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MICROBIOLOGICAL CONTROL OF HYDROCARBON FLUIDS

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The instant invention is directed toward a method of control of microbes. More specifically, the present invention is concerned with a process of inhibition of growth and reproduction of microorganisms existing in hydrocarbon fluids containing minor amounts of aqueous liquids.

Recently, it has been discovered that certain microbiological problems have arisen with respect to storage of hydrocarbon fluids. More specifically, it has been determined that degradation of these stored products, resulting in sludge formation and in increased corrosivity, has been a result, at least in part, from activity of such microbe species as bacteria and fungi. While essentially pure hydrocarbon fluids are not appreciably susceptible to bacterial or fungal attack, those fluids containing even as low as 10 p.p.m. of water are prone to attack, since the aqueous phase becomes an excellent environmental medium for the microbes. While the microorganisms exist in pure hydrocarbon medium, they can only thrive in the impure aqueous liquid phase, whether the latter is emulsified throughout the oil, or forms an impure bottom layer in the oil.

The problem of microbiological attack of hydrocarbon becomes increasingly severe as storage time increases, since generally the amount of microorganism activity-promoting portion of the oil, namely, the water phase, likewise increases upon long term standing. Such accumulated water in the hydrocarbon fluid occurs as a result of multiple handling steps and/or because of atmospheric water condensation. Thus, while a newly refined hydrocarbon oil species may be almost completely free from water, and therefore not appreciably susceptible to microbiological attack, the finished product, even after short-time storage picks up water, which becomes a potential breeding ground for deleterious microorganisms.

As generally mentioned above, two primary problems occur as a result of microbiological attack of hydrocarbon liquids containing minor amounts of water. The microbes, while existing in the aqueous phase of the predominately hydrocarbon system, actually feed on the hydrocarbon fluid, which is used as a source of carbon in the life cycle of the microorganisms. It is generally accepted that these microorganisms feed at the interface between the oil and water phases to carry out their attack upon hydrocarbon. Such attack then causes two harmful effects. First, the hydrocarbon fractions, fed upon by the microbes, are broken down to other generally useless products. These materials cause a sludging or thickening condition in the oil. In many instances the impure bodies produced by microbiological attack catalyze further formation of sludge bodies, until large amounts of the hydrocarbons are ineffective for their intended use. Secondly, in the breakdown of hydrocarbon fluids by microorganisms such as bacteria and fungi, acidic substances are produced. These materials have a tendency to attack the storage containers in which the hydrocarbon fluids are kept. In particular, the acids produced by the microbes have a strong corrosive effect upon drum liners, storage tanks, etc. Again, in many situations, the corrosive media produced catalyze further corrosion attack.

As a result of the above dual effects resulting from microbiological attack, the hydrocarbon fluid becomes less

efficient and sometimes even useless in the process in which it is to be employed. For example, the sludge formed as a result of microorganism feeding has a tendency to block filters employed in internal combustion engines of vehicles, or filters of the type employed in home oil burner units. Another specific result of microbiological degradation of hydrocarbon fluids is serious corrosion of aircraft tanks. In many instances, airplanes have wingtanks containing many thousands of gallons of hydrocarbon fluid such as jet fuel. Since, in many cases, such planes are kept in a state of immediate readiness, the fuel must remain in continual storage in the tanks. In turbine powered aircraft, a brown slime is often noted in the fuel tanks, even after a relatively short storage period. This slime, as result of microbiological activity in the jet fuel, has a tendency to perforate protective tank coatings, such as rubber, and cause severe pitting corrosion of underlying aluminum metal. The aluminum metal is attacked by acids produced at least in part by bacterial metabolism. Such a corrosion problem not only leads to frequent replacement of aircraft parts, but may cause structural cracking and failure of critical parts in service.

Generally, all hydrocarbon stocks are susceptible to microbiological attack of the type described above. Specific species of petroleum fractions such as catalytically cracked gasoline, fuel oils such as diesel fuel, furnace distillate, No. 2 fuel oil, etc., kerosene, jet fuels and others, need some type of microorganism control.

