Synthesis of Novel fuel additives

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Abstract: Powders are typically magnesium oxide or hydroxide. Particle sizes range from a couple of microns up to tens of microns. The concentration of magnesium in powders is the highest of any magnesium products with magnesium oxide being 60% magnesium. Powders are very inexpensive. Handling problems make powders less than desirable to use. The inclusion of any moisture in a powder will cause clumping. For this reason it is necessary to keep sacks of powders dry. Powders are often added to the back end of a boiler between the superheater and the economizer. They cannot be added to the fuel since they are insoluble and would separate from fuel if the fuel were not kept in motion. **Methods:** Preparation of magnesium carboxylates by added of sodium hydroxide to the carboxylic acids than added magnesium chloride. Preparation of magnesium sulphonate. Preparation of magnesium complexes as oil additives. **Results:** The oil molecules dissolve the magnesium carboxylate when the polarity of magnesium carboxylate became less. Two factors determine the solubility of carboxylate salts in oil. One is the nature of the carboxylate ion, i.e. its length, shape, amount of branching and so on. The larger and less polar this group is, the more soluble it is in oil. Solubility of five-carbon-atom in water is not appropriate for carboxylate ions. The reason is that the carboxylate functional group is not merely polar, it is ionic. This allows for stronger ion-dipole bonds to be formed with the water molecules and pull longer carbon chains into solutions. Soaps, for example, generally have from twelve to eighteen carbon atoms in the carbon chain. The other factor is the positive ion. Ammonium, potassium and sodium salts are generally soluble in water. Magnesium and calcium salts are generally less soluble. Many others are generally insoluble. For example, a soap containing sodium ion will dissolve in water. **Conclusion**: The metal content of the emulsion additives can be increased by increasing the water content with respect of the total volume. Generally it can be shown that a wide variety of additive formulations have been presented with varying degree of solubility and metal content, the choice among them can be judged depending on the user requirements. **Suggestions:** Due to the unavailability of the technique required to study the effectiveness of the prepared magnesium complexes, it is of great importance to test their effectiveness as corrosion inhibitors using small oil burning unit. In order to have higher metal content by using metal oxide or salts, a particle size reduction technique has to be used to get a nanoparticale size of these compound to obtain miscible oil mixture. [Researcher. 2010;2(5):5-13]. (ISSN: 1553-9865).

Key words: Emulsion additives, magnesium carboxylate, nanoparticale, petroleum

1. Introduction

The word of petroleum come from Latin words (Petra; rock and oleum; oil). It is a dark viscous liquid, found trapped in certain porous geological strata. The composition of petroleum is essentially a mixture of hydrocarbon of paraffin series, cycloparaffins and hydrocarbon of the aromatic series. The actual composition varies with the place of origin. It is classified as paraffin base if the crude oil remaining after the removal of volatile hydrocarbon is composed mainly of alkanes and as asphalt base if the residual crude oil is composed of cycloalkanes (Kirk, 1996; Nelson, 1958). The origin of heavy oil (or bunker fuel) being considered is crude oil, when crude oil is subjected to refining, the lighter fractions (gasoline, kerosene, diesel, etc…) are removed by distillation. The heaviest materials in crude petroleum are not distilled, the boiling points are too high to be conveniently recovered. These materials (asphaltenes, waxes, and very large molecules) carry through refining and become residual (or resid). During various operations, in the refining (heating at high temperature), rearrangement of molecules many take place forming even large molecules materials that have still higher boiling points. These materials also become part of the resid. Finally, any contaminants in the crude will also be in the rised. This includes any salts (chemically elements that are typically soluble in water), sediment, and the heavy organic molecules from various sources. The color of heavy oil fuel is always black, dark brown, or at least very dark. This color arises from the asphaltenes in the crude oil. Asphaltenes are very large molecules containing carbon, hydrogen, oxygen, sulfur, and some nitroge. Vanadic attack was first observed in the early 1940's in naval ships burning residual fuel oils (Elorenzi, 1950).Vanadium is a common fuel

