

Soot Dispersant Comprising Block Copolymer and Lubricant Composition
Containing the Same

5 The present invention relates to a soot dispersant comprising a block copolymer. The soot dispersant as described herein provides utility in lubricant fluids and lubricated systems; it is particularly suitable for use in diesel engines. The soot dispersant comprising a block copolymer imparts improved soot dispersancy to a lubricant fluid when in use providing engine efficiencies.

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Soot particles in engine lubricant fluids result from the incomplete combustion of fuel by the engine when in use. Soot can be generated in any combustion engine utilising a hydrocarbon based fuel, whether the engine is automotive or stationary. Soot production is particularly a problem in heavy duty diesel engines where incomplete combustion occurs
15 when the engine is operated at lower temperatures, which is now common, as lower operating temperatures may be beneficial in reducing some types of fuel emissions.

Most of the soot particles generated in an engine are only around 30 nm in size and not problematic in and of themselves. However, once present in a lubricant fluid, the soot
20 particles may form low density aggregates which can adversely affect the lubricant fluids ability to perform its lubricating function by increasing the viscosity of the lubricant fluid. As such, engine efficiency can be improved if the presence of soot agglomerates in an engine's lubricant fluid can be reduced or eliminated.

25 Wear of engine components may also increase when lubricant fluids contain high levels of soot aggregates as these soot aggregates create wear particles within the lubricant fluid. Additionally, at high temperatures, or high concentrations, the aggregated soot particles may crash out of the lubricant fluid resulting in sooty deposits forming upon the working parts of the engine; this may result in the parts of the engine becoming blocked, or coated,
30 with soot to such an extent that the engine fails necessitating engine downtime and maintenance. As such, the reduction or elimination of the formation of soot aggregates may beneficially provide a reduction in engine downtime and maintenance costs; this will be of particular benefit to stationary engines operating in industrial settings.

The anticipated presence of soot aggregates in a lubricant fluid also results in an engine requiring frequent lubricant oil changes. In the case of automotive engines, the need to perform an oil change may dictate the engine's service interval. Reduction in formation of soot aggregates in the engine's lubricant fluid, therefor, has direct consumer benefits if the
5 service interval time can be increased, or service costs reduced as an oil change does not need to be performed so often.

As such, while individual soot particles pose little risk to engine parts, aggregates of soot can cause damage in engine. Therefore, Additives (soot dispersants) are required in engine
10 oils to keep the individual soot particles from forming such damaging aggregates. Soot dispersant additives for lubricant fluids (including engine oils) are known and attempt to address some of the problems identified above. Currently used soot dispersants are small-molecules and random copolymers (that is polymers consisting of two or more monomers in a random distribution). However, a need remains to provide improved soot dispersants,
15 particularly improved soot dispersants that can be prepared and manufactured at a commercially acceptable cost with a high degree of control and reproducibility. Other advantages of the present invention may also be appreciated from the description below.

According to the present invention there is provided a soot dispersant comprising:
20 an A-B type block copolymer, wherein:
the A block is a soot anchoring unit, and
the B block is an oil soluble unit.

There is also provided a lubricant fluid composition comprising the soot dispersant as
25 described herein.

In accordance with an alternative embodiment of the present invention there is provided a method of manufacturing the soot dispersant as described herein.

30 Additionally, there is provided use of the lubricant fluid composition of the present invention as an engine oil.

As such, in accordance with one embodiment of the present invention there is provided a soot dispersant comprising an A-B type block copolymer, wherein:
35 the A block is a soot anchoring unit, and
the B block is an oil soluble unit.

Block copolymers consist of two or more monomers present in discrete separate segments, conveniently referred to as units or "blocks". Block copolymers will be understood by the skilled person in the art to be distinct to random copolymers which form with a random
5 distribution of monomers. In the soot dispersants of the present invention, the A block soot anchoring unit can be adsorbed or "anchored" onto a target soot nano-particles, and an alternative B block oil soluble unit can be dissolved in a fluid, suitably an oil based lubricant fluid as further described below. The present block copolymers are strongly anchored onto the soot particles via the A block soot anchoring unit, whilst the oil solubility, coupled with
10 the steric hindrance, of the B block oil soluble unit prevents the soot particles from aggregating; this ensures that any soot particles present in the fluid are well dispersed in use. Random copolymer dispersants are adsorbed onto soot nano-particles at random wherever the suitable anchoring monomer A "units" occur in the random copolymer; in such materials anchoring may not be achieved due to the location in the random copolymer of the suitable anchoring monomer unit, anchoring may be weak due to physical hindrance of
15 the alternative monomer units present, reproducibility of dispersants effect may be limited, and/or relatively high levels of dispersant may be required to achieve a desired result. The problems encountered with use of random copolymers may be overcome by use of the highly regular and reproducible nature of the presently described block copolymers.

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Suitably, in the present soot dispersant comprising an A-B type block copolymer, one or both of the A and B block units comprise one or more vinyl containing monomer, preferably one or more methacrylate containing monomer. The presence of methacrylate containing monomers in both the A and B block units ensure compatibility and ease of addition of the
25 two distinct units to one another during manufacturing, as such, preferably both of the A and B block units comprise one or more methacrylate containing monomer. Each A or B block may individually contain a single monomer (i.e. is a homopolymer block) or two or more different monomers (i.e. is a random copolymer block). The molecular weight, or number of monomer units, can also be variable in each individual A or B block.