It has been found, however, that conventional biocides, as for example, those which have found wide use in inhibiting growth and reproduction of microorganisms in substantially aqueous media, such as those used in paper-mills, cooling towers, etc., have unexpectedly shown little promise in solving the special microbiological problem of hydrocarbon attack. In addition, many commercially known microbiocides due to the nature of their chemical structure cannot be employed as hydrocarbon additives. As an example, in some instances, substances containing a halogen atom, sulfur, or heavy metal atom cannot be added to hydrocarbon fluids even if such materials would give some measure of microbiological control. These materials are themselves known to cause degradation of hydrocarbon fluid medium to some degree upon storage of the petroleum fraction. In addition, other substances such as certain amines, which might have possible use as hydrocarbon biocides, promote emulsion of the water and oil phase, producing an overall composition having less efficiency due to a lesser degree of combustibility.

A specific example of a well-known microbiocidal agent which has suitable activity in a predominantly aqueous environment is sodium pentachlorophenate. Yet, this substance, surprisingly enough, has been found to be virtually useless in inhibiting growth and reproduction of microorganisms existing in a substantially hydrocarbon environment. Additional known biocides which demonstrated little or no activity in oil media include peracetic acid, boric acid, sodium methyl dithiocarbamate, sulfur heterocycles as thiadiazine derivatives and many others.

It would therefore be an advantage to the microbiocidal art if a class of compounds were discovered which would prove useful in inhibiting growth and reproduction of microorganisms existing in a system predominantly composed of hydrocarbon fluid. If such substances had requisite microbiocidal activity, and would not themselves cause deleterious effects such as sludge promotion, or increased emulsion of water-in-oil or oil-in-water, these additives would find wide use and ready acceptance in the art. Specifically, employment of such microbiocidal agents would obviate the problems of corrosion and hycarbon breakdown caused by microbes, and likewise do

away with all of the subsidiary problems resulting from these primary causes.

It therefore becomes an object of the invention to provide a method of inhibiting the growth and reproduction of microorganisms existing in a substantially hydrocarbon medium which contains minute amounts of aqueous liquid impurity.

Another object of the invention is to provide a class of substances which show microbiocidal activity in oil media, thereby substantially preventing corrosion effects and sludge formation due to microbial degradation of these hydrocarbon fluids.

A specific object of the invention is to achieve the above aims by addition of certain chemicals which themselves do not deleteriously affect the condition of the hydrocarbon fluid so treated.

Yet another object of the invention is to provide a substantially microbe-inhibited hydrocarbon fluid such as jet fuel, gasoline, and fuel oils containing use amounts of chemical biocide.

Other objects will appear hereinafter.

The above described objects and others have been achieved by discovery of the following microbiological method which forms the basis of the instant invention. In its broadest aspects, the invention is concerned with inhibiting growth and reproduction of microorganisms existing in an environmental system which comprises a hydrocarbon fluid as a major portion and an aqeuous liquid as a minor portion. Such microorganism control is effected by treating such above system with at least a microbiocidal amount of a nickel composition. It is preferred for best results that the nickel composition be capable of furnishing to the predominantly hydrocarbon system under conditions of storage, at least 0.5 p.p.m. of nickel calculated as elemental nickel.

The nickel compositions of the invention have found use in inhibiting growth and reproduction of microorganisms in virtually any type of hydrocarbon fluid containing residual amounts of water. The additives have shown special promise with respect to fuel oils, jet fuels and gasoline. When these types of hydrocarbons or others are treated with a nickel substance, attack by microorganisms is either done away with completely or diminished to the point where the resultant effects of such attack, such as sludge formation in the hydrocarbon fluid and production of corrosive acids, no longer become a problem.

The nickel composition itself may be added to the hydrocarbon fluid at any time subsequent to its final refining step. For example, the nickel substance may be added to large storage tanks as a part of tank farms, to storage drums, to the storage tank of a vehicle itself employing the hydrocarbon as a source of fuel, to a storage tank, for example, of a home burner unit etc. The biocide may even be added to the hydrocarbon when it is still at the oil refinery, for example, to the rundown line leading from the last operation of refining the petroleum fluid, or to any storage or transfer area which contains the finished petroleum product. The nickel inhibitor may be added directly to the oil itself, or to the aqueous bottom phase by means of injection pumps or lines leading directly thereto. In case of addition to the hydrocarbon phase, it is believed the nickel compositions of the invention migrate to the aqueous phase. Such migration is enhanced by gentle agitation of the storage tank and/or periodical addition or withdrawal of hydrocarbon fluid which cause a certain degree of turbulence in the storage tank.

