

A PYROLYSIS OIL WITH REDUCED POUR POINT AND/OR VISCOSITY

TECHNICAL FIELD OF THE INVENTION

5 The invention relates to a composition comprising a pyrolysis oil and a polymeric additive for reducing the pour point, viscosity, or both the pour point and viscosity of the pyrolysis oil. The invention further relates to a method of manufacturing said composition, the use of a polymeric additive for reducing the pour point, viscosity, or both the pour point and viscosity of a pyrolysis oil. The invention further relates to a method for transporting or storing a pyrolysis oil.

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BACKGROUND OF THE INVENTION

Plastic production continues to grow rapidly, and plastic products remain to be a crucial part of our lives due to the versatility of the material and the low cost associated with plastic production. It is estimated that 15 250 million tons of plastic per year are either landfilled or dispersed into the environment. It is also predicted that the use of plastic will continue to increase in the future. The increase in plastic production will also be associated with the increase in associated plastic waste, especially with single-use plastic items. The increase in plastic waste has also brought interest in how to effectively recycle or convert plastic waste back into usable materials.

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One effective way to treat plastic waste is by thermochemically converting plastic waste via a pyrolysis process. Pyrolysis is a thermal cracking process that occurs in the absence of oxygen at temperatures above 400°C. The process breaks down polymer chains into smaller chains and molecules. The pyrolysis process can therefore convert plastic waste material into usable products thereby addressing the plastic waste management issues. There are many types of plastics, but the majority of plastic waste is made up of low-density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET). Of those plastics, polyethylene and polypropylene constitute the greatest portion of plastic waste. The pyrolysis provides a final product termed in the art 'pyrolysis oil'. The main products produced from plastic pyrolysis include 25 liquid oil, wax, solid residues, and gas. All such residues are then processed further as part of existing plastic processing plants or steam crackers used in refineries.

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In the pyrolysis process, the conversion of plastic to usable materials, e.g. oil, gas, and wax, is dependent on several factors. The most influential factors are the reactor design, the process temperature, the type of plastic used, and the type of catalyst.

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The wax residue comprises those pyrolysis products having alkyl chains of 16 or more carbon atoms. The wax residue is a valuable product in the pyrolysis process. The amount of wax residue produced can greatly influence the final pyrolysis oil properties. The main driver in the amount of wax residue produced is the plastic feedstock being introduced into the pyrolysis process. For example, olefinic plastics such as polyethylene and polypropylene are more linear polymers, which therefore break down into waxy linear 40

alkyl chains when converted in the pyrolysis process. Pyrolysis oils produced from polyethylene and polypropylene can yield over 50wt% wax residue depending on the specific pyrolysis oil process conditions.

Specific process conditions including catalyst types can also influence oil-to-wax ratio. To obtain a lower wax residue content in the final product, certain catalysts can be used. Also, conditions such as residence time in the reactor can be influential. For example, 'fast' pyrolysis leads to the production of waxy hydrocarbon mixtures, whereas 'slow' pyrolysis typically produces more oil than wax. (Materials 2021, 14, 2586).

However, waxy chains can also cause a variety of transportation and storage issues. The waxy chains of 12 or more carbon atoms can begin to crystallize as the pyrolysis oil cools to ambient temperature after the pyrolysis process. Pyrolysis oils also typically have a large quantity of paraffins with waxy chains of 16 to more than 40 carbon atoms. These wax chains are most problematic since the melting point is much higher. The wax crystals can then build up and cause an increase in viscosity, making the thicker oil more difficult to pump or move. If there is enough wax residue in the pyrolysis oil, especially in polyolefin pyrolysis oils, then the wax crystals may cause the entire product to solidify at lower temperatures heading towards ambient temperature. Once solidified, expensive heating must be used to melt the product in order to move or process it further. The wax crystals may also clog equipment such as filters and pipelines, thus increasing servicing costs. Lastly, high wax amounts can lead to paraffin deposition on pipelines in the production lines. As wax builds up, the efficacy and lifetime of the equipment is decreased.

Despite this, wax is a valuable pyrolysis product, and existing plastic processing plants have been designed and built to use the wax residue. However, the wax residue made in the pyrolysis process, especially from increasingly used olefin feedstocks, is making transportation and storage of the pyrolysis oil more difficult and more expensive.

As previously explained, the amount of wax residue varies depending on the plastic feedstock used, and the specific process conditions. And, polyolefin-based pyrolysis oils produced via current or standard pyrolysis processes, tend to produce the most amount of wax, which therefore have the most problems, especially at ambient conditions. The 'pour point' is the lowest temperature at which the pyrolysis oil will still flow, and pyrolysis oils with high wax residue have relatively high pour points (for example, above 50°C), which are usually above standard operating conditions and storage temperatures. This leads to difficulty in processing such pyrolysis oils, as the oil may solidify and become unable to transport. Heat is typically applied to the oil to liquefy it for storage and transportation. This expends heat energy and takes time. Therefore, even slight reductions in the pour point could drastically reduce the amount of heat energy expended and time taken to liquefy or to keep in liquid form the pyrolysis oil for transportation and storage.

One solution for reducing the pour point of the pyrolysis oil is to change the process conditions or the catalysts type to produce pyrolysis oils with lower pour points. But to do this, expensive catalysts need to be employed, the processes must run longer, or special reactors are required. Increasing process times or changing the reactor also increases the cost or decreases the overall efficiency. Furthermore, the valuable wax product is no longer produced at the same amount, and so cannot be available for subsequent

processing set up to expect the wax product. Other solutions have been implemented to isolate the wax by introducing a dewaxing step and reprocessing the oil to crack the wax into smaller molecules. However, these solutions also add costs and decrease efficiency to the process.

- 5 US2012/0310023A1 discloses that oils obtained in pyrolysis of polyolefin containing plastics mixtures are frequently wax-like semisolid products, and that the use of specific catalysts can result in the production of more light and less waxy products.

10 Lee *et al.* in the Journal of Analytical and Applied Pyrolysis 94 (2012) 209–214 explain that most of the plastic waste consisting of polyethylene is mainly converted in waxy oils. The waxy oils can be problematic because they could result in a breakdown of plant operations, ranging from pipeline blockages to shorter instrument life cycles. Thus, upgrading technology for pyrolysis to produce high-quality oils is needed. The authors demonstrated the efficacy of zeolite catalysts in the catalytic upgrading of the pyrolysis process.

- 15 Hakeem *et al.* in Applied Petrochemical Research (2018) 8:203–210 describe the problem with higher wax contents in pyrolysis oils and propose that catalysis could also be used to reduce the amount of wax in the final products and upgrade the oil to a lower wax quality in order to improve final properties.

20 KR100994244B1 discloses the need to remove the wax from the process and proposes the use of a separation device for wax removal. Therefore, the pyrolysis process will require an additional step to the process.

25 US2022/081634 discloses the use of a polymeric additive for improving the cold flow properties of a plastic-derived synthetic feedstock composition (see [0008]). Among the disclosed polymeric additives, the polymer can be a copolymer of an alpha-olefin monomer with an ethylenically unsaturated carboxylic acid monomer or derivatives thereof, such as maleic anhydride monomer with a range of weight-average molecular weight from 20,000 to 70,000 g/mol (see [0070], [0076] and example 3 of Table 1). This document is focused on the treatment of plastic pyrolysis oil with a high wax residue content of alkanes with long carbon chains (high content of waxes having C₁₆ or longer carbon chains - see e.g. [0048], [0086],
30 [0097], [0115], [00127], as well as the two treated pyrolysis oils of the experimental part [0153]).

WO2023/183460 discloses a composition comprising a pyrolysis oil and an additive composition comprising (a) one or more nitrogen containing antioxidants; and optionally, (b) a copolymer comprising maleic anhydride derived units and α -olefin derived units; and/or (c) the reaction product of a carboxylic acid and
35 a polyamine. It also relates to a method of improving the oxidation stability of a composition comprising a pyrolysis oil by adding to the composition the above-indicated additive composition (see abstract). The optional copolymer comprising maleic anhydride derived units and alpha-olefin derived units, has preferably a number average molecular weight of from 1,000 to 50,000 g/mol, more preferably from 8,000 to 17,000 g/mol (pages 12-14 and copolymer C of Table 1 with a M_n of 15,000 g/mol).