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The A block soot anchoring unit may preferably comprise one or more vinyl containing monomer. The vinyl containing monomer may contain a methacrylate or a styrene functional group. Specific examples of suitable vinyl containing monomers include the following: styrene, methoxystyrene, butoxystyrene, and hydroxy styrene, acrylamide and its
35 derivatives such as phenyl acrylamide, benzyl acrylamide, N-isopropyl acrylamide, N,N-dimethyl acrylamide, N-methylol acrylamide, and N-hydroxyethyl acrylamide,

methacrylamide and its derivatives such as phenyl methacrylamide, benzyl methacrylamide, N-isopropyl methacrylamide, N,N-dimethyl methacrylamide, N-methylol methacrylamide, and N-hydroxyethyl methacrylamide, acrylic acid and acrylate derivatives such as phenyl acrylate, benzyl acrylate, hydroxyalkyl acrylates such as 2-hydroxy ethyl acrylate, 2-hydroxypropyl acrylate and glyceryl monoacrylate, polyalkylene glycols acrylates such as diethylene glycol acrylate and polyethylene glycol acrylate, alkoxy polyalkylene glycols acrylates such as methoxy tetraethylene glycol acrylate and methoxypolyethylene glycol acrylate, dialkyl amino alkyl acrylates such as 2-(dimethylamino) ethyl acrylate methacrylate, 2-hydroxy-3-phenoxypropyl acrylate, and methacrylic acid and methacrylate derivatives such as phenyl methacrylate, benzyl methacrylate, hydroxyalkyl methacrylates such as 2-hydroxy ethyl methacrylate, 2-hydroxypropyl methacrylate and glyceryl monomethacrylate, polyalkylene glycols methacrylates such as diethylene glycol methacrylate and polyethylene glycol methacrylate, alkoxy polyalkylene glycols methacrylates such as methoxy tetraethylene glycol methacrylate and methoxypolyethylene glycol methacrylate, dialkyl amino alkyl methacrylates such as 2-(dimethylamino) ethyl methacrylate. Preferred vinyl containing monomer examples may be selected from: methacrylic acid, glyceryl monomethylacrylate, hydroxyethyl methacrylate, styrene, methylstyrene, benzyl methacrylate, diethylamino methacrylate and 2-(dimethylamino)ethyl methacrylate.

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More especially, preferably the A block soot anchoring unit comprises one or more methacrylate containing monomer. Said monomer is necessarily functional such that it may anchor to a soot particle when in use. The necessary functionality may be provided by the presence of an aromatic, basic or hydrophilic group in the methacrylate monomer. Suitable functional groups may preferably include nitrogen or oxygen, such as amine and hydroxyl groups. Preferably the methacrylate monomer contains an aromatic or basic functional group, alone or in combination, most preferably the methacrylate monomer contains an amine or aromatic groups as these groups are found to have particularly good anchoring properties suitable for anchoring to soot particles. Preferably the methacrylate monomer does not contain a hydrophilic groups, and in particular does not contain a hydroxyl group; such functional groups have found to be only weakly anchoring to soot particles, although some affinity to soot may be observed for hydroxyl groups, and so they present a less preferred embodiment of the present invention. Benzyl methacrylate and 2-(dimethylamino)ethyl methacrylate are particularly preferred methacrylate containing monomer examples.

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More especially, preferably the B block oil soluble unit comprises one or more methacrylate containing monomer, suitably said monomers are alkyl-methacrylates, and most suitably said alkyl-methacrylate monomers comprise an alkyl chain containing between 4 and 20 carbons. Preferably the B block alkyl-methacrylate alkyl group is not functionalised, that is to say that the alkyl group carbon chain does not contain any substitution. The alkyl-methacrylate alkyl group may be linear or branched. Suitably, the alkyl-methacrylate alkyl group is saturated, that is to say that no double bonds are present, such that reference to alkyl- groups is not to be considered as also encompassing alkenyl groups. As such, preferably the alkyl-methacrylate alkyl group is a saturated linear alkyl chain containing between 4 and 20 carbons. Specific examples of suitable alkyl-methacrylates monomers include the following: butyl methacrylate, isopentyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, nonyl methacrylate, lauryl methacrylate, tetradecyl methacrylate, octadecyl methacrylate, and hexadecyl methacrylate. More preferably the alkyl-methacrylate alkyl group carbon chain has between 4 and 16 carbons, even more preferably between 6 and 14 carbons, and most preferably between 8 and 12 carbons. Such monomers are found to provide good oil solubility for the intended use in lubricant fluids. Particularly preferred B block oil soluble unit monomers may be selected from butyl methacrylate, 2-ethylhexyl methacrylate and lauryl methacrylate, and selection of lauryl methacrylate is especially preferred.

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Suitably, the soot dispersant comprises a majority of the B type block, and preferably the A-B type block copolymer has a ratio of A block monomeric soot anchoring units to the B block monomeric oil soluble units (A:B) may be in the range of between 3 and 100 (A): 25 and 100 (B). More preferably the ratio of A block monomeric soot anchoring units to the B block monomeric oil soluble units (A:B) may be in the range of between 5 and 20 (A): 25 and 50 (B). In addition, as described above, individually each of the A and B blocks may be formed from one or more monomer; in this case the ratio of each monomer in each block may suitably be between 1:1 and 1:4. In the case of the B type block, homopolymers are preferred, and in the case of the A type block a random copolymer comprising two monomers is preferred; in this case, and as is evident in the Examples provided below, the ratio of A:B units can be expressed as, for example, (2.5:2.5):50, meaning that the block copolymer comprises a ratio of 5 A block units to 50 B block units, and the A block is formed from two monomer units in a 1:1 ratio relative to each other.

35 Preferably the soot dispersant comprises an A block soot anchoring unit having a number average molecular weight of between 8000 and 30000, preferably between 8500 and

25000, and more preferably between 9000 and 20000. Here, number average molecular weight is measured by a tetrahydrofuran eluent gel permeation chromatography (GPC) method relative to a polymethylmethacrylate (PMMA) calibration standard, according to the method described in Ohtsuki, A.; Lei, L.; Tanishima, M.; Goto, A.; Kaji, H. J. Am. Chem. Soc. 2015, 137, 5610-5617.