As mentioned above, the nickel composition after addition should preferably be present in the aqueous-hydrocarbon environment in an amount such that at least 0.5 p.p.m. of nickel is available. Therefore, the nickel composition itself should possess the property or inherent ability to release at least 0.5 p.p.m. of nickel when added to the hydrocarbon in use amounts. This means that at least that amount of nickel composition as calculated in terms of Ni content should preferably be added to the aqueous-hydrocarbon system.

The amount of nickel composition as a molecular entity which must be additively employed to usefully inhibit growth and reproduction of bacteria and fungi existing in the hydrocarobn fluid, should be adjusted according to the severity of the problem, amount of water phase present in relation to hydrocarbon, and specific activity of the particular species of nickel composition employed. Generally, however, it has been determined that from about 2 p.p.m. to about 1,000 p.p.m. of additive nickel composition, capable of releasing at least 0.5 p.p.m. of nickel in such use ranges, is effective in achieving the requisite aim of microbiological control. More preferably, from about 5 p.p.m. to about 200 p.p.m. of nickel chemical are added to the hydrocarbon fluid-water system.

As mentioned above, almost any type of hydrocarbon fluid may be inhibited from microbial attack by application of the nickel compositions of the invention. Particularly, hydrocarbon fluids containing at little as 10 p.p.m. of aqueous liquid are susceptible to such attack, and therefore must be protected. Normally, commercial microbe-susceptible hydrocarbon fluids contain from about 0.001% of water to about 10.0% of water, and more often 0.001–3.0%. It is understood, of course, that hydrocarbon fluids having greater or lesser amounts of water may likewise be protected by addition of the nickel compositions of the invention. The above recited ranges of aqueous liquid impurity in hydrocarbon fluids merely recite the more common condition of petroleum stocks after varying periods of storage. Again, the hydrocarbon liquid itself may contain water in form of a bottom layer, or as minute droplets dispersed throughout the hydrocarbon fluid. In any case, all hydrocarbon fluids containing even minute amounts of aqueous liquids require microbiological control.

The particular microbiological organisms which are normally present in hydrocarbons as the harmful agent, are comprised of many types and varieties, primarily bacteria and fungi. One bacterial species which particularly utilizes hydrocarbons and is normally present in these fluids is *Pseudomonas aeruginosa.* Other types of organisms include bacteria such as *Desulfovibrio desulfuricans,* Flavobacterium species, *Micrococcus paraffinae, Mycobacterium phlei, Bacterium aliphaticum,* etc., and fungi such as Cladosporium, Nocardia, Aspergillus, *Candida lipolytica,* Penicillium, etc.

It has been determined that the nickel compositions of the invention are useful in inhibiting growth and reproduction and/or in killing any of the aforementioned types of microorganisms, and are particularly active against the Pseudomonas group.

The nickel compositions useful in the invention may be chosen from a wide variety and a number of classes of specific nickel compounds. As mentioned above, the nickel compositions should preferably be capable of releasing at least 0.5 p.p.m. of nickel metal into the aqueous phase of the hydrocarbon fluid when added in use amounts, whether such aqueous phase exists in the form of a distinct bottom layer or as droplets dispersed throughout the petroleum. Greatly preferred nickel substances usually exist in partial or complete ionic form in the aqueous phase, and the nickel itself is thereby immediately available in ionized form to act upon the microbes contained therein. As an adjunct of this then, it is preferred that the inorganic, or organic nickel compositions have sufficient solubility in water to furnish at least microbiocidal amounts of nickel to the aqueous phase of the hydrocarbon fluid. As also mentioned above, it has been determined that biocidal activity is generally present when the nickel composition, regardless of its structural composition, is present in sufficient amounts in the aqueous phase to dotate thereto at least 0.5 p.p.m. of

nickel. Preferred nickel compositions then are those which have some solubility or dispersibility in water, even if such characteristic is only to the extent of the aforementioned use amounts of the nickel additive. The most preferred nickel compositions have the property of donating at least 1 p.p.m. of nickel to the oil-water system when the nickel composition itself is added in at least an amount of 2.0 p.p.m.

The nickel composition as furnished to the hydrocarbon fluid may exist in a wide variety of forms, organic and inorganic. These may be in form of organic or inorganic salts, as covalent organo-nickel compounds, as nickel metal complexes of organics, etc.

