

Overbased Magnesium Sulphonates

The present invention relates to a process for the production of overbased magnesium sulphonates and to overbased magnesium sulphonates prepared by the process. In particular the present invention is concerned with overbased magnesium sulphonates prepared from high molecular weight sulphonic acids. The overbased magnesium sulphonates prepared by the process are particularly useful as additives for oil-based compositions, especially lubricating oils, and the invention also relates to oil-based compositions containing these overbased metal sulphonates.

Overbased magnesium sulphonates are well known, as is their use as additives in oil-based compositions, for example, lubricants, greases and fuels. They function as detergents and acid neutralizers, thereby reducing wear and corrosion and, when used in engines, extending engine life.

Many processes have been proposed for producing overbased sulphonates, the preferred processes generally involving the carbonation, in the presence of an organic solvent or diluent, of a mixture of an oil-soluble sulphonate and/or an oil-soluble sulphonic acid and an excess of a compound of the desired metal above that required to react with any acid present. It is known that overbased magnesium sulphonates are in general more difficult to prepare than the corresponding calcium compounds, and processes proposed for preparing overbased magnesium sulphonates have involved various special measures, for example, the use of particular reaction conditions and/or the incorporation of one or more additional substances into the mixture to be carbonated, such additional substances including, for example, water, alcohols, and promoters of various types. It has proved particularly difficult to prepare overbased magnesium sulphonates from high molecular weight sulphonic acids.

It is important that overbased materials for use as additives in oil-based compositions such as lubricating oils and fuels are clear liquids and are free of sediment. The product obtained at the end of carbonation in processes for preparing overbased magnesium sulphonates will contain some unwanted material (normally hard sediment and/or gelatinous material formed during the overbasing process referred to as post carbonation sediment (PCS). From an

economic standpoint, it is desirable to be able to remove the sediment quickly and simply, preferably by filtration, and it is also desirable that the amount of sediment to be removed be as low as possible.

- 5 Gelatinous material, if present, will tend to inhibit or prevent filtration by blocking the filter. Where purification by filtration is possible, it is desirably effected as rapidly as possible. If large amounts of sediment are present, the sediment must normally be removed by centrifuging rather than by filtration, and even small
10 amounts of sediment may have a tendency to block filters if the process is carried out on a large scale, this tendency being particularly marked if the system contains gelatinous material formed during the overbasing process.

- It is desirable that overbased materials for use as additives for oil-based compositions have a relatively high basicity. These are high base number
15 additives. The terms low base number and high base number as used to define sulphonates should be understood in relation to ASTM D2896-88 "Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration". This test method is concerned with the determination of basic constituents in petroleum products by potentiometric titration with perchloric acid in
20 glacial acetic acid. The result of this test method is quoted as a base number which is the base equivalence in mg KOH g⁻¹. Thus, the term low base number refers to numerical values of base number which are less than 50 mg KOH g⁻¹ and the term high base number refers to numerical values of base number which are greater than 50 mg KOH g⁻¹ and may be as high as 400 mg KOH g⁻¹ or even
25 higher e.g. 600 mg KOH g⁻¹. For some applications, it is preferred that the TBN be at least 350, preferably at least 380 and most preferably at least 400, mg KOH g⁻¹, as measured by ASTM D2896-88. Processes for the production of overbased materials of high TBN, however, frequently result in significantly higher sediment levels at the end of the carbonation step than do processes for producing
30 overbased materials of lower TBN.

- In particular it is difficult to produce high base number sulphonates from synthetic high molecular weight sulphonic acids, that is synthetic acids of average molecular weights of 500 or greater, which also have low viscosity and low levels of
35 sediment (PCS). If this is attempted with conventional processes high viscosity products are obtained which have a lower than expected base number and which may have unacceptably high levels of post carbonation sediment, high viscosity, a low filtration rate or a combination of these deficiencies.

The proportion of sediment in the reaction mixture immediately after carbonation (that is, before centrifuging or filtration to remove sediment) is usually known as the "post carbonation sediment", or "PCS", and is normally expressed as volume % PCS based on the volume of the reaction mixture. When comparing
5 proportions of sediment in different systems, it is important that the % PCS be calculated on comparable systems, preferably "stripped" systems free from any volatile materials, for example, water, methanol, and solvents, which are included in the reaction mixture for the purposes of the reaction but which are not required in the final overbased product. In some processes these volatile materials are not
10 removed until after removal of the sediment, and the % PCS reported is thus based on the volume of a reaction system which still contains the volatile materials, but by appropriate calculation it is possible to arrive, for comparison purposes, at a value for the % PCS in a notional system free from the volatile materials.

15 When carbonating overbased magnesium sulphonates, the magnesium oxide and/or magnesium hydroxide present are converted to carbonate. There are various carbonates which may be produced either alone or in admixture with one or more of each other. These carbonates are natural artinite ($\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), hydromagnesite ($3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) and nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$). It is preferred for colloidal stability and low sediment that the carbonate present is predominately hydromagnesite. When overbased magnesium
20 sulphonates are prepared from sulphonic acids of low molecular weight (400 to 500) the carbonation reaction appears to be self limiting so that the most desirable carbonate, hydromagnesite, is preferentially formed at the end of carbonation. With very low molecular weight sulphonic acids (less than 300), which have high levels of water solubility, the product is over-carbonated and the undesirable nesquehonite form predominates. When high molecular weight sulphonic acids are used in these conventional processes, artinite is produced during carbonation
25 which is undesirable. It has hitherto not been possible to provide overbased magnesium sulphonates from high molecular weight sulphonic acids which at the end of carbonation predominately contain the hydromagnesite form of magnesium carbonate. On removal of the volatile solvents, a basic magnesium carbonate is formed which is sterically stabilised in suspension by the magnesium sulphonate
30 soap.

35 There remains therefore a need for a process suitable for preparing overbased magnesium sulphonates from high molecular weight sulphonic acids and which have high TBN, low levels of post carbonation sediment, and where relatively

rapid filtration of the sediment-containing reaction product is possible.

The applicants have surprisingly found that, by using a wholly or partially water-soluble sulphonic acid or a magnesium salt thereof in the preparation of
5 overbased magnesium sulphonates from high molecular weight sulphonic acids, it is possible to ensure that at the end of carbonation practically all the magnesium oxide used in the process is converted to the desired hydromagnesite ($3 \text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 3\text{H}_2\text{O}$) and consequently it is possible to prepare overbased magnesium sulphonates from high molecular weight sulphonic acids which have high TBN and
10 low levels of PCS and acceptable viscosities and filtration rates. The amount of hydromagnesite or artinite produced can be determined by carrying out a mass balance on the amount of CO_2 absorbed during carbonation after allowing for the amount of MgO consumed in reacting with the sulphonic acid charge. For hydromagnesite to be formed, each molecule of overbasing magnesium will react
15 with 0.75 molecules of CO_2 ; for artinite to be formed, each molecule of overbasing magnesium will react with only 0.5 molecules of CO_2 . The amount of each can be readily determined by solving simultaneous equations and then, after determination of the quantity of CO_2 absorbed, the amount of hydromagnesite and artinite can readily be determined by simple arithmetic.

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The use of a low molecular weight sulphonic acid that is partially or wholly water-soluble, or a magnesium salt thereof, in the process of their manufacture makes it possible to obtain overbased magnesium sulphonates of high TBN which have low % PCS values from high molecular weight sulphonic acids.

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According to the present invention there is provided a process for the production of an overbased magnesium sulphonate which comprises the steps of (i) carbonating a mixture comprising an admixture of at least components (a) to (g) inclusive below, where

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- (a) is at least one oil-soluble high molecular weight sulphonic acid;
- (b) is at least one low molecular weight sulphonic acid that is wholly or partially water-soluble, or magnesium salt thereof;
- (c) is magnesium oxide in excess of that, required to react completely with component (a) and with component (b);

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- (d) is a hydrocarbon solvent;
- (e) is water;
- 5 (f) a water-soluble alcohol; and
- (g) is a promoter, and
- (ii) removing volatile solvent from the admixture of step (i).