Preferably the soot dispersant comprises a B block oil soluble unit having a number average molecular weight of between 2000 and 30000, preferably between 2500 and 25000, more preferably between 3000 and 20000, and most preferably between 6000 and 15000. Here, number average molecular weight is measured by a tetrahydrofuran eluent gel permeation chromatography (GPC) method relative to a polymethylmethacrylate (PMMA) calibration standard, according to the method described in Ohtsuki, A.; Lei, L.; Tanishima, M.; Goto, A.; Kaji, H. J. Am. Chem. Soc. 2015, 137, 5610-5617.

Preferably the soot dispersant comprises an A block soot anchoring unit having a polydispersity index (PDI) of between 1 and 2, preferably between 1 and 1.7, more preferably between 1 and 1.2, and most preferably between 1 and 1.1.

Preferably the soot dispersant comprises a B block oil soluble unit having a polydispersity index (PDI) of between 1 and 1.4, preferably between 1 and 1.3, more preferably between 1 and 1.2, and most preferably between 1 and 1.1.

Most preferably, the soot dispersant comprises an A block soot anchoring unit and a B block oil soluble unit each having a polydispersity index (PDI) of between 1 and 1.1.

The PDI of a polymer is calculated as the weight average molecular weight divided by the number average molecular weight. PDI values at or close to 1 indicate that polymers with a single chain length are being produced, i.e. the bulk polymer is highly uniform. PDI values of 1, or close to 1, are achievable by preparation of the block copolymers by controlled radical polymerisation (CRP) methods.

Suitably, the soot dispersant comprises an A-B type block copolymer prepared by a controlled radical polymerization (CRP) process. Such a process allows for high degree of control and reproducibility in the manufacture of the block copolymer units. More especially, the soot dispersant comprises an A-B type block copolymer prepared by an organocatalyzed CRP (OCRCP) process; such a process has all of the benefits of a CRP

process, but is low-cost, odour-free, and metal-free, all of which are advantageous features for a soot dispersant for use in a lubricant fluid.

Furthermore, there is provided a lubricant fluid composition comprising the soot dispersant,
5 as described above, and a lubricating oil.

Suitable lubricating oils are known in the art and may be selected based on their intended use.

10 The choice of lubricating oil can have a major impact on properties such as oxidation and thermal stability, volatility, low temperature fluidity, solvency of additives, contaminants and degradation products, and traction. The American Petroleum Institute (API) currently defines five groups of lubricating oils, commonly referred to as lubricant base stocks (API Publication 1509).

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Groups I, II and III are lubricating mineral oils which are classified by the amount of saturates and sulphur they contain and by their viscosity indices. Table 1 below illustrates these API classifications for Groups I, II and III.

20 Table 1

<u>Group</u>	<u>Saturates</u>	<u>Sulphur</u>	<u>Viscosity Index (VI)</u>
I	<90%	>0.03%	80-120
II	At least 90%	Not more than 0.03%	80-120
III	At least 90%	Not more than 0.03%	At least 120

Group I base stocks are solvent refined lubricating mineral oils, which are the least expensive base stock to produce. They provide satisfactory oxidation stability, volatility, low temperature performance and traction properties and have very good solvency for
25 additives and contaminants.

Group II base stocks are mostly hydroprocessed lubricating mineral oils, which typically provide improved volatility and oxidation stability as compared to Group I base stocks.

Group III base stocks are severely hydroprocessed lubricating mineral oils or they can be produced via wax or paraffin isomerisation. They are known to have better oxidation stability and volatility than Group I and II base stocks but have a limited range of commercially available viscosities.

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Group IV base stocks differ from Groups I to III in that they are synthetic lubricating oils e.g. polyalphaolefins (PAOs). PAOs have good oxidative stability, volatility, and low pour points. Disadvantages include moderate solubility of polar additives, for example anti-wear additives.

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Group V base stocks include all lubricating oils that are not included in Groups I to IV. Examples include alkyl naphthalenes, alkyl aromatics, vegetable oils, esters (including polyol esters, diesters and monoesters), polycarbonates, silicone oils and polyalkylene glycols.

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The lubricant fluid composition of the present invention may comprise a lubricating oil selected from any of the base stocks described above. As such, preferably the lubricating oil is selected from an API Group I, II, III, IV, V base stock or mixture thereof. Suitably, for some end uses, the lubricating oil may be a mixture of Group IV and Group V base stocks or Group IV and Group I, II or III base stocks; the selection of suitable lubricating oil depends on the intended end use of the lubricant fluid and can be selected by the person skilled in the art based on their existing knowledge of the technical field.

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The lubricant fluid composition may comprise at least 0.1 wt%, suitably at least 0.2 wt%, preferably at least 0.5 wt%, more preferably at least 1 wt%, and even more preferably at least 2 wt%, of the soot dispersant based on the total weight of the composition. The lubricant composition may comprise no more than 15%wt, preferably no more than 12 wt%, and more preferably no more than 10 wt%, of the soot dispersant based on the total weight of the composition. The present block copolymer dispersants are able to disperse the soot particles more efficiently than equivalent random copolymers when in use in a lubricating fluid. Therefore, at the same treatment rate, block copolymer based soot dispersants significantly prolong the lifetime of the lubricant fluids (or engine oils) in comparison to equivalent random copolymer dispersants.

