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# (54) USE OF POLYMERS AS ADDITIVES FOR LUBRICANT OIL COMPOSITIONS

(57) The present invention is concerned with the use of polymeric additives in lubricant oil compositions, wherein the polymers comprise styrene and maleic acid dialkyl ester building blocks and increase the shear stability of the composition.

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## Description

**[0001]** The present invention is concerned with the use of polymers as additives for lubricant oil compositions, wherein the polymers comprise styrene and maleic acid dialkyl ester building blocks and increase the shear stability of the compositions.

### *Background of the invention*

**[0002]** In the fields of lubricants, the degree of susceptibility of viscosity of a fluid to temperature variations is quantitatively expressed by an empirical term known as viscosity index (VI). A higher VI value signifies a lesser effect of temperature on viscosity. Polymers employed as additives in lubricants to enhance the VI (i.e. to minimize the temperature dependency of viscosity) are called viscosity index improvers (VII) and corresponding VII-treated lubricants are categorized as multigrade oils as opposed to monograde oils which contain no VII.

**[0003]** Polymer containing fluids exhibit less reduction in viscosity with increase in temperature than the corresponding base fluids containing no polymer. The hydrodynamic volume of the polymer in the fluid increases with increase in temperature thereby resulting in an increase in viscosity, which greatly compensates the opposing effect of commonly observed reduction in viscosity of a fluid with rise in temperature.

**[0004]** The shear stability of the additive has strong influence on multigrade engine oil's ability to retain its viscosity under shearing conditions, experienced by the lubricant while in use. The loss of viscosity of a lubricant under shear can be of two kinds, namely a temporary viscosity loss or a permanent viscosity loss. One of the major problems with many of the VII is their tendency to undergo permanent reduction of viscosity as a result of mechanical shearing which occurs in most of the mechanical system.

**[0005]** In order to increase vehicle efficiency and thereby limit $CO_2$ emissions, there is a general trend to use lower and lower viscosity engine lubricants in order to reduce hydrodynamic friction losses. While engine oil viscosity is controlled primarily by the viscosity of the base oil present, it is considerably modified by the VII.

**[0006]** The prime function of these additives is to increase the viscosity index of their blends, but it is now recognized that they may also contribute to reducing hydrodynamic friction by undergoing temporary shear thinning at the high shear rates present in some engine components. Unfortunately, while temporary shear thinning may be desirable, it is often accompanied by permanent shear thinning resulting from the scission of polymer molecular chains at high shear rates, and this is always undesirable. Thus, viscosity modifiers are required that show considerable temporary but very little permanent shear thinning.

**[0007]** The performance of lubricant oil compositions has increased in recent years and will increase even further due to more demanding environmental and governmental standards. Many functional fluids like hydraulic oils, gear oils, transmission oils and crankcase oils comprise VII and/or pour point depressants (PPD) in order to maintain a certain viscosity and flowability over a wide temperature regime. Those additives are marketed based upon features such as cold temperature deposit control, stable viscosity and fluid durability. While VII improve the viscosity index of a lubricant oil, PPDs are applied to maintain low temperature flowability (pour point) and cold filterability (cold filter plugging point). Where polymers are applied, the polymers are usually based on polyolefins and polymethacrylates, acrylates or styrene-maleic anhydride co-polymers and esterified derivatives thereof. These polymers can be altered in their structures by using different alcohols for their production. Especially, poly(alkylmethacrylates) (PAMA) and poly-styrene-maleic anhydrides (PSMA) represent a class of VII or PPD which have been used for many years in lubricant oil compositions.

**[0008]** Base oils are produced by means of refining crude oils via distillation. While the lighter oils are used for fuels, the heavier cuts are suitable as base oils. By hydroprocessing sulfur and aromatics are removed using hydrogen under high pressure in order to obtain, purified base oils, which are desired when quality requirements are particularly stringent. Depending on the properties and the refining methods, base oils can be classified into 5 groups according to the American Petroleum Institute (API).

Group I

**[0009]** The least refined type which is produced by solvent refining. It usually consists of conventional petroleum base oils. API defines group I as "base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120".

Group II

**[0010]** Better grade of petroleum base oil, which may be partially produced by hydrocracking. Impurities are removed from the base stock leading to clearer color. API defines group II as "base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120".

Group III

**[0011]** The best grade of petroleum base oil, since it is fully produced by hydrocracking, which make these oils purer. API defines group III as "base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 120". This group may be described as synthetic technology oils or hydro-cracked synthetic oil.