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In the process of the present invention, the magnesium oxide may be reacted with component (b) before addition of component (g), or the magnesium oxide may be mixed with component (g) before addition of component (b) or component (a). Also, component (g) may be mixed with component (b) before addition of
15 component (a) and component (c).

The present invention further provides an overbased magnesium sulphonate composition from which volatile solvents have not been removed (eg unstripped) comprising at least one magnesium sulphonate derived from an oil-soluble high
20 molecular weight sulphonic acid and at least one magnesium sulphonate derived from a low molecular weight sulphonic acid that is wholly or partially water soluble wherein at least 50 wt% of the total sulphonate in the composition is derived from the high molecular weight sulphonic acid or acids and the magnesium carbonate in the composition is in its hydromagnesite form.

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Such composition is the product produced on completion of carbonation (step (i)) and before removing volatile solvents (step(ii)). On removal of the volatile solvents, both CO₂ and H₂O are lost from the hydromagnesite and a sterically stabilised colloidal suspension of basic magnesium carbonate is formed.

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The present invention therefore further provides an overbased magnesium sulphonate composition comprising at least one magnesium sulphonate derived from an oil-soluble high molecular weight sulphonic acid and at least one magnesium sulphonate derived from a low molecular weight sulphonic acid that is
35 wholly or partially water soluble and a stabilised colloidal suspension of basic magnesium carbonate, wherein at least 50 wt% of the total sulphonate in the composition is derived from the high molecular weight sulphonic acid or acids. The TBN of the composition may, for example, be at least 400 mg KOHg⁻¹.

It is preferred that the compositions comprises at least 60 wt% based on sulphonate of the sulphonate derived from the high molecular weight sulphonic acid and most preferably at least 75 wt% weight of the metal sulphonate. It is
5 preferably in the range of 50 to 92 wt%, most preferably 75 to 94 wt%.

It is also preferred that the kinematic viscosity of the overbased magnesium sulphonate composition at 100°C is 700 centistokes (cS) or less e.g. 300 cS or less most preferably 150 cS or less and most preferably in the range 30 - 150 cS
10 (1 cS = $10^{-6} \text{m}^2 \text{s}^{-1}$).

The PCS of the resultant overbased magnesium sulphonate may be 2% or less preferably 1.8 % or less, most preferably 1.6 % or less and in some cases can be 1 % or less, based on a reaction system free from volatile materials. The fact that
15 very low amounts of sediment may be obtained in accordance with the invention is advantageous from the ecological viewpoint when working on a large scale, as there is less waste material to be disposed of.

The resultant overbased magnesium sulphonates also filter rapidly after stripping
20 of the solvent, typically at a rate of at least 150, preferably at least 200, and especially at least 250, $\text{kg/m}^2/\text{hour}$. The products also have relatively low viscosities.

The overbased magnesium sulphonate composition of the present invention from
25 which volatile solvents have not been removed may comprise at least 16 wt% based on the total weight of the composition of sulphonate. Even higher concentrations of sulphonate in the composition are possible. Accordingly, it is preferred that the composition comprises at least 20 wt% sulphonate, more preferably at least 25 wt% sulphonate. It is preferred that the sulphonate is
30 present in the range of 16 to 30 wt% and most preferably in the range 20 to 30 wt% based on the total weight of the composition.

The term "oil-soluble high molecular weight" sulphonic acid means a synthetic oil
35 soluble alkyl sulphonic acid, or an alkary sulphonic acid, the acid having a number average molecular weight of greater than 500, preferably 600 or greater such as up to 700. The high molecular weight sulphonic acid may be a single high molecular weight sulphonic acid or it may be a mixture of high molecular weight sulphonic acids; that is a mixed sulphonic acid. The mixed sulphonic acid may be

a mixture of different high molecular weight sulphonic acids. Number average molecular weight may be determined by available techniques such as that described in ASTM D-3712. It is preferred that the high molecular weight sulphonic acid is an alkaryl sulphonic acid such as for example an alkyl benzene sulphonic acid, alkyl toluene sulphonic acid or alkyl xylene sulphonic acid. It is also preferred that it is a mixed sulphonic acid of C₁₅ to C₆₀ + alkyl benzene or C₁₅ to C₆₀ + alkyl xylene or C₁₅ to C₆₀ + alkyl toluene sulphonic acids or mixtures of two or more of these acids. The preferred high molecular weight sulphonic acids are those which are derived from aromatic alkylates prepared from C₂, C₃ or C₄ polyolefins such as polyethylene, polypropylene or polynormal butene. It is most preferred that they are prepared from polynormal butene. When the sulphonic acid is a mixed sulphonic acid and is derived from polynormal butene it is preferred that it has a number average molecular weight of at least 600 and preferably 600 to 700. It is also possible to replace some or all of the high molecular weight acid with the neutral magnesium sulphonate of the acid in the process of the present invention. However it is preferred to use the acid rather than the neutral sulphonate in the process of the present invention.

The wholly or partially water-soluble sulphonic acid is preferably a low molecular weight alkaryl sulphonic acid and most preferably is a mixture of C₉ to C₃₆ + alkyl substituted alkyl benzene or alkyl toluene or alkyl xylene sulphonic acids. The alkyl group may be a branched or straight chain hydrocarbyl group which is free of heteroatoms such as oxygen and nitrogen. It is preferred that the wholly or partially water-soluble sulphonic acid has a number average molecular weight of less than 500, preferably less than 490 and most preferably less than 450. It is preferred that the molecular weight is in the range 300 to 490 and preferably 310 to 450 and most preferably 320 to 400. The wholly or partially water-soluble sulphonic acid may be a mixture of wholly or partially water soluble sulphonic acids for example a mixture of C₁₈ straight chain alkylaryl sulphonic acid and C₁₅ to C₃₆+ branched chain alkylaryl sulphonic acid. A particularly preferred water soluble sulphonic acid is a C₁₀ to C₁₄ dodecylbenzene sulphonic acid e.g commercially available sulphonic acids know as Sinnozon DBS, LAS-sirene 113 and branched Sinnozon TBP.

By "wholly or partially water-soluble sulphonic acid" is meant a sulphonic acid which, when agitated in contact with water, is either completely miscible with water forming a solution or shows a significant degree of miscibility with water such that some of the acid is transferred to the aqueous phase. In this context a partially

water-soluble sulphonic acid is preferably an acid which has at least 5% by weight transferred to the water phase when 100 g of acid is shaken with 100 g of water under ambient conditions. More preferably at least 10 wt% is transferred and most preferably at least 20 wt% is transferred. It is preferred that this sulphonic acid is wholly water-soluble and has an average molecular weight of less than 380 and most preferably in the range of 320 to 380. It is also possible to replace some or all of the wholly or partially water-soluble acid with the neutral magnesium sulphonate of the acid in the process of the present invention. However it is preferred to use the wholly or partially water-soluble acid rather than the neutral sulphonate in the process.

The amount of wholly or partially water-soluble sulphonic acid used in the process of the present invention depends in part on the solubility of the sulphonic acid. As the solubility decreases, greater amounts of wholly or partially water-soluble sulphonic acid are required. If too much wholly or partially water-soluble sulphonic acid is used, the undesirable nesquehonite form of magnesium carbonate is formed. At least 2 wt% of the wholly or partially water soluble sulphonic acid should be used in the process of the present invention based on the total weight of sulphonic acid used, preferably at least 6 wt % is used and most preferably 6 to 25 wt% is used.