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In one preferred embodiment, the lubricant fluid composition is non-aqueous. However, it will be appreciated that components of the lubricant fluid composition may contain small amounts of residual water (moisture) which may therefore be present in the non-aqueous lubricant fluid composition. The lubricant fluid composition may comprise less than 5% water by weight based on the total weight of the composition. More preferably, the lubricant fluid composition is substantially water free, i.e. contains less than 2%, less than 1%, or preferably less than 0.5% water by weight based on the total weight of the composition. Preferably the lubricant fluid composition is substantially anhydrous.

Lubricant fluids for use as automotive engine oils typically comprise a lubricating oil (also referred to as a lubricant base stock) and further additives, typically in an additive package, both the lubricating oil and the additive package can contribute significantly to the properties and performance of the automotive engine oil. Lubricant fluids for stationary engines may also include further additives to enhance their performance in use. As such, the lubricant fluid composition may comprise at least 0.5 wt% of a further additive or a mixture of further additives, preferably at least 1 wt%, and more preferably at least 5 wt%, based on the total weight of the composition. The lubricant composition may comprise up to 30 wt% of a further additive or a mixture of further additives, preferably up to 20 wt%, and more preferably up to 10 wt%, based on the total weight of the composition.

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Suitably, the lubricant fluid composition may comprise one or more of the following further additives:

1. Friction reducing agents such as esters, partial esters, phosphonates, organomolybdenum-based compounds, fatty acids, higher alcohols, fatty acid esters, sulfur containing esters, phosphate esters, acid phosphoric acid esters, and amine salts of phosphoric acid esters.
2. Additional dispersants: for example, alkenyl succinimides, alkenyl succinate esters, alkenyl succinimides modified with other organic compounds, alkenyl succinimides modified by post-treatment with ethylene carbonate or boric acid, pentaerythritols, phenate-salicylates and their post-treated analogues, alkali metal or mixed alkali metal, alkaline earth metal borates, dispersions of hydrated alkali metal borates, dispersions of alkaline-earth metal borates, polyamide ashless dispersants and the like or mixtures of such dispersants.
3. Anti-oxidants: Anti-oxidants reduce the tendency of mineral oils to deteriorate in service which deterioration is evidenced by the products of oxidation such as sludge

- and varnish-like deposits on the metal surfaces and by an increase in viscosity. Examples of anti-oxidants include phenol type (phenolic) oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-butyl-4-dimethylamino-p-cresol, 2,6-di-tert-butyl-4-(N,N'-dimethylamino-methylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)-sulfide, and bis(3,5-di-tert-butyl-4-hydroxybenzyl). Other types of oxidation inhibitors include alkylated diphenylamines (e.g., Irganox L-57 from Ciba-Geigy), metal dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis(dibutyldithiocarbamate).
4. Anti-wear agents: As their name implies, these agents reduce wear of moving metallic parts. Examples of such agents include phosphates, phosphites, carbamates, esters, sulfur containing compounds, and molybdenum complexes.
 5. Emulsifiers: for example, linear alcohol ethoxylates.
 6. Demulsifiers: for example, addition products of alkylphenol and ethylene oxide, polyoxyethylene alkyl ethers, and polyoxyethylene sorbitan esters.
 7. Extreme pressure agents (EP agents): for example, zinc dialkyldithiophosphate (primary alkyl, secondary alkyl, and aryl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate. A preferred EP agent is zinc dialkyl dithiophosphate (ZnDTP), e.g. as one of the co-additive components for an antiwear hydraulic fluid composition.
 8. Multifunctional additives: for example, sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglycethide, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.
 9. Viscosity index improvers: for example, polymethacrylate polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrogenated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.
 10. Pour point depressants: for example, polymethacrylate polymers.

11. Foam inhibitors: for example, alkyl methacrylate polymers and dimethyl silicone polymers.

Additionally, there is provided a method of manufacturing a soot dispersant comprising an
5 A-B type block copolymer, wherein:

the A block is a soot anchoring unit, and

the B block is an oil soluble unit,

as described above.

10 As mentioned above, most suitably the soot dispersant comprises an A-B type block copolymer prepared by a controlled radical polymerization (CRP) process. Such a process allows for a high degree of control and reproducibility in the manufacture of the block copolymer units. This can also advantageously provide a more controlled and reproducible final lubricant fluid comprising the soot dispersant.

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Although traditional CRP techniques are suitable for the preparation of the present block copolymer soot dispersants, they are less preferred as such methods have limitations such as use of special agents, unpleasant odour and presence of toxic metals; the high cost of the agents and removal of odorous and toxic agents are problems associated with
20 traditional CRP techniques limit their use here.

Therefore, preferably the present method of manufacturing employs an organocatalyzed CRP (OCRCP) as described in Goto, A.; Ohtsuki, A.; Ohfuchi, H.; Tanishima, M.; Kaji, H. J. Am. Chem. Soc. 2013, 135, 11131-11139, the content of which is incorporated herein in its
25 entirety. The OCRCP manufacturing method uses alkyl iodides as initiators and organic molecules as catalysts. Utilisation of such an OCRCP method of manufacturing is low-cost, odor-free, and metal-free and overcomes the problems associated with preparing the soot dispersant via a traditional CRP method.

30 In one embodiment, the lubricant fluid composition of the present invention is used as an engine oil, preferably an automotive engine oil, and this includes use as both gasoline and diesel (including heavy duty diesel (HDDEO)) engine oils. However, the soot dispersants of the present invention (and hence the present lubricating fluids) find particular utility in use in diesel engine oils, and in particular heavy duty diesel engine oils (HDDEOs). HDDEOs
35 are potentially exposed to very high levels of soot particles when in use in a lubricating system within a heavy duty diesel engine.

The present invention will now be described with reference to the following examples and accompanying Figures in which,

5 Figure 1. shows the soot particle size distribution of Samples CR2-1, CR3-1 and CR3-2.

Figure 2. shows the soot particle size distribution of Samples CR4-3, CR4-4, CR4-5 and CR4-6.

