges from 0.82 to 0.86 g/mL, wherein commercial specification limits density to 0.86 g/mL according to ASTM D1298 (ISO 3675, IP 160).

[0036] The term **"LPG"** refers to the general definition used in the oil and gas industry. It refers to a hydrocarbon essentially comprised of C3 (propane) with some C4 isomers; n-butane and isobutene.

[0037] The term **"pyrolysis plastic oil", "plastic pyrolysis oil"** or **"oil resulting from the pyrolysis of plastic"** refers to the liquid products obtained once waste plastic or plastic waste have been thermally pyrolyzed. The pyrolysis process shall be understood as an unselective thermal cracking process. The plastic to be pyrolyzed can be of any type. For instance, the plastic to be pyrolyzed can be polyethylene, polypropylene, polystyrene, polyester, polyamide, polycarbonate, etc. These pyrolysis plastic oils contain paraffins, i-paraffins (iso-paraffins), dienes, alkynes, olefins, naphthenes, and aromatic components. Pyrolysis plastic oil may also contain impurities such as organic chlorides, oxygenated and/or silylated organic compounds, organic silicon compounds, metals, salts, phosphorous, sulfur and nitrogen compounds. The plastic used for generating pyrolysis plastic oil is a waste plastic, irrespective of its origin or nature. The composition of the pyrolysis plastic oil is dependent on the type of plastic that is pyrolyzed. Pyrolysis plastic oil is mainly (especially over 80wt%, most often over 90wt%) constituted of hydrocarbons having from 1 to 150 carbon atoms and impurities.

[0038] The term **"Diene Value"** (DV) or **"Maleic Anhydride Value"** (MAV) is a measure of the conjugated double bonds (dienes) in the oil. For the Maleic Anhydride Value (MAV), one mole of Maleic anhydride corresponds to 1 mole of conjugated double bond and the result corresponds to the amount of maleic anhydride in milligrams that will react with 1 gram of oil. One known method to quantify dienes is the UOP 326-17: Diene Value by Maleic Anhydride Addition Reaction. The term "diene value" (DV) refers to a similar analytical method to quantify dienes by titration, which is expressed in g of iodine per 100 g of sample. There is a correlation between the MAV = DV x 3,863 since 1 mole of conjugated double bond is titrated by 1 mole of Maleic Anhydride or 1 mole of Iodine.

[0039] The term **"bromine number"** corresponds to the amount of reacted bromine in grams by 100 grams of sample. The number indicates the quantity of olefins in a sample. It is determined in grams of Br_2 per 100 grams of sample (gBr_2/100g) and can be measured according to ASTM D1159-07R17 method.

[0040] The term **"boiling point"** refers to boiling point generally used in the oil and gas industry. Boiling point is measured at atmospheric pressure. The initial boiling point is defined as the temperature value when the first bubble of vapor is formed. The final boiling point is the highest temperature that can be reached during a standard distillation. At this temperature, no more vapor can be driven over into the condensing units. The determination of the initial and final boiling points is known in the art. Depending on the boiling range of the mixture, various standardized methods can be used, such as ASTM D2887-19ae2 relating to the boiling range distribution of petroleum fractions by gas chromatography. For compositions containing heavier hydrocarbons ASTM D7169-05 may alternatively be used. Boiling range of distillates is advantageously measured using ASTM D7500, D86 or D1160.

[0041] The concentration of metals in the matrix of hydrocarbon can be determined by any method known in the art. Relevant characterization methods include XRF or ICP-AES methods. Those skilled in the art know which method is the most adapted to each metal measurement and to which hydrocarbon matrix. Features, structures, characteristics or embodiments may be combined in any suitable manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments.

[0042] « **Potential gums »** inform on the tendency of a fuel to form gum and deposits under accelerated aging conditions. They give an indication on the stability of a fuel during its storage. Potential gums can be determined by means of method ASTM D873-12(2018).

[0043] « **Existing gums »** correspond to quantity of residue remaining after evaporation of a fuel under specific conditions. They give an indication on the stability of a fuel when heated. Existing gums can be determined by means of method NF EN ISO 6246 (2018) et ASTM D381-19

Detailed description of the invention

[0044] **As regards the hydrocarbon stream,** it has a diene value of at least 0.5 g I_2/100 g, preferably at least 1 g I_2/100 g, as measured according to UOP 326, a bromine number of at least 5 g Br_2/ 100g as measured according to ASTM D1159.

