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CA 2348538 C 2008/09/16

(11)(21) **2 348 538**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 1999/11/03
(87) Date publication PCT/PCT Publication Date: 2000/05/18
(45) Date de délivrance/Issue Date: 2008/09/16
(85) Entrée phase nationale/National Entry: 2001/04/27
(86) N° demande PCT/PCT Application No.: EP 1999/009668
(87) N° publication PCT/PCT Publication No.: 2000/027956
(30) Priorité/Priority: 1998/11/06 (EP98309090.3)

(51) Cl.Int./Int.Cl. *C10M 143/12* (2006.01),
C10M 143/10 (2006.01), *C10L 1/16* (2006.01)
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(54) Titre : COMPOSITION D'HUILE LUBRIFIANTE
(54) Title: LUBRICATING OIL COMPOSITION

(57) **Abrégé/Abstract:**

A lubricating oil composition comprising a di-block copolymer of poly(monovinyl aromatic hydrocarbon) and hydrogenated poly(conjugated diene) as a dispersant additive is described. The said di-block copolymer preferably comprises poly(monovinyl aromatic hydrocarbon) in the molecular weight range 8,000 - 30,000. The diblock copolymers are useful as dispersant additives in lubricant oils, reduce heavy metal corrosion, reduce degradation of elastomeric seals and are less sensitive to the presence of over-based detergents.



**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷: C10M 143/12, C10L 1/16 // (C10M 143/12, 143:10), C10N 20:04, 30:04, 60:02	A1	(11) International Publication Number: WO 00/27956 (43) International Publication Date: 18 May 2000 (18.05.00)
(21) International Application Number: PCT/EP99/09668 (22) International Filing Date: 3 November 1999 (03.11.99) (30) Priority Data: 98309090.3 6 November 1998 (06.11.98) EP (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel Van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: DE JONG, Feike; Carel Van Bylandtlaan 30, NL-2596 HR The Hague (NL). WEDLOCK, David, J.; Shell Centre, London, Greater London SE1 7NA (GB). (74) Agent: MANSELL, Keith, Rodney; PO Box 1, Milton Hill, Abingdon, Oxfordshire OX13 6BB (GB).		(81) Designated States: CA, JP, SG, European patent (BE, DE, ES, FR, GB, IT, NL). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: LUBRICATING OIL COMPOSITION (57) Abstract A lubricating oil composition comprising a di-block copolymer of poly(monovinyl aromatic hydrocarbon) and hydrogenated poly(conjugated diene) as a dispersant additive is described. The said di-block copolymer preferably comprises poly(monovinyl aromatic hydrocarbon) in the molecular weight range 8,000 – 30,000. The diblock copolymers are useful as dispersant additives in lubricant oils, reduce heavy metal corrosion, reduce degradation of elastomeric seals and are less sensitive to the presence of over-based detergents.		

LUBRICATING OIL COMPOSITIONFIELD OF THE INVENTION

The present invention relates to lubricating oil compositions, in particular, lubricating oil compositions having di-block co-polymers of poly(monovinyl aromatic hydrocarbon) and poly(conjugated diene) as dispersants.

BACKGROUND OF THE INVENTION

High molecular weight oil-soluble di-block copolymers can be used for improving the effective viscosity index (VI) of lubricating oil formulations. The VI is a measure of the tendency of a fully formulated oil to resist decrease in viscosity with increasing temperature. The higher the viscosity index - the more the fully formulated oil can resist viscosity decrease with increasing temperature. Base oils have an inherent VI but this is normally not adequate for all engine operational needs.

Specifically synthesised ashless dispersants are added to fully formulated crankcase lubricant oils to keep combustion-derived soots and oxidation-derived sludges in dispersion. Generally, these are surface active molecules of 2000 to 6000 Daltons molecular weight. For example, polyisobutylene (PIB) is chemically linked to maleic anhydride (MALA) to give a covalently bonded compound PIBMALA. This may then be reacted with a variety of polyamines or polyalcohols to give a range of molecules; PIBMALA amines and PIBMALA esters. Typically the PIB will be in the molecular weight range 1000 to 3000 Dalton, and the polyamine will be diethylene triamine (DETA), triethylene tetramine (TETA) or higher polyamine homologues. These molecules are surface active and can maintain in a stable colloid state, soots and sludges in a crankcase lubricating oil.

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Certain oil-soluble polymers can effectively increase the viscosity of a lubricant oil formulation at higher temperatures (typically above 100°C) while not excessively increasing high shear rate viscosity at lower temperatures (typically -10 to -15°C). These oil-soluble polymers are generally relatively high molecular weight (>100,000 Dalton) compared to base oil and additive components. They may be polymers such as OCPs (olefin copolymers), star polymers, or association di-block copolymers, generally handled for convenience as a dissolved technical concentrate in base oil carrier. It is known that such di-block copolymers associate or aggregate to form micelles in order to reduce exposure of the insoluble chain section to the base oil. This assists their thickening tendency over a limited temperature range.

Di-block copolymers may act as colloid (small particle) stabilisers or dispersants in solid-in-oil dispersions, when one block of the chain is capable of adsorbing to a particulate substrate and when the other block is readily soluble in the liquid oil-continuous phase. Such di-block copolymers can function as both dispersants with respect to soot and sludge, and viscosity index improvers (VIIs).

Among the groups of polymers which can give this VI credit to fully formulated internal combustion engine lubricant oils (gasoline and diesel type) are di-block copolymers of polystyrene (PS) and hydrogenated polyisoprene (HPIP). The polystyrene units are not soluble in the base oil, the hydrogenated polyisoprene is and the polymers are synthesised to give a net balance of base oil solubility. For instance, VIIs comprising PS/HPIP diblock copolymers of high molecular weight can cause improved dispersancy as compared with HPIP star

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polymer VII alone (figure 1). However, it is understood that di-block copolymers cannot function as dispersants as well as functioning as VIIs at lower molecular weight because the micellisation is expected to be overly compact and this would compromise dispersancy and their thickening tendency over a limited temperature range. Furthermore, the polystyrene chain length is expected to be too short to achieve absorption/stability in relation to soots and sludges.

10 Known formulations of high molecular weight di-block copolymers of polystyrene and hydrogenated polyisoprene have shown that for dispersions of a carbon black (Vulcan XC72R™, Cabot) in a base oil of lubricating quality, the viscosity of the dispersion at a given shear rate or shear stress is lower for the oil containing the polystyrene-hydrogenated polyisoprene di-block copolymers of total molecular weight 100,000 or 135,000 respectively. The styrene/isoprene ratio required is normally such as to confer base oil solubility of the di-block copolymer but is typically 35,000 (polystyrene) + 65,000 (hydrogenated polyisoprene) in the case of the 100,000 molecular weight di-block, and 50,000 (polystyrene) + 85,000 (hydrogenated polyisoprene) in the case of the 135,000 molecular weight di-block. In either case, for good solubility a high hydrogenated polyisoprene: polystyrene ratio of at least 3:2 is expected to give good results.