10 Figure 3. shows the soot particle size distribution (including long-term stability test) for Sample CR 3-6-1.

Figure 4. shows the soot particle size distribution of Samples 4, CR 3-7, and CR 3-8.

15 Figure 5. shows the soot particle size distribution of Samples CR3-8 and CR4-1.

Figure 6. shows the soot particle size distribution of Samples CR4-1 and CR4-2.

Figure 7. shows the soot particle size distribution of Samples CR4-1 and CR5-1.

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Figure 8. shows the soot particle size distribution of Samples CR5-1, CR5-2 and CR5-3.

Figure 9. shows the soot particle size distribution of Samples CR4-1, CR4-1/CR6-1 blend and CR4-1/CR6-6 blend.

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Figure 10. shows the soot particle size distribution of Sample CR4-1 and comparative CR 4-1 Random.

Examples

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Materials used in the following examples are identified as follows:

Butyl methacrylate (BMA) ex. Tokyo Chemical Industry (TCI)

Lauryl methacrylate (LMA) ex. Tokyo Chemical Industry (TCI)

2-ethylhexyl methacrylate (EHMA) - Tokyo Chemical Industry (TCI)

35 2-(dimethylamino)ethyl methacrylate (DMAEMA) ex. Tokyo Chemical Industry (TCI)

Styrene (St) ex. Tokyo Chemical Industry (TCI)

Benzyl methacrylate (BzMA) ex. Tokyo Chemical Industry (TCI)
 Hydroxyethylmethacrylate (HEMA) ex. Tokyo Chemical Industry (TCI)
 Glyceryl Monomethacrylate (GLMMA) ex. Alfa Chemistry
 Yubase 3 (A Topaz oil and exemplary lubricant fluid base oil) - ex. SK Lubricants
 5 Soot - Carbon Black ex. Vulcan XC72R
 Tetrahydrofuran (THF) ex. VWR Chemicals
 Iodine (I₂) ex. Tokyo Chemical Industry (TCI)
 2,2-azobis(2,4-dimethylvaleronitrile) (V65) ex. FUJIFILM Wako Pure Chemical
 Bu₄NI (BNI) ex. Tokyo Chemical Industry (TCI)

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Test methods:

Soot Particle Dispersion Test – as described below

Soot Dispersion Stability Test – as described below

15 Example 1 preparation of a soot dispersants comprising block copolymer

In the following examples of soot dispersants comprising block copolymers Samples as detailed in Table 1 were prepared in accordance with the preparation method provided below:

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Table 1

Sample	Block Copolymer Composition	
	A Block Soot Anchoring	B Block Oil Soluble
CR2-1	DMAEMA/BzMA (10/10 units)	BMA (50 units)
CR3-1	DMAEMA/St (10/10 units)	BMA (50 units)
CR3-2	DMAEMA/St (5/15 units)	BMA (50 units)
CR3-6-1	DMAEMA/St (5/5 units)	BMA (25 units)
CR3-7	DMAEMA/St (2.5/2.5 units)	BMA/LMA (12.5/12.5 units)
CR3-8	DMAEMA/St (2.5/2.5 units)	LMA (25 units)
Sample 4	DMAEMA/St (2.5/2.5 units)	BMA (25 units)
CR4-1	DMAEMA/BzMA (2.5/2.5 units)	LMA (25 units)
CR4-2	DMAEMA/BzMA (5/5 units)	LMA (25 units)
CR4-3	DMAEMA/St (5/15 units)	LMA/BMA (25/25 units)
CR4-4	DMAEMA/St (10/10 units)	LMA/BMA (25/25 units)

CR4-5	DMAEMA/St (10/10 units)	LMA/BMA (37.5/12.5 units)
CR4-6	DMAEMA/St (5/15 units)	LMA/BMA (37.5/12.5 units)
CR 5-1	DMAEMA/BzMA (2.5/2.5 units)	EHMA (25 units)
CR 5-2	DMAEMA/BzMA (2.5/5 units)	EHMA (25 units)
CR 5-3	DMAEMA/BzMA (5/2.5 units)	EHMA (25 units)
CR 6-1	HEMA (5 Units)	LMA (25 Units)
CR 6-6	GLMMA (5 Units)	LMA (25 Units)

Block Copolymer Sample Preparation Method

5 Yubase 3 oil (to provide a solvent, and also to provide a suitable lubricant fluid base oil) was added to a reaction vessel. The B block i.e. the oil soluble block, was prepared first by charging the desired monomer (or combination of LMA/BMA monomers as stipulated in Table 1) iodine, tetrabutylammonium iodide, and 2,2'-Azodi(2-methylbutyronitrile) to the reaction vessel with stirring to mix the ingredients together. The oxygen was removed from the reaction vessel with vacuum and replaced with nitrogen to inert the vessel. The reactor was heated to 80°C and once at temperature left to react until the reaction was complete. The reaction was conducted under a nitrogen blanket with continuous stirring. After the reaction was complete the reactor was cooled to room temperature. For the Samples where BMA/LMA monomer combinations were utilised random copolymers were produced as the B block.

Subsequently, the A block i.e. the soot anchoring block, monomer (or combination for monomers), Yubase 3 oil and 2,2'-Azodi(2-methylbutyronitrile) were added to the reaction vessel with stirring. The oxygen was removed from the reaction vessel with vacuum and replaced with nitrogen to provide an inert atmosphere to the reaction vessel. The reaction vessel was heated to 80°C and once at temperature left to react, under a nitrogen blanket with stirring. After 6 hours the reaction was complete.