The overbased magnesium sulphonates with which this invention is concerned comprise an oil solution of the magnesium sulphonate which acts as a surfactant to disperse colloidal magnesium derivatives, for example, magnesium carbonate, oxide and/or hydroxide. It is thus important that the high molecular weight sulphonic acid be oil-soluble.

The proportion of dispersed colloidal magnesium derivatives such as magnesium carbonate, oxide and/or hydroxide in the overbased magnesium sulphonates determines the basicity of the products. The magnesium oxide used as a starting material is used in an amount sufficient to give the desired TBN in the product. Advantageously, the magnesium oxide is used in a total quantity corresponding to 1 to 45, preferably 1 to 25, equivalents of magnesium for each equivalent of sulphonic acid used including both the sulphonic acids used.

The magnesium oxide used may be any magnesium oxide. Relatively reactive forms of magnesium oxide, are commonly known as "light", "active", or "caustic burned" magnesium oxides. These forms of magnesium oxide have a relatively

low density and relatively high surface area, in contrast to "heavy" or "deadburned" forms of magnesium oxide, which are relatively dense and of relatively low surface area and tend to be relatively inert chemically. The preferred magnesium oxides used in accordance with the invention are "heavy" or a mixture of "light" and "heavy". Preferably the "heavy" magnesium oxide has a citric acid number (as hereinafter defined) of greater than 200 seconds and a surface area measured by the BET single point method of less than $12 \text{ m}^2/\text{g}$, the particle size of at least 92 volume % of the magnesium oxide being greater than $2 \mu\text{m}$. Preferably the "light" magnesium oxide which can be a portion of the mixture has a citric acid number of less than 200 seconds and a surface area higher than $12 \text{ m}^2/\text{g}$.

As defined herein, the citric acid number is the time in seconds required to neutralise, at 22°C , a stirred mixture of 1.7 g of the magnesium oxide, 100 ml water, and 100 ml of a citric acid solution containing 26 g citric acid monohydrate and 0.1 g phenolphthalein in 1 litre of aqueous solution. Neutralisation is indicated by the mixture turning pink. The citric acid number of the "heavy" magnesium oxide used in accordance with the invention is advantageously at most 700 seconds, and is most advantageously in the range of from 200 to 600 seconds, preferably 400 to 500 seconds. The citric acid number of the "light" magnesium oxide is at most 200 seconds and is preferably in the range 20 to 140 seconds.

The BET single point method for measuring the surface areas of particulate solids is described in the Journal of Analytical Chemistry, Vol. 26, No. 4, pages 734 to 735 (1954) - M. J. Katz, An Explicit Function for Specific Surface Area. The surface area, measured by this method, of the "heavy" forms of magnesium oxide for use in accordance with the invention is advantageously less than $10 \text{ m}^2/\text{g}$, and is preferably in the range of from 2 to $10 \text{ m}^2/\text{g}$. The surface area of the "light" magnesium oxide is greater than $12 \text{ m}^2/\text{g}$ and is preferably in the range 20 to $70 \text{ m}^2/\text{g}$.

The particle size of at least 92 volume % of the "heavy" magnesium oxide used in accordance with the invention is greater than $2 \mu\text{m}$. Advantageously, at least 94 volume of the magnesium oxide has a particle size of greater than $2 \mu\text{m}$.

The preferred magnesium oxides used in accordance with the invention preferably has a purity, as measured by EDTA titration, of at least 95 %. In the EDTA titration

method, a sample of the magnesium oxide is dissolved in dilute hydrochloric acid, and the solution is buffered to a pH of about 10 and then titrated with a solution of the disodium salt of ethylene diamine tetra-acetic acid. The disodium salt forms a complex with the magnesium ions in the solution, so that the concentration of magnesium ions can be calculated from the amount of the disodium salt used. The mass of magnesium, expressed as magnesium oxide, is compared with the mass of the original sample to give the percentage purity.

When a mixture of "heavy" and "light" magnesium oxides are used it is preferred that the "light" magnesium oxide is present at 50 wt% or less most preferably 40 wt % or less and is preferably in the range 25 to 45 wt% most preferably in the range 30 to 40 wt% of the total weight of magnesium oxide.

The hydrocarbon solvent used in the carbonation mixture is a solvent in which the high molecular weight sulphonic acid and the overbased sulphonate are at least partially soluble, and is used in an amount sufficient to keep the mixture fluid during carbonation. The solvent is advantageously volatile, preferably with a boiling point at atmospheric pressure of below 150°C, so that it can be removed after the completion of carbonation. Examples of suitable hydrocarbon solvents are aliphatic hydrocarbons, for example, hexane or heptane, and aromatic hydrocarbons, for example, benzene, toluene or xylene, the preferred solvent being toluene. Typically, the solvent is used in an amount of about 3 to 4 parts by mass per part by mass of the magnesium oxide.

As well as the hydrocarbon solvent, the carbonation mixture may comprise a nonvolatile diluent oil, for example, a mineral oil, although the use of such an oil during carbonation is not essential. In the process of the invention a non-volatile diluent oil is preferably only used if such an oil is present in the high molecular weight sulphonic acid starting material. Diluent oil may however be added to the magnesium sulphonate after the completion of carbonation which may in some cases be advantageous for facilitating handling of the product.

The total amount of water introduced into the mixture is at least 0.5 mole, advantageously at least 1 mole, per mole of the excess magnesium oxide (that is, the magnesium oxide available to form colloiddaily dispersed basically-reacting products). Advantageously, the total amount of water introduced does not exceed 5 moles, and -preferably does not exceed 2.5 moles, per mole of overbasing magnesium oxide.

As examples of suitable water-soluble alcohols for use in accordance with the invention there may be mentioned lower aliphatic alkanols, alkoxy alkanols, and mixtures of two or more of such compounds, wherein the maximum number of carbon atoms is usually at most 5. Examples of suitable alkanols are methanol, ethanol, isopropanol, n-propanol, butanol and pentanol. Methanol is preferred. An example of a suitable alkoxy alkanol is methoxy ethanol.

For guidance, the mass ratio of water to alcohol will typically be in the range of from 10 to 0.1 : 1, especially 7 to 1.0 : 1 more preferably 5 to 1.5 to 1 and most preferably 5 to 1.6 : 1.

Examples of suitable promoters for use in the process of the present invention are ammonia, ammonium compounds, monoamines and polyamines (for example, ethylene diamine) and carbamates of these amines. The preferred promoters are carbamates and in particular the carbamates prepared from polyamines. The most preferred carbamates are those prepared from ethylene polyamines and in particular ethylene diamine. Such a carbamate may be prepared by the reaction of ethylene diamine in a methanol/water solvent with carbon dioxide. The reaction is exothermic and produces a solution of the carbamate.

The promoter may advantageously be pre-reacted with the wholly or partially water soluble sulphonic acid before or after addition of the magnesium oxide. Preferably the mole ratio of promoter to wholly or partially water soluble sulphonic acid to 0.1 : 5 preferably 0.1 to 1 : 2.5 most preferably 0.1 to 1 : 1 whether prereacted or not. Preferably the promoter when it is in the form of a carbamate is always added to a basic reaction mixture that is after the addition of the magnesium oxide. If it is added before addition of the magnesium oxide it is preferred that the sulphonic acids are added after the addition of the magnesium oxide. It is most preferred therefore that the magnesium oxide and wholly or partially water soluble sulphonic acid are reacted initially followed by addition of the carbamate promoter to a reaction mixture which is basic due to the presence of excess magnesium oxide over that required to neutralise the wholly or partially water soluble sulphonic acid.

