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Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

0 267 674
A1

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EUROPEAN PATENT APPLICATION

21 Application number: **87307863.8**

51 Int. Cl.4: **C10G 9/16 , C23F 15/00**

22 Date of filing: **04.09.87**

30 Priority: **30.09.86 US 913450**

43 Date of publication of application:
18.05.88 Bulletin 88/20

64 Designated Contracting States:
BE DE ES FR GB IT NL

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54 **Antifoulant compositions and uses thereof.**

57 Overbase complexes of metal oxides and carbonates associated with metal salts of organic acids are useful as antifoulants for oil, gas and petrochemical refining processes.

The invention provides an antifoulant composition comprising at least one overbase complex of (A) an oxide of a metal selected from the group consisting of Mg, Ca, Ba, Sr and Mn and mixtures thereof and (B) a metal salt of at least one organic acid complexing agent.

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ANTIFOULANT COMPOSITIONS AND USES THEREOF

Background of the Invention

5 The processes involved in oil, gas and petrochemical refining, for example, reforming, hydroforming, absorption, hydrocracking, isomerization, extraction, cracking, fractionation, hydrofining, desalting and the like, expose hydrocarbon streams to relatively elevated temperatures. These temperatures are most commonly attained by the use of heaters and heat exchangers in which the hydrocarbon feeds, products and intermediates are intimately contacted with heated surfaces. These conditions are known to promote the formation of fouling deposits which can drastically limit refining capacities and flow rates.

10 Many areas in refining operations are subject to fouling, including such areas as preheat exchangers on crude units, hydrodesulfurizers, fluid catalytic cracking units, overhead condensers, reformer reboilers, coker furnaces, vacuum towers, alkylation reboilers and the like.

15 Although the problems associated with fouling are most acute in the oil refining industry, they are also a persistent problem in gas plant refining operations and in petrochemical processes involving, for example, ethylene, styrene, butadiene, isoprene, acrylonitrile and other chemicals.

The formation of fouling deposits accompanying the thermally initiated physical or chemical modification of hydrocarbons and derivatives is observed any time a hydrocarbon or derivative phase is exposed to a retaining surface, metallic or otherwise, at elevated temperatures in process equipment. Deposits of this nature are known to materially decrease heat transfer characteristics of the affected systems and are generally removed only with considerable difficulty. The consequent increases in operating and maintenance expense accompanying the formation and removal of such deposits is often substantial. Consequently, considerable effort has been devoted to attempts to eliminate fouling problems, with the result that numerous methods have been proposed for either preventing foulant deposition or removing fouling deposits. These methods have met with varying degrees of success but the essential problem remains.

25 The fouling deposits which are encountered as a result of the physical and/or chemical modification of hydrocarbon feeds initiated by elevated process temperatures may consist of sticky, tarry, polymeric or carbonaceous material. The most common fouling deposits can be generally classified as inorganic salts, corrosion products, metal-organic compounds, organic polymers and coke. The inorganic salts such as sodium, calcium and magnesium chloride are probably carried into the process system with the crude feed stock. Metal-organic compounds may also be present in the feed stock or may be formed on heat transfer surfaces by combinations with corrosion products or other metals carried into the system. The formation of organic polymers is most commonly attributed to reaction of unsaturated hydrocarbons. Coke deposition is usually associated with the occurrence of hot spots caused by the accumulation of fouling deposits. Consequently, it can be shown that, in such processes, the metal and organic elements of fouling deposits interact with each other.

35 Several approaches have been taken to minimize the accumulation of foulant materials in process equipment. Some approaches involve polishing or coating process equipment in an effort to reduce affinity for fouling materials. It is practically impossible, however, to prevent the formation of fouling deposits by coating metal surfaces with protective permanent coatings without a consequent loss of process efficiency due to the loss of heat transfer capacity attributable to the coating itself.

40 Another approach, which does not necessitate the expense involved in process equipment coating and does not result in the accompanying loss in heat transfer capacity, involves the addition of chemicals to the hydrocarbon feed which act to either prevent the formation of fouling material or to prevent adhesion thereof to process equipment. Numerous compositions have been suggested for the purpose of preventing or mitigating the effects of fouling deposit formation in process systems but none is considered completely successful.

Field of the Invention

This invention relates to novel antifoulant compositions and to the use thereof to inhibit fouling of equipment used in the refining of crude oil, gas and petrochemicals and in the thermal processing of other organic materials. In particular, the invention relates to the use of colloidally dispersed overbase complex antifoulants in oil refineries, gas plants and petrochemical refineries. More particularly, the invention relates to overbase complexes of metal oxides and/or carbonates with at least one complexing agent and to their use as antifoulants in oil, petrochemical and gas refining operations.

Prior Art

A wide variety of antifoulants has been used in attempts to inhibit fouling associated with the decomposition of crude and refined oils, gases and petrochemical feed streams. A partial, but representative, listing of patents relating to antifoulant compositions and their uses is set forth below.