Chain end removal and purification

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After the synthesis of copolymer as described above the reactor was cooled to room temperature. 2-aminoethanol was added to the reaction vessel with stirring. Again, the

oxygen was removed from the reaction vessel with vacuum and replaced with nitrogen to provide an inert atmosphere to the vessel. The reaction vessel was heated to 60°C and once at temperature left to react for 5 hours, under a nitrogen blanket with stirring. The reactor was cooled to room temperature and tetrahydrofuran added to the reactor to dissolve and thin the solution. Alumina was charged to the vessel and stirred at room temperature for 2 hours to remove the release the iodide. The alumina was removed from the solution using a filter press leaving the purified polymer in tetrahydrofuran. The tetrahydrofuran was removed from the product by distillation to leave the desired block copolymer dissolved in Yubase 3 oil; this provides a suitable lubricant fluid comprising a soot dispersant block copolymer.

Table 2, below, provides block polymer conversion rate (conv), molecular weight by molecular number (Mn) and poly dispersity index (PDI) information for each Sample prepared.

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Table 2

Sample No.	Block 1 conv	Block 1 Mn	Block 1 PDI	Block 2 conv	Total (Block 1 + Block 2) Mn	Total (Block 1 + Block 2) PDI
CR2-1	79%	10500	1.07	>95%	17500	1.07
CR3-1	65%	8800	1.09	>95%	16200	1.16
CR3-2	>95%	10000	1.12	>95%	11700	1.31
CR3-6-1*	90%	2900	1.14	>95%	4200	1.89
CR3-7	94%	8300	1.19	>95%	9700	1.18
CR3-8	90%	10900	1.11	>95%	13000	1.13
Sample 4*	90%	2900	1.14	>95%	4200	1.80
CR4-1	88%	10000	1.06	>95%	11700	1.11
CR4-2	92%	11400	1.05	>95%	12000	1.08
CR4-3	80%	22700	1.24	>95%	22900	1.59

CR4-4	80%	26300	1.18	>95%	29100	1.31
CR4-5	56%	21900	1.14	>95%	24800	1.63
CR4-6	95%	19100	1.10	>95%	20900	1.38
CR 5-1	>95%	7600	1.06	>95%	8700	1.07
CR 5-2	>95%	7400	1.06	>95%	9100	1.06
CR 5-3	>95%	7600	1.07	>95%	9100	1.08
CR 6-1	88%	9600	1.06	>95%	11400	1.06
CR 6-6	84%	9100	1.05	>95%	10100	1.06

*Analysed with DMF-GPC instead of THF GPC i.e. where dimethylformamide is used as an alternative eluent.

Testing

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Soot Particle Dispersion Test

The obtained soot dispersants containing the block copolymers Samples as detailed in Table 1, above, were then tested for soot dispersion effect. Each soot dispersant Sample (5 wt%) and Yubase 3 oil were mixed in a beaker and mechanically stirred at a speed of 200 rpm utilising an overhead stirrer (a Hei-TORQUE Precision 400 ex. Heidolph) with an impeller head fitted, at a temperature of 60°C for 1 hour. Subsequently, whilst maintaining stirring, soot (5 wt%) was added (the soot dispersant, soot, and oil all together weighed a total of 50 g) and the temperature increased and maintained at a temperature of 80 °C for 24 hours.

Subsequently, the ability of a Sample to disperse the soot was analysed using a Malvern Mastersizer 3000. For each Sample tested, a small sample of the soot, dispersant and oil mixture as prepared above was diluted in THF to provide a slightly translucent test sample mixture. Prior to commencing the test, the Mastersizer particle size type was set to Carbon Back, and the solvent type was set to THF. Initially, a sample of pure THF was introduced to the Mastersizer to provide a background correction. Thereafter, a small amount of the test sample mixture was introduced, using a pipette, until the amount of test sample introduced falls within the necessary obscuration range (15%-45%), and the test sample

mixture is then analysed and the soot dispersion results provided by way of particle size distribution curve as shown in the Figures annexed hereto, and described below.

Figures 1 and 2 show the soot dispersion results using some of the example soot dispersant block copolymers prepared in Example 1. More especially, Samples CR 2-1, CR 3-1, CR 3-2, CR 4-3, CR 4-4, CR 4-5, and CR 4-6 were tested. All the samples tested exhibit a soot dispersancy effect, and it can be seen from Figures 1 and 2 that the block copolymers containing an aromatic monomer (St or BzMA) in combination with a basic DMAEMA monomer in the soot anchoring block exhibit good soot dispersion capabilities.

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Soot dispersant monomer unit ratio variation test

To better understand the effect of the monomers present in the soot dispersant block copolymers, the number of the monomer units of BMA, DMAEMA, and St for the identified CR 3 samples was varied as shown in Table 1, above. Compared with the BMA (50 units) + DMAEMA/St (10/10 units) of Sample CR 3-1, Sample CR 3-6-1 was provided with half of the DMAEMA/St (5/5) units. Figure 3 shows the soot dispersion results obtained for CR 3-6-1 which exhibited a high-level of soot dispersion (i.e. provided a smaller soot particle size).

20 Soot Dispersion Stability Test

The remaining CR 3-6-1 containing dispersion, as prepared for the soot particle dispersion test described above, was kept at room temperature for 20 days. After 20 days the soot dispersed by CR 3-6-1 was not significantly aggregated, demonstrating the long-term stability of the dispersion. Figure 3 shows the long-term stability test data, showing the “fresh” dispersion described in the test above and the dispersion after 20 days.

30 Soot Particle Dispersion Test for Monomer Variants

The Soot Particle Dispersion Test described above was utilised to investigate monomer variant Samples, as detailed in Table 1.