This beneficial dispersion behaviour is seen for fully formulated diesel engine lubricants containing such di-block VIIs in specification diesel engine tests such as the Mack T8 test within the API (American Petroleum Institute) CG-4 performance category. This test measures soot-induced thickening of the oil during engine use. This dispersant behaviour of polystyrene-hydrogenated

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polyisoprene di-block copolymers manifests itself as beneficial performance in a range of crankcase lubricant specification engine tests, typically reducing soot-induced thickening of diesel engine lubricants and enhancing engine cleanliness by acting as a sludge and soot dispersant in diesel and gasoline engine lubricants. However, such relatively high molecular weight dispersant additives are incompatible with most additive packages.

Corrosion and degradation of parts is a significant problem in lubrication technology. Succinimide dispersants are known to cause some corrosion of heavy metal bearings for instance, copper and lead components, and, similarly, degrade elastomeric seals. Much research has gone into reducing corrosion levels for heavy metals and degradation rates for elastomeric seals.

Succinimide dispersants are also known to have reduced effectiveness in the presence of over-based detergents.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides a lubricating oil composition comprising: a major amount of a lubricating base oil, and a minor amount of a di-block copolymer of poly(monovinyl aromatic hydrocarbon) and hydrogenated poly(conjugated diene) as a dispersant additive, said di-block copolymer comprising poly(monovinyl aromatic hydrocarbon) in the number average molecular weight (M_n) range 8,000-30,000, wherein the poly(monovinyl aromatic hydrocarbon): hydrogenated poly(conjugated diene) number average molecular weight ratio is in the range of 3:2 to 10:1.

In another aspect, the present invention provides a di-block copolymer of poly(monovinyl aromatic hydrocarbon) and hydrogenated poly(conjugated diene) for use as a dispersant in a lubricant oil composition, said di-block

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copolymer comprising poly(monovinyl aromatic hydrocarbon)
in the number average molecular weight (M_n) range 8,000-
30,000, wherein the poly(monovinyl aromatic hydrocarbon):
hydrogenated poly(conjugated diene) number average
5 molecular weight ratio is in the range of 3:2 to 10:1.

In a further aspect, the invention provides a
dispersant for a lubricant oil composition comprising the
di-block copolymer in accordance with the invention.

In another aspect, the present invention provides an
10 additive package for a lubricant oil composition
comprising the di-block copolymer in accordance with the
invention.

In a further aspect, the present invention provides a
use of the lubricating oil composition in accordance with
15 the invention, as a dispersant.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 graphically plots kinematic viscosity
response of a lubricant as a function of dispersant and
20 VII content.

Figure 2 illustrates the dispersity index of specified
diblock copolymers in a Type A (5.5cst) basestock.

Figure 3 compares viscosity to shear rate for
specified diblock copolymers in a Type A (5.5cst)
25 basestock.

Figure 4 compares the dispersing properties of diblock
copolymers of Examples 7 and 8 in a base oil.

Figure 5 illustrates a comparison of the dispersing
properties of diblock copolymers of Examples 7 and various
30 reference dispersants in a base oil.

5 DETAILED DESCRIPTION

According to the present invention there is provided a lubricating oil composition comprising a di-block copolymer of poly(monovinyl aromatic hydrocarbon) and poly(conjugated diene) as a dispersant additive, the said
10 di-block copolymer comprising poly(monovinyl aromatic hydrocarbon) in the molecular weight range 8,000 - 30,000.

Preferably, the molecular weight range of the poly(monovinyl aromatic hydrocarbon) is in the range 8,400 - 25,000. Most preferably, the poly(monovinyl aromatic
15 hydrocarbon) molecular weight range is between 8,400 and 20,000.

According to the second aspect of the present invention there is provided a lubricating oil composition comprising a di-block copolymer of poly(monovinyl aromatic
20 hydrocarbon) and poly(conjugated diene) as dispersant, the poly(monovinyl aromatic hydrocarbon): poly(conjugated diene) molecular weight ratio being in the range from 0.2:1 to 10:1.

Preferably, the poly(monovinyl aromatic hydrocarbon):poly(conjugated diene) ratio is in the range
25 3:2 to 10:1. More preferably, the poly(monovinyl aromatic hydrocarbon):poly(conjugated diene) ratio is in the range of 3:2 to 5:1.

Preferably, the percentage of poly(monovinyl aromatic hydrocarbon) in the poly(monovinyl aromatic
30 hydrocarbon)/poly(conjugated diene) di-block copolymer is at least 60% by weight, more preferably between 60% and 90% by weight, most preferably between 60% and 85% by

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weight. Preferred monovinyl aromatic hydrocarbon monomers for use in preparing the poly(monovinyl aromatic hydrocarbon) blocks for use in the present invention include styrene, alkyl-substituted styrene, and alkoxy-substituted styrene, vinyl naphthalene, and alkyl-substituted vinyl naphthalene. The alkyl and alkoxy substituents may typically comprise from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms. The number of alkyl or alkoxy substituents per molecule, if present, may range from 1 to 3, and is preferably one.

Preferred conjugated diene monomers for use in preparing the poly(conjugated diene) block for use in the present invention include those conjugated dienes containing from 4 to 24 carbon atoms such as 1,3-butadiene, isoprene, piperylene, methylpentadiene, 2-phenyl-1,3-butadiene, 3,4-dimethyl-1,3-hexadiene, and 4,5-diethyl-1,3-octadiene.

Preferably, the block copolymer(s) in accordance with the present invention comprise(s) at least one poly(monovinylaromatic hydrocarbon) block and at least one poly(conjugated diene) block. Preferred block copolymers are selected from the group consisting of those of the formulae $A_n(BA)_m$, wherein A represents a block polymer of predominantly poly(monovinyl aromatic hydrocarbon), wherein B represents a block of predominantly poly(conjugated diene), wherein m represents an integer ≥ 1 , preferably 1 to 8, more preferably 1 to 4, in particular 1, and n represents 0 or 1.

More preferably, the monovinyl aromatic hydrocarbons are styrene and/or alkyl-substituted styrene, in particular styrene.

Preferred conjugated dienes are those containing from 4 to 12 carbon atoms, more preferably from 4 to 6 carbon

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atoms. Isoprene and butadiene are the most preferred conjugated diene monomers for use in the present invention because of their low cost and ready availability.

More preferably, the A blocks represent predominantly
5 poly(styrene) blocks and the B blocks represent predominantly poly(butadiene) blocks, predominantly poly(isoprene) blocks or isoprene/butadiene copolymer blocks.