2,895,913	4,410,418
3,364,130	4,425,223
3,492,219	4,431,514
3,546,097	4,440,625
3,666,656	4,444,649
3,772,182	4,456,526
4,024,051	4,469,586
4,107,030	4,510,041
4,200,518	4,511,457
4,319,063	4,529,500
4,397,737	4,552,643
4,404,087	4,556,476

These patents describe the use of oil dispersible magnesium-containing organic compositions in lubricating oils (2,895,913); amide condensation products in petroleum processing equipment, metal deactivators for use in hot petroleum charge stock; mixtures of methacrylate polymers and a nitrogen-containing material; oil-soluble addition type copolymers; a mixture of nitrogen-containing methacrylate polymer, a Schiff's base and a diarylamine; inorganic phosphorous-containing acids and salts; sulfanilic acid amine salts; polyalkylene amines; a mixture of a sulfonate, amine and phenylhydrazine; poly(oxyalkylene)-carbamates; metals such as tin, antimony and germanium; halogen-containing silicon compounds; mixtures of a phosphorus acid ester and a hydrocarbon sulfonic acid; the reaction product of a polyalkylene amine and a hydroxy fatty acid; a mixture of a hydroxylamine and an organic surfactant; phosphates; a mixture of a hydroxylamine and a catechol; saturated sulfoxides; mixtures of phenothiazines and phenols; mixtures of phenothiazines, catechols and hydroquinones; phenothiazine dimers; combinations of tin, copper and antimony and mixtures of phenothiazines and hydroxylamines. Additionally, UK Patent Appln. 2017747 A describes sodium di-2-ethylhexylsulphosuccinates as fouling inhibitors for crude petroleum oil and UK Patent 2021144 B describes polyalkylenoxy sulfoxy salts for preventing and removing fouling deposits on refining equipment for hydrocarbon food streams.

Overbased oil-stable, fluid dispersions or "solutions" of complexes, containing, e.g., magnesium and calcium, and their preparation and use are well known to those skilled in the art. The term "overbase" historically refers to metal base/acid reaction products containing an amount of metal in stoichiometric excess of that required to form a neutral organic acid salt of such base. Synonymous terms frequently used include "basic", "highly basic" and "hyperbased".

Many processes are known for preparing overbased; metal-containing dispersions. Representative U.S. Patents which disclose processes for preparing overbased metal complexes include the following:

U.S. 2,585,520 discloses the preparation of highly basic magnesium and calcium petroleum sulfonates useful as additives for lubricating oils.

U.S. 2,895,913 discloses the preparation of stable oil-dispersible overbased organo-magnesium compounds useful as additives in lubricating oils.

U.S. 3,057,896 discloses the preparation of overbased calcium sulfonates useful as additives for lubricating oils.

U.S. 3,150,089 discloses stable dispersions of overbased organo-magnesium compounds useful as additives for lubricating oils.

U.S. 3,629,109 discloses the preparation of overbased organo-magnesium complexes which are useful as

lubricant and fuel additives.

U.S. 3,764,536 discloses the preparation of an overbased calcium salt of alkenylsuccinimide which is useful as a dispersant additive for lubricating oils.

Additionally, U.S. 3,776,835 discloses detergent-dispersant compositions used as antifoulants for fouling caused by high temperature hydrocarbon streams. Such compositions include sulfonates, especially normal and basic metal salts of benzene sulfonic acids, normal and basic salts of phosphonic and thiophosphonic acids, the normal and basic salts of phenates and carboxylate and carboxylate-phenate salts, alkenyl succinimides, alkali metal naphthenates and amines and carboxylic acids. Various commercial antifoulants are also mentioned, including ethoxylated catechol, polyhydroxyl ethoxylated amines, combination of a metal deactivator, a phenolic amine and a succinimide, and a combination of morpholine and a water soluble salt of an ethoxylated imidazoline.

U.S. 3,865,737 discloses the preparation of fluid, overbased organomagnesium complex dispersion which is useful as a lubricating composition additive. U.S. 4,129,589 discloses the preparation of overbased magnesium salts of sulfonic acids which are useful as lubricant additives.

U.S. 4,163,728 discloses the preparation of a stable, fluid organo-magnesium complex dispersion useful as an acidic neutralization additive for lubricating oils. The compounds disclosed are overbased.

U.S. 4,293,429 discloses the preparation of an overbased mixture of a magnesium carboxylate and magnesium oxide in the form of a fluid dispersion of submicron-sized magnesium oxide. The compounds are useful as additives for lubricants.

U.S. 4,295,981 discloses the preparation of overbased magnesium phenates useful as lubricating oil additives.

U.S. 4,298,482 describes the preparation of an overbased mixture of magnesium salts and magnesium hydroxide in the form of a dispersion of very small particles. The overbased material is useful as an acid neutralizer for lubricating oils and fuels.

U.S. 4,347,147 discloses the preparation of magnesium sulfonates and magnesium oxide having a small particle size.

U.S. 4,474,710 discloses the preparation of overbased mixtures of magnesium hydroxide or magnesium carbonate in a liquid magnesium sulfonate dispersant. The materials are useful as lubricant additives.

None of the above-described patents suggests the use of overbase complexes of metals and mixed overbase complexes as described herein to reduce the fouling problems associated with refining operations.

Of the above-described patents, the disclosures of U.S. 3,865,737, 4,163,728, 4,293,429 and 4,298,482 are particularly informative with regard to the elucidation of the state of the art and the preparation of overbased metal complexes in the form of dispersions. Accordingly, the disclosures of those patents, as regards the discussion of the preparation and composition of overbased metal compounds, is incorporated herein by reference. In particular, Cols. 1-9 of U.S. 3,865,737 is incorporated herein by reference as are Cols. 1-4 of U.S. 4,163,728, Cols. 1-3 of U.S. 4,293,429 and Cols. 1-4 of U.S. 4,298,482.

Summary of the Invention

The present invention pertains to novel antifoulant, compositions which are overbase complexes comprising oil-stable colloidal dispersions of fine particles of a metal salt, e.g., a metal oxide or carbonate, and a complexing agent and their use in the inhibition of fouling, particularly high temperature fouling, e.g., 500-1200° F, in refining processes.