[0045] The hydrocarbon stream contains at least 2 wt% of plastic pyrolysis oil. In a preferred embodiment, said hydrocarbon stream contains at least 25 wt % of pyrolysis plastic oil, preferably at least 50 wt% more preferably 75 wt %, even more preferably at least 90 wt % of pyrolysis plastic oil. It is also possible to use pure pyrolysis plastic oil, and this is the most preferred embodiment. In the latter case, the hydrocarbon stream is only consisting of pyrolysis plastic oil.

[0046] Contaminants contained in plastic pyrolysis oil may comprise constituents which are not boiling below 700°C, preferably not below 600°C, such as gums in the form of plastic oligomers and residues of pyrolysis of plastic, optionally metals and optionally solids.

[0047] Advantageously, the plastic pyrolysis oil is originating from the stream of pyrolyzed waste plastic for which the

C1 to C4 hydrocarbons have been removed and/or the components having a boiling point higher than 350°C have been removed and/or preferably further converted in a steam cracker, and/or a FCC, or a hydrocracking unit, a coker or a visbreaker or blended in crude oil or crude oil cut to be further refined.

[0048] The other component of said hydrocarbon stream may include any diluent miscible with the pyrolysis plastic oil. Such diluent preferably has a diene value of at most 0.5 g I_2/100 g as measured according to UOP 326-17, a bromine number of at most 5 g Br_2/ 100g as measured according to ASTM D1159.

[0049] The diluent according to the invention is preferably selected from a naphtha and/or a paraffinic solvent and/or a diesel or a straight run gasoil, containing at most 1 wt% of sulfur, preferably at most 0.1 wt% of sulfur, and/or a hydrocarbon stream having a boiling range between 50°C and 150°C or a boiling range between 150°C and 250°C or a boiling range between 200°C and 350°C, having preferably a bromine number of at most 5 gBr_2/100g, and/or a diene value of at most 0.5 gI_2/100g or any combination thereof.

[0050] **As regards the additives capable to reduce gums formation or buildup,** one can cite an antipolymerant such as a stable free radicals or a precursor thereof, such as a hydroxylamine compound.

[0051] Any stable free radical (or precursor thereof under conditions which produce the stable free radical in situ) as defined may be used in the present invention. The stable free radicals suitable for use in this invention may be selected from, but are not limited to, the following groups of chemicals: nitroxides (e.g., di-tert butylnitroxide), hindered phenoxys (e.g., galvinoxyl), hydrazyls (e.g., diphenylpicrylhydrazyl), and stabilized hydrocarbon radicals (e.g., triphenylmethyl), as well as polyradicals, preferably biradicals of these types. In addition, certain precursors that produce stable free radicals in situ may be selected from the following groups: nitrones, nitrosos, thioketones, benzoquinones, amines and hydroxylamines.

[0052] These stable free radicals exist over a wide range of temperatures up to about 260°C. A limiting factor in their use is the temperature of the processing wherein they are employed. Specifically, the present method applies to processing carried on at temperatures at which said stable free radical exists. Pressure has not been seen to be significant to the present method, hence, atmospheric, sub or superatmospheric conditions may be employed.

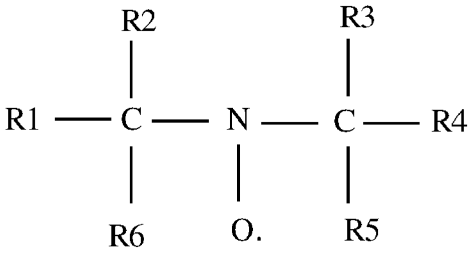
[0053] In an advantageous embodiment the stable free radical may be a stable nitroxide and may be substituted with at least one alkyl, aryl or alkylaryl group.

[0054] In an advantageous embodiment the hydroxylamine may be substituted with at least one alkyl, aryl or alkylaryl group.

[0055] Preferably, the stable nitroxide free radical or the hydroxylamine may be substituted with a straight or branched chain alkyl of 1 to 20 carbon atoms, a straight or branched chain alkyl of 1 to 20 carbon atoms which is substituted by one to three aryl groups, an aryl of 6 to 12 carbon atoms, or an aryl of 6 to 12 carbon atoms which is substituted by one to three alkyl groups of 1 to 6 carbon atoms.

[0056] Specific examples of such suitable hydroxylamines substituted with at least one alkyl, aryl or alkylaryl group as detailed above include, but are not necessarily limited to N-ethylhydroxylamine (EHA); N,N'-diethylhydroxylamine (DEHA); N-ethyl N-methylhydroxylamine (EMHA); N-isopropylhydroxylamine (IPHA); N,N' dibutylhydroxylamine (DBHA); N-amylhydroxylamine (AHA); N-phenylhydroxylamine (PHA); and the like and mixtures thereof.