With the term "predominantly" in relation to block A
10 is meant that the said block is mainly derived from a monovinylaromatic hydrocarbon monomer (eg styrene) and up to 20% by weight of another monovinylaromatic hydrocarbon monomer (eg a-methylstyrene), preferably up to 10% by weight; or up to 10% by weight of a conjugated diene
15 monomer (eg butadiene and/or isoprene), preferably up to 5% by weight.

With the term "predominantly" in relation to block B is meant that the said block is mainly derived from a conjugated diene monomer or a mixture of two or more,
20 preferably two, conjugated diene monomers and up to 10% by weight of a monovinylaromatic hydrocarbon monomer, preferably up to 5% by weight.

Multivalent coupling agents may be used and include those commonly known in the art.

25 Examples of suitable multivalent coupling agents contain from 2 to 8, preferably 2 to 6, more preferably 2, 3 or 4 functional groups.

More preferably, the block copolymers contain pure poly(styrene), and pure hydrogenated poly(isoprene)
30 blocks.

Block copolymers and selectively hydrogenated block copolymers comprising at least one poly(monovinylaromatic hydrocarbon) block and at least one poly(conjugated diene)

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block, are well known in the art and available commercially.

The block copolymers can be made by anionic polymerisation with an alkali metal initiator such as sec-
5 butyllithium as disclosed for instance in U.S. 4,764,572, U.S. 3,231,635, U.S. 3,700,633, and U.S. 5,194,530.

The poly(conjugated diene) block(s) of the block copolymer may be selectively hydrogenated, typically a residual ethylenic unsaturation of at most 20%, more
10 preferably at most 5%, and most preferably at most 2% of its original unsaturation content prior to hydrogenation. Preferably, the block copolymers to be used in the compositions according to the invention are selectively hydrogenated. Hydrogenation may be effected selectively
15 as disclosed in U.S Patent Reissue 27,145. The hydrogenation of these polymers and copolymers may be carried out by a variety of well established processes including hydrogenation in the presence of such catalysts as Raney Nickel, noble metals such as platinum and the
20 like, soluble transition metal catalysts and titanium catalysts as in U.S. Patent 5,039,755. The polymers may have different diene blocks and these diene blocks may be selectively hydrogenated as described in U.S. Patent 5,001,199. As set out above, the ethylenic unsaturation
25 in the block copolymers may be removed by selective hydrogenation. In addition, it is also possible to selectively remove the ethylenic unsaturation in some arms whilst leaving the ethylenic unsaturation in other arms intact as disclosed for example in EP 0540109, 0653453 and
30 0653449.

The vinyl content of (hydrogenated) poly(isoprene) block(s) may vary within wide limits and is typically in the range from 0 to 75% mol, preferably 0 to 20% mol.

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Advantageously, such dispersant additives have little deleterious effect on heavy metal bearing corrosion and seal elastomers compared to PIBMALA amines and, more importantly, have dispersancy largely independent of
5 detergent soap levels unlike succinimides. Furthermore, surprisingly, the lower molecular weight di block copolymers form micellar structures in base oil which dissociate above certain temperatures.

The present invention preferably provides a
10 lubricating oil composition comprising a major amount (more than 50%w) of a lubricating base oil and a minor amount (less than 50%w), preferably from 0.1 to 20%w, especially from 0.5 to 10%w (active matter), of the di-block copolymer according to the present invention, the
15 percentages by weight being based on the total weight of the composition.

A lubricant formulation may be produced by addition of an additive package to the lubricating oil. A minor amount of viscosity modifier may be included if the final
20 lubricant formulation is to be a multigrade version. The type and amount of additive package used in the formulation depends on the final application, which can include spark-ignition and compression-ignition internal combustion engines, including automobile and truck
25 engines, marine and railroad diesel engines, gas engines, stationary power engines and turbines.

The lubricant formulation is blended to meet a series of performance specifications as classified in the US by a tripartite arrangement between the Society of Automotive
30 Engineers (SAE), American Petroleum Institute (API) and American Society for Testing and Materials (ASTM). Also the American Automobile Manufacturers Association (AAMA) and Japan Automobile Manufacturers Association Inc.

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(JAMA), via an organisation called the International Lubricant Standardisation and Approval Committee (ILSAC), jointly develop minimum performance standards for gasoline-fuelled passenger car engine oils.

5 In Europe, engine oil classifications are set by the Association des Constructeurs Europeens de l'Automobile (ACEA) in consultation with the Technical Committee of Petroleum Additive Manufacturers (ATC) and Association
10 Technique de l'Industries Europeens des Lubrifiants (ATIEL). Besides these internationally recognised oil classification systems, many, if not all, Original Equipment Manufacturers (OEMs) have their own in-house performance requirements that must be met by lubricant formulations used for first (i.e. factory) fill.

15 Suitable lubricating base oils are natural, mineral or synthetic lubricating oils.

 Natural lubricating oils include animal and vegetable oils, such as castor oil. Mineral oils comprise the lubricating oil fractions derived from crude oils, e.g. of
20 the naphthenic or paraffinic types or mixtures thereof, coal or shale, which fractions may have been subjected to certain treatments such as clay-acid, solvent or hydrogenation treatments. Synthetic lubricating oils include synthetic polymers of hydrocarbons, e.g. derived
25 from polyalphaolefins, isomerised slack wax, modified alkylene oxide polymers and esters, which are known in the art. These lubricating oils are preferably crankcase lubricating oil formulations for spark-ignition and compression-ignition engines, but include also hydraulic
30 lubricants, metal-working fluids and automatic transmission fluids.

 Preferably the lubricating base oil component of the compositions according to the present invention is a

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mineral lubricating oil or a mixture of mineral lubricating oils, such as those sold by member companies of the Royal Dutch/Shell Group of Companies under the designations "HVI", or the synthetic hydrocarbon base oils sold by member companies of the Royal Dutch/Shell Group of Companies under the designation "XHVI" (trade mark).

The viscosity of the lubricating base oils present in the compositions according to the present invention may vary within wide ranges, and is generally from 3 to 35 mm²/s at 100°C.