contaminant in "black" oils. When these fuels are combusted, vanadium forms (primarily) vanadium pentoxide (V_2O_5). Vanadium pentoxide melts about 675 ℃. When it is molten, vanadium pentoxide behaves as an excellent solvent for the metal oxides that high temperature alloys form to protect their surfaces. When in a molten state and while a solvent, vanadium pentoxide strips away these oxides. The metal surface atoms respond by forming a new layer of oxide coating which is again stripped away. As the process continues, the metal surface undergoes corrosion as each successive layer is stripped away. Fuel additives which are formulated to control high temperature corrosion ,were designed to address particular contaminant situation and operating condition. All of them based on the following active component and may offered in combination and concentration : magnesium, chromium, silicon, iron and manganese. Additives containing magnesium are used primarily control vanadic oxidation through combination with V_2O_5 at an appropriate Mg /V treatment ratio, magnesium orthovanadate [$3MgO.V_2O_5$] with a high melting point of about 1243c^o is formed as a new ash component. Chromium additives are specially designed to inhibit sulfidation corrosion promoted by alkali metals contaminants such as sodium and potassium, chromium has also been shown to reduce ash fouling, and the mechanism is believed to involve the formation of volatile compounds which pass through the turbine without depositing. Additives containing silicon are also used to provide added corrosion protection and improved ash friability in specific application (Walter, 1998). Oil-soluble iron compound in the form of salts of aliphatic carboxylic acid were used as additives for improving the combustion of liquid fuels, and the other side iron oxide dispersion is also used in this respect. The dispersion product reached maximum smoke reduction at 55 ppm iron as compared with an oil soluble product that reached a maximum reduction at 30 ppm iron. This may be attributable to the difference between level with dispersion having an average particle size of 0.5 to 1.0 micrometer. Magnesium has been used because it has a relatively low atomic weight that means that more atoms of magnesium can be added to fuel for a given weight of additive. And since magnesium is relatively plentiful and easy to obtain from nature, the cost can be bearable for this application. Magnesium is magnesium; the reactions discussed will occur no matter the source of the magnesium. What is different is the nature of the products, their reactivity and the manner in which the products are used. The following is a quick summary of the different types of magnesium products that have been used over the years (Kirk, 1983).

Materials and Methods

General: All chemical used were of reagent grade (supplied by Either Merck or Fluka) and used as supplied. The FTIR spectra in the range (4000–400) cm^{-1} were recorded on FTIR 8300 Shimadzu Spectrophotometer. Atomic absorption spectrophotometer, PERKIN-ELMER Flame atomic absorption spectrophotometer, model 5000 (USA). Ca, Cu, Fe, Mg and Pb hollow cathode lamps were obtained from PERKIN-ELMER instruments. Melting Points: The melting points of the prepared compounds were obtained using Gallenkamp Melting Point Apparatus.

Preparation of magnesium complexes:
Preparation of magnesium carboxylates: 0.0025 mole (0.1gm) of sodium hydroxide dissolved in 20 ml of distilled water was added to 0.0025 mole (0.5 gm) of the corresponding acid where all the acid was dissolved. 0.00125 mole (0.25gm) of magnesium chloride dissolved in 5.0 ml distilled water was added to the above solution or salt solution(in case oleate and stearate).The resulting precipitate, was filtered and washed with small amounts of water. The resulting complex was dried in vacuum for 6 hrs. Table(1)show the types of base and acid (or it's salts)used in the preparation of the magnesium carboxylate.

Preparation of magnesium sulfonate: 1.0 gm of commercial sulfonic acid was converted to it's sodium salt by addition of sodium hydroxide solution(10%) until the pH of the resulting solution became 7.00, and the brown color of original acid became light brown. To the resulting clear solution, saturated aqueous solution of magnesium chloride was added, then the solvent (water) was evaporated. 70.0 ml of (1:1) ethanol-carbon tetrachloride mixture was added to the residual precipitate, a light yellow solution was obtain and white precipitate of NaCl and excess $MgCl_2$ was separated. The solvent was evaporated until dryness, where yellow precipitate of magnesium sulfonate was obtain.