Detailed Description of the Invention

As set forth above, prevention of fouling in oil, gas and petrochemical refining has been a particularly troublesome problem. The problem is complicated not only because of the nature of the fouling materials but because the various areas or units of a refining operation present different environments, different feed stocks and different objectives. A fouling problem in one area of a refinery may not necessarily respond to the same antifoulant treatment as does a different area of a refinery. Accordingly, treatment of refining operations must be broken down, unit by unit, and the particular fouling characteristics of each unit must be defined and treated appropriately.

Use of antifoulant chemicals in an oil refinery are particularly important in the following areas:

1. Addition of antifoulant to the raw crude stream after the desalting operation but prior to entering the crude unit, i.e., the desalted process stream entering the preheat train.

2. Addition of antifoulant to the effluent exchanger train (atmospheric resid), i.e., the effluent from the atmospheric crude column of the crude unit.

3. Addition of antifoulant to the reactor influent and affluent stream to the hydrotreating and hydroprocessing units.

5 4. Addition of antifoulant to the effluent (bottoms) from the atmospheric crude column, including pumparound circuits and the influent to the gas and oil vacuum furnaces and columns.

5. Addition of antifoulant to the feed to the coker furnace (delayed or fluid) and to the coker furnace itself and the transfer lines and pumparound circuits attached to the coker furnace.

6. Addition of antifoulant to the main fractionator effluent of the alkylation unit prior to the reboiler and 10 the reboiler pumparound circuit. Antifoulant should also be added to the reboiler itself.

7. Addition of antifoulant to the feed to the preheater of the fluid catalytic cracking unit and to the effluent from the cracking unit to the slurry exchange system, including the bottoms from the main fractionator tower and pumparound and the catalytic cracker unit pumparound circuit.

8. Addition of antifoulant to the preheater and feed to the furnace on the visbreakers and to the 15 effluent from the main fractionating column on the visbreaker.

Each of the above areas of a refinery operate in individually characteristic manners in view of their special environments which do not necessarily have characteristics in common with other areas of the refinery.

The following is a summary of the important units of, for example, an oil refinery which require addition 20 of antifoulant chemicals:

Crude unit preheat exchanger
Crude unit vacuum resid exchanger
Crude unit vacuum distillation heater and resid
Fluid catalytic cracker preheat
25 Fluid catalytic cracker slurry pumparound
Fluid catalytic cracker furnace
Delayed coker
Fluid coker
Visbreaker
30 Hydrotreater
Hydrocracker
Reboilers
Hydrodesulfurizers
Heat exchangers
35 Hot separators
Pumparound circuits
Process stream tubes

In accordance with the present invention, it has been found that if an oxide or carbonate of Mg, Ca, Ba, Sr or Mn is prepared in conjunction with at least one complexing agent, a product results which is an 40 overbase complex of a metal oxide or carbonate, in an extremely fine, preferably submicron particle size, and the metal salt of the complexing agent. It is theorized that the presence of the complexing agent, during preparation of the metal oxide or carbonate, protects the fine particles of metal oxide or carbonate from agglomerating and allows the fine particles to remain dispersed in a stable manner in the diluent used in the reaction and, later, in a hydrocarbon stream.

45 The exact nature of overbases is not understood. It has been suggested that they comprise dispersions of salts formed by contacting an acidic material with a basically reacting metal compound, e.g., a metal hydroxide. Alternatively, it has been suggested that they comprise "polymeric salts". It is believed that neither theory is incorrect but that neither is completely correct. In accordance with the present invention, it is believed that the preparation of an "overbased" material results in an "overbase complex" of a metal 50 oxide or carbonate with an organic acid dispersant or stabilizer (i.e., "complexing agent"). The nature of the complex so-formed is not completely understood.

Accordingly, as used in the present specification, an "overbase complex" is a complex of an oxide or carbonate of Mg, Ca, Ba, Sr or Mn and a metal salt of an organic acid "complexing agent". The overbase complex contains a stoichiometric excess of metal, relative to the number of equivalents of acid complexing 55 agent which is reacted with a basic metal compound to afford the complex, based on the normal stoichiometry of the particular metal base and acid. For example, a "neutral" or "normal" metal salt of an acid is characterized by an equivalent ratio of metal to acid of 1:1, while an overbased salt is characterized by a higher ratio, e.g., 1.1:1, 2:1, 5:1, 10:1, 15:1, 20:1, 30:1 and the like. The term "metal ratio" is used to

designate the ratio of (a) equivalents of metal to acid in an overbased salt to (B) the number of equivalents expected to be present in a normal salt, based on the usual stoichiometry of the metal or metals involved and the acid or acids present. Thus, an oil dispersion of an overbased magnesium salt containing two equivalents of acid and twenty equivalents of magnesium would have a metal ratio of 10 (i.e., $20 \div (1 + 1)$).

5 In the present specification, magnesium, for example, is regarded as having two equivalents per atomic weight; magnesium oxide (MgO) and magnesium hydroxide (Mg(OH)₂), two equivalents per mole. Organic acids are regarded as having one equivalent of acid per acidic hydrogen or acid group. Thus, a monocarboxylic acid or monosulfonic acid or their equivalent derivatives, such as esters and ammonium and metal salts, have one equivalent per mole of acid, ester or salt; a disulfonic acid or dicarboxylic acid, or
10 equivalent derivative, has two equivalents per mole. The basically reacting metal compounds such as the oxides and carbonates of calcium, barium and manganese have two equivalents per mole (i.e., two equivalents per atomic weight of metal).