Preferred among the nickel compositions which may be employed in practice of the invention, are two broad classes. First are inorganic nickel compounds, which are generally water soluble in nature. Among those most useful are nickel halides, nitrates, sulfates, etc.

Another extremely useful class of compounds are nickel complexes of organic compounds which contain at least one basic nitrogen group. Such complexes are easily formed by reaction of any inorganic nickel compound and the specific organic amine to be thereby complexed. Such amine reactants may include alkylene polyamines; polyalkylene polyamines; primary, secondary and tertiary monoamines such as dimethylamine, trimethylamine, ethylamine, butylamine, N-ethyl-butylamine, etc.; arylamines such as aniline and substituted anilines; heterocyclic amines such as ethylene imine, morpholine, etc.; cyclic amines such as cyclohexylamine; alkaryl amines such as dodecyl aniline; fatty amines such as C_2-C_{22} N-substituted primary, secondary and tertiary amines and polyamines; amino acids such as glycine; imidazolines and substituted imidazolines, etc. As mentioned above, these amine complexes are easily prepared by merely stirring together a source of nickel, such as an inorganic salt, with the amine in any desired ratio. The complexing reaction may be run with or without heat application.

Other nickel complexes such as ketonates, hydroxy carboxylates, citrates, tartarates, certain Schiff's bases and the like may also be used.

The following examples are presented by way of illustrating the simplicity and ease of preparing typical nickel compositions, useful as microbiocides in hydrocarbon media.

Example I

0.1 mole of nickel sulfate were mixed with 0.2 mole sodium phenoxyacetate in water solution. A blue-green precipitate was formed which was washed and then dried. The dried product can be directly employed as a useful biocide in oils.

Example II

0.1 mole of nickel sulfate were added to 0.1 mole of an imidazoline prepared from diethylene triamine and tall oil fatty acids which had previously been dissolved in a water-ethanol solution. The solution was mixed for 10 minutes, the precipitate filtered, and washed successively with water and acetone. A water soluble biocide was produced by further reacting the product complex with an aqueous solution of acetic acid. Likewise, an oil soluble product was obtained by reacting the product in a benzene solution of oleic acid.

Example III

0.1 mole of nickel sulfate were added to an aqueous solution containing 0.2 mole of glycine. The solution was evaporated in an air stream to a syrup and the complex precipitated and washed with acetone to produce a relatively pure solid usable complex.

In order to test the efficacy of the invention, the following specific laboratory test was devised.

A test medium was first prepared as follows: Into a sample bottle was placed 400 ml. of sterile kerosene and 40 ml. of an aqueous mineral medium containing one gram each of the following inorganic salts added to 1,000 ml. of water; NH_4NO_3, K_2HPO_4, KH_2PO_4, $MgSO_4$, and $CaCl_2$. This aqueous mineral medium had been previously adjusted with sodium hydroxide to a pH of 7.4 and to it had also been added two drops of a concentrated solution of ferric chloride.

Each test for microbiocidal effectiveness was carried out in groups of three samples. Solutions of prepared test chemicals were added in varying amounts to the above test solutions along with one drop of stationary phase culture of Pseudomonas. The bottles were then stoppered and incubated at 90° F. for four weeks. The performance of the material under test was based on inhibition or kill of the above bacteria. Growth values at one month greater than 100 times that of the original bacteria added indicated failure of the chemical. The number of cells added was determined before and after the experiments by means of plate counts. Those chemicals showing activity and the various dosages generally required for excellent results are shown in Table I below.

Weighed iron coupons which had been also placed in the sample bottles were inspected for corrosion after the test period. Also, the weight of any sludge formed in the oil was determined in each case. It was noted that those test samples which showed good growth inhibition and kill, correspondingly did not corrode to any appreciable extent the iron metal coupon placed therein, nor did sludge formation increase to any appreciable extent.

Table I below points out that a number of varying nickel compositions may be usefully employed in the invention at relatively low dosage levels and still exhibit good activity in inhibiting the growth and reproduction of microorganisms. The letter "F" indicates failure as above defined in terms of bacterial growth greater than 2 log values of additional bacteria over that added. In some cases the organic compound, making up a nickel complex or in some way forming a part or moiety of a nickel composition itself had known activity as a microbiocide and this reactant organic compound was also tested. It is noted that in these cases where the organic precursors had activity, the complexes formed from these organics showed at least a two-fold increase in activity over the organic reactant. In other cases, the organic parent reactant alone showed absolutely no activity, while the nickel product of this organic reactant showed excellent additive effect.