To ensure maximum conversion of magnesium oxide to colloidal products, carbonation is normally continued until there is no further significant uptake of carbon dioxide. The minimum temperature that may be used is that at which the

carbonation mixture remains fluid, and the maximum is the decomposition temperature of the component with the lowest decomposition temperature, or the lowest temperature at which an unacceptable amount of one or more volatile components is lost from the mixture. Carbonation is preferably carried out with the apparatus set for total reflux. The temperature of the reactants is normally adjusted to a chosen value before carbonation is commenced, and is then allowed to vary during carbonation as the reaction proceeds. Generally carbonation is effected at a temperature in the range of from 20 to 200°C, preferably 40 to 80°C more preferably 40 to 70°C most preferably 40 to 66°C. It is preferred that carbonation is commenced at least 35°C preferably 40°C or slightly less.

When there is no further significant uptake of carbon dioxide, the carbonation mixture is stripped to remove volatile materials such as water, the alcohol, and volatile solvent(s), and any solids remaining in the mixture are removed, preferably by filtration. The mixture may be stripped before or after the solids are removed. Further carbon dioxide may if desired be passed through the reaction mixture during stripping, the carbon dioxide acting primarily to flush out volatile materials. As indicated above, the invention surprisingly makes it possible to obtain overbased magnesium sulphonates having high TBNs, having an extremely low proportion of post carbonation sediment, and capable of purification by filtration. It is preferred that stripping is commenced within 1 hour of carbonation.

Advantageously the magnesium sulphonate may be post treated with a carboxylic acid or anhydride materials. This has been found to be particularly advantageous when the sulphonate is to be used in formulated oils which come into contact with fluoroelastomer seals. This has also been found to improve the water compatibility and tolerance of the sulphonate. Preferred carboxylic acids or anhydride materials are dicarboxylic acids and their anhydrides in particular aliphatic hydrocarbyl dicarboxylic acids and anhydrides. The most preferred dicarboxylic acids are vicinyl dicarboxylic acids examples of which include maleic, and fumaric with fumaric being particularly preferred. It is preferred that the post treatment is undertaken after carbonation and that the carboxylic acid or anhydride is used in sufficient quantity to react with any active nitrogen hydrogen groups which are present in the carbonated product. Such groups are present in the product due to residual promoter which has not been removed after reaction. Advantageously the acid or anhydride is used in excess and in doing so imparts improved water tolerance to the sulphonate. Typically the acid is used at 1.0 to 5 wt % preferably 1 to 2.5 wt% and most preferably 1 to 2.0 wt% based on the

weight of the overbased magnesium sulphonate. The exact amounts used are dependant on the amount of promoter used and on the residual amount of promoter after the carbonation and stripping of the product.

- 5 Overbased magnesium sulphonates obtained by the process of the invention are useful as additives for oil-based compositions, for example, lubricants, greases and fuels, and the invention thus also provides such compositions containing the overbased magnesium sulphonates. When used in engine lubricants, the overbased magnesium sulphonates neutralise acids formed by the operation of
10 the engine and help to disperse solids in the oil to reduce the formation of harmful deposits. They also enhance the antirust proper-ties of the lubricants. The amount of overbased magnesium sulphonate that should be included in the oil-based composition depends on the type of composition and its proposed application. Automotive crankcase lubricating oils preferably contain 0.01 % to 6
15 mass % preferably 0.2 to 4 mass % of the overbased magnesium sulphonate, on an active ingredient basis, based on the mass of the oil.

The overbased magnesium sulphonates prepared in accordance with the invention are oil-soluble or (in common with certain of the other additives referred
20 to below) are dissolvable in oil with the aid of a suitable solvent, or are stably dispersible materials. Oil-soluble, dissolvable, or stably dispersible as that terminology is used herein does not necessarily indicate that the materials are soluble, dissolvable, miscible, or capable of being suspended in oil in all proportions. It does mean, however, that the materials are, for instance, soluble
25 or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

- 30 The lubricating oil may be selected from any of the synthetic or natural oils used as crankcase lubricating oils for spark-ignited and compression-ignited engines. The lubricating oil base stock conveniently has a viscosity of about 2.5 to about 12 cSt or mm²/s and preferably about 2.5 to about 9 cSt or mm²/s at 100°C . Mixtures of synthetic and natural base oils may be used if desired.

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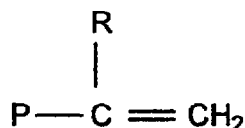
Examples of additives which may be included in lubricating oil compositions are viscosity index improvers, corrosion inhibitors, oxidation inhibitors, friction

modifiers, dispersants, detergents, metal rust inhibitors, anti-wear agents, pour point depressants, and anti-foaming agents.

5 The ashless dispersants comprise an oil soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless dispersant may be, for example, selected from oil soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon
10 substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto, and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

15 The oil soluble polymeric hydrocarbon backbone is typically an olefin polymer or polyene, especially polymers comprising a major molar amount (i.e., greater than 50 mole %) of a C₂ to C₁₈ olefin (e.g., ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a C₂ to C₅ olefin. The oil soluble
20 polymeric hydrocarbon backbone may be a homopolymer (e.g., polypropylene or polyisobutylene) or a copolymer of two or more of such olefins (e.g., copolymers of ethylene and an alpha-olefin such as propylene or butylene, or copolymers of two different alpha-olefins). Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is an α,ω -diene, such
25 as a C₃ to C₂₂ non-conjugated diolefin (e.g., a copolymer of isobutylene and butadiene, or a copolymer of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene). Atactic propylene oligomer typically having $\overline{M}_n$ of from 700 to 5000 may also be used, as described in EP-A-490454, as well as heteropolymers such as polyepoxides.

30 One preferred class of olefin polymers is polybutenes and specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C₄ refinery stream. Other preferred classes of olefin polymers are ethylene alpha-olefin (EAO) copolymers and alpha-olefin homo- and
35 copolymers having in each case a high degree (e.g., >30%) of terminal vinylidene unsaturation. That is, the polymer has the following structure:



wherein P is the polymer chain and R is a C₁ - C₁₈ alkyl group, typically methyl or ethyl. Preferably the polymers will have at least 50% of the polymer chains with terminal vinylidene unsaturation. EAO copolymers of this type preferably contain 1 to 50 wt.% ethylene, and more preferably 5 to 48 wt.% ethylene. Such polymers may contain more than one alpha-olefin and may contain one or more C₃ to C₂₂ diolefins. Also usable are mixtures of EAO's of varying ethylene content. Different polymer types, e.g., EAO and PIB, may also be mixed or blended, as well as polymers differing in $\overline{M}_n$; components derived from these also may be mixed or blended.

Suitable olefin polymers and copolymers may be prepared by various catalytic polymerization processes. In one method, hydrocarbon feedstreams, typically C₃-C₅ monomers, are cationically polymerized in the presence of a Lewis acid catalyst and, optionally, a catalytic promoter, e.g., an organoaluminum catalyst such as ethylaluminum dichloride and an optional promoter such as HCl. Most commonly, polyisobutylene polymers are derived from Raffinate I refinery feedstreams. Various reactor configurations can be utilized, e.g., tubular or stirred tank reactors, as well as fixed bed catalyst systems in addition to homogeneous catalysts. Such polymerization processes and catalysts are described, e.g., in US-A 4,935,576; 4,952,739; 4,982,045, and UK-A 2,001,662.

Conventional Ziegler-Natta polymerization processes may also be employed to provide olefin polymers suitable for use in preparing dispersants and other additives. However, preferred polymers may be prepared by polymerizing the appropriate monomers in the presence of a particular type of Ziegler-Natta catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl-transition metal compound) and, preferably, a cocatalyst or an activator, e.g., an alumoxane compound or an ionizing ionic activator such as tri (n-butyl) ammonium tetra (pentafluorophenyl) boron.