Test of solubility of magnesium complexes in different solvent: 10.00 gm of magnesium complexes was dissolved in 100 ml hot solvent (benzene, toluene, and gas oil), the mixture was filtrated under vacuum at 25 ℃, the filtrate was dried in vacuum oven ,the resulting solid mass was weighted to a constant weight.

Preparation of magnesium complexes as oil additives(stock solution): 10.0 gm of soluble magnesium complex was mixed with heating and stirring with 50.0 ml fuel oil for 3hr.

Preparation of oil emulsion of magnesium
Preparation of oil emulsion of magnesium by using sodium laurel sulfonate: 10.0ml saturated solution of magnesium chloride was mixed with 0.5gm sodium

laurel sulfonate, the mixture was heating with stirring for 20 min. and then added to 50ml of crude oil, the mixture was heated and stirred for 1 hr. to complete emulsifying process.

Preparation of oil emulsion of magnesium by using magnesium sulfonate: 50% of magnesium acetate solution was added to 0.2 gm of magnesium sulfonate the mixture was added to 10 ml of crude oil, the mixture heated and stirred for 1 hr. to complete emulsifying process.

Determination of magnesium content in fuel additives: Determination of magnesium content in the standard commercial additives: 5.0 ml of (10%) sodium hydroxide solution was added to 5.0 ml of standard commercial additive ,the mixture was stirred for 4 min. and then 10.0ml of xylene and 10.0ml of water were added to the above mixture and then heated for 30min, finally   20.0ml of conc. hydrochloric acid was added to the resulting   and then stirred for 1hr. the two layers were separated using separating funnel and the magnesium content in the aqueous layer was determined using atomic absorption technique.

Determination of magnesium content in the prepared additives: Determination of magnesium content in magnesium carboxylate: 0.14gm of magnesium carboxylate was added to 5ml of xylene,to the resulting mixture 2.0ml of hydrochloric acid and 5.0ml of distilled water were added, then the mixture was   shaken for 15min and left for 2hrs. The aqueous layer was separated using separating funnel, the volume was completed to 25ml in a volumetric flask. A sample of this solution was analyzed for magnesium content using atomic absorption spectroscopy.

Determination of magnesium content in magnesium sulfonate: 0.3268 gm of magnesium sulfonate was dissolved in 2.0 ml of distilled water and, then the volume was completed to 25ml in a volumetric flask. A sample of this solution was analyzed for magnesium content using atomic absorption spectroscopy.

Determination of magnesium content in emulsion stock: To 0.5 gm of emulsion solution 10 ml ethanol was added, to the resulting solution 10.0ml of carbon tetrachloride was added, the resulting two layers were separated using separating funnel. to the aqueous layer 5ml conc. hydrochloric acid was added and the volume of this solution was completed to 25 ml with distilled water in volumetric flask, in which the magnesium content was determined using atomic absorption technique.

Results

General: The more efficient use of petroleum make the necessity for developing process which guarantee the optimum possible utilization of this raw material, especially with the shortage and increased costs of it.
The efficiency which can be achieved depends on the completeness of the combustion of the fuel with no side effect. One way of achieving this aim is to add certain substance to the heating oil, which promote it's combustion and to minimize destructive side effects. The description of the prior art in using various metals, presented in chapter one, known to improve combustion in boilers and combustion turbines show the magnesium to be the most widely used as a combustion catalyst in boilers with residual oil that often contains fuel contaminants, such as vanadium. Due to incomplete description of the magnesium additives with respect to it's composition (the structure and the percent of the active magnesium), and also the relationship between the type of additive and the type of combustion engine, we found that it is necessary to prepare a wide range of magnesium compounds which include oil soluble (organic complexes), and emulsions. The aim is also to find a new formulation of higher magnesium content with higher possible oil solubility.

Magnesium carboxylate: Eleven sodium salts of mono and di-carboxylic acid including derivatives of open chain, alicyclic, and aromatic have been prepared by reaction of sodium hydroxide with the acid, except arachidic acid for which the sodium salt was not soluble, therefore it's potassium salt was prepared , on the other hand sodium oleate and sodium stearate were used as supplied.