[0057] A stable nitroxide free radical that can be used in this invention is a nitroxide having the formula (I) shown below or an amine precursor thereof.



$$R1-\overset{R2}{\underset{R6}{C}}-\underset{O.}{N}-\overset{R3}{\underset{R5}{C}}-R4$$

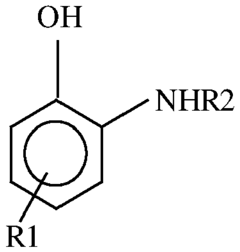
(I)

wherein R1, R2, R3 and R4 are alkyl groups or heteroatom substituted alkyl groups and no hydrogen is bound to the remaining valences on the carbon atoms bound to the nitrogen. The alkyl (or heteroatom substituted) groups R1-R4 may be the same or different, and preferably contain 1 to 15 carbon atoms. Preferably R1-R4 are methyl, ethyl, or propyl groups. In addition to hydrogen the heteroatom substituents may include, halogen, oxygen, sulfur, nitrogen and the like.

[0058] The remaining valences R5-R6 in the formula above may be satisfied by any atom or group except hydrogen which can bond covalently to carbon, although some groups may reduce the stabilizing power of the nitroxide structure and are undesirable. Preferably R5 and R6 are halogen, cyano,-COOR wherein R is alkyl or aryl, --CONH2, --S--C6H5, --S--COCH3,-OCOC2H5, carbonyl, alkenyl where the double bond is not conjugated with the nitroxide moiety or alkyl of 1 to 15 carbon atoms, R5 and R6 may also form a ring of 4 or 5 carbon atoms and up to two heteroatoms, such as O, N or S by R5 and R6 together. Examples of suitable compounds having the structure above and in which R5 and R6 form part of the ring are pyrrolidin-1-oxys, piperidinyl-1-oxys, the morpholines and piperazines. Particular examples wherein the R5 and R6 above form part of a ring are 4-hydroxy-2,2,6,6-tetramethyl-piperindino-1-oxy, 2,2,6,6-tetramethyl-piperidino-1-oxy, 4-oxo-2,2,6,6-tetramethyl-piperidino-1-oxy and pyrrolin-1-oxyl. Suitable R5 and R6 groups are methyl, ethyl, and propyl groups. A specific example of a suitable compound where R1-R6 are alkyl groups is di-tert-butylnitroxide. The preferred carbonyl containing nitroxides are those wherein the R5 and R6 form a ring structure with the nitrogen, preferably a six number ring, for example, 4-oxo-2,2,6,6-tetramethylpiperidino-1-oxy. Examples of nitroxides that can be used in the present invention are the 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (also referred as 4 OH Tempo), the 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (also referred as 4 NH Tempo), and 4 butoxy Tempo, or their amine precursors.

[0059] **As regards the additives capable to reduce gums formation or buildup,** one can also cite the unhindered phenols, the hindered phenols, the aminophenols, the phenylenediamines.

[0060] The aminophenol may be selected from the compounds given by the following formula (II):



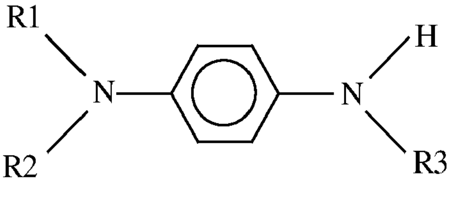
(II)

[0061] Where R1 is selected from hydrogen, a C1-C20 alkyl group, C6-C12 aryl group, or OR', with R' being a H, an C1-C20 alkyl or a C6-C12 aryl group. R2 is selected from an C1-C20 alkyl, a phenyl group, or OR', with R' having the same meaning as before.

[0062] Non-exclusive examples of such compounds are 2-aminophenol (2 AP), 3-hydroxy-2-aminophenol, 2-amino-naphthalen-1 -ol, 3-amino-naphthalen-2-ol, 1-amino-naphthalen-2-ol, 2-amino-tert-butyl-phenol, and 2-amino-4-methylphenol.

[0063] Suitable hindered or unhindered phenols may include, but are not necessarily limited to, 4-tert butylcatechol (TBC); tert-butyl hydroquinone (TBHQ); 2,6-di-tert-butyl-4-methoxyphenol (DTBMP); 2,4 di-tert-butylphenol; 2,5-di-tert-butylphenol; 2,6-di tertbutylphenol; 2,4, tri-tert-butylphenol; butylated hydroxyltoluene (BHT, also known as 2,6 di-tert-butyl-paracresol and 2,6 di-tert-butyl methylphenol); 2,6 di-tert-butyl-4-nonylphenol; 2,6-di-tert-butyl-4-sec-butylphenol; 2-butyl-4-methylphenol; 2-tert-butyl-4-methoxyphenol (also known as butylated hydroxyanisole or BHA); 2, di-tert-butyl hydroquinone 15 (DTBHQ); tert-amyl hydroquinone; 2,5-di-amyl hydroquinone; 3, di-tert-butylcatechol; hydroquinone; hydroquinone monomethyl ether; hydroquinone monoethyl ether; hydroquinone monobenzyl ether; or 3,3,3',3'-tetramethyl, 1,1-spirobis-indane-5,5',6,6' tetrol (Tetrol); topanol® AN (mixture of BHT and 2,4 Dimethyl-6-tert-butylphenol), tocopherols ($C_{29}H_{50}O_2$) including alpha-, beta-, gamma-, delta-tocopherol, and mixtures thereof.