Group IV

**[0012]** Consists of synthetic oils made of Poly-alpha-olefins PAO. Poly-alpha-olefins PAO oils are much more stable in extreme temperatures, which make them suitable for use in very cold weather (as found in northern Europe) as well as very hot weather (as in Middle East).

Group V

**[0013]** Any type of base oil other than mentioned in the previously defined groups. Group V oils include, among others, naphthenic oils and esters.

**[0014]** Industrial lubricants and base oils are further often classified according to the ISO 3448 viscosity grade classification. The mid-point viscosity at 40 °C ($mm^2/s$) represents the viscosity grade, respectively. The range comprise classes from ISO VG 2 (1.98 - 2.42 $mm^2/s$ at 40 °C) to ISO VG 1500 class (1350 - 1650 $mm^2/s$ at 40 °C).

**[0015]** As stated above there is a need for improved VII/PPD which provide within a wider temperature regime a good viscosity temperature profile and shear stability for the base oils of the different groups. It is known from the prior art that adding a certain degree of branching has a negative impact on shear stability, viscosity index and low temperature viscosity for PAMA based polymers. US8343900 B2 suggested to use OXO based alcohols (linear and branched) in combination with 2-alkyl branched GUERBET type alcohols to improve PSMA additives with respect to shear stability and viscosity index.

**[0016]** It is known in the art that for viscosity index improvers, where the ester functional groups have some degree of branching, the viscosity index and the shear stability of the lubricating oil composition are an issue [US8343900 B2].

**[0017]** US2570846 A discloses the use of esters of styrene/maleic acid-copolymers to reduce the pour point and to increase the viscosity index of lubricating oils. The alcohol moieties are based on linear C6- to C18- alkanols.

**[0018]** US3574575 A discloses esters of styrene/maleic acid-copolymers as fluidity improvers in liquid hydrocarbons. The alcohol moieties of the ester groups are based on alcohols having at least 20 carbon atoms in the alkyl portion.

**[0019]** US5703023 A discloses polymeric viscosity index improvers made from styrene/maleic anhydride copolymers esterified with C8- to C18- alcohols, of which 50-90% are linear and the balance being branched (preferably 2-ethylhexanol).

**[0020]** US8293689 B2 discloses lubricating compositions containing styrene/maleic anhydride copolymers esterified with 2-decyltetradecanol (Isofol24) or 2-ethylhexanol and linear C12-15-alcohols (Neodol25) further comprising an anti-wear agent.

**[0021]** From WO2017/012716 A1 the use of styrene-maleic acid dialkyl ester polymers as pour point depressants in paraffin-containing fluids is known. The reference teaches that these polymers alter the tertiary structure of the paraffin in the fluid and thus lower the pour point of the fluids, which are mainly crude oils. This application is different from the use as viscosity index improver in base oils, firstly because base oils and paraffin-containing fluids are different and secondly because the effect is different.

**[0022]** For example, paraffin-containing fluids have a much higher viscosity and are mostly crude oils, whereas base oils are already refined fractions, from which the long-chain paraffins (wax) have been removed by dewaxing steps (see above).

**[0023]** Furthermore, the efficiency of depressing the pour point in crude oils is greatly influenced by the side chains of the polymer, respectively their carbon chain length and branching. In crude oils the pour point is determined by ASTM D5985 and mainly caused by the precipitation of wax crystals in the liquid, whereas in base oils much shorter alkanes tend to pour out and the pour point is determined according to ASTM D97. Therefore, the pour point of crude oils is usually at much higher temperatures than the one of base oils.

**[0024]** Therefore, WO2017/012716 A1 teaches away from using the polymer additives in base oils. In addition, shear stability does not play any role for additives that are exclusively pour point depressants.

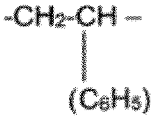
**[0025]** The object of the present invention is to provide a polymer as an additive for use as shear stable viscosity index improvers with a high thickening efficiency and at the same time increased low temperature performance (pour point).

*Summary of the invention*

**[0026]** Surprisingly polystyrene-maleic anhydride (PSMA) based copolymers having linear alkyl and branched alkyl moieties, in particular 2-alkyl branched, generate high shear stable polymers with high thickening efficiency and increased low temperature performance (pour point) in a lubricant oil composition.