The lubricating oil compositions according to the present invention may contain various other additives known in the art, such as:

- (a) Viscosity index improvers or modifiers. The viscosity modifier may be of the solid type or a concentrate in a natural or synthetic base stock and can be defined as a substance, usually a polymer, which substantially improves (e.g. by at least 5 units) the viscosity index (e.g. as determined by ASTM procedure D2270) by its incorporation. These can all be incorporated into the final lubricant formulation to give the desired performance properties thereof. Examples of such viscosity modifiers are linear or star-shaped polymers of a diene such as isoprene or butadiene, or a copolymer of such a diene with optionally substituted styrene. These copolymers are suitably block copolymers and are preferably hydrogenated to such an extent as to saturate most of the olefinic unsaturation. A number of other types of viscosity modifier are known in the art, and many of these are described in Proceedings of Conference "Viscosity and flow properties of multigrade engine oils", Esslingen, Germany, December

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1977. It is also known in the art that viscosity modifiers can be functionalised to incorporate dispersancy (e.g. dispersant viscosity index improvers based on block copolymers, or polymethacrylates) and/or antioxidant functionality as well as viscosity modification and they can also have pour point depressants mixed in to give handleable products in cold climates.
- 5
- (b) Ashless or ash-containing extreme pressure/anti-wear additives, such as, for example, those of the metal containing dithiophosphate or ashless dithiocarbamate type, and mixtures thereof. The actual composition of the individual components will vary depending upon final application and hence can be based on a range of metal ion types and various alcohols, in which both alkyl and aryl moieties may be of varying size. Preferred are zinc dithiophosphates (ZDTPs) or sodium dithiophosphates.
- 10
- 15
- (c) Dispersants including succinimides and Mannich bases, both of various molecular weights and amine type, including borated versions, or esters also of varying type and molecular weight. Preferred are ashless dispersants such as polyolefin-substituted succinimides, e.g. those described in GB-A-2231873.
- 20
- 25
- (d) Anti-oxidants, for example of the aminic type such as "IRGANOX" (trade mark) L57 (tertiary C₄-C₁₂ alkyl diphenylamine) or phenolic type such as "IRGANOX" (trade mark) L135 (2,6-ditertiary-butyl-4-(2-carboxy(alkyl)ethyl)phenol) (ex. CIBA Speciality Chemicals) or a soluble copper compound at a copper concentration of between 50 and 500 ppm.
- 30
- (e) Anti-rust compounds of, for example, the ethylene/propylene block copolymer type.

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- (f) Friction modifiers for fuel economy, either metal (e.g. molybdenum) containing, or metal free esters and amines, or synergistic mixtures thereof.
- (g) Metal containing detergents such as phenates, sulphonates, salicylates or naphthenates, or mixtures thereof, all of which detergents may be either neutral or overbased, such overbased detergents being carbonates, hydroxides or mixtures thereof. The metals are preferably calcium, magnesium or manganese, although alkali metals such as sodium or potassium could also be used.
- (h) Copper passivators, preferably of the alkylated or benzylated triazole type.

The di-block copolymer of the present invention may also be used in fuels. Accordingly, the present invention further provides a fuel composition comprising a major amount (more than 50%w) of a base fuel and a minor amount (less than 50%w), preferably from 0.001 to 2%w, more preferably from 0.001 to 0.5%w and especially from 0.002 to 0.2%w (active matter), of a di-block copolymer according to the present invention, the percentages by weight being based on the total weight of the composition.

Suitable base fuels include gasoline and diesel fuel. These base fuels may comprise mixtures of saturated, olefinic and aromatic hydrocarbons, and may contain a range of sulphur levels, e.g. in the range 0.001 to 0.1%w. They can be derived from straight-run gasoline, synthetically produced aromatic hydrocarbon mixtures, thermally catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions or catalytically reformed hydrocarbons.

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The fuel compositions according to the present invention may contain various other additives known in the art, such as:

- 5 (a) Anti-knock additives, such as lead compounds, or other compounds such as methyl cyclopentadienyl-manganese tricarbonyl or orthoazidophenyl.
- (b) Co-antiknock additives, such as benzoylacetone.
- (c) Dehazers, such as those commercially available as
10 "NALCO" (trade mark) EC5462A (ex. Nalco), "TOLAD" (trade mark) 2683 (ex. Baker Petrolite), EXP177, EXP159M, EXP175, EP409 or EP435 (ex. RE Speciality Chemicals), and T9360-K, T9305, T9308, T9311 or T327 (ex. Baker Petrolite™).
- (d) Anti-foaming agents, such as those commercially
15 available as "TEGOPREN" (trade mark) 5851, Q 25907, MR1027, MR2068 or MR2057 (ex. Dow Corning), "RHODORSIL" (trade mark) (ex. Rhone Poulenc), and "WITCO" (trade mark) SAG TP325 or SAG327 (ex. Witco).
- (e) Ignition improvers (e.g. 2-ethylhexyl nitrate,
20 cyclohexyl nitrate, di-tertiary-butyl peroxide and those disclosed in US-A-4208190 at Column 2, line 27 to Column 3, line 21)
- (f) Anti-rust agents (e.g. that commercially sold by
25 Rhein Chemie, Mannheim, Germany as "RC 4801", or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms (e.g. the pentaerythritol
30 diester of polyisobutylene-substituted succinic acid)
- (g) Reodorants.
- (h) Anti-wear additives.

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- (i) Anti-oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine).
- (j) Metal deactivators.
- 5 (k) Lubricity agents, such as those commercially available as EC831, "PARADYNE" (trade mark) 631 or 655 (ex. Paramins™) or "VEKTRON" (trade mark) 6010 (ex. Shell Additives International Limited).
- 10 (l) Carrier fluids such as a polyether e.g. a C₁₂-C₁₅ alkyl-substituted propylene glycol ("SAP 949"), "HVI" or "XHVI" (trade mark) base oil, which are commercially available from member companies of the Royal Dutch/Shell Group of Companies, a polyolefin derived from C₂-C₆ monomers, e.g. polyisobutylene
15 having from 20 to 175, particularly 35 to 150, carbon atoms, or a polyalphaolefin having a viscosity at 100°C in the range 2×10^{-6} to 2×10^{-5} m²/s (2 to 20 centistokes), being a hydrogenated oligomer containing 18 to 80 carbon atoms derived from at
20 least one alphaolefinic monomer containing from 8 to 18 carbon atoms.

The lubricating oil and fuel compositions of the present invention may be prepared by adding the di-block copolymer of the present invention to a lubricating base
25 oil or base fuel. Conveniently, an additive concentrate is blended with the lubricating base oil or base fuel. Such a concentrate generally comprises an inert carrier fluid and one or more additives in a concentrated form. Hence the present invention also provides an additive
30 concentrate comprising an inert carrier fluid and from 10 to 80%w (active matter) of the di-block copolymer according to the present invention, the percentages by weight being based on the total weight of the concentrate.

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Examples of inert carrier fluids include hydrocarbons and mixtures of hydrocarbons with alcohols or ethers, such as methanol, ethanol, propanol, 2-butoxyethanol or methyl tert-butyl ether. For example, the carrier fluid
5 may be an aromatic hydrocarbon solvent such as toluene, xylene, mixtures thereof or mixtures of toluene or xylene with an alcohol. Alternatively, the carrier fluid may be a mineral base oil or mixture of mineral base oils, such as those sold by member companies of the Royal
10 Dutch/Shell Group of Companies under the designations "HVI", e.g. "HVI 60" base oil, or the synthetic hydrocarbon base oils sold by member companies of the Royal Dutch/Shell Group of Companies under the designation "XHVI" (trade mark).