TABLE I.—MICROBIOLOGICAL ACTIVITY OF NICKEL COMPOSITIONS

	Composition	Activity Range (p.p.m.)	Molar Ratio of Ni Compound to Organic or Percent Ni in Product
1	$NiCO_3$-Ethylenediamine Complex	50-100	----------
2	$NiCO_3$-Ethylenediamine Oleate Complex.	25-50	----------
3	Nickel Bromoacetate	50-100	30%
4	Nickel Dipicrylamine Complex	25-50	8.5%
5	Dipicrylamine	50-100	----------
6	Nickel Hexamethylenetetramine	25-50	17.5%
7	Hexamethylenetetramine	50-100	----------
8	Nickel Fluoroborate	10-25	25.2%
9	Nickel Chloride Adduct of Glycine.	10-25	13%
10	Nickel Pentachlorophenate	10-25	10%
11	Sodium Pentachlorophenate	F	----------
12	$NiSO_4$ Complex of Imidazoline formed as reaction product of aminoethyl ethanolamine and oleic acid.	25-50	----------
13	Acetate Salt of 12	25-50	----------
14	Imidazoline formed as reaction product of aminoethyl ethanolamine and oleic acid.	50-100	----------
15	$NiSO_4$-Ethanolamine Complex	50-100	----------
16	Nickel Nonylphenoxy-acetate	50-100	17.5%
17	Nickel 2,4 Dichlorophenoxy acetate.	50-100	22.2%
18	Nickel Tributyl Phosphine acetate.	50-100	1:1
19	$NiSO_4$ R-$NHCH_2CH_2CH_2NH_2$ Complex where R is a radical derived from coco fatty acid.	10-25	1:1
20	Acetate Salt of 19	5-10	----------

TABLE I.—MICROBIOLOGICAL ACTIVITY OF NICKEL COMPOSITIONS—Continued

	Composition	Activity Range (p.p.m.)	Molar Ratio of Ni Compound to Organic or Percent Ni in Product
21	$Ni(C_2H_3O_2)_2$ Complex of $RNHCH_2CH_2CH_2NH_2$ where R is a radical derived from coco fatty acid.	10–25	1:1
22	do	10–25	1:2
23	do	10–25	1:3
24	do	10–25	1:6
25	$Ni(NO_3)_2$ Complex of $RNHCH_2CH_2CH_2NH_2$ where R is a radical derived from coco fatty acid.	10–25	1:1
26	do	10–25	1:2
27	$Ni(NO_3)_2$-Pyridine N Oxide Complex.	10–25	1:2
28	$NiSO_4$ Complex of $(CH_3)_3CCH_2$-$C(CH_3)_2CH_2C(CH_3)_2NH_2$.	10–25	1:1
29	$(CH_3)_3CCH_2C(CH_3)_2CH_2$-$C(CH_3)_2NH_2$.	F	
30	$Ni(C_2H_3O_2)_2$ Complex of $RNH(CH_2)_3NH_2$ where R is a radical derived from oleic acid.	25–50	
31	$Ni(C_2H_3O_2)_2$ Complex of $RNH(CH_2)_3NH_2$ where R is a radical derived from hydrogenated tallow fatty acid.	50–100	1:1
32	do	25–50	1:3
33	$Ni(NO_3)_2$ Complex of $RNH(CH_2)_3NH_2$ where R is a radical derived from hydrogenated tallow fatty acid.	25–50	
34	Acetate Salt of 31	25–50	
35	$NiSO_4$ Complex of imidazoline formed from reaction of diethylene triamine and tall oil fatty acid.	10–25	
36	Phenolic Salt of 35	25–50	
37	Acetate Salt of 35	10–25	
38	$Ni(C_2H_3O_2)_2$ Complex of imidazoline from reaction of diethylene triamine and tall oil fatty acids.	25–50	1:1
39	do	50–100	1:3
40	do	50–100	1:3
41	do	50–100	1:6
42	$NiCl_2.6H_2O$	5–10	24.8%
43	$Ni(NO_3)_2.6H_2O$	2.5–5	20.2%
44	$NiSO_4$	5–10	22.4%
45	$Ni(OOCH)_2.2H_2O$	5–10	39.9%

Many of the above nickel compositions shown to be effective against Pseudomonas may also be employed in other hydrocarbon systems involving a great number of different bacteria, fungi and Actinomyces. Equally good microbiocidal results may be realized in addition to those clearly demonstrated above, regardless of the types of hydrocarbon media to be controlled or variety of microorganisms contained therein.