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Jin *et al.* in the Chinese Journal of Chemical Engineering 26 (2018) 400–406 explain that reactor design can help influence the wax quantity in the final pyrolysis oil product. The authors studied falling film reactor

in comparison to other reactor types to improve the liquid/wax ratio. The authors showed that the liquid wax ratio in the vertical falling film pyrolysis reactor is slightly higher than that achieved in the tubular reactor, equal to that in the rotary kiln reactor, and slightly lower than that in the medium fluidized bed.

5 Thus, as exemplified above, the conventional solutions to reduce viscosity and pour point of pyrolysis oils have been to reduce or eliminate production of the wax by changing the reactor design, adding special catalyst, increasing processing times or having an additional dewaxing process step. Although those methods help in producing liquid pyrolysis oils with a lower wax content, it creates additional costs, maintenance work, increased processing times, which decrease production efficiency and are thus not
10 good industrially viable solutions. Furthermore, the industry looks for high wax residue content pyrolysis oils for cracking processes, without having the transportation and storage disadvantages.

However, the properties of the plastic pyrolysis oils strongly depend on the production process, which leads to plastic pyrolysis oils having different wax residue content of alkanes. Therefore, there is still a need to
15 investigate further to find effective and cost-efficient solutions for the treatment of plastic pyrolysis oils from a plastic pyrolysis process in order to keep them liquid, improving the transport and storage of these oils before the cracking process.

The present invention is therefore directed to provide a pyrolysis oil with a lower pour point, lower viscosity
20 or both lower pour point and viscosity, as well as other objectives.

BRIEF SUMMARY OF THE INVENTION

According to a first aspect of the invention there is provided a composition comprising a plastic pyrolysis oil
25 a) and a polymeric additive b), for reducing the pour point, viscosity, or both the pour point and viscosity of the pyrolysis oil.

According to a second aspect of the invention there is provided a method of manufacturing the composition of the first aspect of the invention comprising the steps of:
30 providing a plastic feedstock;
pyrolyzing the plastic feedstock to generate a plastic pyrolysis oil a);
preparing a polymeric additive b) as described herein; and
adding polymeric additive b) to the pyrolysis oil a).

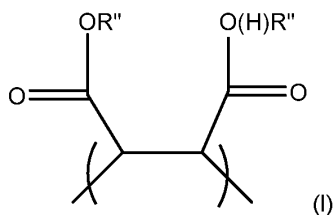
35 According to a third aspect of the invention there is provided the use of a polymeric additive b), as described herein to reduce the pour point of a plastic pyrolysis oil a), or to reduce the viscosity of the pyrolysis oil, or both.

According to a fourth aspect of the invention there is provided a method of transporting or storing a plastic
40 pyrolysis oil a) comprising the step of adding a polymeric additive b) to the pyrolysis oil to form the composition of the first aspect of the invention

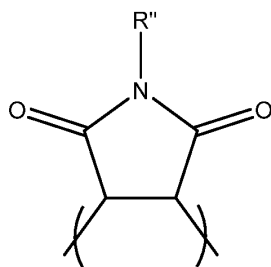
DETAILED DESCRIPTION OF THE INVENTION

According to the invention, there is provided a composition comprising a plastic pyrolysis oil a) and a polymeric additive b), wherein the polymeric additive b) is a copolymer P) prepared by polymerizing a monomer composition comprising

- i) 10 to 70 % by weight of monomers selected from alkyl maleate compound of Formula (I), maleimide compound of Formula (II) or a mixture thereof, based on the total weight of the copolymer P),



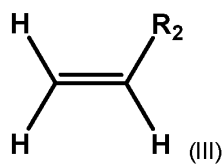
(I)



(II)

wherein R'' in Formula (I) and Formula (II) is a linear or branched alkyl group having from 10 to 40 carbon atoms, preferably from 10 to 30 carbon atoms, more preferably from 12 to 30 carbon atoms, even more preferably from 18 to 22 carbon atoms; and

- ii) 30 to 90 % by weight of a non-functionalized alpha-olefin of Formula (III) or a mixture thereof, based on the total weight of the copolymer P),



(III)

wherein R₂ is a linear alkyl group having from 8 to 40 carbon atoms, preferably from 10 to 40 carbon atoms, more preferably from 15 to 35 carbon atoms, even more preferably from 20 to 32 carbon atoms, and

wherein the plastic pyrolysis oil a) comprises 12 % by weight or less of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil a).

The polymeric additive b) reduces the pour point of the pyrolysis oil. The polymeric additive may also reduce the viscosity of the pyrolysis oil. The polymeric additive may also reduce both the pour point and the viscosity of the pyrolysis oil.

- 5 Preferably, the pour point of a pyrolysis oil a) is reduced by at least 1 °C, more preferably by at least 2 °C, even more preferably by at least 3 °C, most preferably by at least 5 °C, by the addition of the polymeric additive as described herein, when compared to the same pyrolysis oil with no polymeric additive.

- 10 The reduction in viscosity is preferably of at least 10 %, preferably at least 20 %, even more preferably 30 %, 40 %, 50 %, or 60 % or more, at a temperature from -20 °C to +80 °C, preferably from -10 °C to +50 °C, when the polymeric additive is added to the pyrolysis oil with a wax residue as described herein, when compared to the same pyrolysis oil with no polymeric additive.

- 15 The polymeric additive b) has a wax inhibition of greater than 1 % relative to the pyrolysis oil a) as determined by the cold finger test measured using CF-15 cold finger device manufactured by PSL with rack temperature set at 5 °C above the Wax Appearance Temperature (WAT) and finger temperature set 20 °C below the WAT for a test period of 24 hours as described in detail in the experimental part of the present invention. The wax inhibition is preferably greater than 5 %, 10 %, 15 %, 25 % or 30 % (measured according to the cold finger test described above and more detail in the experimental part).

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Plastic pyrolysis oil a)

- 25 The term “plastic pyrolysis oil” or “pyrolysis oil” as used herein includes any pyrolysis oil produced from the pyrolysis of plastics or plastic waste. Pyrolysis is a thermal cracking process that occurs in the complete or substantial absence of oxygen, at temperatures above 250 °C to convert plastic into energy, in the form of solid, liquid and gaseous fuels. The process breaks down polymer chains into smaller chains and molecules.

- 30 The plastic pyrolysis oil is preferably a plastic waste pyrolysis oil, namely a pyrolysis oil produced from plastic waste. The pyrolysis of plastic waste with a thermal degradation of plastic waste at different temperatures (300–900 °C), to produce liquid oil is for example described in Rehan *et al.*, 2017, Int. Biodeterior. Biodegrad. 119, 162–175.

- 35 Preferably, the plastic pyrolysis oil is a plastic pyrolysis oil and/or a plastic waste pyrolysis oil, wherein the plastic and plastic waste are both selected from polyolefins, more preferably polyolefins selected from high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) and a mixture thereof; polyethylene terephthalate (PET); polyvinyl chloride (PVC); polystyrene (PS); or a mixture thereof.

- 40 The term “polyolefin pyrolysis oil” and “polyolefin waste pyrolysis oil” as used herein defines an oil produced from the pyrolysis of polyolefins or waste polyolefin respectively, wherein the plastic and plastic waste are selected from high-density polyethylene (HDPE), low-density polyethylene (LDPE) and polypropylene (PP).

Pyrolysis oils having a wax content of at least 1 % by weight typically have problems regarding storage and transportation, due to the high pour point and high viscosity of the pyrolysis oil. The terms “wax residue” or “wax content” include that portion of the pyrolysis oil that comprises linear hydrocarbons containing 16 or more carbon atoms.

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In the context of the present invention, the term “linear hydrocarbons containing 16 or more carbon atoms” used herein means “n-paraffin waxes with C₁₆ or longer carbon chains”, namely, “n-paraffin waxes being a mixture of C₁₆ to C₁₉ n-paraffin waxes, C₂₀ to C₂₉ n-paraffin waxes, C₃₀ to C₃₉ n-paraffin waxes, and n-paraffin waxes with C₄₀ or longer carbon chains”.