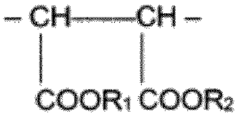
**[0027]** The present invention relates to the use of styrene-maleic acid dialkyl ester polymers in lubricant oil compositions. In more detail, the invention relates to the use of styrene-maleic acid alkyl ester polymers, where the ester groups are made from mixtures of long-chain linear and branched fatty alcohols. The styrene-maleic acid alkyl ester polymers comprise at least the following building blocks:

a)



$$-CH_2-\underset{\substack{|\\(C_6H_5)}}{CH}-$$

b)



$$-\underset{\substack{|\\COOR_1}}{CH}-\underset{\substack{|\\COOR_2}}{CH}-$$

wherein

- R1, R2 = are independent from each other a C10- to C50- alkyl group, the alkyl group being branched or linear;
- the ratio of the linear alkyl groups to the branched alkyl groups is in the range from 95:5 to 5:95, preferably 90:10 to 10:90, more preferably 80:20 to 20:80, most preferably 70:30 (all in weight%);
- at least 90% by the number, preferably more than 98% by the number, of the building blocks are a) and b), relative to the total number of all building blocks incorporated into the polymer; and
- the building blocks a) and b) are present in the polymer in a (number) ratio of from 80:20 to 20:80, relative to each other, or according to preferred embodiments 75:25 to 50:50, preferably 60:40 to 50:50.

**[0028]** The branched alkyl groups R1, R2 are preferably branched at the 2 position and also independent thereof the branched alkyl groups have 12 to 26, more preferably 12 to 20, carbon atoms. The linear alkyl groups R1, R2 have 12 to 20, more preferably 12 to 14, carbon atoms.

**[0029]** The polymer preferably has an acid value of less than 2 mg KOH/g, measured according to DIN EN 14104.

**[0030]** The polymer chain preferably comprises in total 50 to 150 building blocks a) and b) per polymer chain plus optionally other building blocks or end groups.

**[0031]** The mass average molecular weight Mw of the non-esterified polymer (without R1 and R2 or in other words with R1 = H and R2 = H) preferably is in the range of 18,000 g/mol to 22,000 g/mol. The polydispersity index (PDI) $M_w/M_n$ thereof preferably is between 2 and 3. Both are determined by gel permeation chromatography (GPC).

**[0032]** The styrene-maleic acid dialkyl ester polymers preferably have a molecular weight Mw in the range of 40,000 to 52,000 g/mol.

**[0033]** In a further embodiment 1 to 10 weight% of the polymers are used in the lubricant oil composition.

**[0034]** The lubricant oil composition of the present invention is a composition comprising at least one base oil and at least one styrene-maleic acid dialkyl ester polymer as defined herein. The lubricant oil composition may comprise further additives customary in the lubricant industry such as thickeners, antioxidants, antiwear agents, anticorrosives, metal deactivators, detergents, dyes, lubricity improvers, friction modifiers and high-pressure additives. The base oil can be a mineral oil or a synthetic oil. The base oil may have a kinematic viscosity of 20 to 2500 $mm^2/s$, in particular of 40 to 500 $mm^2/s$, at 40°C.

**[0035]** Preferably the base oil is at least one Group I-V base oil, preferably Group I-IV base oil, as well as mixtures thereof.

**[0036]** The base oil may also be at least one oil with a viscosity class according to ISO 3448 in the range of VG10 to VG320, preferably VG15 to VG68.

**[0037]** Furthermore, the base oil may have a pour point according to ASTM D97 equal to or below -10° C.

**[0038]** According to another aspect the polymers defined above are used to improve the Permanent Shear Stability Index (PSSI) of the lubricant oil composition at 100° C after 20 h to a value below 40%, preferably below 30%.

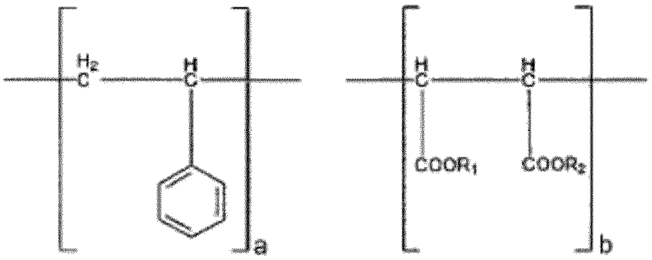
**[0039]** The polymer may also increase the permanent shear stability of the lubricant oil composition and/or act as viscosity index improver and/or pour point depressant therein.