The magnesium derivatives (or complexes)of all those salts were obtained by their reactions with magnesium chloride in aqueous medium It can be shown that all the magnesium complexes have higher melting points than their respective acids, this was expected since the metal salts are known to have higher melting points especially when the size / charge ratio decreases, which is case with the studied metal ion (Mg^{+2}). Increasing the ionic charges will certainly increase the lattice energy of a crystal. For compounds which are predominantly ionic charges will result in increased melting points, and according to Fagan's rules, increasing charge results in increasing covalency, especially for small cation and large anions. Covalency does not necessarily favor either high or low melting points. For species which are strongly covalently bonded in the solid, but have weaker or fewer covalent bonds in the gas phase, melting and boiling points can be extremely high. It was found that low melting point salts have higher oil solubility (Turbeville , 1999). Table (2)also show the yield percent for the magnesium complexes, which are generally more than 87% excepted that of arachidate complex having 51% yield,

this may be due to it's solubility difficulties. The selected acid were chosen to get more than one variation, i.e. structural varieties and molecular weight varieties, in order to obtain magnesium complexes with higher possible metal content and in the same time higher oil solubility.

The oil is a pure hydrocarbon so it is non-polar. The non-polar hydrocarbon tail of the magnesium carboxylate dissolves into the oil. That leaves the polar carboxylate ion of the molecules are sticking out of the oil droplets, the surface of each oil droplet is negatively charged. As a result, the oil molecules dissolve the magnesium carboxylate when the polarity of magnesium carboxylate became less (Anjolye, 2003). Two factors determine the solubility of carboxylate salts in oil. One is the nature of the carboxylate ion, i.e. its length, shape, amount of branching and so on. The larger and less polar this group is, the more soluble it is in oil. Solubility of five-carbon-atom in water is not appropriate for carboxylate ions. The reason is that the carboxylate functional group is not merely polar, it is ionic. This allows for stronger ion-dipole bonds to be formed with the water molecules and pull longer carbon chains into solutions. Soaps, for example, generally have from twelve to eighteen carbon atoms in the carbon chain. The other factor is the positive ion. Ammonium, potassium and sodium salts are generally soluble in water. Magnesium and calcium salts are generally less soluble. Many others are generally insoluble. For example, a soap containing sodium ion will dissolve in water. However, if the water contains magnesium, calcium or iron, these ions will take the place of the sodium ions, combine with the carboxylate ion to make an insoluble compound and precipitate out of solution to form what is commonly called metal carboxylates. However, if the water contains magnesium, calcium or iron, these ions will take the place of the sodium ions, combine with the carboxylate ion to make an insoluble compound and precipitate out of solution to form what is commonly called metal carboxylates.

Table (3) and figure (1) show that magnesium oleate to be higher solubility among the magnesium carboxylate, the reason of it's higher solubility may be related to the length of the hydrocarbon chain of the oleate molecules and the presence of unsaturated double bond which affect it's solubility. On comparison of the solubility of two(C_{18}) acids (stearate, and oleate), magnesium oleate have higher solubility than it's stearate analogue, this is due to the presence of a double bond in the oleate only. The solubility of the studied magnesium carboxylate was generally higher in gas-oil than in the other solvent, as seen in figure (2). The magnesium salt of an organic acid with sufficient lipophilic character to achieve oil solubility contains less than 6% magnesium by weight. It was thought that the reason is that a molecular weight of about 200 is required for the organic acid to have oil solubility and the elemental weight of magnesium is 24. Magnesium is a divalent element and two acid molecules are required for each atom of magnesium.

Table (4) show that magnesium adipate has higher magnesium content (14.28 %) and magnesium arachidate has lower metal content (3.715%). figure (4) show that as molecular weight increases metal content decreases. An attempt was made to get a complex of higher possible solubility with simultaneous higher possible metal content. Complexes with high metal content but poor solubility are of no use. It's was found that magnesium oleate and magnesium stearate were of higher solubility and higher possible metal content, as seen in tables (3,4) and figures (1,2,3) (Walter, 2006).