[0064] The phenylenediamines of this invention have at least one N-H group and are advantageously of the following formula (III):



(III)

wherein R1, R2, and R3 are the same or different and are hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, straight or branched chain alkyl of 1 to 20 carbon atoms which is substituted by one to three aryl groups, aryl of 6 to 12 carbon atoms, or aryl of 6 to 12 carbon atoms which is substituted by one to three alkyl groups of 1 to 6 carbon atoms.

[0065] Suitable examples of phenylenediamines include N-phenyl-N'-methyl-1,4-phenylediamine, N-phenyl-N'-ethyl-1,4-phenylediamine, N-phenyl-N'-n-propyl-1,4-phenylediamine, N-phenyl-N'-isopropyl-1,4-phenylediamine (NIPP PP-

DA), N-phenyl-N'-n-butyl-1,4-phenylediamine, N-phenyl-N'-iso-butyl-1,4-phenylediamine, N-phenyl-N'-sec-butyl-1,4-phenylediamine, N-phenyl-N'-t-butyl-1,4-phenylediamine, N-phenyl-N'-n-pentyl-1,4-phenylediamine, N-phenyl-N'-n-hexyl-1,4-phenylediamine, N-phenyl-N'-(1-methylhexyl)-1,4-phenylediamine, N-phenyl-N'-(1,3-dimethylbutyl)-1,4-phenylediamine, N-phenyl-N'-(1,4-dimethylpentyl)-1,4-phenylediamine, N-phenyl-N', N'-dimethyl-1,4-phenylenediamine, N-phenyl-N',N'-diethyl-1,4-phenylenediamine, N-phenyl-N',N'-di-n-butyl-1,4-phenylenediamine, N-phenyl-N,N'-di-sec-butyl-1,4-phenylenediamine, N-phenyl-N'-methyl-N'-ethyl-1,4-phenylenediamine, N,N'-dimethyl-1,4-phenylenediamine, N, N'-di ethyl-1,4-phenylenediamine, N,N'-diisopropyl-1,4-phenylenediamine, N,N'-di-iso-butyl-1,4-phenylenediamine, N,N'-di-sec-butyl-1,4-phenylenediamine (DSB PPDA), N,N'-bis(1,4-dimethylpentyl)-1,4-phenylenediamine, N,N'-bis(1,3-dimethylbutyl)-1,4-phenylenediamine, N,N'-diphenyl-1,4-phenylenediamine, N,N,N'-trimethyl-1,4-phenylenediamine, and N,N,N'-triethyl-1,4-phenylenediamine and N-phenyl-p-phenylenediamine (NP PPDA), and mixtures thereof.

[0066] In a preferred embodiment, the additive capable to reduce gums formation or buildup is selected among the unhindered phenols, the hindered phenols, the aminophenols, the phenylenediamines, and mixtures thereof.

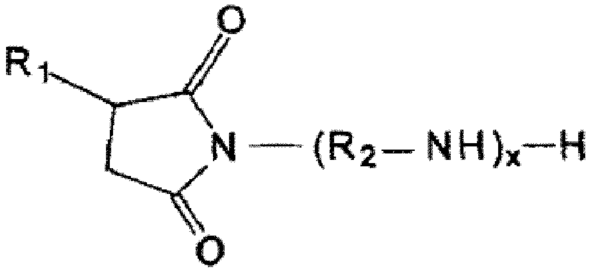
[0067] In a most preferred embodiment, the additive capable to reduce gums formation or buildup is selected among the unhindered phenols, the hindered phenols, aminophenols and mixtures thereof. In another most preferred embodiment, the additive capable to reduce gums formation or buildup is selected among phenylenediamines.

[0068] In a preferred embodiment, suitable additives include 4-tert butylcatechol (TBC); 2,6-di tertbutylphenol; butylated hydroxyltoluene (BHT), tocopherols including alpha-, beta-, gamma-, delta-tocopherol, phenylenediamines, in particular those of the above list, and mixtures thereof.