Metallocene catalysts are, for example, bulky ligand transition metal compounds of the formula:



where L is a bulky ligand; A is a leaving group, M is a transition metal and m and n are such that the total ligand valency corresponds to the transition metal valency. Preferably the catalyst is four co-ordinate such that the compound is ionizable to a
5 1⁺ valency state.

The ligands L and A may be bridged to each other, and if two ligands A and/or L are present, they may be bridged. The metallocene compound may be a full sandwich compound having two or more ligands L which may be cyclopentadienyl
10 ligands or cyclopentadienyl derived ligands, or they may be half sandwich compounds having one such ligand L. The ligand may be mono- or polynuclear or any other ligand capable of η -5 bonding to the transition metal.

One or more of the ligands may π -bond to the transition metal atom, which may be
15 a Group 4, 5 or 6 transition metal and/or a lanthanide or actinide transition metal, with zirconium, titanium and hafnium being particularly preferred.

The ligands may be substituted or unsubstituted, and mono-, di-, tri, tetra- and penta-substitution of the cyclopentadienyl ring is possible. Optionally the
20 substituent(s) may act as one or more bridge between the ligands and/or leaving groups and/or transition metal. Such bridges typically comprise one or more of a carbon, germanium, silicon, phosphorus or nitrogen atom-containing radical, and preferably the bridge places a one atom link between the entities being bridged, although that atom may and often does carry other substituents.

25 The metallocene may also contain a further displaceable ligand, preferably displaced by a cocatalyst - a leaving group - that is usually selected from a wide variety of hydrocarbyl groups and halogens.

30 Such polymerizations, catalysts, and cocatalysts or activators are described, for example, in US 4,530,914; 4,665,208; 4,808,561; 4,871,705; 4,897,455; 4,937,299; 4,952,716; 5,017,714; 5,055,438; 5,057,475; 5,064,802; 5,096,867; 5,120,867; 5,124,418. 5,153,157; 5,198,401. 5,227,440; 5,241,025; USSN 992,690 (filed Dec. 17, 1992. EP-A- 129,368; 277,003; 277,004; 420436;
35 520,732; W091/04257; 92/00333.1 93/08199 and 93/08221.1 and 94/07928.

The oil soluble polymeric hydrocarbon backbone will usually have a number average molecular weight ($\bar{M}_n$) within the range of from 300 to 20,000. The $\bar{M}_n$

of the polymer backbone is preferably within the range of 500 to 10,000, more preferably 700 to 5,000 where its use is to prepare a component having the primary function of dispersancy. Polymers of both relatively low molecular weight (e.g., $\overline{M}_n = 500$ to 1500) and relatively high molecular weight (e.g., $\overline{M}_n = 1500$ to 5,000 or greater) are useful to make dispersants. Particularly useful olefin polymers for use in dispersants have $\overline{M}_n$ within the range of from 1500 to 3000. Where the oil additive component is also intended to have a viscosity modifying effect it is desirable to use a polymer of higher molecular weight, typically with $\overline{M}_n$ of from 2,000 to 20,000; and if the component is intended to function primarily as a viscosity modifier then the molecular weight may be even higher, e.g., $\overline{M}_n$, of from 20,000 up to 500,000 or greater. Furthermore, the olefin polymers used to prepare dispersants preferably have approximately one double bond per polymer chain, preferably as a terminal double bond.

Polymer molecular weight, specifically $\overline{M}_n$, can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC), which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). Another useful method, particularly for lower molecular weight polymers, is vapor pressure osmometry (see, e.g., ASTM D3592).

The oil soluble polymeric hydrocarbon backbone may be functionalized to incorporate a functional group into the backbone of the polymer, or as one or more groups pendant from the polymer backbone. The functional group typically will be polar and contain one or more hetero atoms such as P, O, S, N, halogen, or boron. It can be attached to a saturated hydrocarbon part of the oil soluble polymeric hydrocarbon backbone via substitution reactions or to an olefinic portion via addition or cycloaddition reactions. Alternatively, the functional group can be incorporated into the polymer in conjunction with oxidation or cleavage of the polymer chain end (e.g., as in ozonolysis).

Useful functionalization reactions include: halogenation of the polymer at an olefinic bond and subsequent reaction of the halogenated polymer with an ethylenically unsaturated functional compound (e.g., maleation where the polymer is reacted with maleic acid or anhydride); reaction of the polymer with an unsaturated functional compound by the "ene" reaction without halogenation; reaction of the polymer with at least one phenol group (this permits derivatization

in a Mannich base-type condensation); reaction of the polymer at a point of unsaturation with carbon monoxide using a Koch-type reaction to introduce a carbonyl group in an iso or neo position; reaction of the polymer with the functionalizing compound by free radical addition using a free radical catalyst;
5 reaction with a thiocarboxylic acid derivative; and reaction of the polymer by air oxidation methods, epoxidation, chloroamination, or ozonolysis.

The functionalized oil soluble polymeric hydrocarbon backbone is then further derivatized with a nucleophilic reactant such as an amine, amino-alcohol, alcohol,
10 metal compound or mixture thereof to form a corresponding derivative. Useful amine compounds for derivatizing functionalized polymers comprise at least one amine and can comprise one or more additional amine or other reactive or polar groups. These amines may be hydrocarbyl amines or may be predominantly hydrocarbyl amines in which the hydrocarbyl group includes other groups, e.g.,
15 hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Particularly useful amine compounds include mono- and polyamines, e.g. polyalkylene and polyoxyalkylene polyamines of about 2 to 60, conveniently 2 to 40 (e.g., 3 to 20), total carbon atoms and about 1 to 12, conveniently 3 to 12, and preferably 3 to 9 nitrogen atoms in the molecule. Mixtures of amine compounds
20 may advantageously be used such as those prepared by reaction of alkylene dihalide with ammonia. Preferred amines are aliphatic saturated amines, including, e.g., 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane-1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; and polypropyleneamines such as 1,2-
25 propylene diamine; and di-(1,2-propylene)triamine.

Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines. A particularly useful class of amines are the polyamido and related
30 amido-amines as disclosed in US 4,857,217; 4,956,107; 4,963,275; and 5,229,022. Also usable is tris(hydroxymethyl)amino methane THAM) as described in US 4,102,798; 4,113,639. 4,116,876; and UK 989,409. Dendrimers, star-like amines, and comb-structure amines may also be used. Similarly, one may use the condensed amines disclosed in US 5,053,152. The functionalized polymer is
35 reacted with the amine compound according to conventional techniques as described in EP-A 208,560; US 4,234,435 and US 5,229,022 .

The functionalized oil soluble polymeric hydrocarbon backbones also may be derivatized with hydroxy compounds such as monohydric and polyhydric alcohols or with aromatic compounds such as phenols and naphthols. Polyhydric alcohols are preferred, e.g., alkylene glycols in which the alkylene radical contains from 2 to 8 carbon atoms. Other useful polyhydric alcohols include glycerol, mono-oleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, and mixtures thereof. An ester dispersant may also be derived from unsaturated alcohols such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexane-3-ol, and oleyl alcohol. Still other classes of the alcohols capable of yielding ashless dispersants comprise the ether-alcohols and including, for example, the oxy-alkylene, oxy-arylene. They are exemplified by ether-alcohols having up to 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to 8 carbon atoms. The ester dispersants may be di-esters of succinic acids or acidic esters, i.e., partially esterified succinic acids, as well as partially esterified polyhydric alcohols or phenols, i.e., esters having free alcohols or phenolic hydroxyl radicals. An ester dispersant may be prepared by one of several known methods as illustrated, for example, in US 3,381,022.