Non-limiting examples of suitable additive concentrations in final blended lubricating oil compositions are:

Oil component % by weight	A	B	C	D	E	F
Alkaline earth sulphonate detergent	3.8	3.4	--	--	--	--
Alkaline earth phenate detergent	1.2	1.1	--	--	--	--
Alkaline earth salicylate detergent	--	--	4.6	2.5	3.6	10.5
High molecular weight dispersant	--	5.5	8.0	5.0	11.5	--
Low molecular weight dispersant	6.0	2.0	--	--	--	9.0
Primary ZDTP	0.5	--	--	0.3	--	0.7
Secondary ZDTP	0.4	1.0	0.9	0.7	1.2	0.6
Aminic antioxidant	--	--	0.6	0.8	0.3	--
Phenolic antioxidant	0.7	1.2	--	--	--	--
Base oil	balance	balance	balance	balance	balance	balance

Non-limiting examples of suitable additive concentrates for blending lubricating oil compositions are:

Oil component % by weight	A	B	C	D	E	F
Alkaline earth sulphonate detergent	29.9	23.8	--	--	--	--
Alkaline earth phenate detergent	9.4	7.7	--	--	--	--
Alkaline earth salicylate detergent	--	--	32.4	26.6	21.6	50.2
High molecular weight dispersant	--	38.5	56.3	53.2	68.9	--
Low molecular weight dispersant	47.2	14.0	--	--	--	43.1
Primary ZDTP	3.9	--	--	3.2	--	3.3
Secondary ZDTP	3.1	7.0	6.3	7.4	7.2	2.9
Aminic antioxidant	--	--	4.2	8.5	1.8	--
Phenolic antioxidant	5.5	8.4	--	--	--	--
Base oil	balance	balance	balance	balance	balance	balance

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The present invention still further provides the use of a di-block copolymer according to the present invention as a dispersant additive.

5 The invention will now be described with reference to the accompanying examples.

The preparations were living polymer anionic polymerisations with sequential addition of monomer using butyl lithium as the anion initiator, at ~50C. Hydrogenations were performed using Pd on carbon catalyst
10 (Degussa 450) at ~130°C.

Examples of di-block copolymers synthesised and evaluated

	PS (Mn) Molecular weight	HPiP (Mn) Molecular weight	Total Molecular weight	% PS
Example 1	561	755	1316	43
Example 2	867	970	1837	47
Example 3	1032	1536	2568	40
Example 4	2519	4481	7000	36
Example 5	4970	4517	9487	52
Example 6	8400	5600	14000	60
Example 7	17380	4620	22000	79
Example 8	35000	65000	100000	35
Example 9	~48000	105000	153000	31

Dispersancy

15 Dispersant samples were assessed rheologically in a variable shear rate rheometer as carbon black dispersions (5% by weight Vulcan XC72R, Cabot), in either base oil solution or in a fully formulated screener oil at 100°C.

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The samples were assessed first for carbon black (CB) dispersancy as solutions in Type A base stock at 0.5% by weight (active matter (a.m.)), since this was felt to be likely to give the best possible chance of demonstrating a dispersancy lift. In essence only Example 7 showed a significant dispersancy lift and in fact the Example 1, with the lowest total molecular weight, appeared to thicken the carbon black dispersion, see figures 2 and 3.

For examples 5-7 the PS chain was synthesised to a higher molecular weight than the HPIP chain, for an essentially constant HPIP mol. weight. Only a slight dispersancy performance at 8400 MW in Type A base stocks was observed until the molecular weight of PS was shifted from 8.4 to 17.5K dalton (Example 7) - for the HPIP held in the range 4 to 5 K dalton.

Since the transition in behaviour from non-dispersant to dispersant for Example 5 through to 7 demonstrates clearly a critical chain length of PS required, this may suggest a 'statistical' adsorption process where the adsorption energy per monomer unit is weak but multi-point attachment ensures no desorption once attachment has occurred ie a typical 'homopolymer' adsorption process. In figure 2, the complete rheogram shows that Example 7 is probably directionally stronger as a dispersant than Example 8 at the same active matter level. This same effect is shown in figure 3, which plots kinematic viscosity vs shear rate.

Example 7 was also assessed in the more aromatic Type B base oil to see if similar base oil sensitivity to dispersancy performance, as noted for Example 8, persisted for this polymer also at 0.5% by weight (a.m.). This was found to be the case, see figure 4.

When assessed in a fully formulated oil screener, it performed perfectly well when compared to conventional

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succinimide dispersants. Further, while conventional succinimide dispersants have acceptable soot dispersancy in low polar base stocks, such as Type A and synthetic base stock - it has been found that the copolymers of the invention have significant treat rate advantages combined with non-engine performance bonuses.

Comparative data are shown in figure 5 ranking Example 7 against succinimide and post-treated succinimide dispersants, where it is seen that at 0.5% by weight (a.m.) of Example 7, a dispersancy response is seen which is equivalent to 2.0% by weight (a.m.) of Reference 2 (a high nitrogen content succinimide dispersant) in a detergent inhibitor (DI) containing screener formulation.

As an example of a fully blended product, it was found possible to blend a 15W40 fully formulated oil containing a shear stable VII with 1% by weight (a.m.) of Example 7 and 6% polybutenyl succinimide (molecular weight range of polybutene 1500-2500) and other DI components with no viscometric problems.

It has been demonstrated in principle that is possible to obtain carbon black soot dispersancy from low molecular weight analogues of diblock copolymers. It has been surprisingly demonstrated that a critical chain length of poly(monovinyl aromatic hydrocarbon) is required to achieve adsorption/stability and that dispersancy is surprisingly not compromised by overly compact micelle formation.

The isoprene/styrene diblocks dispersants show significantly lower corrosion activity (Table 1) than succinimide dispersants in the Cummins L10 bench corrosion test.

The isoprene/styrene diblocks do not degrade engine elastomer seals to the same extent as succinimide dispersants.