[0069] **As regards the additive which is a dispersant agent, such** additive is a dispersant/detergent capable to prevent the agglomeration of insoluble compounds, formed during oxidation reactions. Such additive does not reduce the gum content.

[0070] The dispersant/detergent agent used in the present invention may be selected from:

(i) substituted amines such as N-polyisobutene amine R1-NH_2, N-polyisobutene-ethylenediamine R1-NH-R2-NH_2,
(ii) alkenyl succinimides, for example obtained by reacting an akenyl succinic anhydride or acid with an amine or a polyamine, or their bissuccinimide, succinnamic, succinamide structural equivalents, for example succinimides of formula (IV):

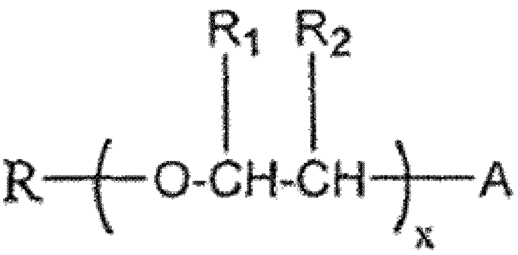


(IV)

where R1 represents a C2-C120 or C2-C100 alkenyl group, for example a polyisobutene group of weight-average molecular weight between 140 and 5000 and preferably between 500 and 2000 or preferably between 750 and 1250;, and where R2 represents at least one of the following segments -CH_2-CH_2-, CH_2-CH_2-CH_2, -CH-CH(CH_3)- and x represents an integer between 1 and 6.

(iii) the polyethylenamines. They are for example described in detail in the reference "Ethylene Amines," Encyclopedia of Chemical Technology, Kirk and Othmer, Vol. 5, pp. 898-905, Interscience Publishers, New York (1950).

(iv) the polyetheramines of formula (V):



$$R\left(O\text{-}\underset{|}{\overset{R_1}{CH}}\text{-}\overset{R_2}{CH}\right)_x A$$

(V)

where R is an alkyl or aryl group having from 1 to 30 carbon atoms; R1 and R2 are each independently a hydrogen atom, an alkyl chain with 1 to 6 carbon atoms or -O-CHR1-CHR2-; A is an amine or N-alkylamine with 1 to 20 carbon atoms in the alkyl chain, an N,N-dialkylamine having from 1 to 20 carbon atoms in each alkyl group, or a polyamine with 2 to 12 nitrogen atoms and from 2 to 40 carbon atoms and x is in the range from 5 to 30. Such polyetheramines are marketed for example by the companies BASF, HUNSTMAN or CHEVRON.

(v) the products of reaction between a phenol substituted with a hydrocarbon chain, an aldehyde and an amine or polyamine or ammonia. The alkyl group of the alkylated phenol can comprise from 9 to 110 carbon atoms. This alkyl group can be obtained by polymerization of olefinic monomer containing from 1 to 10 carbon atoms (ethylene; propylene; 1-butene, isobutylene and 1-decene). The polyolefins that are used in particular are polyisobutene and/or polypropylene. The polyolefins generally have a weight-average molecular weight Mw between 140 and 5000 and preferably between 500 and 2000 or preferably between 750 and 1250.

[0071] The alkyl phenols can be prepared by an alkylation reaction between a phenol and an olefin or a polyolefin such as polyisobutylene or polypropylene. The aldehyde used can contain from 1 to 10 carbon atoms, generally formaldehyde or paraformaldehyde.

[0072] The amine used can be an amine or a polyamine including the alkanolamines having one or more hydroxyl groups. The amines used are generally selected from ethanolamine, diethanolamines, methylamine, dimethylamine, ethylenediamine, dimethylaminopropylamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine and/or 2-(2-aminoethylamino)ethanol. This dispersant can be prepared by a Mannich reaction by reacting an alkylphenol, an aldehyde and an amine as described in patent U.S. Pat. No.5,697,988.
other dispersants, such as:

(vi) carboxylic dispersants such as those described in U.S. Pat. No.3,219,666;

(vii) the amine dispersants resulting from reaction between halogenated aliphatics of high molecular weight with amines or polyamines, preferably polyalkylene polyamines, described for example in U.S. Pat. No.3,565,804;

(viii) polymeric dispersants obtained by polymerization of alkyl acrylates or alkyl methacrylates (C8 to C30 alkyl chains), aminoalkyl acrylates or acrylamides and acrylates substituted with poly(oxyethylene) groups. Examples of polymeric dispersants are described for example in U.S. Pat. No.3,329,658 and U.S. Pat. No.3,702,300;