A preferred group of ashless dispersants includes those derived from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines (e.g., tetraethylene pentamine, pentaethylene (di)(pent)amine(?), polyoxypropylene diamine) aminoalcohols such as trimethylolaminomethane and optionally additional reactants such as alcohols and reactive metals e.g., pentaerythritol, and combinations thereof). Also useful are dispersants wherein a polyamine is attached directly to the long chain aliphatic hydrocarbon as shown in US 3,275,554 and 3,565,804 where a halogen group on a halogenated hydrocarbon is displaced with various alkylene polyamines.

Another class of ashless dispersants comprises Mannich base condensation products. Generally, these are prepared by condensing about one mole of an alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compounds (e.g., formaldehyde and paraformaldehyde) and about 0.5 to 2 moles polyalkylene polyamine as disclosed, for example, in US 3,442,808. Such Mannich condensation products may include a long chain, high molecular weight hydrocarbon (e.g., $\overline{M}_n$ of 1,500 or greater) on the benzene group or may be reacted with a compound containing such a hydrocarbon, for example, polyalkenyl succinic anhydride, as shown in US 3,442,808.

- Examples of functionalized and/or derivatized olefin polymers based on polymers synthesized using metallocene catalyst systems are described in US 5,128,056; 5,151,204; 5,200,103; 5,225,092; 5,266,223; USSN 992,192 (filed Dec. 17, 1992); 992,403 (filed Dec. 17, 1992); 070,752 (filed Jun. 2, 1993); EP-A-440,506;
- 5 513,157; 513,211. The functionalization and/or derivatizations and/or post treatments described in the following patents may also be adapted to functionalize and/or derivative the preferred polymers described above: US 3,087,936; 3,254,025; 3,275,554; 3,442,808, and 3,565,804.
- 10 The dispersant can be further post-treated by a variety of conventional post treatments such as boration, as generally taught in US 3,087,936 and 3,254,025. This is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from the group consisting of boron oxide, boron halides, boron acids and esters of boron acids, in an amount to provide from about
- 15 0.1 atomic proportion of boron for each mole of the acylated nitrogen composition to about 20 atomic proportions of boron for each atomic proportion of nitrogen of the acylated nitrogen composition. Usefully the dispersants contain from about 0.05 to 2.0 wt. %, e.g. 0.05 to 0.7 wt. % boron based on the total weight of the borated acyl nitrogen compound. The boron, which appears to be in the product
- 20 as dehydrated boric acid polymers (primarily $(\text{HBO}_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts e.g., the metaborate salt of the diimide. Boration is readily carried out by adding from about 0.05 to 4, e.g., 1 to 3 wt. % (based on the weight of acyl nitrogen compound) of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and
- 25 heating with stirring at from 135° to 190°C, e.g., 140°-170°C, for from 1 to 5 hours followed by nitrogen stripping. Alternatively, the boron treatment can be carried out by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine while removing water.
- 30 Viscosity modifiers (or viscosity index improvers) impart high and low temperature operability to a lubricating oil. Viscosity modifiers that also function as dispersants are also known and may be prepared as described above for ashless dispersants. In general, these dispersant viscosity modifiers are functionalized polymers (e.g. inter polymers of ethylene-propylene post grafted with an active monomer such as
- 35 maleic anhydride) which are then derivatized with, for example, an alcohol or amine.

The lubricant may be formulated with or without a conventional viscosity modifier and with or without a dispersant viscosity modifier. Suitable compounds for use as viscosity modifiers are generally high molecular weight hydrocarbon polymers, including polyesters. Oil soluble viscosity modifying polymers generally have
5 weight average molecular weights of from about 10,000 to 1,000,000, preferably 20,000 to 500,000, which may be determined by gel permeation chromatography (as described above) or by light scattering.

Representative examples of suitable viscosity modifiers are polyisobutylene,
10 copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene
isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially
15 hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing
20 wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as
25 may be measured by ASTM D2896) of from 0 to 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises neutralised detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of
30 150 or greater, and typically of from 250 to 450 or more.

Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline
35 earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and

overbased calcium sulfonates having TBN of from 20 to 450 TBN, and neutral and overbased calcium phenates and sulfurized phenates having TBN of from 50 to 450.

5 Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene,
10 chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

15 The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from
20 about 100 to 220 wt % (preferably at least 125 wt %).

Metal salts of phenols and sulfurised phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art.

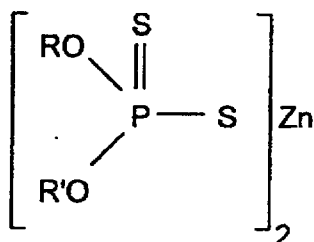
25 Sulfurised phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

30 Dihydrocarbyl dithiophosphate metal salts are frequently used as anti-wear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 wt. %, based upon the total weight of the lubricating oil composition. They
35 may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. The zinc dihydrocarbyl dithiophosphates can be made from mixed

DDPA which in turn may be made from mixed alcohols. Alternatively, multiple zinc dihydrocarbyl dithiophosphates can be made and subsequently mixed.

Thus the dithiophosphoric acid containing secondary hydrocarbyl groups used in this invention may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralization reaction.

The preferred zinc dihydrocarbyl dithiophosphates useful in the present invention are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



Wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. At least 50 (mole) % of the alcohols used to introduce hydrocarbyl groups into the dithiophosphoric acids are secondary alcohols.

Additional additives are typically incorporated into the compositions of the present invention. Examples of such additives are antioxidants, anti-wear agents, friction modifiers, rust inhibitors, anti-foaming agents, demulsifiers, and pour point depressants.

5

Oxidation inhibitors or antioxidants reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline
10 earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, ashless oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in US 4,867,890, and molybdenum containing compounds. Examples of molybdenum
15 compounds include molybdenum salts of inorganic and organic acids (see, for example, US 4,705,641), particularly molybdenum salts of monocarboxylic acids having from 1 to 50, preferably 8 to 18, carbon atoms, for example, molybdenum octoate (2-ethyl hexanoate), naphthenate or stearate; overbased molybdenum-containing complexes as disclosed in EP 404 650A- molybdenum
20 dithiocarbamates and molybdenum dithiophosphates; oil-soluble molybdenum xanthates and thioxanthates as disclosed in US 4,995,996 and 4,966,719; oilsoluble molybdenum- and sulfur-containing complexes; and aromatic amines, preferably having at least two aromatic groups attached directly to the nitrogen.

25 Typical oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen contain from 6 to 16 carbon atoms. The amines may contain more than two aromatic groups. Compounds having a total of at least three aromatic groups in which two aromatic groups are linked by a covalent bond or by an atom or group (e.g., an oxygen or sulfur atom, or a -CO-, -SO₂- or
30 alkylene group) and two are directly attached to one amine nitrogen also considered aromatic amines having at least two aromatic groups attached directly to the nitrogen. The aromatic rings are typically substituted by one or more substituents selected from alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups.

35

Friction modifiers may be included to improve fuel economy. In addition to the oil soluble aliphatic, oxyalkyl, or arylalkyl amines described above to add nitrogenous TBN, other friction modifiers are known. Among these are esters formed by

reacting carboxylic acids and anhydrides with alkanols. Other conventional friction modifiers generally consist of a polar terminal group (e.g. carboxyl or hydroxyl) covalently bonded to an oleophilic hydrocarbon chain. Esters of carboxylic acids and anhydrides with alkanols are described in US 4,702,850. Examples of other
5 conventional friction modifiers are described by M. Beizer in the "Journal of Tribology" (1992), Vol. 11 4, pp. 675-682 and M. Belzer and S. Jahanmir in "Lubrication Science" (1988), Vol. 1, pp. 3-26.

Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic
10 acids may be used. When the formulation of the present invention is used, these anti-rust inhibitors are not generally required.