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All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

Table 1

Corrosion data

Dispersant	% w (a.m.)	Cummins L-10 bench corrosion test data			
		tin corrosion/ppm	lead corrosion/ppm	copper corrosion/ppm	
succinimide	0.9	<1	10	4	
succinimide	1.35	<1	17	5	
succinimide	1.8	<1	29	6	
diblock (sty/iso)	1.25	<1	2	3	

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CLAIMS:

1. A lubricating oil composition comprising:
a major amount of a lubricating base oil, and
a minor amount of a di-block copolymer of
poly(monovinyl aromatic hydrocarbon) and hydrogenated
poly(conjugated diene) as a dispersant additive, said di-
block copolymer comprising poly(monovinyl aromatic
hydrocarbon) in the number average molecular weight (M_n)
range 8,000-30,000, wherein the poly(monovinyl aromatic
hydrocarbon): hydrogenated poly(conjugated diene) number
average molecular weight ratio is in the range of 3:2 to
10:1.
2. The lubricating oil composition according to claim 1,
wherein the number average molecular weight (M_n) range of the
poly(monovinyl aromatic hydrocarbon) is in the range 8,400-
25,000.
3. The lubricating oil composition according to claim 1 or
2, wherein the di-block copolymer is selected from the group
consisting of di-block copolymers of the formula $A_n(BA)_m$,
wherein A represents a block polymer of predominately
poly(monovinyl aromatic hydrocarbon), wherein B represents a
block of predominately poly(conjugated diene), wherein m
represents an interger ≥ 1 , and wherein n represents 0 or 1.
4. The lubricating oil composition of claim 3, wherein
m = 1 to 4.
5. The lubricating oil composition of claim 3, wherein
m = 1.
6. The lubricating oil composition according to any one of
claims 1 to 5, wherein the monovinyl aromatic hydrocarbon
used to prepare the poly(monovinyl aromatic hydrocarbon)

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block of said di-block copolymer is styrene, alkyl-substituted styrene, or alkoxy substituted styrene.

7. The lubricating oil composition according to any one of claims 1 to 6, wherein the conjugated diene used in preparing the hydrogenated poly(conjugated diene) block is a conjugated diene containing from 4 to 24 carbon atoms.

8. The lubricating oil composition according to claim 7, wherein the conjugated diene is 1,3-butadiene; isoprene; piperylene; methylpentadiene; 2-phenyl-1,3-butadiene; 3,4-dimethyl-1,3-hexadiene; or 4,5-diethyl-1,3-octadiene.

9. The lubricating oil composition according to any one of claims 1 to 8, wherein the poly(monovinyl aromatic hydrocarbon) is polystyrene.

10. The lubricating oil composition according to any one of claims 1 to 9, wherein the hydrogenated poly(conjugated diene) is hydrogenated polyisoprene.

11. A di-block copolymer of poly(monovinyl aromatic hydrocarbon) and hydrogenated poly(conjugated diene) for use as a dispersant in a lubricant oil composition, said di-block copolymer comprising poly(monovinyl aromatic hydrocarbon) in the number average molecular weight (M_n) range 8,000-30,000, wherein the poly(monovinyl aromatic hydrocarbon): hydrogenated poly(conjugated diene) number average molecular weight ratio is in the range of 3:2 to 10:1.

12. The di-block copolymer according to claim 11, wherein the number average molecular weight (M_n) range of the poly(monovinyl aromatic hydrocarbon) is in the range 8,400-25,000.

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13. The di-block copolymer according to claim 11 or 12, wherein the di-block copolymer is selected from the group consisting of di-block copolymers of the formula $A_n(BA)_m$, wherein A represents a block polymer of predominately poly(monovinyl aromatic hydrocarbon), wherein B represents a block of predominately poly(conjugated diene), wherein m represents an integer ≥ 1 , and wherein n represents 0 or 1.
14. The di-block copolymer of claim 13, wherein $m = 1$ to 4.
15. The di-block copolymer of claim 13, wherein $m = 1$.
16. The di-block copolymer according to any one of claims 11 to 15, wherein the monovinyl aromatic hydrocarbon used to prepare the poly(monovinyl aromatic hydrocarbon) block of said di-block copolymer is styrene, alkyl-substituted styrene, or alkoxy substituted styrene.
17. The di-block copolymer according to any one of claims 11 to 16, wherein the conjugated diene used in preparing the hydrogenated poly(conjugated diene) block is a conjugated diene containing from 4 to 24 carbon atoms.
18. The di-block copolymer according to claim 17, wherein the conjugated diene is 1,3-butadiene; isoprene; piperylene; methylpentadiene; 2-phenyl-1,3-butadiene; 3,4-dimethyl-1,3-hexadiene; or 4,5-diethyl-1,3-octadiene.
19. The di-block copolymer according to any one of claims 11 to 17, wherein the poly(monovinyl aromatic hydrocarbon) is polystyrene.
20. The di-block copolymer according to any one of claims 11 to 19, wherein the hydrogenated poly(conjugated diene) is hydrogenated polyisoprene.

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21. An additive package for a lubricant oil composition comprising the di-block copolymer in accordance with any one of claims 11 to 20 and oil of lubricating viscosity.

22. A use of the lubricating oil composition according to any one of claims 1 to 10 as a dispersant.

Fig.1.