(ix) dispersants containing at least one aminotriazole group such as described for example in U.S. Patent Publication No. 2009/0282731 resulting from reaction of a dicarboyxlic acid or anhydride substituted with a hydrocarbyl and an amine compound or salt of the (amino)guanidine type;

(x) oligomers of polyisobutylsuccinic anhydride (PIBSA) and/or of dodecylsuccinic anhydride (DDSA) and of hydrazine monohydrate, such as those described in EP 1,887,074;

(xi) oligomers of ethoxylated naphthol and of PIBSA, such as those described in EP 1,884,556;

(xii) quaternized ester, amide or imide derivatives of PIBSA, such as those described in WO2010/132259;

(xiii) mixtures of Mannich bases such as substituted phenols/aldehydes/mono-or polyamines, for example dodecylphenol/ethylenediamine/formaldehyde, and of polyisobutylene succinimides (PIBSI), such as those described in WO2010/097624 and WO 2009/040582;

(xiv) quaternized terpolymers of ethylene, of alkenyl ester(s) and of monomer(s) with at least one ethylenic unsaturation and containing an at least partially quaternized tertiary nitrogen, such as those described in WO2011/134923.

[0073] In a preferred embodiment, the dispersant/detergent agent used in the present invention may be selected from the above compounds (ii) and (v). Such preferred dispersant/detergent agent(s) may be added to the above described additive(s) capable to reduce gums formation or buildup and more particularly to the preferred additive(s)..

[0074] **As regards the stabilized composition,** it is of use in industrial processes for plastic recycling in which hydrocarbon streams is handled or manipulated other than the intentional polymerization of the olefin. Such processes include but are not limited to hydrocarbon cracking processes, preheating, distillation, hydrogenation, extraction, etc.

[0075] The proportion of b) with reference to a) can be up to 5000wppm, advantageously up to 3000 wppm, in particular from 50 to 5000 wppm, preferably from 50 to 3000 wppm, most preferably from 300 to 1500wppm, or within any of these limits.

[0076] The proportion of c) with reference to a) can be up to 5000wppm, advantageously up to 3000 wppm, in particular from 50 to 5000 wppm, preferably from 50 to 3000 wppm, most preferably from 300 to 1500wppm, or within any of these limits.

[0077] The additives of this invention may also be used with other additives known to prevent fouling such as metal deactivators, corrosion inhibitors and the like. The stabilizer combination of this invention may be applied at any point in an industrial plant stream or process where it is effective.

As regards the process for preparing a composition stabilized against premature polymerization

[0078] Step (a) for providing a hydrocarbon stream as defined above may comprise :

(i) providing at least one plastic pyrolysis oil by pyrolysis of plastic waste,
(ii) optionally providing a diluent,
(iii) preparing a hydrocarbon stream having a diene value of at least 0.5 g I_2/100 g, preferably at least 1 g I_2/100 g, as measured according to UOP 326, a bromine number of at least 5 g Br_2/ 100g as measured according to ASTM D1159 by mixing said at least one plastic pyrolysis oil provided in step (i) with the diluent provided in step (ii) when present, said composition comprising at least 2wt% of plastic pyrolysis oil, the remaining part of said hydrocarbon stream being a diluent.

[0079] In one embodiment, in step (b), said at least one additive capable to reduce gums formation or buildup is added to said at least one plastic pyrolysis oil provided by step (i), prior to step (iii). In an embodiment, the additives are added to the pyrolysis plastic oil immediately after the pyrolysis of the plastic waste.

[0080] In one embodiment, in step (c), said at least one additive is added to said at least one plastic pyrolysis oil provided by step (i), prior to step (iii), preferably immediately after the pyrolysis of the plastic waste.

[0081] In one embodiment, steps (b) and (c) are performed simultaneously, preferably immediately after the pyrolysis of the plastic waste.

[0082] Whatever the embodiment, the additives can be introduced as pure or as a dilute solution in a hydrocarbon or equivalent and/or they can be introduced simultaneously or separately. For example, the additives may be diluted in hydrocarbons, for example C6-C20 aromatic hydrocarbons substituted or not, including toluene, benzene, naphthalene, substituted or not, and their mixtures, heavy aromatic naphtha, a middle distillate (boiling range 180-360°C) such as a jet fuel or a diesel, or in polar solvents, in particular alcohols such as glycols, ethanol, or water.

[0083] The stabilized composition described in the present invention or obtained by the process of the present invention may be used as such or further processed alone or in combination with another feedstock such as naphtha, gasoil or any crude oil refining product. It may for example be fractionated according to distillation temperature ranges, to feed a steam cracker, a FCC, a hydrocracker, a catalytic hydrogenation unit or a pool of fuels or combustibles such as naphtha, gas oil, heavy fuel oil and/or for the preparation of lubricants.