**[0040]** The polymers used are not uniform compounds but a mixture of compounds comprising above building blocks a) and b) and in so far above values refer to a mixture of compounds or in other words the overall composition of the polymers is defined by above values.

**[0041]** The polymer may comprise building blocks other than a) or b), for example maleic acid anhydride, or maleic acid mono-esters.

*Detailed Description*

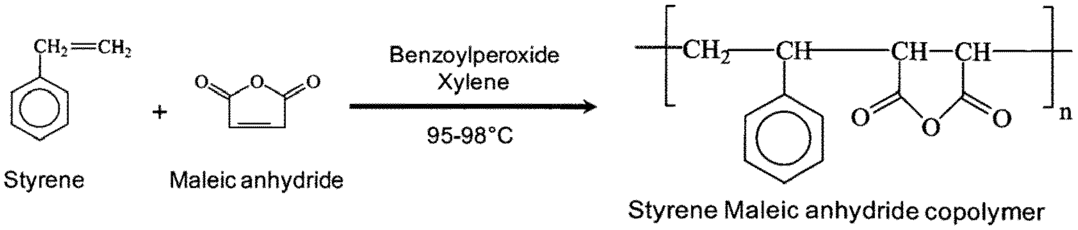
**[0042]** The invention makes use of styrene-maleic acid alkyl ester polymers having the following building block:



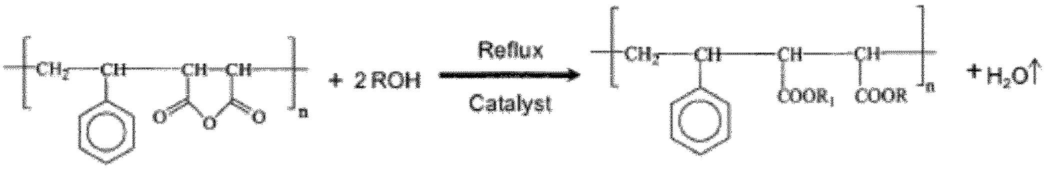
with R1 and R2 = alkyl, without that the sequence of building blocks resulting from styrene a) and maleic acid dialkyl ester b) necessarily need to be of an alternating nature (a)b)a)b)a)b) ....). The building blocks can also have a random distribution or a block structure. R1 and R2 may be different for each b.

**[0043]** The following examples and results will illustrate the preparation of the polymers and demonstrate the advantages obtained. However, it should be understood that the examples may not be understood to limit to subject matter of the claims.

**[0044]** The reaction scheme below illustrates the synthesis of styrene-maleic acid dialkyl ester polymers with an alternating structure. However, the product can also be synthesized via alternative synthetic pathways (such as performing the esterification of maleic anhydride before copolymerising with styrene).



**[0045]** The styrene-maleic anhydride copolymer is then esterified as follows:



*Experimental Section*

**[0046]** The following general preparation method was followed:

0.66 mol Maleic anhydride (from Merck and used as received) and 7.28 mol xylene were charged to a reactor and heated up to 95°C under nitrogen. 0.75 mol Styrene (from Merck and used as received) and the initiator benzoylperoxide (0.002 mol), dissolved in xylene were simultaneously added dropwise over a period of 90-120 min into the reactor. The polymerisation was carried out for 6-8 hours at 95-98 °C.

**[0047]** The completion of the polymerization to the desired level was measured by the acid number of the unreacted maleic anhydride in the filtered polymerisation solution. The acid value is preferably less than 2 mg KOH/g. The copolymer average molecular weight (mass) Mw was determined by using GPC analysis (MZGel SDplus 100 Å 5 µm 300x8 mm/

MZ-Gel SDplus 1000 Å 5μm 300x8mm/Agilent polyPore 5μm 300x7.5 mm equipped with a pre-column Mz-Gel SDplus linear 5μm 20 50x8mm, injection volume 20 μL, solvent THF, flow rate 1 ml/min, detection via UV (254 nm) and refractive index) and was 20,000 g/mol.

**[0048]** The subsequent esterification reaction took place in the same reactor. 1.24 mol fatty alcohol was charged to the copolymer/xylene suspension and heated up until the suspension turned into a clear solution.

**[0049]** Methane sulfonic acid (0.13 mol) was charged as catalyst and the reactor was heated up until the reflux of xylene started. The esterification reaction was carried out until the theoretical amount of water was collected.