The complex antifoulants of the invention are overbase complexes of metal oxides and/or carbonates and a metal salt of at least one complexing agent. Thus, in general,

Table 1

<u>Metal oxide/carbonate</u>			
20	Mg, Ca, Ba, Sr, Mn	)	
	oxide and/or carbonate	) +	(carboxylic acid
25	Mg, Ca, Ba, Sr, Mn oxide	) +	(noncarboxylic acid
	Mg, Ba, Sr, Mn carbonate	) +	(noncarboxylic acid

30 Hereinafter, for want of better terms, "carboxylate" refers to the reaction product of a metal base and an organic carboxylic acid have the general formula R-COOH, where R is a hydrocarbon radical, and "noncarboxylate" refers to the reaction product of a metal base and an organic acid other than an organic carboxylic acid, i.e., "noncarboxylic" acids such as organic sulfur acids and organic phosphorus acids,
35 which latter materials have substantially greater dispersant capabilities than do the carboxylates which appear to have more stabilizing capabilities.

The role of the complexing agent in the preparation and use of the antifoulants of the invention is not clear. As stated above, some may function as stabilizers while others may function as dispersants. Certainly, some may have both functions or another, unknown, function. It is clear, however, that, during the
40 preparation of the complex, the presence of at least one complexing agent is essential to provide the complex antifoulants of the invention. It is also clear that the preferred antifoulants are characterized by the presence of a noncarboxylate, especially a sulfonate.

The overbase complexes used in the present invention may be prepared in any manner known to the prior art for preparing overbased salts, provided that the overbase complex resulting therefrom is in the
45 form of finally divided, preferably submicron, particles which form a stable dispersion in oil. Thus, a preferred method for preparing the antifoulants of the present invention is to form a mixture of a base of the desired metal, e.g., Mg(OH)₂, a complexing agent, e.g., a fatty acid such as a tall oil fatty acid, which is present in a quantity much less than that required to stoichiometrically react with the hydroxide, and a non-volatile diluent. The mixture is heated to a temperature of about 250-350° C, whereby there is afforded the
50 overbase complex of the metal oxide and metal salt of the fatty acid. The metal carbonate/complexing agent overbase complex is prepared in the same manner as described above, except that carbon dioxide is bubbled through the initial reaction mixture.

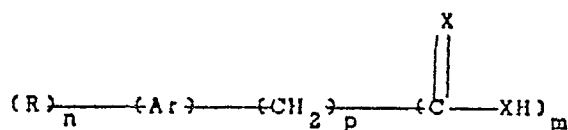
The above described method of preparing the overbase complexes of the present invention is particularly set forth in U.S. P. 4,163,728 which is incorporated herein by reference in its entirety, wherein,
55 for example, a mixture of Mg(OH)₂ and a carboxylic acid complexing agent is heated at a temperature of about 280-330°C. In a suitable non-volatile diluent.

Complexing agents which are used in the present invention are carboxylic acids, phenols, organic phosphorus acids and organic sulfur acids. Included are those acids which are presently used in preparing

overbased materials (e.g., those described in U.S. Patents 3,312,618, 2,695,910 and 2,616,904) and constitute an art-recognized class of acids. The carboxylic acids, phenols, organic phosphorus acids and organic sulfur acids which are oil-soluble per se, particularly the oil-soluble sulfonic acids, are especially useful. Oil-soluble derivatives of these organic acidic substances, such as their metal salts, ammonium salts, and esters (particularly esters with lower aliphatic alcohols having up to six carbon atoms, such as the lower alkanols), can be utilized in lieu of or in combination with the free acids. When reference is made to the acid, its equivalent derivatives are implicitly included unless it is clear that only the acid is intended.

Suitable carboxylic acid complexing agents which may be used herein include aliphatic, cycloaliphatic, and aromatic mono and polybasic carboxylic acids such as the naphthenic acids, alkyl- or alkenyl-substituted cyclopentanoic acids, alkyl- or alkenyl-substituted cyclohexanoic acids and alkyl- or alkenyl-substituted aromatic carboxylic acids. The aliphatic acids generally are long chain acids and contain at least eight carbon atoms and preferably at least twelve carbon atoms. The cycloaliphatic and aliphatic carboxylic acids can be saturated or unsaturated. Specific examples include 2-ethylhexanoic acid, alphalinolenic acid, propylene-tetramer-substituted maleic acid, behenic acid, isostearic acid, pelargonic acid, capric acid, palmitoleic acid, linoleic acid, lauric acid, oleic acid, ricinoleic acid, undecylic acid, dioctylcyclopentane carboxylic acid, myristic acid, dilauryldecahydronaphthalene carboxylic acid, stearyl-octahydroindene carboxylic acid, palmitic acid, commercially available mixtures of two or more carboxylic acids such as tall oil fatty acids, rosin acids, and the like. Also included as representative acids are saturated aliphatic monocarboxylic acids, e.g. formic, acetic, propionic, butyric, valeric, caproic, heptanoic, caprylic, pelargonic, capric, undecylic, lauric, tridecylic, myristic, isoacetic, palmitic, margaric and stearic; alicyclic unsaturated monocarboxylic acids, e.g., hydnocarpic and chaulmoogric; saturated aliphatic dicarboxylic acids, e.g. oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic; alicyclic saturated dicarboxylic acids, e.g. cyclohexane dicarboxylic acid; unsaturated aliphatic monocarboxylic acids, e.g. acrylic, crotonic, decenoic, undecenoic, tridecenoic, pentadecenoic, oleic, linoleic and linolenic; unsaturated dicarboxylic acids, e.g., fumaric and maleic.