Viscosity increase response as a function of dispersant and VII

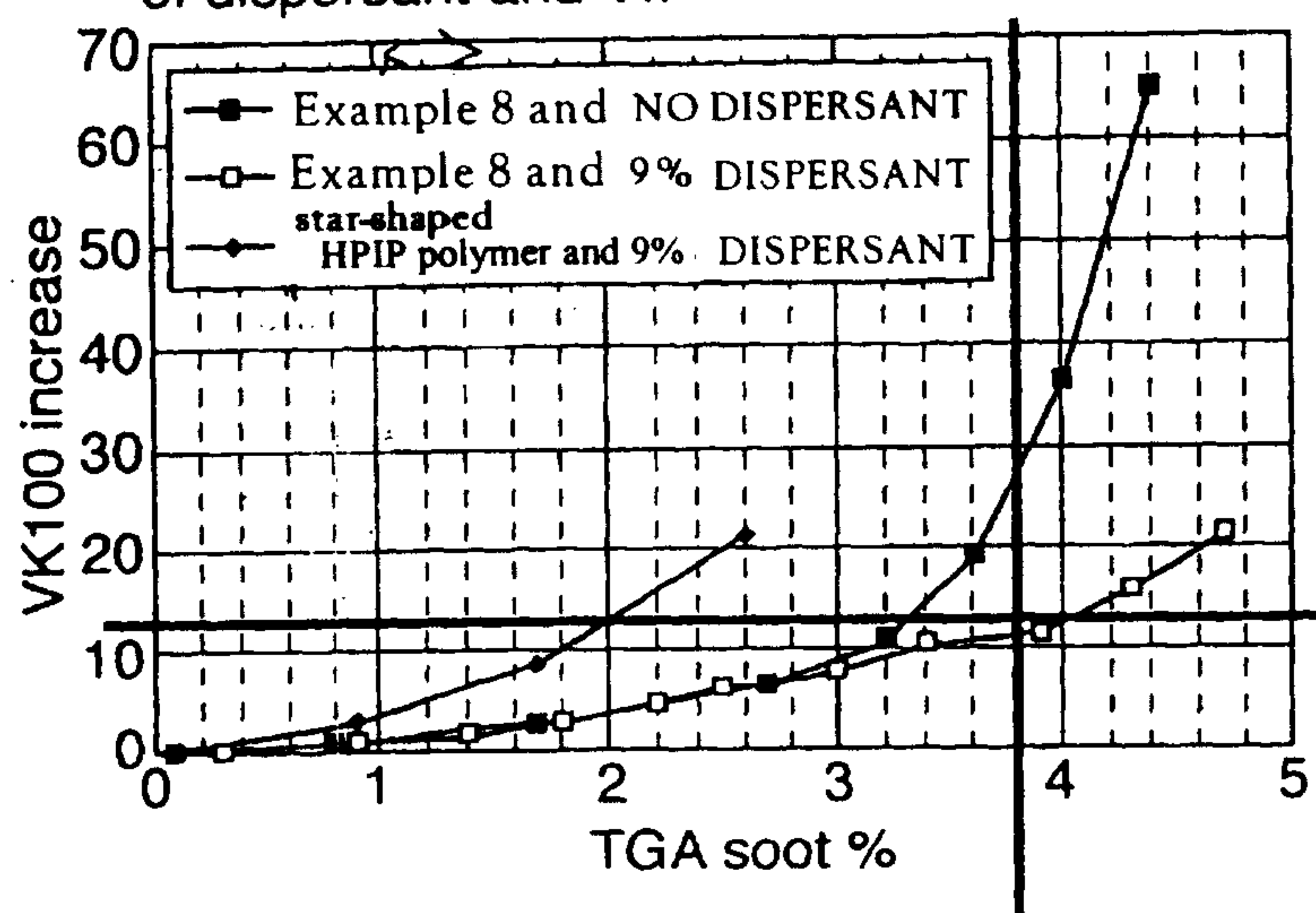


Fig.2.

Dispersancy index of di-block copolymer Examples 1 to 9.

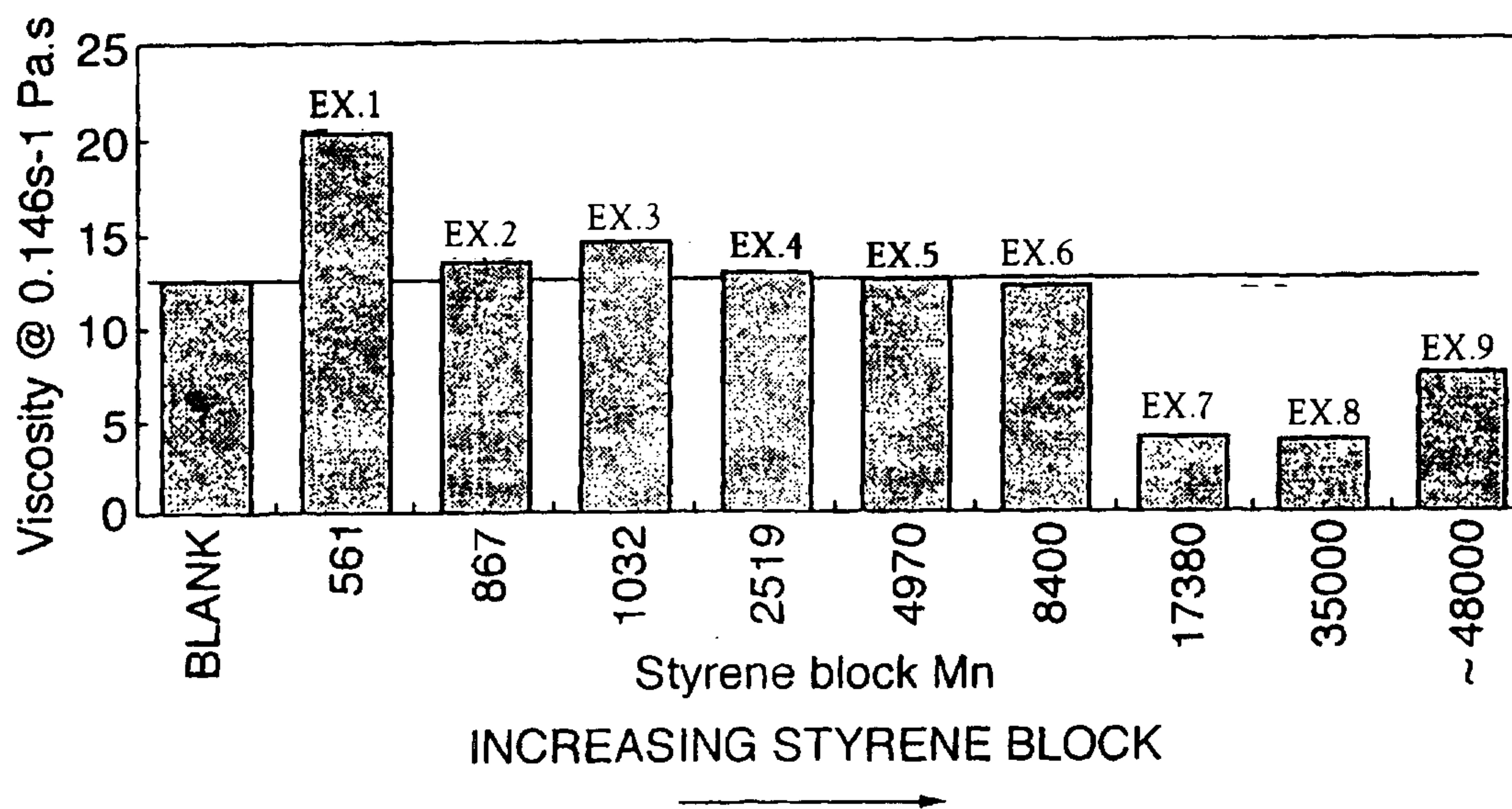


Fig.3.