**[0050]** The polystyrene-maleic anhydride copolymer ester solution was treated with activated carbon and filtrated before removal of xylene. Xylene was removed by distillation to obtain the neat copolymer ester.

**[0051]** The fatty alcohols / fatty alcohol mixtures specified in below table were used in the esterification step for preparation of the polymers described in table 1.

**Table 1:**

| Typical analysis of long chain fatty alcohols used for preparation of the styrene m copolymer esters maleic | | | | | | | |
|---|---|---|---|---|---|---|---|
| in [wt.%] | ISOFOL 12 | ISOFOL 16 | ISOFOL 20 | ISOFOL 24 | ISOFOL 2426S | NAFOL 1214 | NAFOL 1620 |
| Chemical description | 2-buty-octanol | 2-hexyldecanol | 2-octyl-decanol | 2-decyltetradecanol | Branched Alcohols, C24-26 | Alcohols, C12-14 | Alcohols, C16-20 |
| | [wt.%] | [wt.%] | [wt.%] | [wt.%] | [wt.%] | [wt.%] | [wt.%] |
| C10 OH | | | | | | 1.5 max. | |
| C12 OH | 97 min. | | | | | 68-73 | 0.2 max. |
| C14 OH | | | | | | 24-30 | 2.0 max. |
| C16 OH | | 97 min. | | | | 1.5 max. | 47-55 |
| C18 OH | | | | | | | 26-34 |
| C20 OH | | | 97 min. | | | | 10-18 |
| C22 OH | | | | | | | 3.0 max. |
| C24 OH | | | | 97 min. | 96 min. | | 0.2 max. |
| C26 OH | | | | | | | |
| Average molecular weight | 186 | 242 | 298 | 354 | 368 | 190-197 | 255-269 |

*min = minimum, max = maximum*

ISOFOL alcohols are branched Guerbet alcohols, more specifically, saturated primary alcohols with defined branching at the two position of the carbon chain. The Guerbet alcohols can chemically be described as 2-alkyl-1-alkanols, with the alkyl and the alkanol group both being linear.

NAFOL 1214 refers to a C12-14 synthetic linear alcohol mixture, NAFOL 1620 refers to a C16-20 synthetic linear alcohol mixture and NAFOL 1218 refers to a C12-18 synthetic linear alcohol mixture. The number of carbon atoms given above refers to the complete molecule and not only to the backbone of the alcohol.

**[0052]** Six different polymers were prepared using various fatty alcohols as described above, according to the general synthesis procedure as set out above and compared to reference esters based on linear alcohols alone or based on poly(alkylmethacrylates). The acronyms for the different neat copolymer esters (polymeric additives) prepared are described below:

| | |
|---|---|
| PSMA-1214: | The alcohol NAFOL 1214 was used to esterify the styrene-maleic anhydride copolymer. |
| PSMA-1214/112: | A mixture of alcohols esterified with styrene-maleic an-hydride copolymer: 70 weight% NAFOL 1214 and 30 weight% ISOFOL 12. |
| PSMA-1214/116: | A mixture of alcohols esterified with styrene-maleic an-hydride copolymer: 70 weight% NAFOL 1214 and 30 weight% ISOFOL 16. |

PSMA-1214/I20: A mixture of alcohols esterified with styrene-maleic an-hydride copolymer: 70 weight% NAFOL 1214 and 30 weight% ISOFOL 20.
PSMA-1214/124: A mixture of alcohols esterified with styrene-maleic an-hydride copolymer: 70 weight% NAFOL 1214 and 30 weight% ISOFOL 24.
PSMA-1214/I2426S: A mixture of alcohols esterified with styrene-maleic an-hydride copolymer: 70 weight% NAFOL 1214 and 30 weight% ISOFOL 2426S.
PAMA-1214: The alcohol NAFOL 1214 esterified with alkylmethacrylates copolymer.
PAMA-1214/1620: A mixture of alcohols esterified with alkylmethacrylates copolymer: 70 weight% NAFOL 1214 and 30 weight% NAFOL 1620.