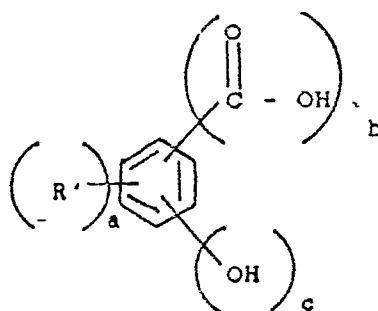
Aromatic acids which are used herein are represented by the general formula:



Where R is a hydrocarbon or essentially hydrocarbon radical containing at least four aliphatic carbon atoms, n is an integer of from one to four, Ar is a polyvalent aromatic hydrocarbon radical having a total of up to fourteen carbon atoms in the aromatic nucleus, each X is independently a divalent sulfur or oxygen group, p is zero or an integer of from one to six and m is an integer of from one to four, with the proviso that R and n are such that there is an average of at least eight aliphatic carbon atoms provided by the R substituents for each acid molecule represented. Examples of aromatic radicals represented by the variable Ar are the polyvalent aromatic radicals derived from benzene, naphthalene, anthracene, phenanthrene, indene, fluorene, biphenyl, and the like. Generally, the radical represented by Ar will be a polyvalent radical derived from benzene or naphthalene such as phenylenes and naphthalene, e.g., methylphenylenes, ethoxyphenylenes, nitrophenylenes, isopropylphenylenes, hydroxyphenylenes, mercaptophenylenes, N,N-diethylaminophenylenes, chlorophenylenes, dipropoxynaphthylenes, triethylnaphthylenes, and similar tri-, tetra-, and pentavalent radicals thereof.

The R variables are usually hydrocarbon groups, preferably aliphatic hydrocarbon groups such as alkyl or alkenyl radicals. However, the R groups can contain such substituents as phenyl, cycloalkyl (e.g., cyclohexyl, cyclopentyl, etc.) and nonhydrocarbon groups such as nitro, amino, halo (e.g., chloro, bromo, etc.), lower alkoxy, lower alkyl mercapto, oxo substituents (i.e., =O), thio groups (i.e., =S), interrupting groups such as -NH-, -O-, -S-, and the like, provided the essentially hydrocarbon character of the R variable is retained. Examples of R groups include butyl, isobutyl, pentyl, octyl, nonyl, dodecyl, docosyl, tetracontyl, t-chlorohexyl, 4-ethoxypentyl, 4-hexenyl, 3-cyclohexyloctyl, 4-(p-chlorophenyl)-octyl, 2,3,5-trimethyl, 4-ethyl-5-methyloctyl, and substituents derived from polymerized olefins such as polychloroprenes, polyethylenes, propypropylenes, polyisobutylenes, ethylenepropylene copolymers, chlorinated olefin polymers, oxidized ethylene-propylene copolymers, and the like. Likewise the variable Ar may contain nonhydrocarbon substituents, for example, such diverse substituents as lower alkoxy, lower alkyl mercapto, nitro, halo, alkyl or alkenyl groups of less than four carbon atoms, hydroxy, mercapto, and the like.

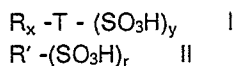
Another group of aromatic carboxylic acids are those of the formula:



Where R' is an aliphatic hydrocarbon radical containing at least four carbon atoms, a is an integer of from 1 to 3, b is 1 or 2, c is zero, 1, or 2 and preferably 1, with the proviso that R' and a are such that the acid molecules contain at least an average of about twelve aliphatic carbon atoms in the aliphatic hydrocarbon substituents per acid molecule.

Phenols which are used herein include 3,5,5-trimethyl-n-hexyl phenol, n-decyl phenols, cetyl phenols, nonyl phenols, alkylphenyl phenols, resorcinol, octyl catechol, triisobutyl pyrogallol, alkyl alpha naphthol and the like.

Other acids, like the phenols (i.e. "noncarboxylic acids" which may be used in preparing the antifoulants are the organic sulfur acids, e.g., oil-soluble sulfonic acids, including the synthetic oil-soluble sulfonic acids. Suitable oil-soluble sulfonic acids are represented by the general formulae:



In Formula I, T is a cyclic nucleus of the mono-or polynuclear type including benzenoid, cycloaliphatic or heterocyclic nuclei such as a benzene, naphthalene, anthracene, 1,2,3,4-tetrahydronaphthalene, thianthrene, cyclopentene, pyridine or biphenyl nucleus and the like. Ordinarily, however, T will represent an aromatic hydrocarbon nucleus, especially a benzene or naphthalene nucleus. The variable R in the radical R_x can be, for example, an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, carboalkoxyalkyl, an aralkyl group, or other hydrocarbon or essentially hydrocarbon groups, while x is at least 1 with the proviso that the variables represented by the group R_x are such that the acids are oil-soluble. This means that the groups represented by R_x should contain at least about eight aliphatic carbon atoms and preferably at least about twelve aliphatic carbon atoms. Generally x will be an integer of 1-3. The variables 4 and y in Formulae I and II have an average value of one to about four per molecule.