Figure 4 shows the soot dispersion results of Sample 4, CR3-7, and CR3-8, which provide samples with different BMA/LMA unit ratios from 25/0 to 12.5/12.5 and 0/25, and demonstrating similarly high levels of soot dispersion by the three dispersants. CR 3-8 with 25 units of LMA is the most hydrophobic and was the most soluble in the engine oil selected, with no negative effect to the soot dispersion ability. Therefore, oil solubility was improved by selecting LMA for the oil soluble unit.

As can be seen in Figure 5, Sample CR4-1 (LMA (25 units) + DMAEMA/BzMA (2.5/2.5 units)) afforded even better dispersion (smaller soot particle size) than Sample CR 3-8. The number of units of DMAEMA and BzMA was further increased to synthesize Sample CR4-2 (LMA (25 units) + DMAEMA/BzMA (5/5 units)). Figure 6 shows that CR4-1 performed better than CR4-2. Therefore, across the range of samples prepared and tested CR4-1 (LMA (25 units) + DMAEMA/BzMA (2.5/2.5 units)) was identified as the best performing dispersant in the Topaz oil used in the present tests.

Use of EHMA monomer instead of LMA was also utilised in several of the prepared block copolymers (Samples CR 5-1 to CR 5-3); a soot dispersancy effect was also observed for these samples. However, these samples were not as effective as Sample CR4-1, and this reduced effectiveness may be due to the solubility of the block copolymer in the Topaz oil selected. Figure 7 shows the soot particle size distribution of CR4-1 and CR5-1, whereas Figure 8 shows soot particle size distribution of CR5-1, CR5-2 and CR5-3.

Example 2 – Block Copolymer Blends

Two example materials were also produced where the soot dispersant comprised two distinct block copolymers blended together. In this case the examples were a) a blend of Samples CR4-1 and CR6-1 present in the base Yubase 3 oil at 1.25wt% each, and b) a blend of Samples CR4-1 and CR6-6 present in the Yubase 3 oil at 1.25wt% each. Figure 9 shows the particle size distribution of soot particles in the these block copolymer blend materials compared to Sample CR4-1; the blended materials show an improvement over CR4-1 as seen in the tail end portion.

Although the CR6-1 and CR6-6 block copolymers had been found to perform less favourable than CR4-1, when these block copolymers were blended with CR4-1 an improvement in the performance of CR4-1 was observed, as seen in Figure 9. The reason

for this performance enhancement is not yet understood, however, this may be an indication that dispersants comprising blends of block copolymers in accordance with the present invention could be “tuned” to provide optimal performance for a given base oil or for a given type of soot expected to be generated when in use.

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Example 3 - Random Copolymer (Comparative)

In the following example a soot dispersant comprising a block copolymer, Sample CR 4-1, is compared to a chemically equivalent random copolymer (identified as CR 4-1 Random).
10 As can be seen in Figure 10, the random copolymer is not as effective at dispersing the soot particles; a broader particle size tail end is evident. Although the CR 4-1 Random sample is capable of providing some soot dispersancy capabilities, the CR 4-1 sample has improved properties and this improvement is derived from the block copolymer nature of the sample.

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To prepare the comparative random copolymer in a reaction vessel there was provided a mixture of LMA (8000 mM), DMAEMA (1000 mM), BzMA (1000 mM), iodine (I₂) (120 mM), 2,2-azobis(2,4-dimethylvaleronitrile) (V65) (400 mM), and Bu₄NI (BNI) (20 mM) in Yubase 3 Topaz oil (40 wt%) at 60 °C for 16 hours. I₂ and V65 (R-N=N-R) generated an alkyl iodide
20 (R-I) initiator. V65 generated the alkyl radical (R•) which reacted with I₂ to generate R-I. BNI was used as a catalyst, and Yubase 3 was used as the reaction solvent. After 16 hours, the monomer conversion reached >95% for all three monomers. The number-average molecular weight (M_n) and PDI values of the obtained random copolymer P(LMA/DMAEMA/BzMA) were 18,800 and 1.12. Subsequently, to the reaction solution, 2-
25 aminoethanol (1000 mM) was added and heated at 60 °C for 5 hours to remove iodide from the polymer chain end. To the mixture, THF (270g), Na₂S₂O₃ (34g) and Al₂O₃ (27g) were added and stirred for 2 hours. After which, the resulting mixture was filtered and evaporated at 60 °C to remove residual THF solvent.

EXAMPLE CLAIMS

1. A soot dispersant comprising an A-B type block copolymer, wherein:
the A block is a soot anchoring unit, and
5 the B block is an oil soluble unit.
2. A soot dispersant comprising an A-B type block copolymer in accordance with claim 1, wherein one or both of the A and B block units comprise one or more vinyl containing monomer, preferably one or more methacrylate containing monomer.
- 10 3. A soot dispersant comprising an A-B type block copolymer according to claim 2, wherein the A block soot anchoring unit comprises said one or more methacrylate containing monomer.
- 15 4. A soot dispersant comprising an A-B type block copolymer according to claim 3, wherein the A block soot anchoring unit comprises said one or more methacrylate containing monomer comprising an aromatic, basic or hydrophilic group.
- 20 5. A soot dispersant comprising an A-B type block copolymer according to claim 4, wherein said methacrylate containing monomer contains an amine or aromatic group.
- 25 6. A soot dispersant comprising an A-B type block copolymer according to any one of claims 2 to 5, wherein the A block soot anchoring unit comprises one or more vinyl containing monomer selected from: methacrylic acid, glyceryl monomethylacrylate, hydroxyethyl methacrylate, styrene, methylstyrene, benzyl methacrylate, diethylamino methacrylate and 2-(dimethylamino)ethyl methacrylate.
- 30 7. A soot dispersant comprising an A-B type block copolymer according to claim 6, wherein the A block soot anchoring unit comprises one or more methacrylate containing monomer selected from benzyl methacrylate and 2-(dimethylamino)ethyl methacrylate.
- 35 8. A soot dispersant comprising an A-B type block copolymer according to any one of claims 2 to 7, wherein the B block oil soluble unit comprises said one or more methacrylate containing monomer.