Dispersancy comparison : Examples 6 to 9

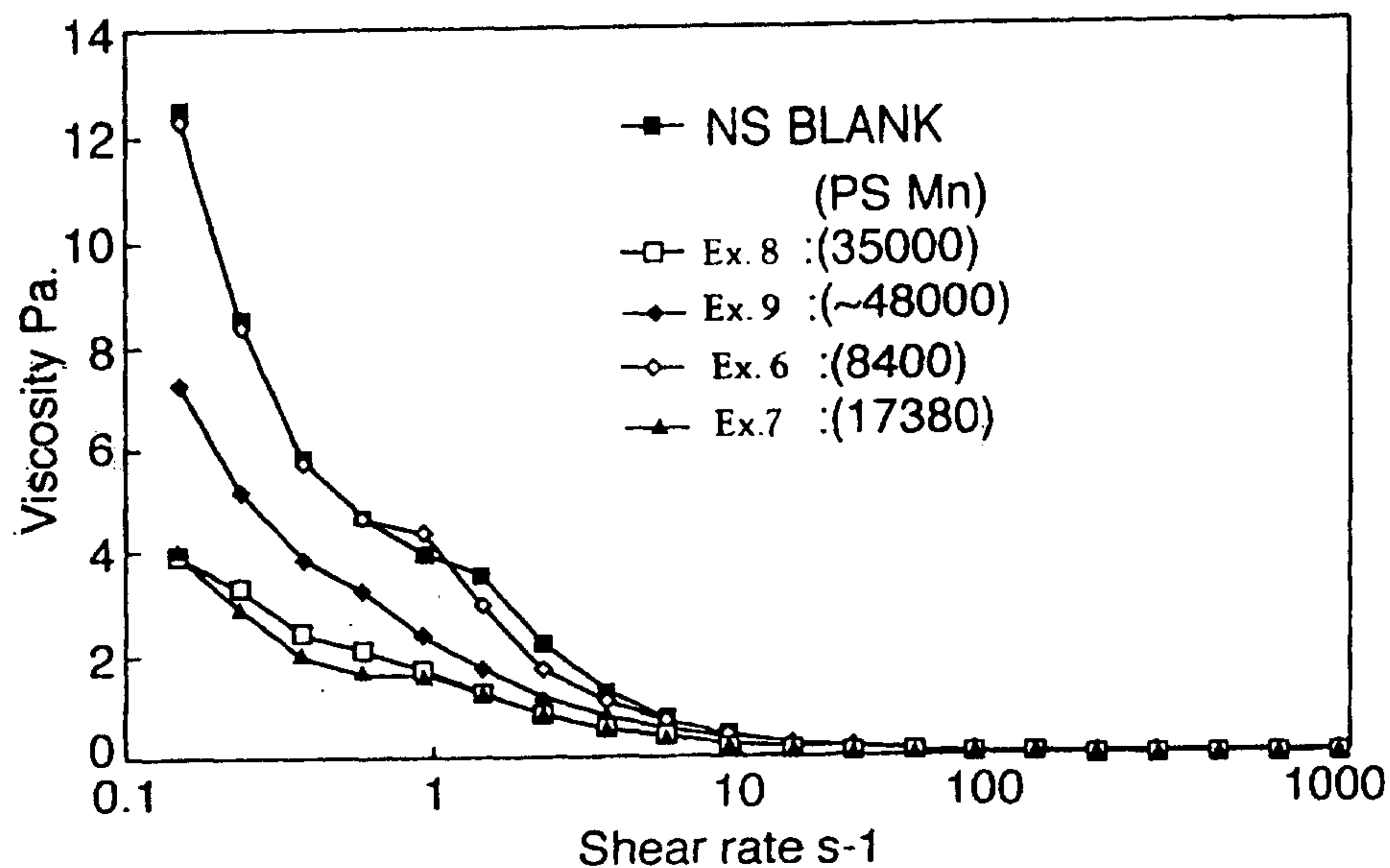


Fig.4.

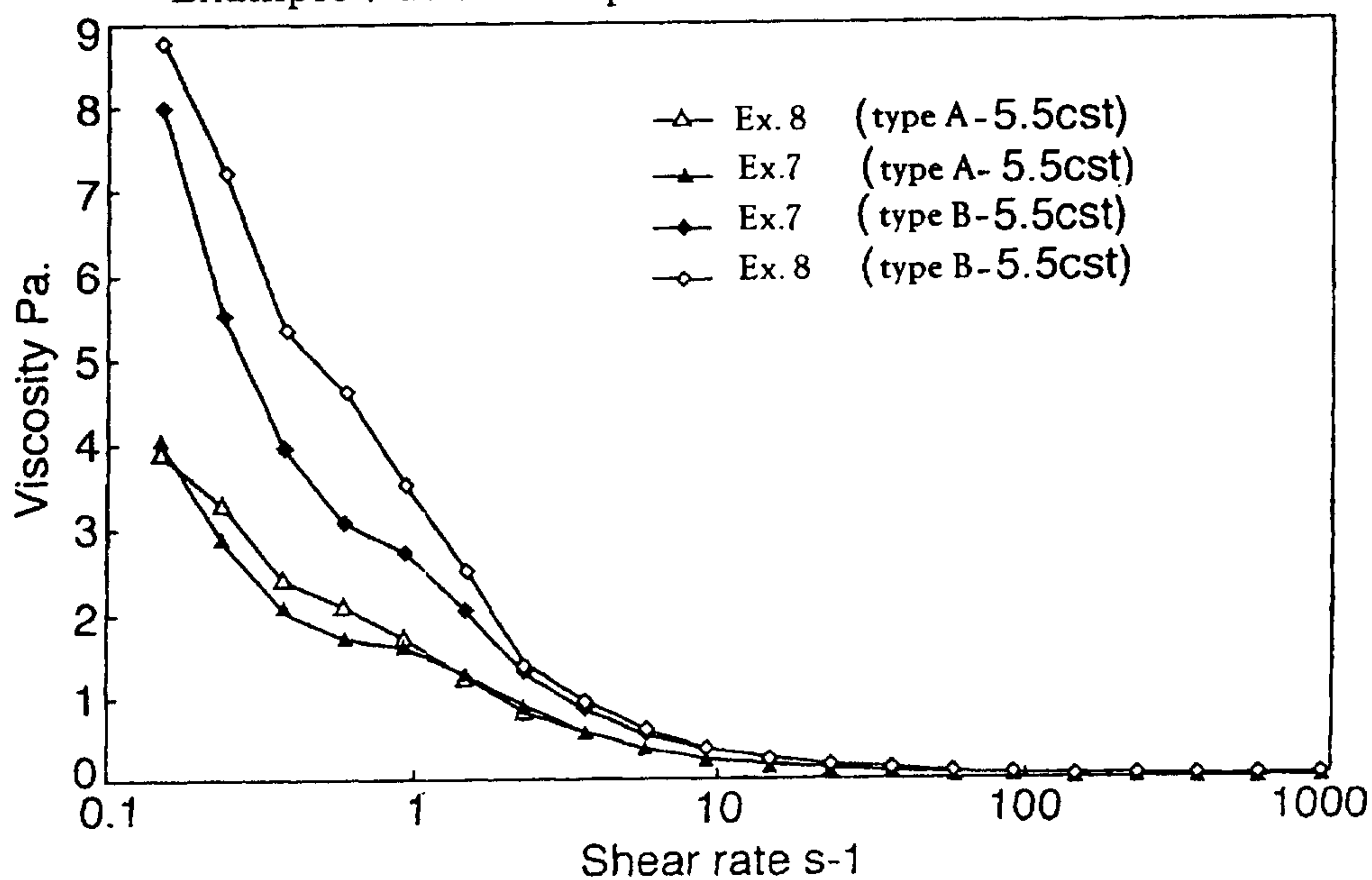
Dispersancy comparison in various baseoil :
Example 7 and Example 8

Fig.5.