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The pyrolysis oil a) of the composition of the present invention has a wax residue of 12 % by weight or less of n-paraffin waxes with C₁₆ or longer carbon chains, preferably from 0.01 % by weight to 12 % by weight of n-paraffin waxes with C₁₆ or longer carbon chains, more preferably from 0.05 % by weight to 12 % by weight of n-paraffin waxes with C₁₆ or longer carbon chains. The pyrolysis oil a) of the composition of the present invention may also preferably have a wax residue of 10 % by weight or less of n-paraffin waxes with C₁₆ or longer carbon chains, more preferably from 0.01 % to 10 % by weight of n-paraffin waxes with C₁₆ or longer carbon chains, even more preferably from 0.05 % by weight to 10 % by weight of n-paraffin waxes with C₁₆ or longer carbon chains based on the total weight of the plastic pyrolysis oil a).

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According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 12 % by weight of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 12 % by weight of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 12 % by weight of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 12 % by weight of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up to 12 % by weight or less, based on the total weight of the plastic pyrolysis oil.

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According to a preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 12 % by weight of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 12 % by weight of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 12 % by weight of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 12 % by weight of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 to 12 % by weight, based on the total weight of the plastic pyrolysis oil.

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According to another preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 10 % by weight of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 10 % by weight of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 10 % by weight of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 10 % by weight of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up to 10 % by weight or less, based on the total weight of the plastic pyrolysis oil.

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According to another preferred embodiment of the invention, the plastic pyrolysis oil a) preferably comprises from 0 % to 10 % by weight of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 10 % by weight of C₂₀ to C₂₉ n-

paraffin waxes, from 0 % to 10 % by weight of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 10 % by weight of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up from 0.01 to 10 % by weight, based on the total weight of the plastic pyrolysis oil.

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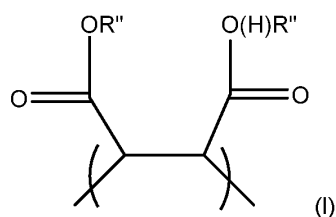
Advantageously, reducing or lowering the pour point or the viscosity or both of a pyrolysis oil makes it easier to transport and store a pyrolysis oil having a wax residue. In this way, the present invention obviates the current requirements to modify the reactor, or to modify the reaction process (for example, by the addition of a catalyst) when processing a pyrolysis oil having a wax residue that it is desired to maintain. In this way,

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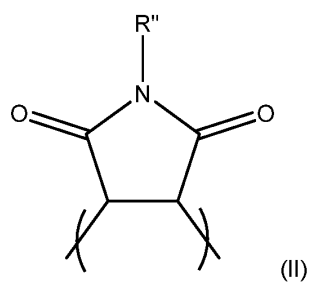
current plastic processing plants designed to expect the use of a wax residue pyrolysis oil can continue to operate without redesign.

Polymeric additive b)

- 15 The polymeric additive b) is a copolymer P) prepared by polymerizing a monomer composition comprising i) from 10 to 70 % by weight of monomers selected from alkyl maleate compound of Formula (I), maleimide compound of Formula (II) or a mixture thereof, based on the total weight of the copolymer P),



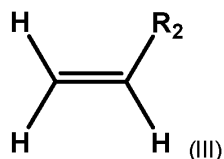
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wherein R'' in Formula (I) and Formula (II) is a linear or branched alkyl group having from 10 to 40 carbon atoms; and

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- ii) from 30 to 90 % by weight of one or more non-functionalized alpha-olefin of formula (III), based on the total weight of the copolymer P),



wherein R_2 is a linear alkyl group having from 8 to 40 carbon atoms, preferably from 10 to 40 carbon atoms, more preferably from 15 to 35 carbon atoms, even more preferably from 20 to 32 carbon atoms.

According to the present invention, the polymeric additive b) is one polymer P), or a mixture of one or more polymer P).

Within the context of the present invention, the monomer composition corresponds to the total amount of monomers to prepare the copolymer P).

In a preferred embodiment, the polymeric additive b) is a copolymer P) prepared by polymerizing a monomer composition comprising

- i) 10 to 70 % of alkyl maleate compound of Formula (I), based on the total weight of the copolymer, and
- ii) 30 to 90 % by weight of one or more non-functionalized alpha-olefin of formula (III), based on the total weight of the copolymer P).

Preferably R^1 in Formula (I) and Formula (II) is a linear or branched alkyl group having from 10 to 40 carbon atoms, more preferably from 12 to 30 carbon atoms, even more preferably from 18 to 22 carbon atoms.

Preferably R_2 in Formula (III) is a linear alkyl group having from 10 to 40 carbon atoms, more preferably from 10 to 35 carbon atoms, even more preferably from 10 to 32 carbon atoms.

The content of alkyl maleate i) in the copolymer P) is preferably from 20 to 50 % by weight, more preferably from 25 to 40% by weight, based on the total weight of the copolymer P).

The content of alpha-olefin ii) in the copolymer P) is preferably from 50 to 80 % by weight, more preferably from 60 to 75 % by weight, based on the total weight of the copolymer P).

In one embodiment the polymeric additive b) is a polymer prepared by polymerizing a monomer composition comprising C_{18} - C_{22} alkyl maleate and C_{20} - C_{32} non-functionalized alpha-olefin.

In another embodiment, the polymeric additive b) is a polymer prepared by polymerizing a monomer composition comprising C_{18} - C_{22} alkyl maleate and C_{20} - C_{24} non-functionalized alpha-olefin.

In a further embodiment, the polymeric additive b) is a polymer prepared by polymerizing a monomer composition comprising C_{18} - C_{22} alkyl maleate and C_{10} - C_{18} non-functionalized alpha-olefin.

A copolymer is a polymer formed from two or more different types of monomers linked in a polymeric chain.

According to the present invention, the polymeric additive b) is one polymer P), or a mixture of one or more polymer P). Preferably, the polymeric additive b) comprises one or more copolymers P), even more preferably copolymers P) selected from the group consisting of a polymer prepared by polymerizing a monomer composition comprising C₁₈-C₂₂ alkyl maleate and C₂₀-C₃₂ non-functionalized alpha-olefin, a polymer prepared by polymerizing a monomer composition comprising C₁₈-C₂₂ alkyl maleate and C₂₀-C₂₄ non-functionalized alpha-olefin, a polymer prepared by polymerizing a monomer composition comprising C₁₈-C₂₂ alkyl maleate and C₁₀-C₁₈ non-functionalized alpha-olefin, or a mixture thereof.

As used herein, the term "maleate" refers to esters of maleic acid. The term "alkyl maleate" refers to esters of maleic acid and aliphatic alcohols. The alkyl maleate described herein are characterized by the number of carbon atoms in the alkyl chain derived from the alcohol.

For example, the term "C₁₈-C₂₂ alkyl maleate" refers to esters of maleic acid and linear or branched alcohols having 18 to 22 carbon atoms. The term encompasses individual maleic esters with an alcohol of a particular length, and likewise a mixture of maleic esters with alcohols of different lengths. Likewise, the term "C₂₀-C₂₄ alkyl maleate" refers to esters of maleic acid with linear or branched alkyl chain having 20 to 24 carbon atoms. The term encompasses individual maleic esters with an alcohol of a particular length, and likewise mixtures of maleic esters with alcohols of different lengths.

Alpha-olefin is compound made up of hydrogen and carbon that contains one or more pairs of carbon atoms linked by a double bond. As used herein, the term C₁-C₄₀ olefin, C₁₀-C₁₈ olefin or C₂₀-C₃₂ olefin refers to an olefin comprising a linear, branched or cyclic residue with 1 to 40 carbon atoms, 10 to 18 carbon atoms or 20 to 32 carbon atoms, respectively.

As an optional component, the monomer composition to prepare the copolymer P) may contain further monomer iii) derived from one or more comonomers, or a mixture thereof.

Preferably, these comonomers iii) are selected from the list consisting of:

hydroxyalkyl (meth)acrylates, preferably hydroxyalkyl (meth)acrylates selected from 3-hydroxypropyl (meth)acrylate, 3,4-dihydroxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,5-dimethyl-1,6-hexanediol (meth)acrylate, 1,10 decanediol (meth)acrylate;

aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides, preferably aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides selected from N-(3-dimethyl-aminopropyl)methacrylamide, 3-diethylaminopentyl (meth)acrylate, 3-dibutyl-aminohexadecyl (meth)acrylate;

nitriles of (meth)acrylic acid and other nitrogen-containing (meth)acrylates, preferably nitriles of (meth)acrylic acid and other nitrogen-containing (meth)acrylates selected from N-(methacryloyloxyethyl)diisobutylketimine, N-(methacryloyloxyethyl)dihexadecyl-ketimine, (meth)acryloylamidoacetonitrile, 2-methacryloyloxyethylmethylcyanamide, cyanomethyl

(meth)acrylate;

aryl (meth)acrylates like benzyl (meth)acrylate or phenyl (meth)acrylate, where the acryl residue in each case can be unsubstituted or substituted up to four times;

carbonyl-containing (meth)acrylates, preferably carbonyl-containing (meth)acrylates selected from 2-carboxyethyl (meth)acrylate, carboxymethyl (meth)acrylate, N-methacryloyloxy-formamide, acetonyl (meth)acrylate, N-methacryloyl-2 pyrrolidinone, N-(2-methacryloyloxyethyl)-2-pyrrolidinone, N-(3-methacryloyloxy-propyl)-2-pyrrolidinone, N-(2-methacryloyloxy-pentadecyl)-2-pyrrolidinone, N-(3-methacryloyloxy-heptadecyl)-2-pyrrolidinone;

(meth)acrylates of ether alcohols, preferably (meth)acrylates of ether alcohols selected from tetrahydrofurfuryl (meth)acrylate, methoxyethoxyethyl (meth)acrylate, 1-butoxypropyl (meth)acrylate, cyclohexyloxyethyl (meth)acrylate, propoxyethoxyethyl (meth)acrylate, benzyloxyethyl (meth)acrylate, furfuryl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxyethyl (meth)acrylate, 2-methoxy-2-ethoxypropyl (meth)acrylate, ethoxylated (meth)acrylates, 1-ethoxybutyl (meth)acrylate, methoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxy-2-ethoxyethyl (meth)acrylate, esters of (meth)acrylic acid and methoxy polyethylene glycols;

(meth)acrylates of halogenated alcohols, preferably (meth)acrylates of halogenated alcohols selected from 2,3-dibromopropyl (meth)acrylate, 4-bromophenyl (meth)acrylate, 1,3-dichloro-2-propyl (meth)acrylate, 2-bromoethyl (meth)acrylate, 2-iodoethyl (meth)acrylate, chloromethyl (meth)acrylate;

oxiranyl (meth)acrylate, preferably oxiranyl (meth)acrylate selected from 2,3-epoxybutyl (meth)acrylate, 3,4-epoxybutyl (meth)acrylate, 10,11-epoxyundecyl (meth)acrylate, 2,3-epoxycyclohexyl (meth)acrylate, oxiranyl (meth)acrylates such as 10,11-epoxyhexadecyl (meth)acrylate, glycidyl (meth)acrylate;

phosphorus-, boron- and/or silicon-containing (meth)acrylates, preferably phosphorus-, boron- and/or silicon-containing (meth)acrylates selected from 2-(dimethyl-phosphato)propyl (meth)acrylate, 2-(ethylphosphito)propyl (meth)acrylate, 2-dimethylphosphinomethyl (meth)acrylate, dimethylphosphonoethyl (meth)acrylate, diethylmethacryloyl phosphonate, dipropylmethacryloyl phosphate, 2-(dibutylphosphono)ethyl (meth)acrylate, 2,3-butenemethacryloylethyl borate, methyldiethoxymethacryloylethoxysilane, diethylphosphatoethyl (meth)acrylate;

sulfur-containing (meth)acrylates, preferably sulfur-containing (meth)acrylates selected from ethylsulfinylethyl (meth)acrylate, 4-thio-cyanatobutyl (meth)acrylate, ethylsulfonylethyl (meth)acrylate, thiocyanatomethyl (meth)acrylate, methylsulfinylmethyl (meth)acrylate, bis(methacryloyloxyethyl) sulfide;

heterocyclic (meth)acrylates, preferably heterocyclic (meth)acrylates selected from 2-(1-imidazolyl)ethyl (meth)acrylate, oxazolidinylethyl (meth)acrylate, N-methacryloylmorpholine and 2-(4-morpholinyl)ethyl (meth)acrylate;

maleic acid and maleic acid derivatives, preferably mono- and diesters of maleic acid, maleic anhydride, methylmaleic anhydride, maleinimide, methylmaleinimide;

fumaric acid and fumaric acid derivatives, preferably mono- and diesters of fumaric acid;

vinyl halides, preferably vinyl halides selected from vinyl chloride, vinyl fluoride, vinylidene chloride and vinylidene fluoride;

- vinyl esters, preferably vinyl acetate;
- vinyl monomers containing aromatic groups, preferably vinyl monomers containing aromatic groups selected from styrene, substituted styrenes with an alkyl substituent in the side chain, such as alpha-methylstyrene and alpha-ethylstyrene, substituted styrenes with an alkyl substituent on the ring such as vinyltoluene and p-methylstyrene, halogenated styrenes such as monochlorostyrenes, dichlorostyrenes, tribromostyrenes and tetrabromostyrenes;
- heterocyclic vinyl compounds, preferably heterocyclic vinyl compounds selected from 2-vinylpyridine, 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, 2-vinylpyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinyloxolane, vinylfuran, vinylthiophene, vinylthiolane, vinylthiazoles and hydrogenated vinylthiazoles, vinyloxazoles and hydrogenated vinyloxazoles;
- vinyl and isoprenyl ethers;
- methacrylic acid and acrylic acid, or a mixture thereof.

In an embodiment, the comonomer iii) is styrene.

- As used herein, the term “(meth)acrylate” refers to esters of acrylic and methacrylic acid, and to mixtures thereof. The term “alkyl (meth)acrylate” refers to esters of (meth)acrylic acid and aliphatic alcohols. The alkyl (meth)acrylates described herein are characterized by the number of carbon atoms in the alkyl chain derived from the alcohol.

- The proportion of comonomers in the monomer composition can vary depending on the use and property profile of the polymeric additive b). Preferably, the content of comonomer iii) in the monomer composition to prepare the copolymer P) is in the range from 0 to 20 % by weight, preferably from 0 to 15 % by weight, more preferably from 0.1 to 15 % by weight, based on the total weight of the monomer composition.

- Preferably, the amounts of monomers and comonomers sum up from 95 to 100 % by weight, more preferably sum up to 100 % by weight, based on the total weight of the monomer composition.

- Preferably, the weight-average molecular weight of the polymeric additive b) is from 8,000 to 600,000 g/mol, preferably from 8,000 to 300,000 g/mol even more preferably from 8,000 to 100,000 g/mol and most preferably from 10,000 to 50,000 g/mol, determined by gel permeation chromatography using poly(methyl-methacrylate) calibration standards according to DIN 55672-1 (as described in more details below).

Preparation process for polymeric additive b)

- Preparation of olefin-co-ester of maleic acid and olefin-co-imide-derivative of maleic acid are well known in the art and described in literature such as in US10738138B2 and US4192930.

Olefin-co-ester of maleic acid polymer: These polymers include are a combination of one or more olefins and an ester of maleic acid or a maleic acid derivative such as citraconic acid, nadic acid. Such polymers can be made by copolymerizing an unsaturated ester of maleic anhydride (or a derivative thereof) with one or more alpha-olefins or by reacting an alcohol (a hydroxyl-bearing moiety) with a copolymer of maleic anhydride (or a derivative thereof) and one or more alpha-olefins.

R" represents the alkyl group from the alcohol or hydroxy bearing moiety used to create the ester of maleic anhydride. Depending on the esterification conversion, the R" group may appear once or twice in the maleic anhydride derivative portion of the polymer.

The term alkyl maleate refers to esters of maleic acid or a maleic acid derivative. The structure is represented by Formula (I).

"C₁₈-C₂₂ alkyl maleate" refers to esters of maleic acid or a maleic acid derivative where the alkyl chain length is 18-22 carbon atoms. The esterification of the maleic anhydride can be partial or full and R" in Formula (I) is a linear or branched alkyl group having from 18 to 22 carbon atoms.

Olefin-co-imide-derivative of maleic acid polymers: These polymers are a combination of one or more olefins and an N-alkyl, N-aryl, or N-alkaryl maleimide or maleimide derivative. Such polymers may be made by copolymerizing an unsaturated imide with one or more alpha-olefins, or reacting an amine with a copolymer of maleic anhydride (or a derivative thereof) and one or more alpha-olefins.