[0084] **As regards the process for the processing of a composition stabilized against premature polymerization,** it uses a stabilized composition as described in the present invention and in particular obtained by the process for preparing a composition stabilized against premature polymerization of the invention.

[0085] In some embodiments, some or all of the additives contained in the stabilized composition (additive(s) capable to reduce gums formation or buildup and/or additive(s) which is a dispersant agent) may present a two high boiling point to be used in a further processing step and/or may be detrimental to the further processing.

[0086] In such a case, it may be preferable to reduce, or completely remove, some or all of the additives by submitting the stabilized composition provided in step (a) to an evaporation step (b) under operating conditions efficient to obtain a composition containing a reduced amount of additives. Such evaporation may be performed at temperatures and pressure efficient to obtain a gaseous hydrocarbon stream having a final boiling point of at most 650°C, preferably of at most 500°C, more preferably of at most 380°C, and optionally a residue. Such evaporation is optionally performed in presence of steam.

[0087] In one embodiment, in the evaporation step, the stabilized composition may be heated using steam, at a temperature which is high enough to avoid condensation of steam when direct mixing is envisioned, since steam condensation could lead to hammering issues. Non-vaporized products are removed in a separation section to produce the gaseous hydrocarbon stream. Alternatively, the stabilized composition may be heated using a hot oil, which is collected in admixture with the non-vaporized products and may be recycled.

[0088] The evaporation step may be performed using a flash drum, a kettle, a single or double wall thin film evaporator, a falling film evaporator or a combination of at least two of them.

[0089] Such evaporation step (b) may be particularly useful before processing the stabilized composition in a steam cracker.

[0090] The gaseous hydrocarbon stream obtained from evaporation step (b) is then submitted to the further processing step (c).

[0091] In the process for the processing of a stabilized composition according to the invention, the stabilized composition provided in step (a) or the composition containing a reduced amount of additives provided in step (b) may, prior to step (c), be mixed with naphtha, gasoil or any crude oil refining product to have a pyrolysis plastic oil concentration ranging from 0.01 wt% to at most 90 wt%; preferably 0.1 wt% to 75 wt% even more preferably 1 wt% to 50 wt% or within any of these limits.

Examples

[0092] An additive capable to reduce gums formation or buildup, here a phenolic compound, BHT (butylated hydroxyltoluene), has been added to several pyrolysis plastic oils. Existing gums have been determined by means of NF EN ISO 6246 (2018), potential gums by ASTM D873-12(2018).

[0093] The characteristics of the pyrolysis plastic oils alone and with the additive are presented in table 1.

Table 1

	Unit	**HPP1**	**HPP2**	**HPP3**
bromine number	gBr/g	45	25	<1
diene value	gI_2/g	1.2	2.4	0.8
MAV	mg anhydride	4.6	9.3	3.1
Oxygen content	Wt%	0.12	0.06	0.1
Existing gums HPP	**mg/100mL**	**102**	**13**	**2**
Reproducibility of the method		31	7	3
Existing gums HPP + 1000ppm BHT	mg/100mL	62	12	3
Potential gums HPP	**mg/100mL**	**236**	**89**	**22**
Reproducibility of the method		69	28	9
Potential gums HPP+ 1000ppm BHT	mg/100mL	85	31	0.5

[0094] These results show a reduction of the formation of gums with the addition of BHT, particularly for potential gums.

Claims

1. Composition stabilized against premature polymerization comprising:

a) a hydrocarbon stream having a diene value of at least 0.5 g I_2/100 g as measured according to UOP 326, a bromine number of at least 5 g Br_2/ 100g as measured according to ASTM D1159, and containing at least 2 wt% of plastic pyrolysis oil which is containing contaminants, wherein said contaminants comprise constituents which are not boiling below 700°C, preferably not below 600°C, such as gums in the form of plastic oligomers and residues of pyrolysis of plastic, optionally metals and optionally solids, the remaining part of said hydrocarbon stream being a diluent,
b) at least one additive capable to reduce gums formation or buildup,
c) optionally at least one additive which is a dispersant agent.

2. Composition according to claim 1 wherein at least one additive capable to reduce gums formation or buildup and at least one dispersant agent are present.

3. Composition according to any one of the preceding claims wherein the additive capable to reduce gums formation or buildup is an antipolymerant such as a stable free radical or a precursor thereof.

4. Composition according to claim 3 wherein the antipolymerant is a stable nitroxide free radical and/or a hydroxylamine substituted with at least one alkyl, aryl or alkylaryl group.

5. Composition according to any one of the preceding claims wherein the additive capable to reduce gums formation or buildup is selected among he unhindered phenols, the hindered phenols, the aminophenols, the phenylenediamines and mixtures thereof.

6. Composition according to any one of the preceding claims wherein said at least one additive which is a dispersant agent is selected from products of reaction between a phenol substituted with a C9-110 hydrocarbon chain, an aldehyde and an amine or polyamine or ammonia, from alkenyl succinimides or mixtures thereof.

7. Composition according to any one of the preceding claims wherein the proportion of b) with reference to a) is from is from 20 to 5000wppm, preferably from 50 to 3000wppm, more preferably from 300 to 1500wppm.

8. Composition according to any one of the preceding claims wherein the proportion of c) with reference to a) is from 20 to 5000wppm, preferably from 50 to 3000wppm, more preferably from 300 to 1500wppm.

9. Process for preparing a composition stabilized against premature polymerization, comprising :

(a) providing a hydrocarbon stream having a diene value of at least 0.5 g I_2/100 g as measured according to UOP 326, a bromine number of at least 5 g Br_2/ 100g as measured according to ASTM D1159, and containing at least 2 wt% of plastic pyrolysis oil which is containing contaminants, wherein said contaminants comprise constituents which are not boiling below 700°C, preferably not below 600°C, such as gums in the form of plastic oligomers and residues of pyrolysis of plastic, optionally metals and optionally solids, the remaining part of said hydrocarbon stream being a diluent,
(b) adding to the hydrocarbon stream provided in step (a) at least one additive capable to reduce gums formation or buildup,
(c) optionally adding to the hydrocarbon stream provided in step (a) at least one additive which is a dispersant agent.

10. Process according to claim 9, wherein step (a) comprises :

(i) providing at least one plastic pyrolysis oil by pyrolysis of plastic waste,
(ii) optionally providing a diluent,
(iii) preparing a hydrocarbon stream having a diene value of at least 0.5 g I_2/100 g as measured according to UOP 326, a bromine number of at least 5 g Br_2/ 100g as measured according to ASTM D1159 by mixing said at least one plastic pyrolysis oil provided in step (i) with the diluent provided in step (ii) when present, said composition comprising at least 2wt% of plastic pyrolysis oil, the remaining part of said hydrocarbon stream being a diluent.

11. Process according to claim 10, wherein in step (b), said at least one additive capable to reduce gums formation or buildup is added to said at least one plastic pyrolysis oil provided by step (i), prior to step (iii).

12. Process according to claim 10 or 11, wherein in step (c), said at least one additive is added to said at least one plastic pyrolysis oil provided by step (i), prior to step (iii).

13. Process for the processing of a composition stabilized against premature polymerization, comprising :

(a) providing a composition stabilized against premature polymerization as claimed in any one of claims 1 to 8,
(b) optionally submitting the composition provided in step (a) to an evaporation step under operating conditions efficient to obtain a composition containing a reduced amount of additives,
(c) the stabilized composition provided in step (a) or the composition containing a reduced amount of additives provided in step (b) is (i) processed in a steamcracker, (ii) processed in a fluid catalytic cracker, (iii) processed in a catalytic hydrogenation unit, (iv) processed in a hydrocracking unit and/or (v) separated into usable streams for the preparation of fuels such as LPG, naphtha, gas oil, heavy fuel oil and/or for the preparation of lubricants.

14. The process according to claim 13, wherein the stabilized composition provided in step (a) or the composition containing a reduced amount of additives provided in step (b) is, prior to step (c), mixed with naphtha, gasoil or any crude oil refining product to have a pyrolysis plastic oil concentration ranging from 0.01 wt% to at most 90 wt%; preferably 0.1 wt% to 75 wt% even more preferably 1 wt% to 50 wt%.

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EUROPEAN SEARCH REPORT

Application Number
EP 22 30 5030

DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DE 20 2015 009755 U1 (BLUEALP INNOVATIONS B V [NL]) 6 February 2020 (2020-02-06) * paragraphs [0060], [0079], [0080]; claim 1; figure 1 * -----	1-14	INV. C10G1/10 C10G75/04 C10L1/10
X	WO 2013/119941 A1 (ULLOM WILLIAM [US]) 15 August 2013 (2013-08-15) * page 27, line 6 - line 15; claims 10,25; figure 1 * * page 26, line 23 - line 29 * -----	1-14	
A	WO 02/088055 A1 (BAKER HUGHES INC [US]) 7 November 2002 (2002-11-07) * claim 1 * -----	1-14	
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			C10G C10L

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	16 June 2022	Deurinck, Patricia

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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The members are as contained in the European Patent Office EDP file on
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16-06-2022

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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