*PSMA = Styrene-maleic anhydride copolymer containing 50 mol% maleic acid dialkyl ester*
*PAMA = Poly(alkylmethacrylates)*

**[0053]** The table below describes selected properties of the polymeric additives.

**Table 2:**

| Selected properties of the polymeric additives evaluated | | | | |
|---|---|---|---|---|
| **Polymer** | **PSMA-1214 *** | **PSMA-1214/I12 (70/30)** | **PSMA-1214/I16 (70/30)** | **PSMA-1214/I20 (70/30)** |
| Alcohol | NAFOL 1214 | 70% NAFOL 1214<br>30% ISOFOL 12 | 70% NAFOL 1214<br>30% ISOFOL 16 | 70% NAFOL 1214<br>30% ISOFOL 20 |
| Mw[g/mol] | 48,492 | 46,502 | 48,280 | 41,798 |
| PDI | 1.83 | 1.93 | 1.94 | 2.03 |
| Acid value [mg KOH/g] | 1.69 | 1.72 | 1.14 | 1.18 |
| % esterified COOH | 96.9 | 96.9 | 97.9 | 97.8 |
| | | | | |
| **Polymer** | **PSMA-1214/124 (70/30)** | **PSMA-1214/I2426S (70/30)** | **PAMA-1214**** | **PAMA-1214/1620**** |
| Alcohol | 70% NAFOL 1214<br>30%ISOFOL 24 | 70% NAFOL 1214<br>30%ISOFOL 2426S | NAFOL 1214 | 70% NAFOL 1214<br>30 % NAFOL 1620 |
| Mw[g/mol] | 43,851 | 50,331 | 58,152 | 69,091 |
| PDI | 1.92 | 1.91 | 1.33 | 1.34 |
| Acid value [mgKOH/g] | 1.01 | 0.72 | Not applicable | Not applicable |
| % esterified COOH | 98.1 | 98.6 | Not applicable | Not applicable |
| * comparative product<br>** reference product | | | | |

*Evaluation Tests:*

**[0054]** The inventive polymeric additives were tested by addition of 10 wt% neat polymer to different base oils with regard to the pour point depression (PP), thickening efficiency (TE) and viscosity index (VI). The results are listed in table 3.

**Table 3:**

| Evaluation of the selected polymeric additives in different base oils | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Group II (VG15) Mineral oil light | | | Group II (VG68) Mineral oil heavy | | | Group V (VG22) Nynas T22 | | |
| Property | PP | TE | VI | PP | TE | VI | PP | TE | VI |
| Oil alone | -21 | 3.4 | 89 | -12 | 8.9 | 102 | -42 | 3.9 | 14 |
| PSMA-1214* | -39 | 6.9 | 192 | -33 | 15.6 | 141 | -39 | 8.3 | 144 |
| PAMA-1214** | -41 | 5.4 | 174 | -21 | 14.1 | 114 | -36 | 7.7 | 138 |
| PAMA-1214/1620** | -31 | 5.7 | 201 | -27 | 16.0 | 153 | -36 | 12.8 | 172 |
| PSMA-1214/I12 | -51 | 6.5 | 177 | -12 | 13.7 | 131 | -45 | 7.7 | 132 |
| PSMA-1214/I16 | -31 | 6.7 | 191 | -12 | 15.4 | 138 | -42 | 7.8 | 133 |
| PSMA-1214/I20 | -39 | 6.3 | 166 | -24 | 14.9 | 143 | n.a. | 7.7 | 133 |
| PSMA-1214/I24 | -45 | 7.0 | 192 | -33 | 14.6 | 141 | n.a. | 7.9 | 135 |
| PSMA-1214/I2426S | -42 | 6.3 | 182 | -18 | 15.2 | 138 | -42 | 7.7 | 135 |

*PP = Pour point [° C] according to ASTM D97*
*TE = Thickening efficiency / kinematic viscosity @100° C [cSt] according to ASTM D7042*
*VI = Viscosity index according to ASTM D2270*
** comparative product*
*** reference product*

**[0055]** As one can see from table 3 the polymers as defined in claim 1 improve the pour point depression, thickening efficiency and the viscosity index compared to existing PAMA-additives or PSMA with only linear alkyl chains.

**[0056]** Very important for the use of base oils in the field of lubrication (e.g. in engines) is long time performance of such oils, which is reflected by a high mechanical shear stability. This can be tested by different methods (e.g. DIN 51382 or ASTM D5621). One further method is the so called KRL Tapered Roller Bearing test according to CEC L45-A-99. For this 40 ml of a base oil treated with 10 wt% of the polymeric additive are subjected to a taper roller bearing rig at 60° C and a constant load of 5000 N with the roller bearing rotating at 1450 min$^{-1}$ for a time of 4 and 20 hours. This test is used to simulate the degree of permanent viscosity loss in automotive gear oils, hydraulic fluids and automatic transmission fluids (ATF).