The variable R' in Formula II is an aliphatic or aliphatic-substituted cycloaliphatic hydrocarbon or essentially hydrocarbon radical. Where R' is an aliphatic radical, it should contain at least about 8 to about 20 carbon atoms and where R' is an aliphatic substituted-cycloaliphatic group, the aliphatic substituents should contain about 4 to 16 carbon atoms. Examples of R' are alkyl, alkenyl, and alkoxyalkyl radicals and aliphatic-substituted cycloaliphatic radicals wherein the aliphatic substituents are alkoxy, alkoxyalkyl, carboalkoxyalkyl, etc. Generally the cycloaliphatic radical will be a cycloalkane nucleus or a cycloalkene nucleus such as cyclopentane, cyclohexane, cyclohexene, cyclopentene, and the like. Specific examples of R' are cetyl-cyclohexyl, laurylcyclohexyl, cetyl-oxyethyl and octadecenyl radicals, and radicals derived from petroleum, saturated and unsaturated paraffin wax, and polyolefins, including polymerized mono-and diolefins containing from about 1 to 8 carbon atoms per olefin monomer unit. The groups T, R, and R' in Formulae I and II can also contain other substituents such as hydroxy, mercapto, halogen, nitro, amino, nitroso, carboxy, lower carbalkoxy, etc., as long as the essentially hydrocarbon character of the groups is not destroyed.

The sulfonic acids which are preferred for use herein include alkyl sulfonic acids, alkaryl sulfonic acids, aralkyl sulfonic acids, dialkyl sulfonic acids, dialkylaryl sulfonic acids, aryl sulfonic acids, e.g. ethylsulfonic acid, benzenesulfonic acid, dodecylbenzenesulfonic acid and more complex sulfonic acid mixtures such as mahogany sulfonic acids and petroleum sulfonic acids.

Further, illustrative examples of the sulfonic acids are mahogany sulfonic acids, petrolatum sulfonic acids, mono-and poly-wax-substituted naphthalene sulfonic acids, cetylchlorobenzenesulfonic acids, cetylphenol sulfonic acids, cetylphenol disulfide sulfonic acids, cetoxycaprylbenzene sulfonic acids, dicetyl thianthrene sulfonic acids, di-lauryl betanaphthol sulfonic acids, dicapryl nitronaphthylene sulfonic acids, paraffin wax sulfonic acids, unsaturated paraffin wax sulfonic acids, hydroxy-substituted paraffin wax sulfonic

acids, tetraisobutylene sulfonic acids, tetraamylene sulfonic acids, chloro-substituted paraffin wax sulfonic acids, nitrosyl-substituted paraffin wax sulfonic acids, petroleum naphthene sulfonic acids, cetylcyclopentyl sulfonic acids, lauryl cyclohexyl sulfonic acids, mono-and polywax substituted cyclohexyl sulfonic acids, and the like.

5 As used herein the terminology "petroleum sulfonic acids" or "petrosulfonic acids" is intended to cover that well-known class of sulfonic acids derived from petroleum products according to conventional processes such as disclosed in U.S. Pats. 2,480,638, 2,483,800, 2,717,265; 2,726,261; 2,794,829; 2,832,801; 3,225,086; 3,337,613; 3,351,655; and the like. Sulfonic acids falling within Formulae I and II are discussed in prior U.S. patents 2,616,904; 2,616,905; 2,723,234; 2,723,235; 2,723,236; 2,777,874; and the other U.S.
10 patents referred to in each of these patents. Thus it is seen that these oil-soluble sulfonic acids are well-known in the art and require no further discussion herein.

Organic phosphorus acids used herein are characterized by at least one oil-solubilizing group attached directly to phosphorus via a carbon atom, e.g., oil-soluble phosphoric, phosphinic and phosphonic acids including the oil-soluble thiophosphoric, thiophosphinic and thiophosphonic acids. Preferred phosphorus
15 acids are the alkyl- and dialkyl phosphoric and phosphonic acids and those prepared by reacting olefins with phosphorus sulfides (e.g., phosphorus pentasulfide). Steam-treated reaction products of phosphorus pentasulfide and polyolefins, such as polyisobutylene and polypropylene, are also useful. Such acids are well-known, as shown by U.S. Pats. 2,316,078; 2,316,080; 2,316,091; 2,367,468; 2,375,315; 2,377,955; 2,496,508; 2,507,731; 2,516,119; 2,597,750; 2,647,889; 2,688,612 and 2,915,517.

20 Of course, mixtures of the above-described organic acids and derivatives thereof may be employed in preparing the antifoulants of this invention.

Overbase complex types (see Table I) which are the preferred antifoulants of the invention are the following (where M represents Mg, Ca, Ba, Sr or Mn):

MO/M carboxylate

25 MCO₃/M carboxylate

MO/M noncarboxylate

MCO₃/M noncarboxylate

The use of the terms "carboxylate" and "noncarboxylate" refers, as stated supra, to the partial reaction product of a base of the desired metal and a carboxylic or noncarboxylic acid complexing agent which
30 afford a complex believed to be a dispersion of finely divided metal oxide (or carbonate) associated with the metal carboxylate or metal noncarboxylate.

Of course, more than one oxide or carbonate may be associated with a complexing agent to afford complexes, for example, of the type MO/MCO₃/M noncarboxylate, and more than one complexing agent may be combined with an oxide or carbonate to afford complexes, for example, of the type MO/M
35 carboxylate/M noncarboxylate and MCO₃/M carboxylate/M noncarboxylate.

Additionally, mixed overbase complexes are included in the present invention, e.g. MO/M carboxylate with MO/M noncarboxylate, MCO₃/carboxylate with MCO₃ noncarboxylate, MO/M carboxylate with MCO₃/noncarboxylate, etc.

Species which are intended to be excluded from the above-described general types of complexes are
40 CaCO₃/Ca sulfonate which is disclosed and claimed in copending application Serial No. , filed , of common ownership herewith and the mixed complex MgO/Mg carboxylate with MgCO₃/Mg noncarboxylate which is disclosed and claimed in copending application Serial No. , filed , of common ownership herewith.