The term alkyl maleimide refers to derivatives of the reaction of maleic anhydride and ammonia or an amine derivative. The structure is represented by Formula (II).

"C₁₈-C₂₂ alkyl maleimide" refers to refers to derivatives of the reaction of maleic anhydride and ammonia or an amine derivative. The imidization of the maleic anhydride can be partial or full and R" in Formula (II) is a linear or branched alkyl group having from 18 to 22 carbon atoms.

The polymers of the polymeric additive b) can be obtained by free-radical polymerization and related processes, for example ATRP (Atom Transfer Radical Polymerization), RAFT (Reversible Addition Fragmentation Chain Transfer) or NMP processes (nitroxide-mediated polymerization). More preferably, the polymers b) of the invention are prepared by free-radical polymerization.

Customary free-radical polymerization is described, inter alia, in Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition. In general, a polymerization initiator is used for this purpose. The usable initiators include the azo initiators widely known in the technical field, such as 2,2'-azo-bis-isobutyronitrile (AIBN), 2,2'-azo-bis-(2-methylbutyronitrile) (AMBN) and 1,1-azobiscyclohexanecarbonitrile, and also peroxy compounds such as methyl ethyl ketone peroxide, acetylacetone peroxide, dilauryl peroxide, tert-butyl peroxy-pivalate, tert-butyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, ketone peroxide, tert-butyl peroctoate, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, tert-butyl-peroxybenzoate, tert-butyl-peroxyisopropylcarbonate, 2,5-bis(2-ethylhexanoyl-peroxy)-2,5-dimethylhexane, tert-butyl-peroxy-2-ethylhexanoate, tert-butyl-peroxy-3,5,5-trimethylhexanoate, dicumyl

peroxide, 1,1-bis(tert-butyl-peroxy)cyclohexane, 1,1-bis(tert-butyl-peroxy)-3,3,5-trimethylcyclohexane, cumyl hydroperoxide, tert-butyl-hydroperoxide, bis(4-tert-butylcyclohexyl) peroxydicarbonate, or a mixture of two or more of the aforementioned compounds with one another, and mixtures of the aforementioned compounds with compounds which have not been mentioned but can likewise form free radicals. Preferred initiator for the preparation of polymeric additive b) is tert-butyl-peroxy-2-ethylhexanoate.

Furthermore, a chain transfer agent can be used. It is well-known in the art that a good way to control the molecular weight of a polymer chain is to use chain transfer agents during the polymerization synthesis. Chain transfer agents are molecules with a weak chemical bond which facilitate the chain transfer reaction. During the chain transfer reaction, the radical of the polymer chain abstracts a hydrogen from the chain transfer agent, resulting in the formation of a new radical on the sulfur atom of the chain transfer agent capable of further propagation. Common chain transfer agents are organic compounds comprising SH groups such as n-butyl mercaptan, n-octyl mercaptan, n-dodecyl mercaptan, tert-dodecyl mercaptan, butylthiol glycolate, and octylthiol glycolate. A preferred chain transfer agent is selected from n-dodecyl mercaptan, tert-dodecyl mercaptan or a mixture thereof, most preferably n-dodecyl mercaptan.

Preferably, the monomer mixture to prepare the polymeric additive b) of the present invention may comprise 0.05 to 7 % by weight, preferably 0.05 to 5 % by weight and more preferably 0.1 to 1 % by weight of initiator based on the total weight of the monomer composition to prepare the polymeric additive b). The amount of chain transfer agents to prepare the polymeric additive b) is in the range of 0 to 5 % by weight, preferably 0.01 to 5 % by weight and more preferably 0.05 to 4 % by weight, based on the total weight of the monomer composition.

The polymerization may be carried out at standard pressure, reduced pressure or elevated pressure. The polymerization temperature is not critical. Conventionally the polymerization temperature may be in the range of 0 °C to 200 °C, preferably 0 °C to 140 °C, and more preferably 60 °C to 130 °C.

The polymerization may be carried out with or without solvent. The term solvent is to be understood here in a broad sense. The polymerization is preferably carried out in a nonpolar solvent. These include hydrocarbon solvents, for example aromatic solvents such as toluene, benzene and xylene, saturated hydrocarbons, for example cyclohexane, heptane, octane, nonane, decane, dodecane, which may also be present in branched form, or a mixture thereof, such as naphtha. These solvents may be used individually and as a mixture. Particularly preferred solvents are mineral oils, diesel fuels of mineral origin, naphthenic solvents, natural vegetable and animal oils, biodiesel fuels and synthetic oils (e.g. ester oils such as dinonyl adipate), or a mixture thereof.

Plastic pyrolysis oil composition according to the invention

Preferably, the composition comprises polymeric additive b) at a concentration of from 0.001 % by weight to 1 % by weight of polymeric additive b), based on the total weight of the pyrolysis oil composition. More preferably, the composition comprises polymeric additive b) at a concentration of from 0.005 % by weight to 0.8 % by weight of polymeric additive b), based on the total weight of the pyrolysis oil composition. Even

more preferably, the composition comprises polymeric additive b) at a concentration of from 0.005 % by weight to 0.5 % by weight of polymeric additive b), based on the total weight of the pyrolysis oil composition.

5 In specific embodiments, the plastic pyrolysis oil is a polyolefin pyrolysis oil, wherein the pyrolysis oil is produced at least partially from the pyrolysis of one or more polyolefins. Optionally, the pyrolysis oil is a polyethylene and/or polypropylene pyrolysis oil, wherein the pyrolysis oil is produced at least partially from the pyrolysis of polyethylene and/or polypropylene.

10 Preferably, pyrolysis oil a) and polymeric additive b) sum up from 90 to 98 % by weight, based on the total weight of the pyrolysis oil composition.

15 The composition according to the invention may further comprise an additive c), wherein additive c) is any of the group comprising scale inhibitors, corrosion inhibitors, oxygen scavengers, biocides, emulsion breakers, antifoam agents, drag reducing agents, hydrate inhibitors, paraffin dispersants, asphaltene control agents, a pour point depressant other than copolymer P), or a mixture thereof.

20 Preferably, then the amounts of compounds a), b), c) sum up to 90 to 99 % by weight, more preferably sum up to 95 to 98 % by weight, even more preferably sum up to 100 % by weight, based on the total weight of the composition.

Any specific embodiments or preferred aspects of the polymeric additive b), polymer P) and pyrolysis oil a), as listed herein, apply to the plastic pyrolysis oil composition according to the invention.

Preparation of the plastic pyrolysis oil composition according to the invention

25 The invention also provides a method of manufacturing a composition, as described above, comprising the steps of:

- 30 providing a plastic feedstock;
pyrolyzing the plastic feedstock to generate a plastic pyrolysis oil a);
preparing a polymeric additive b); and
adding polymeric additive b) to the plastic pyrolysis oil a).

35 The method for preparing the plastic pyrolysis oil composition according to the invention preferably comprises the step of mixing the pyrolysis oil and the polymeric additive. More preferably, the method comprises the step of mixing for at least 5, 10, 15, 25 or 30 minutes.

40 The method may also comprise a step of heating the pyrolysis oil and the polymeric additive, preferably to at least 40 °C, even more preferably to at least 50 °C, most preferably to at least 60 °C. The method may comprise heating and mixing the pyrolysis oil simultaneously.

The method of the present invention is able to reduce the pour point of the pyrolysis oil, or to reduce the viscosity of the pyrolysis oil, or to achieve both. The resulting pyrolysis oil is thereby easier to transport and

store compared to the pyrolysis oil with no polymeric additive. In addition, no modifications to plant design are required to provide a pyrolysis oil having a reduced pour point or viscosity, as this can be achieved by adding the polymeric additive of the present invention after the pyrolysis oil is made.

- 5 In specific embodiments, the method comprises the step of providing a plastic feedstock comprising one or more polyolefins and producing the pyrolysis oil at least partially from said feedstock. The polyolefins may be polyethylene and/or polypropylene.

Use of the polymeric additive b)

10

The present invention also extends to the use of a polymeric additive as defined herein to reduce the pour point of a plastic pyrolysis oil or to reduce the viscosity of the pyrolysis oil, or to do both.

- 15 Preferably, the pour point of a pyrolysis oil is reduced by at least 1 °C, more preferably by at least 2 °C, even more preferably by at least 3 °C, most preferably by at least 5 °C, by the addition of the polymeric additive as described herein, when compared to the same pyrolysis oil with no polymeric additive.

- 20 The reduction in viscosity is preferably of at least 10, preferably 20 or 30, even more preferably 40, 50, or 60 % or more, at a temperature from 0 to 80 °C, preferably at either 40 °C, 45 °C or 50 °C, or at a temperature from 40 to 50 °C, when the polymeric additive is added to the pyrolysis oil with a wax residue as described herein, when compared to the same pyrolysis oil with no polymeric additive.

Method for transporting or storing a plastic pyrolysis oil

- 25 Advantageously, as exemplified in the experimental part, the composition according to the invention has a lower pour point and viscosity in comparison to untreated pyrolysis oils. Pyrolysis oils usually solidify making them difficult to transport. In contrast, pyrolysis oils with lower pour point will remain liquid at lower temperatures, thus making them easier to transport and heat does not need to be applied to the composition before transportation and storage.

30

The present invention also extends to a method of transporting or storing a plastic pyrolysis oil a) comprising the step of adding a polymeric additive b) to the pyrolysis oil to form the composition described herein.

- 35 By reducing the pour point of the pyrolysis oil comprising a wax residue of 12 % by weight or less of n-paraffin waxes with C₁₆ or longer carbon chains, or by reducing the viscosity of such pyrolysis oil, or doing both, the manufacturer or user of the pyrolysis oil can maintain current transportation or storage conditions of pyrolysis oils having a total wax content of 12 % by weight or less of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil, by using their existing plant design, or possibly lower the transportation or storage conditions of high or higher wax residue pyrolysis oils using existing plant design, i.e. reduced OPEX.
- 40

The present invention provides a method for transporting or/and storing a plastic pyrolysis oil a) in liquid form at a temperature in the range -20 °C to +50 °C.

In the context of the present invention, all details provided herein above on the composition, pyrolysis oil and polymeric additive do also apply for the method according to the invention.

EXPERIMENTAL PART

The invention is further illustrated in detail hereinafter with reference to examples and comparative examples, without any intention to limit the scope of the present invention.

Methods

In the present invention, the weight-average molecular weights (M_w) and the number-average molecular weights (M_n) of the copolymers (polymeric additives b)) were determined by gel permeation chromatography (GPC) using poly(methyl-methacrylate) calibration standards according to DIN 55672-1 using the following measurement conditions:

Column: the column set consists of a precolumn and 5 SDV columns as disclosed in Table 1:

Table 1

No.	Type	Dimension
Precolumn	SDV 10 μ	8 X 50 mm
Column 1	SDV LXL 10 μ	8 X 300 mm
Column 2	SDV LinL 10 μ	8 X 300 mm
Column 3	SDV 100Å 10 μ	8 X 300 mm
Column 4	SDV 100Å 10 μ	8 X 300 mm
Column 5	KF-800D	8 X 100 mm

Instruments: Agilent 1100 Series Pump; PSS SECcurity Inline-Degaser; Agilent 1260 Series Autosampler; Agilent 1100 Series RI-Detector; Agilent 1260 Series UV-Detector; Techlab column oven;

Oven temperature: 35 °C;

Standards: poly(methyl-methacrylate) (so called PMMA) calibration standards;

Eluent: tetrahydrofuran (THF);

Flow rate: 1 mL/min;

Injected volume: 100 μ L;

Detection: RI at a temperature of 35 °C and UV at a wavelength of 239 nm.

Viscosity was measured using a Discovery HR20 TA instruments rheometer using a 2° cone and Peltier plate geometry. The shear rate was 10x1/s (or s⁻¹). The temperature ramp was 1°C per minute.

Wax content was measured using a Differential Scanning Calorimeter from TA Instruments and analysis via TRIOS software.

Determination of wax species was carried out using an Agilent 6890 series High Temperature Gas Chromatograph.

- 5 Pour points were measured according to ASTM D97 in 1 °C steps. The test involves cooling the pyrolysis oil composition at a defined cooling rate and measuring the temperature at which the composition can no longer be poured from a vessel.

Preparation of the polymeric additives

- 10 The polymeric additives OMAC1, OMAC2, OMAC3, OMAC5, and OMAC6 were prepared according to Example 1 (Step 1 and Step 2b) in US10,738,138, using the weight ratios of monomers as shown in Table 2 below.

- 15 The polymeric additive OMAC4 was prepared according to Example 1 (Step 1 and Step 2a) in US10,738,138, using the weight ratios of monomers as shown in Table 2.

Table 2: Monomer composition, polymer content and weight-average molecular weight of different polymeric additives b) for pyrolysis oils according to the invention

	Polymer		OMAC1	OMAC2	OMAC3	OMAC4	OMAC5	OMAC6
Polymer components	C ₁₈₋₂₂ alkyl maleate	[wt%]	32	43	50		15	25
	C _{10-C18} olefin	[wt%]			50			
	C _{20-C24} olefin	[wt%]		57				
	C ₂₀₋₃₂ olefin	[wt%]	68			51	85	75
	C _{18-C22} alkyl maleimide	[wt%]				49		
	Polymer content	[wt%]	70	70	75	70	70	70
	Weight average molecular weight	[kg/mol]	16	14	18	17	15	14

20

After polymerization, the solvent is not removed and therefore the resulting polymer is mixed with the oil of polymerization. The polymer content of the polymeric additive is provided in Table 2 for the reproducibility of examples.

- 25 Untreated pyrolysis oils:

Table 3 below shows the characteristics of some untreated pyrolysis oils, wherein the pyrolysis oils A, B, D and G are polyolefin pyrolysis oils produced from the pyrolysis of polyolefins which include high-density polyethylene, low-density polyethylene and polypropylene.

30

Table 3: Characteristics of untreated plastic pyrolysis oil (namely, before addition of a polymeric additive of the present invention or a comparative polymeric additive)

Property		Pyrolysis Oil A	Pyrolysis Oil B	Pyrolysis Oil D	Pyrolysis Oil G
Pour Point	[°C]	51	0	18	51
Wax Appearance Temperature	[°C]	59	48	55	47
Wax Disappearance Temperature	[°C]	71	53	65	57
C ₁₂ -C ₁₅ n-hydrocarbons	[wt%]	12.2	0.4	0.8	1.2
C ₁₆ -C ₁₉ n-paraffins	[wt%]	1.6	0.9	1.5	1.1
C ₂₀ -C ₂₉ n-paraffins	[wt%]	9.1	0.4	2	1.7
C ₃₀ -C ₃₉ n-paraffins	[wt%]	3.6	0.2	3.7	0.6
>C ₃₉ n-paraffins	[wt%]	0.5	0	2.2	0.05
Total C ₁₆ or greater n-paraffins	[wt%]	14.8	1.5	9.4	3.45

5

Preparation of compositions according to the invention

Examples 1, Example 8, Example 15, and Example 22 are plastic pyrolysis oils before the addition of any polymeric additive according to the invention (untreated pyrolysis oil).

10

Example 2 was prepared by adding 0.1 g of OMAC1 to 99.9 g of Pyrolysis Oil A. The two components were mixed using an overhead stirrer for 30 minutes while being heated on a hot plate set to 65 °C.

The other composition examples 3-7, 9-14, 16-21, and 23-28 and were prepared in a similar manner as Example 2 using the t polymeric additives and amount indicated in Tables 4-7 below.