Copper and lead bearing corrosion inhibitors may be used, but are typically not
15 required with the formulation of the present invention. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1,3,4 thiadiazoles such as those described in U.S. Pat. Nos. 2,719,125, 2,719,126; and 3,087,932. are typical. Other similar materials are described in U.S. Pat. Nos. 3,821,236; 3,904,537;
20 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882. Other additives are the thio and polythio sulfenamides of thiadiazoles such as those described in UK. Patent Specification No. 1,560,830. Benzotriazoles derivatives also fall within this class of additives. When these compounds are included in the lubricating composition, they are preferably present in an amount not exceeding 0.2 wt %
25 active ingredient.

A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP 330,522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric
30 alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

Pour point depressants, otherwise known as lube oil flow improvers, lower the
35 minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers and polyalkylmethacrylates.

Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

- 5 Some of the above-mentioned additives can provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor. This approach is well known and does not require further elaboration.

10 When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount which enables the additive to provide its desired function. Representative effective amounts of such additives, when used in crankcase lubricants, are listed below. All the values listed are stated as mass percent active ingredient.

15	ADDITIVE	MASS % (Broad)	MASS % (Preferred)
	Ashless Dispersant	0.1 - 20	1 - 8
	Metal detergents	0.1 - 6	0.2 - 4
	Corrosion Inhibitor	0 - 5	0 - 1.5
20	Metal dihydrocarbyl dithiophosphate	0.1 - 6	0.1 - 4
	Supplemental anti-oxidant	0 - 5	0.01 - 1.5
	Pour Point Depressant	0.01 - 5	0.01 - 1.5
	Anti-Foaming Agent	0 - 5	0.001-0.15
	Supplemental Anti-wear Agents	0 - 0.5	0 - 0.2
25	Friction Modifier	0 - 5	0 - 1.5
	Viscosity Modifier 1	0.01 - 6	0 - 4
	Mineral or Synthetic Base Oil	Balance	Balance

1. Viscosity modifiers are used only in multi-graded oils.

30 For non-crankcase applications, the quantities and/or proportions of the above additives may be varied; for example, marine diesel cylinder lubricants use relatively higher amounts of metal detergents, which may form 10 - 50 wt% of the lubricant.

35 The components may be incorporated into a base oil in any convenient way. Thus, each of the components can be added directly to the oil by dispersing or

dissolving it in the oil at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature.

Preferably all the additives except for the viscosity modifier and the pour point depressant are blended into a concentrate or additive package, that is subsequently blended into basestock to make finished lubricant. Use of such concentrates is conventional. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the concentrate is combined with a predetermined amount of base lubricant.

Preferably the concentrate is made in accordance with the method described in US 4,938,880. That patent describes making a premix of ashless dispersant and metal detergents that is pre-blended at a temperature of at least about 100°C. Thereafter the pre-mix is cooled to at least 85°C and the additional components are added.

The final formulations may employ from 2 to 15 mass % and preferably 5 to 10 mass %, typically about 7 to 8 mass % of the concentrate or additive package with the remainder being base oil.

The invention will now be described by illustration only with reference to the following examples.

Example 1

476 g of toluene, 15.4 g of methanol and 44 g of a cut dodecyl benzene linear chain sulphonic acid (Sinnozon DBS, 96.5% a.i.) were mixed with thorough agitation and heated to 30 to 35°C in a reactor fitted with a reflux condenser, a gas distribution tube and a temperature controller. 152 g of magnesium oxide was then added and there was a rapid exotherm as the low molecular weight sulphonic acid was neutralised, and the temperature rose to 40°C. To this mixture was added 56.5 g of ethylene diamine carbamate solution (18.9 wt% in methanol/water). The mixture was held at 40°C for a period of twenty minutes. Then 247 g of an 83 mass % solution of an alkyl benzene high molecular weight sulphonic acid (molecular weight 670) in diluent oil was added along with a further addition of methanol 49 g and water 108 g. There was an immediate exotherm and the temperature was allowed to reach 66°C maximum while commencing,

simultaneously, injection of carbon dioxide into the mixture at a rate of 45 g/h. During carbonation, the temperature of the carbonation mixture was allowed to follow its natural course and slowly increased to about 72°C and then fell again as the reaction subsided and the magnesium oxide was consumed. When the
5 temperature had fallen to about 60°C, heat was applied, and the temperature was maintained at 60°C until carbonation was complete. After 3 hours 30 minutes of carbonation, the apparatus was changed from a reflux to a distillation configuration while maintaining the temperature of the mixture at 60°C, 370 g of diluent oil, also at 60°C, were added, and the mixture so obtained was distilled at
10 atmospheric pressure while introducing a stream of nitrogen. When the distillation temperature reached 165°C, a vacuum was applied, and maintained for a 2 hour period, to remove the last traces of water, methanol and toluene. After releasing the vacuum, a 50 ml sample was removed from the stripped mixture and diluted with 50 ml of toluene. This diluted sample was then centrifuged to show that 1.0
15 vol % of sediment (PCS) remained in the stripped mixture. The product was filtered with the use of a filter aid and the filtered product was bright and clear and had a TBN of 417 mg KOH/g.

Example 2

20

Example 1 was repeated with the exception that 73 g of a linear C₁₈ alkylaromatic sulphonic acid of molecular weight 408 and a.i. 83.4 mass% (MX1245) was used in place of the dodecylbenzene sulphonic acid. Also 309 g of the high molecular weight sulphonic acid of a.i. 60.6 mass % and molecular weight 670 was used.

25 The results are provided in Table 1.

Example 3

30 Example 1 was repeated with the exception that 46 g of a branched dodecylbenzene sulphonic acid was used in place of the dodecylbenzene sulphonic acid. The results are provided in Table 1.

Example 4

35 Example 1 was repeated with the exception that the ethylene diamine was not reacted with carbon dioxide but was pre-reacted in situ with the dodecylbenzene linear chain sulphonic acid. The results are provided in Table 1.

Example 5

Example 1 was repeated with the exception that both the sulphonic acids which were used were added simultaneously at the point where the dodecylbenzene sulphonic acid addition was made in Example 1. The results are provided in Table 1.

Example 6

Example 1 was repeated with the exception that the ethylene diamine charge (9.7 g) in water was pre-reacted with the dodecylbenzene sulphonic acid and this was used in place of the ethylene diamine carbamate promoter. The results are provided in Table 1.

Example 7

Example 1 was repeated with the exception that the magnesium oxide used was a mixture of 70 mass% of a "heavy" magnesium oxide of citric acid number 391 seconds and a surface area BET of 9 m²/g and 30 mass% of a "light" magnesium oxide of citric acid number 80 seconds and a surface area BET of 25 m²/g. The results are provided in Table 1.

Example 8

Example 1 was repeated with the exception that 54.5 of a C₁₈ straight chain alkylaromatic sulphonic acid of molecular weight 427 was used in place of the dodecylbenzene sulphonic acid. The results are provided in Table 1.

Example 9

Example 1 was repeated with the exception that 92 g of a mixture of C₁₈ straight and C₁₅ to C₃₆₊ branched chain sulphonic acids (molecular weight 490 and a.i. 69 mass%) was used in place of the dodecylbenzenesulphonic acid. Also 314 g of a 60 mass% a.i. solution of an alkylbenzene high molecular weight sulphonic acid was used (molecular weight 670). The charge of diluent oil was 260 g. The low molecular weight sulphonic acid was also neutralised separately before addition of the high molecular weight sulphonic acid. The results are provided in Table 1.

Example 10

Example 9 was repeated with the exception that 63 g of a C₁₂ branched alkyl chain xylene sulphonic acid of number average molecular weight 370 and a.i. 82 mass% was used in place of the mixture of C₁₈ straight and C₁₅ to C₃₆+ branched chain sulphonic acids. The results are provided in Table 1.