**Table 4:**

| Shear stability results | | | | | | |
|---|---|---|---|---|---|---|
| | Group II (VG15) | | | | | |
| Property | Rel. viscosity loss [%] 4h | Rel. viscosity loss [%] 20h | Shear stability 4h | Shear stability 20h | PSSI 4h | PSSI 20h |
| PAMA-1214 ** | 3.9 | 9.2 | 96.3 | 90.8 | 10.0 | 24.8 |
| PAMA-1214/1620 ** | 4.2 | 11.5 | 96.0 | 88.5 | 9.8 | 28.0 |
| PSMA1214 * | 5.9 | 15.1 | 94.2 | 84.9 | 11.6 | 30.3 |
| PSMA-1214/I12 | 4.4 | 11.6 | 95.7 | 88.4 | 9.0 | 24.3 |
| PSMA-1214/I16 | 5.4 | 13.1 | 94.7 | 86.9 | 10.8 | 26.8 |

(continued)

| Shear stability results | | | | | | |
|---|---|---|---|---|---|---|
| | Group II (VG15) | | | | | |
| Property | Rel. viscosity loss [%] 4h | Rel. viscosity loss [%] 20h | Shear stability 4h | Shear stability 20h | PSSI 4h | PSSI 20h |
| PSMA-1214/I2426S | 4.3 | 11.9 | 95.7 | 88.1 | 9.2 | 25.7 |
| ** comparative product*<br>*** reference product* | | | | | | |

**[0057]** The relative viscosity loss (C) by mechanical shearing is determined by measuring the viscosity at 100° C before and after the shearing and is calculated as follows:

$$C\ [\%] = (v1 - v2) / v1 * 100 \qquad \begin{array}{l} v1 \text{ - viscosity before shearing} \\ v2 \text{ - viscosity after shearing} \end{array}$$

**[0058]** The Shear stability (S) is calculated as follows:

$$S\ [\%] = v2 / v1 * 100$$

**[0059]** The Permanent Shear Stability Index (PSSI) at 100°C is another factor based on the above test, which represents the permanent viscosity loss of multi-grade lubricants due to polymer degradation and is calculated as follows:

$$PSSI\ [\%] = (v1 - v2) / (v1 - v0) * 100,$$

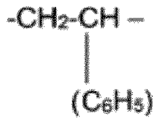
wherein v0 is the viscosity of the pure base oil

**[0060]** As can be seen from table 4, the 20h shear stability of the inventive PSMA based polymeric additive is higher than the PSMA based polymeric additives of the state of the art and at least in the same range as PAMA based ones. It has been surprisingly found that introducing a Guerbet structured alcohol in the PSMA-polymer led to improved shear stability.

## Claims

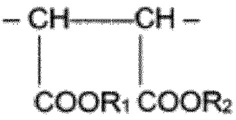
1. Use of styrene-maleic acid dialkyl ester polymers as additive in lubricant oil compositions to improve the shear stability, the polymers comprising the following building blocks:

a)



$$-CH_2-\underset{(C_6H_5)}{\underset{|}{CH}}-$$

b)



$$-\underset{COOR_1}{\underset{|}{CH}}-\underset{COOR_2}{\underset{|}{CH}}-$$

wherein

- R1 and R2 are, independent from each other, a C10- to C50- alkyl group; the alkyl group being branched or linear;
- the ratio of the linear alkyl groups to the branched alkyl groups is in the range from 95:5 to 5:95 (weight% : weight%);
- at least 90 % of the number of the building blocks are either a) or b), relative to the total number of all building blocks incorporated in the polymer; and
- the building blocks a) and b) are, relative to each other, present in the polymer in a ratio of from 80:20 to 20:80 (number: number).

**2.** The use according to claim 1, wherein the polymer consists of more than 98% of the building blocks a) and b).

**3.** The use according to any one of the preceding claims, wherein the branched alkyl groups are branched at the 2 position, wherein preferably the branched alkyl groups comprise 12 to 26 carbon atoms.

**4.** The use according to any one of the preceding claims, wherein the linear alkyl groups comprise 12 to 20 carbon atoms, preferably 12 to 14 carbon atoms.