15

Table 4: Comparative pyrolysis oil compositions compared to the untreated Pyrolysis oil A

Example #		1	2	3	4	5	6	7
Polymer		none	OMAC1	OMAC2	OMAC3	OMAC4	OMAC5	OMAC6
Polymer amount	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil A amount	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	51	42	40	45	43	45	44
PP Reduction	[°C]	n/a	9	11	6	8	6	7
Viscosity, 40°C	[cP]	925	976	2412	3054	5988	3035	985
Viscosity Reduction, 40°C	[%]	n/a	-6	-161	-230	-547	-228	-6

20

n/a: not applicable (baseline) n.m.: not measured

Table 5: Pyrolysis oil compositions according to invention compared to the untreated Pyrolysis oil B

Example #		8	9	10	11	12	13	14
Polymer		none	OMAC1	OMAC2	OMAC3	OMAC4	OMAC5	OMAC6
Polymer amount	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil B amount	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	0	-45	-39	-42	-45	-48	-48
PP Reduction	[°C]	n/a	45	39	42	45	48	48
Viscosity, -10°C	[cP]	6370	4537	3250	4107	4992	1453	2426
Viscosity Reduction, -10°C	[%]	n/a	29	49	36	22	77	62

n/a: not applicable (baseline) n.m.: not measured

5 Table 6: Pyrolysis oil compositions according to invention compared to the untreated Pyrolysis oil D

Example #		15	16	17	18	19	20	21
Polymer		none	OMAC1	OMAC2	OMAC3	OMAC4	OMAC5	OMAC6
Polymer amount	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil D amount	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	18	6	9	12	6	3	3
PP Reduction	[°C]	n/a	12	9	6	12	15	15
Viscosity, 10°C	[cP]	145981	33420	6122	1789	14235	18432	31143
Viscosity Reduction, 10°C	[%]	n/a	77	96	99	90	87	79

n/a: not applicable (baseline) n.m.: not measured

Table 7: Pyrolysis oil compositions according to invention compared to the untreated Pyrolysis oil G

Example #		22	23	24	25	26	27	28
Polymer		none	OMAC1	OMAC2	OMAC3	OMAC4	OMAC5	OMAC6
Polymer amount	[g]	0	0.1	0.1	0.1	0.1	0.1	0.1
Pyrolysis Oil G amount	[g]	100	99.9	99.9	99.9	99.9	99.9	99.9
PP	[°C]	51	15	42	42	45	45	42
PP Reduction	[°C]	n/a	36	9	9	6	6	9
Viscosity, 40°C	[cP]	59973	922	967	845	2404	3208	770
Viscosity Reduction, 40°C	[%]	n/a	98.5	98.4	98.6	96	94.7	98.7

10

n/a: not applicable (baseline) n.m.: not measured

Results

Table 4 shows that addition of OMAC copolymers into a pyrolysis oil with a content of more than 14 wt% of C₁₆ or greater n-paraffins, an undesirable increase in viscosity is observed. Examples 2-7 show that the viscosity of Pyrolysis Oil A, treated with the OMAC copolymers, disadvantageously increases significantly from 6 to 547 %. This large increase in viscosity would make the oil much more difficult to handle and transport.

In contrast, when the OMAC polymers of the invention are combined with a pyrolysis oil having a content of 12 wt% or less of C₁₆ or greater n-paraffins, a reduction in viscosity, as well as a reduction in pour point are advantageously both achieved when compared to the same pyrolysis oil with no polymeric additive. This is the most desirable outcome where the treated pyrolysis oil will flow at a lower temperature (reduced pour point) and have a lower viscosity for improved handling properties.

Similarly, Examples 9-14 demonstrate how the OMAC copolymers achieve this reduction in pour point and viscosity when added to Pyrolysis Oil B. Compared to the untreated oil (Example 8), Examples 9-14 have a 39-48 °C lower pour point and 29-77 % reduction in viscosity.

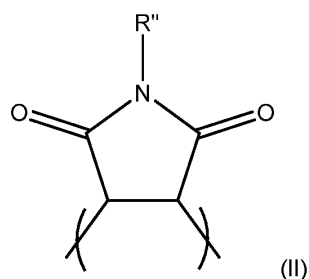
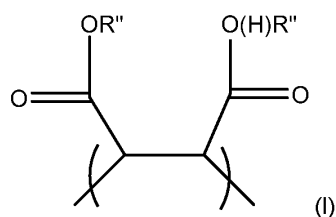
The same is true for Examples 16-21, which demonstrate how the OMAC copolymers achieve this reduction in pour point and viscosity when added to Pyrolysis Oil D. Compared to the untreated oil (Example 15), Examples 16-21 have a 6-15 °C lower pour point and 77-99 % reduction in viscosity.

Examples 23-28 demonstrate how the OMAC copolymers achieve this reduction in pour point and viscosity when added to Pyrolysis Oil G. Compared to the untreated oil (Example 22), Examples 23-28 have a 6-36 °C lower pour point and >95 % reduction in viscosity.

It has been shown that the OMAC copolymers are specifically most effective in the treatment of plastic pyrolysis oils from a plastic pyrolysis process having a content of 12 wt% or less of C₁₆ or greater n-paraffins. The experimental data demonstrate how the addition of OMAC copolymers to plastic pyrolysis oils having a content of 12 wt% or less of C₁₆ or greater n-paraffins advantageously keep them liquid, improving the transport and storage of these oils before the cracking process, by effectively lowering their pour point and/or lowering their viscosity.

CLAIMS

1. A composition comprising a plastic pyrolysis oil a) and a polymeric additive b), wherein the polymeric additive b) is a copolymer P) prepared by polymerizing a monomer composition comprising
- 5 i) 10 to 70 % by weight of monomers selected from alkyl maleate compound of Formula (I), maleimide compound of Formula (II) or a mixture thereof, based on the total weight of the copolymer,

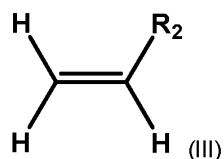


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wherein R'' in Formula (I) and Formula (II) is a linear or branched alkyl group having from 10 to 40 carbon atoms, preferably from 10 to 30 carbon atoms, more preferably from 12 to 30 carbon atoms, even more preferably from 18 to 22 carbon atoms;

15 and

ii) 30 to 90 % by weight of a non-functionalized alpha-olefin of Formula (III) or a mixture thereof, based on the total weight of the copolymer,



20

wherein R₂ is a linear alkyl group having from 8 to 40 carbon atoms, preferably from 10 to 40 carbon atoms, more preferably from 15 to 35 carbon atoms, even more preferably from 20 to 32 carbon atoms, and

25 wherein the plastic pyrolysis oil a) comprises 12 % by weight or less of n-paraffin waxes with C₁₆ or longer carbon chains, based on the total weight of the plastic pyrolysis oil a).

2. The composition according to claim 1, wherein the polymeric additive b) is a copolymer P) prepared by polymerizing a monomer composition comprising
- i) 10 to 70 % of alkyl maleate compound of Formula (I), based on the total weight of the copolymer, and
 - 5 ii) 30 to 90 % by weight of the non-functionalized alpha-olefin of Formula (III), based on the total weight of the copolymer P).
3. The composition according to claim 1 or 2, wherein the monomer composition of copolymer P) comprises 20 to 50 % by weight, preferably 25 to 40 % by weight, of alkyl maleate compound of Formula (I), based on the total weight of the copolymer P).
4. The composition according to any one of the preceding claims, wherein the monomer composition of copolymer P) comprises from 50 to 80 % by weight, preferably from 60 to 75 % by weight, of non-functionalized alpha-olefin of Formula (III), based on the total weight of the copolymer P).
5. The composition according to any one of the preceding claims, wherein the copolymer P) is selected from the group consisting of a polymer prepared by polymerizing a monomer composition comprising C₁₈-C₂₂ alkyl maleate and C₂₀-C₃₂ non-functionalized alpha-olefin, or a polymer prepared by polymerizing a monomer composition comprising C₁₈-C₂₂ alkyl maleate and C₂₀-C₂₄ non-functionalized alpha-olefin, or a polymer prepared by polymerizing a monomer composition comprising C₁₈-C₂₂ alkyl maleate and C₁₀-C₁₈ non-functionalized alpha-olefin, or a mixture thereof.
6. The composition according to any one of the preceding claims, wherein the monomer composition to prepare the copolymer P) further comprises monomers iii) selected from the group consisting of:
- 25 hydroxyalkyl (meth)acrylates, preferably hydroxyalkyl (meth)acrylates selected from 3-hydroxypropyl (meth)acrylate, 3,4-dihydroxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,5-dimethyl-1,6-hexanediol (meth)acrylate, 1,10 decanediol (meth)acrylate;
 - 30 aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides, preferably aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides selected from N-(3-dimethyl-aminopropyl)methacrylamide, 3-diethylaminopentyl (meth)acrylate, 3-dibutyl-aminohexadecyl (meth)acrylate;
 - 35 nitriles of (meth)acrylic acid and other nitrogen-containing (meth)acrylates, preferably nitriles of (meth)acrylic acid and other nitrogen-containing (meth)acrylates selected from N-(methacryloyloxyethyl)diisobutylketimine, N-(methacryloyloxyethyl)dihexadecyl-ketimine, (meth)acryloylamidoacetonitrile, 2-methacryloyloxyethylmethylcyanamide, cyanomethyl (meth)acrylate;
 - aryl (meth)acrylates like benzyl (meth)acrylate or phenyl (meth)acrylate, where the acryl residue in each case can be unsubstituted or substituted up to four times;
 - 40 carbonyl-containing (meth)acrylates, preferably carbonyl-containing (meth)acrylates selected from 2-carboxyethyl (meth)acrylate, carboxymethyl (meth)acrylate, N-methacryloyloxy-formamide, acetyl (meth)acrylate, N-methacryloyl-2 pyrrolidinone, N-(2-methacryloyloxyethyl)-2-pyrrolidinone, N-(3-methacryloyloxy-propyl)-2-pyrrolidinone, N-(2-methacryloyloxy-pentadecyl)-

- 2-pyrrolidinone, N-(3 methacryloyloxyheptadecyl-2-pyrrolidinone;
(meth)acrylates of ether alcohols, preferably (meth)acrylates of ether alcohols selected from tetrahydrofurfuryl (meth)acrylate, methoxyethoxyethyl (meth)acrylate, 1-butoxypropyl (meth)acrylate, cyclohexyloxyethyl (meth)acrylate, propoxyethoxyethyl (meth)acrylate, benzyloxyethyl (meth)acrylate, furfuryl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxyethyl (meth)acrylate, 2-methoxy-2-ethoxypropyl (meth)acrylate, ethoxylated (meth)acrylates, 1-ethoxybutyl (meth)acrylate, methoxyethyl (meth)acrylate, 2-ethoxy-2-ethoxy-2-ethoxyethyl (meth)acrylate, esters of (meth)acrylic acid and methoxy polyethylene glycols;
(meth)acrylates of halogenated alcohols, preferably (meth)acrylates of halogenated alcohols selected from 2,3-dibromopropyl (meth)acrylate, 4 bromophenyl (meth)acrylate, 1,3-dichloro-2-propyl (meth)acrylate, 2-bromoethyl (meth)acrylate, 2-iodoethyl (meth)acrylate, chloromethyl (meth)acrylate;
oxiranyl (meth)acrylate, preferably oxiranyl (meth)acrylate selected from 2, 3-epoxybutyl (meth)acrylate, 3,4-epoxybutyl (meth)acrylate, 10,11-epoxyundecyl (meth)acrylate, 2,3-epoxycyclohexyl (meth)acrylate, oxiranyl (meth)acrylates such as 10,11-epoxyhexadecyl (meth)acrylate, glycidyl (meth)acrylate;
phosphorus-, boron- and/or silicon-containing (meth)acrylates, preferably phosphorus-, boron- and/or silicon-containing (meth)acrylates selected from 2-(dimethyl-phosphato)propyl (meth)acrylate, 2-(ethylphosphito)propyl (meth)acrylate, 2 dimethylphosphinomethyl (meth)acrylate, dimethylphosphonoethyl (meth)acrylate, diethylmethacryloyl phosphonate, dipropylmethacryloyl phosphate, 2 (dibutylphosphono)ethyl (meth)acrylate, 2,3-butylenemethacryloylethyl borate, methyldiethoxymethacryloylethoxysilane, diethylphosphatoethyl (meth)acrylate;
sulfur-containing (meth)acrylates, preferably sulfur-containing (meth)acrylates selected from ethylsulfinylethyl (meth)acrylate, 4-thio-cyanatobutyl (meth)acrylate, ethylsulfonylethyl (meth)acrylate, thiocyanatomethyl (meth)acrylate, methylsulfinylmethyl (meth)acrylate, bis(methacryloyloxyethyl) sulfide;
heterocyclic (meth)acrylates, preferably heterocyclic (meth)acrylates selected from 2-(1-imidazolyl)ethyl (meth)acrylate, oxazolidinylethyl (meth)acrylate, N-methacryloylmorpholine and 2-(4-morpholinyl)ethyl (meth)acrylate;
maleic acid and maleic acid derivatives, preferably mono- and diesters of maleic acid, maleic anhydride, methylmaleic anhydride, maleinimide, methylmaleinimide;
fumaric acid and fumaric acid derivatives, preferably mono- and diesters of fumaric acid;
vinyl halides, preferably vinyl halides selected from vinyl chloride, vinyl fluoride, vinylidene chloride and vinylidene fluoride;
vinyl esters, preferably vinyl acetate;
vinyl monomers containing aromatic groups, preferably vinyl monomers containing aromatic groups selected from styrene, substituted styrenes with an alkyl substituent in the side chain, such as alpha-methylstyrene and alpha-ethylstyrene, substituted styrenes with an alkyl substituent on the ring such as vinyltoluene and p-methylstyrene, halogenated styrenes such as monochlorostyrenes, dichlorostyrenes, tribromostyrenes and tetrabromostyrenes;
heterocyclic vinyl compounds, preferably heterocyclic vinyl compounds selected from 2-vinylpyridine,

3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, 2-vinylpyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinyloxolane, vinylfuran, vinylthiophene, vinylthiolane, vinylthiazoles and hydrogenated vinylthiazoles, vinyloxazoles and hydrogenated vinyloxazoles; vinyl and isoprenyl ethers; methacrylic acid and acrylic acid, or a mixture thereof.

7. The composition according to any one of the preceding claims, wherein the composition comprises from 0.001 to 1 % by weight, preferably from 0.005 to 0.8 % by weight, more preferably from 0.005 to 0.5 % by weight of the polymeric additive b), based on the total weight of the composition.

8. The composition according to any one of the preceding claims, wherein the copolymer P) has a weight-average molecular weight is from 8,000 to 600,000 g/mol, preferably from 8,000 to 300,000 g/mol even more preferably from 8,000 to 100,000 g/mol and most preferably from 10,000 to 50,000 g/mol, determined by gel permeation chromatography using poly(methyl-methacrylate) calibration standards according to DIN 55672-1.

9. The composition according to any one of the preceding claims, wherein the plastic pyrolysis oil a) is a plastic pyrolysis oil and/or a plastic waste pyrolysis oil, wherein the plastic and plastic waste are selected from polyolefins, polyethylene terephthalate, polyvinyl chloride, polystyrene, or a mixture thereof.

10. The composition according to claim 9, wherein the plastic pyrolysis oil a) comprises from 0 % to 12 % of C₁₆ to C₁₉ n-paraffin waxes, from 0 % to 12 % of C₂₀ to C₂₉ n-paraffin waxes, from 0 % to 12 % of C₃₀ to C₃₉ n-paraffin waxes, and from 0 % to 12 % of n-paraffin waxes with C₄₀ or longer carbon chains, wherein the total wax content of n-paraffin waxes with C₁₆ or longer carbon chains sums up to 12 % by weight or less, based on the total weight of the plastic pyrolysis oil.

11. The composition according to any one of the preceding claims, wherein the composition further comprises an additive c), wherein the additive c) is any of the group comprising scale inhibitors, corrosion inhibitors, oxygen scavengers, biocides, emulsion breakers, antifoam agents, drag reducing agents, hydrate inhibitors, paraffin dispersants, asphaltene control agents, a pour point depressant other than copolymer P), or a mixture thereof.

12. The composition according to any one of the preceding claims, wherein the polymeric additive b) reduces the pour point of the pyrolysis oil a) by at least 1 °C, or wherein the polymeric additive b) reduces the viscosity of the pyrolysis oil a) by at least 10% at a temperature from -20 °C to +80 °C, or both.

13. A method of manufacturing the composition as defined in any one of claims 1 to 12 comprising the steps of:

- 5 providing a plastic feedstock;
pyrolyzing the plastic feedstock to generate the plastic pyrolysis oil a);
preparing the polymeric additive b) and
adding the polymeric additive b) to the plastic pyrolysis oil a).

14. Use of a polymeric additive b) as defined in any one of claims 1 to 12 to reduce the pour point of a plastic pyrolysis oil a) or to reduce the viscosity of the plastic pyrolysis oil a), or both.

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15. A method of transporting or storing a plastic pyrolysis oil a) comprising the step of adding a polymeric additive b) to the plastic pyrolysis oil a), to form a composition as defined in any one of claims 1 to 12.