Discussion

It was studied that (3 magnesium : 1 vanadium) ratio is needed to treated the hot corrosion[13], in this work the highest soluble complex was of (3.52%) magnesium content, which is comparable with those additives described in the US patents No. 5145488, 4229309, 4179383, 4293429, 4298482, and 4226739.

Table(1) the types of base and acid (or it's salts)

Base	Acid (or it's salts)	Chemical structure
NaOH	Lauric acid	$CH_3(CH_2)_{10}COOH$
KOH	Arachidic acid	$CH_3(CH_2)_{18}COOH$
NaOH	Palmitic acid	$CH3(CH2)14COOH$
-	Sodium Oleate	$CH3(CH2)_7CH=CH(CH_2)_7COONa$
-	Sodium Stearate	$CH3(CH2)16COONa$
NaOH	Cyclohexane carboxylic acid	$C_7H_{12}O_2$
NaOH	Benzoic acid	$C_7H_6O_2$
NaOH	Cinnamic acid	$C_6H_5CH=CHCOOH$
NaOH	Adipic acid	$HOOC(CH_2)_4COOH$
NaOH	Phathalic acid	$C_8H_5O_2$
NaOH	Terphthalic acid	$C_8H_5O_2$

Table (2): the melting points of the magnesium complexes and their espective carboxylic acid and the yield percent

| Magnesium complex	Chemical structure	M.P.^{o}C of related acid	M.P. ^{o}C	Yield %
Magnesium laurate	(CH$_3$(CH$_2$)$_{10}$COO)$_2$Mg	42-44	140-142	96.78
Magnesium arachidate	(CH$_3$(CH$_2$)$_{18}$COO)$_2$Mg	74-76	162-164	51.72
Magnesium palmitate	(CH$_3$(CH$_2$)$_{14}$COO)$_2$Mg	62-64	300	94.83
Magnesium oleate	(CH3(CH2)$_7$CH=CH(CH$_2$)$_7$COO)2Mg	5-7	54-56	97.56
Magnesium stearate	(CH$_3$(CH$_2$)$_{16}$COO)$_2$Mg	67-69	134-136	95.33
Magnesium Cyclohexane carboxylate	(C6H11COO)$_2$.Mg	29-31	58-60	97.4
Magnesium benzoate	(C$_7$H$_5$O$_2$)$_2$Mg	121-123	330	90.2
Magnesium cinnamate	(C$_6$H$_5$CH=CHCOO)$_2$Mg	132-134	146-148	93.32
Magnesium adipate	(OOC(CH$_2$)$_4$COO)Mg	151-153	>300	87.65
Magnesium phthalate	(C6H4(COO)$_2$)Mg	212-214	296-298	96.71
Magnesium terphthalat	(C$_8$H$_4$O$_2$)Mg	300	328-330	89.49
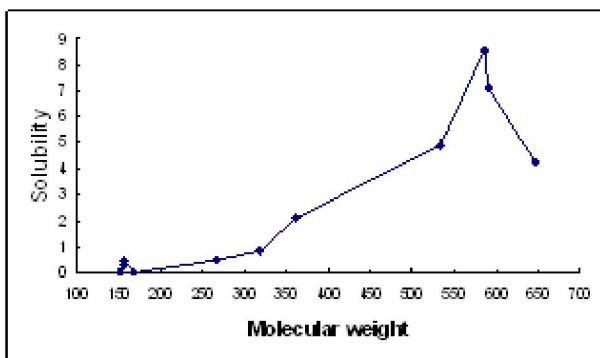
Figure (1) solubility of prepared magnesium carboxylate with it's molecular weight
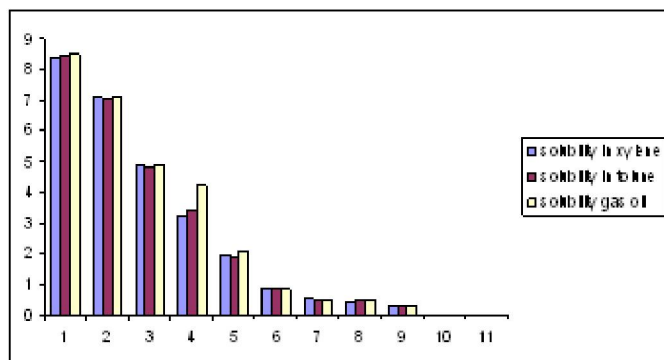