**5.** The use according to any one of the preceding claims, wherein the linear to branched ratio of the alkyl groups is from 90:10 to 10:90, preferably from 80:20 to 20:80 and more preferably 70:30 (in each case weight% : weight%).

**6.** The use according to any one of the preceding claims, wherein the ratio of the number of building blocks a) and b) is from 75:25 to 50:50, preferably 60:40 to 50:50.

**7.** The use according to any one of the preceding claims, wherein the polymers have an acid value of less than 2 mg KOH/g, measured according to DIN EN 14104.

**8.** The use according to any one of the preceding claims, wherein the polymers comprise in total 50 to 150 building blocks a) and b) per polymer chain.

**9.** The use according to any one of the preceding claims, wherein the polymer has an average molecular weight (mass) Mw in the range of 40,000 to 52,000 g/mol.

**10.** The use according to any one of the preceding claims, wherein the non-esterified polymer has an average molecular weight (mass) Mw in the range of 18,000 to 22,000 g/mol and/or a polydispersity index between 2 and 3.

**11.** The use according to any one of the preceding claims, wherein 1 to 10 weight% of the polymers are used in the lubricant oil composition.

**12.** The use according to any one of the preceding claims, wherein the lubricant oil composition comprises at least one Group I-V base oil, preferably Group I-IV base oil, as well as mixtures thereof.

**13.** The use according to any one of the preceding claims, wherein the lubricant oil composition comprises at least one base oil with a viscosity class according to ISO 3448 in the range of VG10 to VG320, preferably VG15 to VG68.

**14.** The use according to any one of the preceding claims, wherein the lubricant oil composition comprises at least one base oil which has a pour point according to ASTM D97 equal to or below -10° C.

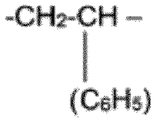
**15.** The use according to any one of the preceding claims, wherein the Permanent Shear Stability Index (PSSI) of the lubricant oil composition at 100° C after 20 hours is below 40%, preferably below 30%.

**16.** The use according to any of the preceding claims, wherein the polymer increases the permanent shear stability of the lubricant oil composition.

**17.** The use according to any of the preceding claims, wherein the polymer also acts as viscosity index improver and/or pour point depressant.

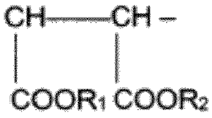
**18.** A method for improving the shear stability of a lubricant oil composition, comprising adding a polymer comprising the following building blocks:

a)



$-CH_2-CH(C_6H_5)-$

b)



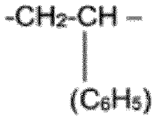
$-CH(COOR_1)-CH(COOR_2)-$

wherein

- R1 and - R2 are, independent from each other, a C10- to C50- alkyl group, the alkyl group being branched or linear;
- the ratio of the linear alkyl groups to the branched alkyl groups is in the range from 95:5 to 5:95 (weight% : weight%);
- at least 90 % of the number of the building blocks are either a) orb), relative to the total number of all building blocks incorporated in the polymer; and
- the building blocks a) and b) are, relative to each other, present in the polymer in a ratio of from 80:20 to 20:80 (number: number).

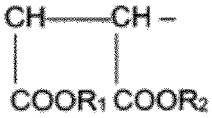
**19.** Styrene-maleic acid dialkyl ester polymers comprising the following building blocks:

a)



$-CH_2-CH(C_6H_5)-$

b)



$-CH(COOR_1)-CH(COOR_2)-$

wherein

- R1 and R2 are, independent from each other, a C10- to C50- alkyl group; the alkyl group being branched or linear;
- the ratio of the linear alkyl groups to the branched alkyl groups is in the range from 95:5 to 5:95 (weight% : weight%);
- at least 90 % of the number of the building blocks are either a) or b), relative to the total number of all building blocks incorporated in the polymer; and
- the building blocks a) and b) are, relative to each other, present in the polymer in a ratio of from 80:20 to 20:80 (number: number);

for the use as additive in in lubricant oil compositions to improve the shear stability.

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# EUROPEAN SEARCH REPORT

Application Number
EP 19 16 1442

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| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (IPC) |
|---|---|---|---|
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C10M
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The present search report has been drawn up for all claims

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| Place of search | Date of completion of the search | Examiner |
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| Munich | 7 August 2019 | Pöllmann, Klaus |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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L : document cited for other reasons
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