Example 11

Example 9 was repeated with the exception that 38 g of a PIB Polymer (polyisobutylene) sulphonic acid of number average molecular weight 397 and a.i. 87 mass% was used in place of the mixture of C₁₈ straight and C₁₅ to C₃₆ branched chain sulphonic acids. The results are provided in Table 1.

Example 12

In a first vessel, the magnesium sulphonate of a cut dodecyl benzene linear chain sulphonic acid (Sinnozon DBS) was made by charging 148g of toluene, 2.2g of methanol and 44g of a cut dodecyl benzene linear chain sulphonic acid (Sinnozon DBS, 96.5 % a.i), commencing mixing and heating the vessel contents to 30 to 35 deg C. 5.9g of magnesium oxide was then added and there was a rapid exotherm as the low molecular weight sulphonic acid was neutralised, and the temperature rose to 40°C.

In a second vessel, the magnesium sulphonate of a high molecular weight sulphonic acid was prepared by charging 328g of toluene, 13.2g of methanol, 7.4g of water and 247g of an 83 mass % solution of an alkyl benzene high molecular weight sulphonic acid (molecular weight 670) in diluent oil, commencing mixing and heating the vessel contents to 40 deg C. 9.6g of magnesium oxide was then added and there was a rapid exotherm to 66 deg C maximum as the high molecular weight sulphonic acid was neutralised.

The contents of the first vessel were transferred to an agitated reactor fitted with a reflux condenser, a gas distribution tube and a temperature controller. To the mixture was added 56.5g of ethylene diamine carbamate solution (18.9 wt % in methanol/water). The mixture was held at 40°C for 15 to 20 minutes. Then 136.5g of magnesium oxide was added. Then the content of the second vessel was

transferred to the reactor along with a further addition of methanol (49g) and water (100.6g). Carbon dioxide was injected into the mixture at a rate of 45g/h as described in Example 1. This diluted sample was then centrifuged to show that 1.2 vol % of sediment (PCS) remained in the stripped mixture. The product was
5 filtered with the use of a filter aid; the filtered product was bright and clear and had a TBN of 408 mg KOH/g.

The result are provided in Table 1.

10 Comparative Example 1

The process of Example 1 was repeated with the exception that no water soluble sulphonic acid was used. The resultant product had unacceptably high levels of sediment and gelled during solvent removal.

15

The data presented in table 1 illustrates that the process of the present invention produces overbased magnesium sulphonates, primarily from high molecular weight sulphonic acids, which have high TBN,s, high filtration rates, low viscosities and low levels of sediment.

TABLE 1

EXAMPLE No	1	2	3	4	5	6	7	8	9	10	11	12	COMP1
End CO ₂ vol%	0.9	1.2	1.0	1.0	1.6	1.0	1.2	1.2	0.8	0.5	0.7	1.2	2.6
End Strip vol%	1.0	1.2	1.0	1.2	1.6	1.2	1.4	1.6	0.9	0.6	0.8	1.2	Gelled
Filtration rate (kg/h/m ²)	1520	950	1200	1476	905	1430	1190	857	650	650	630	1380	-
Viscosity at 100°C -cS	108	116	132	97	120	109	118	113	103	144	109	108	-
TBN mg KOH/g	417	406	408	413	407	414	401	408	413	412	405	408	-



CLAIMS:

1. A process for the production of an overbased magnesium sulphonate which
5 comprises (i) the steps of carbonating a mixture comprising an admixture of at least components (a) to (g) below inclusive, where
- (a) is at least one oil-soluble high molecular weight sulphonic acid;
- 10 (b) is at least one low molecular weight sulphonic acid, that is wholly or partially water-soluble or magnesium salt thereof;
- (c) is magnesium oxide in excess of that required to react completely with component (a) and with component (b);
- 15 (d) is a hydrocarbon solvent;
- (e) is water;
- 20 (f) is a water-soluble alcohol; and
- (g) is a promoter, and
- (ii) removing volatile solvent from the admixture of step (i).
- 25 2. A process as claimed in claim 1 wherein the promoter comprises at least one substance selected from ammonia, ammonium compounds, monoamines, polyamines, and carbamates of said amines.
- 30 3. A process as claimed in any of the preceding claims wherein the high molecular weight sulphonic acid has a number average molecular weight of 600 or greater.
4. A process as claimed in any of the preceding claims wherein the
35 carbonation takes place at a temperature within the range of 40 to 80°C.
5. A process as claimed in any of the preceding claims wherein the magnesium oxide is reacted with component (b) before addition of component (g).





6. A process as claimed in any of claims 1 to 4 wherein the magnesium oxide is mixed with component (g) before addition of component (b) or component (a).
- 5 7. A process as claimed in any of claims 1 to 4 wherein component (g) is mixed with component (b) before addition of component (a) and component (c).
8. A process as claimed in any of the proceeding claims wherein the magnesium oxide has a citric acid number in the range of from 200 to 600
10 seconds.
9. A process as claimed in any of claims 1 to 7 wherein the magnesium oxide is a mixture of at least one magnesium oxide having a citric acid number in the range of from 200 to 600 seconds and at least one magnesium oxide having a
15 citric acid number in the range of from 20 to 140 seconds.
10. An overbased magnesium sulphonate composition from which volatile solvents have not been removed comprising at least one magnesium sulphonate derived from an oil-soluble high molecular weight sulphonic acid and at least one
20 magnesium sulphonate derived from a low molecular weight sulphonic acid that is wholly or partially water-soluble, wherein at least 50 wt% of the total sulphonate in the composition is derived from the high molecular weight sulphonic acid or acids and the magnesium carbonate in the composition is in its hydromagnesite form.
- 25 11. An overbased magnesium sulphonate composition comprising at least one magnesium sulphonate derived from an oil-soluble high molecular weight sulphonic acid and at least one magnesium sulphonate derived from a low molecular weight sulphonic acid that is wholly or partially water-soluble, wherein at least 50 wt% of the total sulphonate in the composition is derived from the high
30 molecular weight sulphonic acid or acids.
12. An overbased magnesium sulphonate composition as claimed in claim 11 having the TBN of at least 400 mg KOH g⁻¹.
- 35 13. An overbased magnesium sulphonate composition as claimed in any of claims 10 to 12 wherein at least 60 wt% of the total sulphonate is derived from the high molecular weight sulphonic acid.





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AMENDED CLAIMS

[received by the International Bureau on 1 April 1997 (01.04.97);
original claim 1 amended; remaining claims unchanged (1 page)]

1. A process for the production of an overbased magnesium sulphonate which comprises (i) the steps of carbonating a mixture comprising an admixture of at
5 least components (a) to (g) below inclusive, where
- (a) is at least one oil-soluble high molecular weight sulphonic acid, having a number average molecular weight of greater than 500;
- 10 (b) is at least one low molecular weight sulphonic acid, that is wholly or partially water-soluble or magnesium salt thereof;
- (c) is magnesium oxide in excess of that required to react completely with component (a) and with component (b);
- 15 (d) is a hydrocarbon solvent;
- (e) is water;
- 20 (f) is a water-soluble alcohol; and
- (g) is a promoter, and
- (ii) removing volatile solvent from the admixture of step (i).
- 25 2. A process as claimed in claim 1 wherein the promoter comprises at least one substance selected from ammonia, ammonium compounds, monoamines, polyamines, and carbamates of said amines.
- 30 3. A process as claimed in any of the preceding claims wherein the high molecular weight sulphonic acid has a number average molecular weight of 600 or greater.
- 35 4. A process as claimed in any of the preceding claims wherein the carbonation takes place at a temperature within the range of 40 to 80°C.
5. A process as claimed in any of the preceding claims wherein the magnesium oxide is reacted with component (b) before addition of component (a)