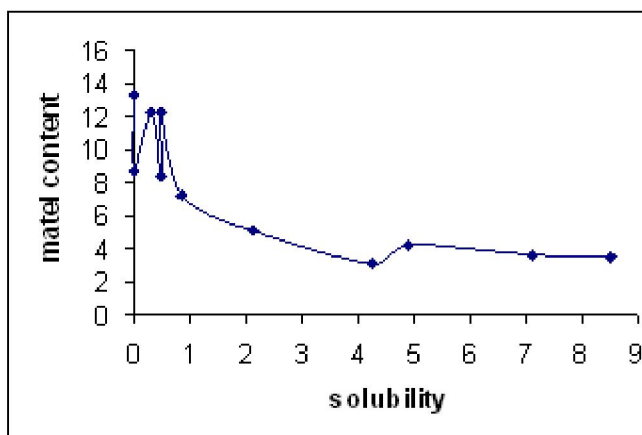Figure (2) solubility of prepared complexes in deferent solvents

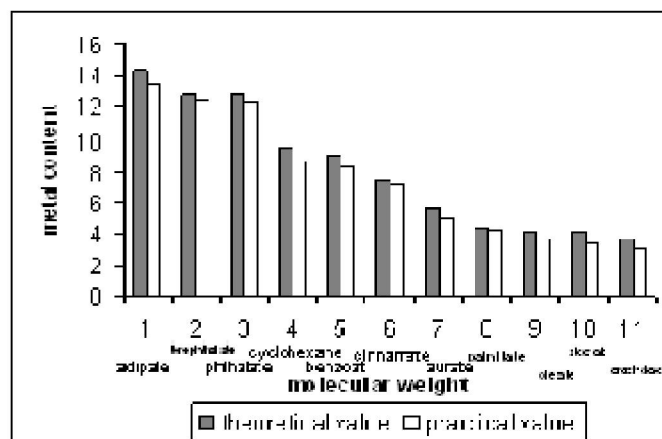Figure (3) solubility of prepared complexes with it's metal content

Figure (4) metal content of prepared complexes

Table (3) solubility of magnesium carboxylate in different solvents

solvent Mg com.	Xylene	Toluene	Gas oil
Magnesium laurate	1.95	1.86	2.11
Magnesium arachidate	3.24	3.44	4.25
Magnesium palmitate	4.86	4.82	4.92
Magnesium oleate	8.41	8.46	8.51
Magnesium stearate	7.08	7.02	7.13
MagnesiumCyclohexane carboxylate	Insoluble	Insoluble	Insoluble
Magnesium benzoate	0.46	0.49	0.47
Magnesium cinnamate	0.88	0.85	0.85
Magnesium adipate	Insoluble	Insoluble	Insoluble
Magnesium phthalate	0.52	0.47	0.48
Magnesium terphthalate	0.29	0.31	0.30

Table (4) magnesium content of the prepared complexes

Compound	Chemical structure	Theoretical value	Practical value
Magnesium laurate	**(CH3(CH2)10COO)2Mg**	**5.68**	**5.06**
Magnesium arachidate	**$(CH_3(CH_2)_{18}COO)_2Mg$**	**3.715**	**3.12**
Magnesium palmitate	**(CH3(CH2)14COO)2Mg**	**4.494**	**4.17**
Magnesium oleate	**$(CH3(CH2)_7CH=CH(CH_2)_7COO)2Mg$**	**4.095**	**3.52**
Magnesium stearate	**(CH3(CH2)16COO)2Mg**	**4.067**	**3.64**
Magnesium phthalate	**$(C_8H_4O_2)Mg$**	**12.765**	**12.28**
Magnesium terphthalate	**$(C_8H_4O_2)Mg$**	**12.765**	**12.33**
Magnesium benzoate	**$(C_7H_5O_5)_2Mg$**	**9.022**	**8.39**
Magnesium Cyclohexane arboxylate	**$(C_7H_{11}O_2)Mg$**	**9.561**	**8.75**
Magnesium cinnamate	**$(C_6H_5CH=CHCOO)_2Mg$**	**7.54**	**7.23**
Magnesium adipate	**$(OOC(CH_2)_4COO)Mg$**	**14.28**	**13.35**