9. A soot dispersant comprising an A-B type block copolymer according to claim 8, wherein the B block oil soluble unit comprises one or more alkyl-methacrylate monomers having an alkyl chain containing between 4 and 20 carbons.
- 5
10. A soot dispersant comprising an A-B type block copolymer according to claim 9, wherein said one or more alkyl-methacrylate monomer is selected from: butyl methacrylate, isopentyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, nonyl methacrylate, lauryl methacrylate, tetradecyl methacrylate, octadecyl methacrylate and hexadecyl methacrylate.
- 10
11. A soot dispersant comprising an A-B type block copolymer according to claim 10, wherein said one or more alkyl-methacrylate monomer is selected from butyl methacrylate, 2-ethylhexyl methacrylate and lauryl methacrylate.
- 15
12. A soot dispersant comprising an A-B type block copolymer according to claim 11, wherein said one or more alkyl-methacrylate monomer is lauryl methacrylate.
13. A soot dispersant comprising an A-B type block copolymer according to any preceding claim, wherein the A-B type block copolymer has a ratio of A block units to B block units (A:B) in the range of between 3 and 100 (A): 25 and 100 (B).
- 20
14. A soot dispersant comprising an A-B type block copolymer according to claim 13, wherein the A-B type block copolymer has a ratio of A block units to B block units (A:B) in the range of between 5 and 20 (A): 25 and 50 (B).
- 25
15. A soot dispersant comprising an A-B type block copolymer according to any preceding claim, wherein individually each of the A block and B block may be formed from two or more monomers and the ratio of each monomer in each block is between 1:1 and 1:4.
- 30
16. A soot dispersant comprising an A-B type block copolymer according to any preceding claim, wherein the A block soot anchoring unit has a number average molecular weight of between 8000 and 30000.
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17. A soot dispersant comprising an A-B type block copolymer according to claim 16, wherein the A block soot anchoring unit has a number average molecular weight of between 8500 and 25000.
- 5 18. A soot dispersant comprising an A-B type block copolymer according to claim 17, wherein the A block soot anchoring unit has a number average molecular weight of between 9000 and 20000.
- 10 19. A soot dispersant comprising an A-B type block copolymer according to any preceding claim, wherein the B block oil soluble unit has a number average molecular weight of between 2000 and 30000.
- 15 20. A soot dispersant comprising an A-B type block copolymer according to claim 19, wherein the B block oil soluble unit has a number average molecular weight of between 2500 and 25000.
- 20 21. A soot dispersant comprising an A-B type block copolymer according to claim 20, wherein the B block oil soluble unit has a number average molecular weight of between 6000 and 15000.
22. A soot dispersant comprising an A-B type block copolymer according to any preceding claim, wherein the A block soot anchoring unit has a polydispersity index (PDI) of between 1 and 2.
- 25 23. A soot dispersant comprising an A-B type block copolymer according to any preceding claim, wherein the B block oil soluble unit has a polydispersity index (PDI) of between 1 and 1.4.
- 30 24. A soot dispersant comprising an A-B type block copolymer according to any preceding claim, wherein the soot dispersant comprises an A block soot anchoring unit and a B block oil soluble unit each having a polydispersity index (PDI) of between 1 and 1.1.
- 35 25. A soot dispersant comprising an A-B type block copolymer according to any preceding claim, wherein the soot dispersant comprises an A-B type block copolymer prepared by a controlled radical polymerization (CRP) process.

26. A soot dispersant comprising an A-B type block copolymer according to claim 25,
wherein the soot dispersant comprises an A-B type block copolymer prepared by an
organocatalyzed CRP (OCRP) process.
- 5
27. A lubricant fluid composition comprising a soot dispersant in accordance with any
one of claims 1 to 26 and a lubricating oil.
28. A lubricant fluid composition according to claim 27, wherein the lubricating oil is
selected from an API Group I, II, III, IV, V base stock or mixtures thereof.
- 10
29. The lubricant fluid composition of claim 27 or 28 comprising at least 0.1 wt% of the
soot dispersant based on the total weight of the composition.
- 15
30. The lubricant fluid composition of any one of claims 27 to 29 comprising no more
than 15%wt of the soot dispersant based on the total weight of the composition.
31. The lubricant fluid composition of any one of claims 27 to 30, wherein the lubricant
composition is non-aqueous.
- 20
32. The lubricant fluid composition of any one of claims 27 to 31, further comprising less
than 5% water by weight based on the total weight of the composition.
33. The lubricant fluid composition of any one of claims 27 to 32, wherein the lubricant
fluid composition is substantially water free.
- 25
34. The lubricant fluid composition of any one of claims 27 to 33 further comprising one
or more of the following further additives: friction reducing agents, additional
dispersants, anti-oxidants, anti-wear agents, emulsifiers, demulsifiers, extreme
pressure agents, multifunctional additives, viscosity index improvers, pour point
depressants, and foam inhibitors.
- 30
35. The lubricant fluid composition of claim 34 further comprising at least 0.5 wt% of a
further additive or a mixture of further additives based on the total weight of the
composition.
- 35

36. The lubricant fluid composition of any one of claims 34 or 35 further comprising up to 30 wt% of a further additive or a mixture of further additives based on the total weight of the composition.
- 5 37. Use of the lubricant fluid composition of any one of claims 27 to 36 as an engine oil.
38. Use according to claim 37, wherein said engine oil is a heavy duty diesel engine oil.