Especially preferred of the above types are:

45 MO/M carboxylate

MCO₃/M sulfonate

MO/M sulfonate

MCO₃/M carboxylate

MO/M sulfonate + MCO₃/M carboxylate

50 MO/MCO₃/M carboxylate

MO/MCO₃/M sulfonate

The most preferred complexes are the following:

MgO/Mg fatty acid carboxylate (especially "tall oil" fatty acid carboxylates)

MgO/Mg benzenesulfonate or dodecylbenzenesulfonate

55 MgCO₃/Mg fatty acid carboxylate

MgCO₃/Mg benzenesulfonate or dodecylbenzenesulfonate

CaO/Ca fatty acid carboxylate

CaO/Ca benzenesulfonate or dodecylbenzenesulfonate

CaCO₃/Ca fatty acid carboxylate

MgO/Mg fatty acid carboxylate + MgO/Mg benzenesulfonate or dodecylbenzene sulfonate

MgCO₃/Mg fatty acid carboxylate + MgCO₃/Mg benzenesulfonate or dodecylbenzenesulfonate

MgO/MgCO₃/Mg fatty acid carboxylate

5 MgO/MgCO₃/Mg benzenesulfonate or dodecylbenzenesulfonate

The mixed overbase complexes, e.g., MgO/Mg fatty acid carboxylate + MgO/Mg benzenesulfonate, are in a weight ratio to each other of from about 0.25/10 to about 10/0.25.

As described in U.S. 4,164,728 referred to earlier, the reaction of metal base and acid affords a product which undergoes decomposition to afford minute particle of metal oxide or carbonate in association with the metal salt of the acid. The minute particles immediately become suspended and stabilized by the metal salt of the acid. The particles of metal oxide or metal carbonate are of a size no greater than about 2 microns in diameter, for example not greater than about 1 micron but, preferably, no greater than about 0.1 micron and, especially, should be less than 0.1 micron in diameter.

The amount of antifoulant which is used to inhibit fouling in a fouling area will vary, depending on the environment of the area, the degree of fouling and the specific antifoulant used. In general, an amount of antifoulant is used which is effective to inhibit fouling in an area. Accordingly, there may be used an amount of from about 5 ppm to about 1000 ppm or more based on the weight of the hydrocarbon stream, depending on specific circumstances. Ordinarily, from about 25 ppm to about 500 ppm are effective, especially from about 50 to 300 ppm.

20 Accordingly, the best mode contemplated of carrying out the present invention is to add, to appropriate fouling areas of an oil refining process, a gas refining process or petro-chemical refining process, an effective fouling inhibiting amount as set forth above, of the antifoulant compositions herein-described.

25 Claims

1. Antifoulant composition comprising at least one overbase complex of (A) an oxide of a metal selected from the group consisting of Mg, Ca, Ba, Sr and Mn and mixtures thereof and (B) a metal salt of at least one organic acid complexing agent.

30 2. Composition of claim 1 wherein said metal is magnesium.

3. Composition of claim 1 wherein said metal is calcium.

4. Composition of claim 1 wherein said metal is barium.

5. Composition of claim 1 wherein said metal is strontium.

6. Composition of claim 1 wherein said metal is manganese.

35 7. Composition of claim 1 wherein said complexing agent is selected from the group consisting of carboxylic acids and an organic acid other than a carboxylic acid.

8. Composition of claim 7 wherein said agent is a carboxylic acid.

9. Composition of claim 8 wherein said acid is a fatty acid.

40 10. Composition of claim 7 wherein said agent which is an organic acid other than a carboxylic acid is an organic sulfur acid.

11. Composition of claim 9 wherein said acid is a sulfonic acid.

12. Composition of claim 10 wherein said sulfonic acid is a benzenesulfonic acid.

13. Composition of claim 7 wherein said agent which is an organic acid other than a carboxylic acid is an organic phosphorus acid.

45 14. Composition of claim 13 wherein said acid is a phosphonic acid

15. Antifoulant composition comprising at least one overbase complex of (A) a carbonate of a metal selected from the group consisting of Mg, Ca, Ba, Sr and Mn and (B) a metal salt of an organic acid complexing agent, provided that said complex is not a complex of calcium carbonate and the calcium salt of a sulfonic acid.

50 16. Antifoulant composition comprising at least one overbase complex of (A) a carbonate of a metal selected from the group consisting of Mg, Ca, Ba, Sr and Mn and (B) a metal salt of at least one carboxylic acid complexing agent.

17. Composition of claim 16 wherein said metal is magnesium.

18. Composition of claim 16 wherein said metal is calcium.

55 19. Composition of claim 16 wherein said metal is barium.