Infrared spectra of the prepared complexes:

All the compounds contain an important diagnostic group; this is a carbonyl group (C=O). In general carbonyl stretching absorption frequency occurs around (1710) cm^{-1} depending on nature of groups linked to it[19]. The compounds containing carbonyl group show basic behavior toward metal ions coordinating via the oxygen atoms, this coordination shifts the stretching frequency of carbonyl (C=O) group toward lower value in some complexes, the decrease value in frequency indicates a decrease in the stretching force constant of (C=O) group as a consequence of the coordination through other groups. The double bond character between carbon and oxygen is reduced. The stretching frequency band of the (O–H) group appeared in the spectra of some carboxylic acids in the rang (3100-3500) cm^{-1}, this band found down field (at about 2990 cm^{-1}) due to strong hydrogen bonding (1976).

When the carboxylic acid react with magnesium salt, magnesium carboxylate have been therefore a red shift in the (v C=O) took place in all of the complexes, this because the bond order of the carbonyl group was decreases. Table (5) summarize the most diagnostic IR absorption frequencies of the magnesium carboxylate. These results indicate the coordination of magnesium ion with the selected carboxylate.

Magnesium sulfonate :

The sulfonic acid used in this work was the commercially available one, which is used liquid detergent industry. This commercial acid may be a mixture of alkane, aromatic, and /or alkaryl oil soluble sulfonic acid. The dark sulfonic acid was converted first to it's light brown sodium salt using sodium hydroxide, which was used to get the magnesium sulfonate of a light yellow oily liquid, this crude product was suitably

treated to get a pure magnesium sulfonate. It was found the prepared magnesium sulfonate was highly soluble in xylene, toluene, and gas-oil. The metal content of the complex was determined and found to be 4.15 % . Because magnesium sulfonate are both water and oil soluble with appreciable metal content, it can be used as surfactant in the production of an overbased magnesium.

Magnesium emulsion: Magnesium emulsion additives which is obtained by mixing heavy oil and water together in the presence of a surfactant. It was prepared following two routes: in the first rout heavy oil(50 ml), containing essentially an aqueous solution of one water soluble metal salt selected from the halides of magnesium (10 ml of saturated solution of magnesium chloride) and 0.5gm of sodium laurel sulfonate as a surfactant. In the second rout from the magnesium acetate solution (5.0gm of magnesium acetate in 10 ml water)was mixed with 10 ml crude oil using magnesium sulfonate as a surfactant(0.2 gm).

Oil-water separation of the resulting emulsion did not took place and the emulsion state was maintained even at temperature range (0- 100 C). The metal content of the emulsion solution obtained by following first rout was (8.5% Mg), while it was (13.5% Mg) in the emulsion of the second rout, the later percent was obtained from two sources ,i.e. (9.35% Mg) from the magnesium acetate and (4.15% Mg) from the surfactant; therefore the magnesium sulfonate, prepared as described in section tow is preferred since it gives higher metal content. The amount of metal salt employed will vary with the particular metal and salt chosen, with the surfactant selected, with the particular heavy oil and fuel burning equipment being treated, and will depend upon whether or not two or more metal salts are utilized together in one aqueous solution. It is an advantage of the aqueous solution heavy fuel oil additives that they permit relatively high concentrations of the metal salts in aqueous solution, and yet afford good stability in use. The economic benefits attendant the use of products with relatively high concentrations of active ingredients is well recognized. The magnesium emulsion are characterized by improved stability, and was proved to be stable at temperatures range (0–100).

One of combustion technologies which was developed an oil-water emulsion additive in which oil is mixed with water. This oil-water emulsion additive has an improved combustion efficiency because water particles micro-explode due to the discrepancy of the boiling points between heavy oil and water (b.p. of heavy oil is 300 C . or more, b.p. of water is 100 C) so that the explosion divides the oil into finer particles and it leads to promotion of diffusion combustion when the emulsion fuel is sprayed into combustion chamber having high temperature. The mixing ratio of water to

oil should be changed and the amount of addition of magnesium salt should be naturally changed. For example, in the paragraph (2.6.1) where 1 weight part of water(10 ml) to 5 weight parts (50 ml) of crude oil was used, about 5 g of magnesium chloride was added, and in paragraph (2.6.2) where 1 weight part of water (10 ml) to   1 weight parts (10 ml) of crude oil was used, about 5.0 g of magnesium acetate was added. As it is clear from above examples, the more inorganic components is needed as the higher ratio of the amount of water to the amount of crude oil is used so that the stabilization of emulsion state is designed. And the amount of magnesium salts depend on the various combination of the water and oil mixture. It was confirmed that the water particles are covered with thin film and are capsulized by oil. This is the phenomenon that a film is formed on the surface of water particle and the water particle is capsulized by oil as a result of the reaction among the components contained in crude oil. While this fuel additive was boiled under atmospheric pressure, it kept a boiling point of additive 100 ^{o}C, and when heating was stopped and the temperature fell to the room temperature (25-30 ^{o}C), the oil-water separation was not occurred and any change in the capsule was not observed. Further, after the fuel of the room temperature was transferred into the room of -5 ^{o}C. and was kept there for one week, it was transferred back to room temperature. After two days, the situation was the same as described above.

Each three pieces of iron nail as the specimen was put in three separate vessels containing the fuel of the present study, heavy oil and water each, and after every one week the degree of corrosion was estimated by visual observation. With nails in the vessel containing water, oxidization phenomenon became clear after 2 weeks and all of three nails were wholly oxidized when 5 weeks passed. With nails in the vessel containing heavy oil, oxidization phenomenon was not observed even after half an year. With nails in the vessel containing the present fuel, the situation was the same as nails in heavy oil. The results of the corrosion in water and in heavy oil was reasonable, but it is natural to be considered that in the fuel of the present study nails would contact with the water particles in the fuel and would be partly oxidized. But as described above, the water particles in the fuel are capsulated by chemical reaction and in this situation the water particles do not come out to the surface. Thus water does not contact to not only vessel wall but also the surface of nails and therefore nails would be never oxidized to corrosion.

Magnesium emulsion additives can retain the very strong emulsion state by the addition of magnesium salt of the inorganic components and surfactant, and the cohesion among water particles does not occurred in any change of temperature and the water particles can

retain a constant size. Therefore the fuel do not bring about oil-water separation and each particle of water is contained in oil without changing from a heating stage to burner spraying stage, and the ideal micro explosion occurs, surrounding oil drops are divided to super fine particles and the evaporation of oil is accelerated and mixing with air is accelerated so that the diffusion combustion is promoted. As the result, a good condition for combustion is prepared and a stable high temperature is maintained in the inside of the combustion chamber (Kemp, 1982; US patent No. 4512774; 6727208; 6296676 B1; 32653).

Conclusion

Taking in account the results of the present work, the following conclusion can be made:

1-The oleate complex of magnesium was found to have the highest oil solubility among the carboxylates derivatives with magnesium content of 3.52% .

2- The prepared magnesium sulfonate have 4.15% metal content with very high oil solubility.

3- The magnesium complex of sulfonate has higher oil solubility and metal content than it's analogue of carboxylates.

4- It was found that the method followed to prepare the magnesium emulsion using magnesium sulfonate as surfactant gave higher metal content (13.5 %) than the product obtained using sodium laural sulfonate as surfactant (8.5 %), with no problems of oil solubility.

5- The emulsion formulations was found to be more suitable as oil additives than the formulations obtained using the soluble products with respect to the higher metal content and good stability in the oil.

6- The metal content of the emulsion additives can be increased by increasing the water content with respect of the total volume.

7- Generally it can be shown that a wide variety of additive formulations have been presented with varying degree of solubility and metal content, the choice among them can be judged depending on the user requirements.

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