It is not known what is the exact effect of the nickel compositions of the invention upon microbiological life. It is believed that the following theory in part explains their activity. It is understood, of course, that the invention is not to be limited to any such theory, and its usefulness does not depend upon such.

It is known that many enzymes contain a metallic ion as part of their reactive sites. These ions usually confer specificity of substrate reaction or determine rate of reaction of the inactive enzyme. If the metal is removed or replaced by another, action of the enzyme, if any, is greatly changed. It can be easily seen that if nickel replaces another metal of, or inserts itself into a vital enzyme, the cell could suffer. The deleterious effect could be due to inability to use the substrate for energy, make or change a needed intermediate, or slow the reaction rate to a point that the cell dies from the lack of the enzyme's product. Also, recent experimentation has indicated that nickel ion may be bound to the well-known DNA molecule. Should the attachment be in a sensitive area, it could very easily destroy cellular functions, resulting in death to the cell. RNA reacts in much the same way as DNA, so that nickel could react with this material and also hinder enzyme formation.

The invention is hereby claimed as follows:

1. A predominantly hydrocarbon system substantially inhibited against microorganism attack, said system comprising a hydrocarbon fluid as a major portion, an aqueous liquid as a minor portion and at least a microbiocidal amount of a nickel composition which is capable of furnishing at least 0.5 p.p.m. of nickel calculated as Ni to the aqueous liquid.

2. The predominantly hydrocarbon system of claim **1** wherein said aqueous liquid comprises 0.001–10.0% by weight of said system.

3. The predominantly hydrocarbon system of claim **1** wherein said hydrocarbon fluid is selected from the group consisting of fuel oil, gasoline and jet fuel.

4. A predominantly hydrocarbon system substantially inhibited against microorganism attack, said system comprising a hydrocarbon fluid as a major portion, an aqueous liquid as a minor portion and at least a microbiocidal amount of a nickel complex of an organic compound containing a basic amino group which is capable of furnishing at least 0.5 p.p.m. of nickel calculated as Ni to the aqueous liquid.

5. The predominantly hydrocarbon system of claim **4** which comprises 0.001–10.0% by weight of aqueous liquid and at least 2 p.p.m. of said complex.

6. The predominantly hydrocarbon system of claim **4** wherein said hydrocarbon fluid is selected from the group consisting of fuel oil, gasoline and jet fuel.

7. A predominantly hydrocarbon system substantially inhibited against microorganism attack, said system comprising a hydrocarbon fluid as a major portion, an aqueous liquid as a minor portion and at least a microbiocidal amount of an inorganic nickel salt which is capable of furnishing at least 0.5 p.p.m. of nickel calculated as Ni to the aqueous liquid.

8. The predominantly hydrocarbon system of claim **7** which comprises 0.001–10.0% by weight of aqueous liquid and at least 2 p.p.m. of said inorganic nickel salt of a mineral acid.

9. The predominantly hydrocarbon system of claim **7** wherein said hydrocarbon fluid is selected from the group consisting of fuel oil, gasoline and jet fuel.

10. A predominately hydrocarbon system substantially inhibited against microorganism attack, said system comprising a hydrocarbon fluid as a major portion, and from 0.001–10% by weight of an aqueous liquid and at least a microbiocidal amount of a nickel composition from the group consisting of nickel salts and nickel complexes of organic amines and their quaternary ammonium salts, said nickel composition being further characterized as being capable of furnishing at least 0.5 p.p.m. of nickel calculated as Ni to the aqueous liquid.

11. The predominately hydrocarbon system of claim **10** where the nickel salt is water soluble.

12. The predominately hydrocarbon system of claim **11** where the nickel salt is a nickel salt of a mineral acid from the group consisting of nickel nitrates, chlorides, sulfates and phosphates.

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