20. Composition of claim 16 wherein said metal is strontium.

21. Composition of claim 16 wherein said metal is manganese.

22. Composition of claim 16 wherein said agent is a fatty acid.

23. Antifoulant composition comprising at least one overbase complex of (A) a carbonate of a metal selected from the group consisting of Mg, Ba, Sr and Mn and (B) a metal salt of an organic sulfur acid complexing agent.
24. Composition of claim 23 wherein said metal is magnesium.
25. Composition of claim 23 wherein said metal is barium.
26. Composition of claim 23 wherein said metal is strontium.
27. Composition of claim 23 wherein said metal is manganese.
28. Composition of claim 23 wherein said acid is a sulfonic acid.
29. Composition of claim 24 wherein said acid is a benzenesulfonic acid.
30. Antifoulant composition comprising at least one overbase complex of (A) an oxide or carbonate of a metal selected from the group consisting of Mg, Ca, Ba, Sr and Mn and (B) a metal salt of an organic phosphorus acid complexing agent.
31. Composition of claim 30 wherein said metal is magnesium.
32. Composition of claim 30 wherein said metal is calcium.
33. Composition of claim 30 wherein said metal is barium.
34. Composition of claim 30 wherein said metal is strontium.
35. Composition of claim 30 wherein said metal is manganese.
36. Composition of claim 30 wherein said acid is a phosphonic acid.
37. Antifoulant composition comprising (A) at least one overbase complex of (1) an oxide of a metal selected from the group consisting of Ca, Ba, Sr and Mn and (2) a metal salt of a carboxylic acid complexing agent and (B) at least one overbase complex of (1) a carbonate of a metal selected from the group consisting of Ca, Ba, Sr and Mn and (2) a metal salt of a carboxylic acid complexing agent and (B) at least one overbase complex of (1) a carbonate of a metal selected from the group consisting of Mg, Ca, Ba, Sr and Mn and (2) a metal salt of an organic sulfur acid complexing agent.
38. Composition of claim 37 wherein said carboxylic acid is a tall oil fatty acid and said sulfur acid is a sulfonic acid.
39. Composition of claim 38 wherein said sulfonic acid is a benzenesulfonic acid.
40. Antifoulant composition comprising (A) at least one overbase complex of (1) an oxide or carbonate of a metal selected from the group consisting of Mg, Ca, Ba, Sr and Mn and (2) a metal salt of a carboxylic acid complexing agent and (B) at least one overbase complex of (1) an oxide or carbonate of a metal selected from the group consisting of Mg, Ca, Ba, Sr and Mn and (2) a metal salt of an organic phosphorus acid complexing agent.
41. Composition of claim 40 wherein said carboxylic acid is a tall oil fatty acid.
42. Composition of claim 40 wherein said organic phosphorus acid is a phosphonic acid.
43. Antifoulant composition comprising (A) at least one overbase complex of (1) an oxide of a metal selected from the group consisting of Mg, Ca, Ba, Sr and Mn and (2) a metal salt of a carboxylic acid complexing agent and (B) at least one overbase complex of (1) a carbonate of a metal selected from the group consisting of Mg, Ba, Sr and Mn and (2) a metal salt of an organic sulfur acid complexing agent.
44. Composition of claim 43 wherein said carboxylic acid is a fatty acid.
45. Composition of claim 43 wherein said sulfur acid is a sulfonic acid.
46. Composition of claim 44 wherein said sulfonic acid is a benzenesulfonic acid.
47. Method of inhibiting fouling in an oil refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 1.
48. Method of inhibiting fouling in an oil refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 15.
49. Method of inhibiting fouling in an oil refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 16.
50. Method of inhibiting fouling in an oil refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 23.
51. Method of inhibiting fouling in an oil refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 30.
52. Method of inhibiting fouling in an oil refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 37.
53. Method of inhibiting fouling in an oil refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 40.
54. Method of inhibiting fouling in an oil refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 43.

55. Method of inhibiting fouling in a gas refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 1.
56. Method of inhibiting fouling in a gas refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 15.
57. Method of inhibiting fouling in a gas refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 16.
58. Method of inhibiting fouling in a gas refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 23.
59. Method of inhibiting fouling in a gas refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 30.
60. Method of inhibiting fouling in a gas refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 37.
61. Method of inhibiting fouling in a gas refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 40.
62. Method of inhibiting fouling in a gas refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 43.
63. Method of inhibiting fouling in a petrochemical refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 1.
64. Method of inhibiting fouling in a petrochemical refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 15.
65. Method of inhibiting fouling in a petrochemical refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 16.
66. Method of inhibiting fouling in a petrochemical refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 23.
67. Method of inhibiting fouling in a petrochemical refining process which comprises adding fouling areas in said process an effective fouling inhibiting amount of a composition of claim 30.
68. Method of inhibiting fouling in a petrochemical refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 37.
69. Method of inhibiting fouling in a petrochemical refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 40.
70. Method of inhibiting fouling in a petrochemical refining process which comprises adding to fouling areas in said process an effective fouling inhibiting amount of a composition of claim 43.
71. Antifoulant composition comprising the overbase complex reaction product of a basically reacting compound of a metal selected from the group consisting of Mg, Ca, Ba, Sr and Mn and at least one organic acid complexing agent.
72. Composition of claim 71 wherein carbon dioxide is introduced during said reaction.



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 87307863.8
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	<u>US - A - 3 328 284</u> (GODAR) * Claims 1,2; column 3, lines 58-67; column 5, lines 46-53 *	1-5,7, 10,47, 50,52, 54-56, 58,60, 62-64, 66,68, 70	C 10 G 9/16 C 23 F 15/00
A	<u>US - A - 4 024 051</u> (SHELL) * Claim 1 *	1,7,47, 48,51, 53,55, 56,59, 61,63, 64,67, 69	
D,A	<u>US - A - 4 347 147</u> (ALLAIN) * Claims 1-5 *	1,2,7- 10,47, 48,50- 56,58- 64,66- 70	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 10 G C 23 F C 23 C C 10 M
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 10-02-1988	Examiner BÖHM
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



☒ CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☒ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid,
namely claims: 47-70
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

☐ LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,
namely:

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid,
namely claims:
- ☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims,
namely claims: