

Properties of Oil-Soluble Magnesium Compounds Used In Gas Turbine Fuel Additives

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Large industrial design combustion turbines can operate on liquid petroleum fuels containing ash components. Engines capable of using these fuels are General Electric Frame 5 and 7 machines, Westinghouse 251 and 501, Asea Brown Boveri Type 11 and 13 and Kraftwerk Union V 84 and V 94 machines. This approach is attractive in situations in which large quantities of ash-bearing fuels are available at low cost, and distillate and gas fuels are not economically available. Saudi Arabia is the largest consumer of ash-bearing fuels in gas turbines; most of the electricity in Saudi Arabia is generated with large frame engines operating on unrefined crude oil.

Ash-bearing fuels include unrefined crude oil, residual oils from the refining process and contaminated refined fuels. Crude oil naturally contains oil-soluble vanadium, nickel and sulfur compounds. Water soluble sodium, potassium and calcium compounds occur naturally in water produced with crude oil and from contamination during transportation. The major contributor to low melting ash is vanadium, ranging from <1 to >500 ppm. Sulfur is found at varying levels up to 5%. Water soluble salts of sodium, potassium and calcium are found at varying levels depending on the history of the fuel. Lead is an equally serious problem in contribution to ash. It does not occur naturally in crude oil but frequently finds its way into residual oils from gasoline treated with lead for anti-knock properties.

Vanadium pentoxide melts at 680° C. Eutectics formed from combinations of sodium, potassium and calcium with vanadium, lead and sulfur have lower melting points ranging into the 500-600° range. Deposits resulting from this ash foul the power section blades and vanes and are catastrophically corrosive above their melting points. The problem is controlled by eliminating and modifying the ash to higher melting species which do not adhere to hot path parts.

Ash-bearing fuels are usually treated with water to form emulsions. The emulsions are broken in centrifuges or electrostatic separators with the aid of chemical demulsifiers to remove most of the water soluble salts of sodium, potassium and calcium. The usual specification for sodium plus potassium in gas turbine fuel is <1 ppm. Magnesium is then introduced into the fuel, generally at a 3 to 1 weight ratio to the vanadium. (1) This converts vanadium into $Mg_3V_2O_8$ which melts at 1,000°, well above the temperature of the metal parts.

The ash passes through the machine without depositing or corroding the hot path area.

A number of misconceptions have developed about magnesium compounds used in fuel additives. The purpose of this paper is to discuss some of those misconceptions.

Overbased Oil-Soluble Magnesium Compounds

The magnesium salt of an organic acid with sufficient lipophilic character to achieve oil solubility contains less than 6% magnesium by weight. 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.

The technique of “over-basing” is used to increase magnesium content. Oil-soluble magnesium compounds are, in reality, emulsions of magnesium oxide, carbonate and/or hydroxide suspended in an oil-soluble surfactant system. The product appears to be a “solution” since it is clear in thin layers. The inorganic phase is less than 0.4 μm particle size which is below the wave length of light. Overbased magnesium products can be manufactured with over 25% metal by weight. Handling characteristics such as viscosity and pour point become impractical for normal applications above 20% magnesium content.

Because of a shortage of materials in a growing market, new techniques in the manufacture of these products and a range of surfactant systems that are available to stabilize the emulsion, as well as unsupported arguments by various competitors in support of their products, a number of misconceptions have developed about these products.

Manufacturers

There are a number of manufacturers of overbased metal compounds, including magnesium, calcium and barium for use as metal soaps in motor oil and grease. These products are designed for high base number and relatively low metal content. There are only three manufacturers of products commonly used in the gas turbine industry. Properties of products made by these manufacturers are compared in Table I.

Manufacturers 1 and 2 formulate their product into finished material which can be used as fuel additives with up to 20% magnesium. Both of these manufacturers use a process involving the decomposition of magnesium hydroxide in the presence of a surfactant system. (2,3) This process can result in trace levels of magnesium hydroxide in the finished product which can cause changes in appearance which are discussed below.

Manufacturer No. 1 is known for producing materials in-house containing up to 20% magnesium as the oxide in carboxylate surfactant systems.

Manufacturer No. 2 uses carbon dioxide in the process which yields magnesium carbonate and magnesium oxide in the emulsion. This manufacturer produces product in carboxylate and sulfonate surfactant systems. This manufacturing approach leads to variations in physical properties such as density and viscosity.

The third manufacturer (No. 3) produces a product designed for use in motor oil additives. It is made in a two-step process by reacting magnesium oxide with carboxylic and sulfonic acids, alcohols and carbon dioxide. (4) It is limited to 14.2% magnesium and requires further processing before it can be used as a gas turbine fuel additive. This product is known in the industry as a "sulfonate". This supplier does not normally market directly to the gas turbine operator.

The finished products sold to the gas turbine operator are formulated into various concentrations of magnesium and combinations with other metals including chromium, silicon, manganese and iron. The products are filtered, mixed in large quantities to insure uniform concentrations and tested for chemical and physical properties including contaminant metal levels.

Manufacturers 1 and 2 mentioned above and other companies formulate and sell finished product to the gas turbine operator. All of these companies purchase concentrates of magnesium from various sources from time to time. The result is that the final user may have considerable difficulty determining the original manufacturer of the magnesium component in the fuel additive.

Sulfonates and Carboxylates Surfactant Systems

A surfactant system is used to stabilize the emulsion of MgO, MgCO₃ or Mg(OH)₂ suspended in the organic solvent which is miscible in liquid petroleum fuels. The surfactant can be virtually any compound with a polar region which will attach to or react with the inorganic crystalline structure of the magnesium compound and a hydrocarbon "tail" which will suspend the system in oil. The most commonly used products are sulfonates and carboxylates.

Overbased metal products made for motor oil and grease applications are generally made from sulfonate oils. These have high viscosities, relatively low metal contents and high total base numbers (TBN). These are generally limited to about 9.2% Mg and have viscosities about 1,000 cSt. These can be made from magnesium oxide or magnesium metal. (5)

There are a number of patents for processes dating back to the 1960's utilizing carboxylates and mixtures of sulfonates and carboxylates to make overbased systems with higher metal content. (6,7). Use of carboxylates lead to higher metal content and lower viscosities than sulfonate products.

Examples of IR spectra from samples made by the three manufacturers referred to above are given in the attached figures. The sulfonate group has a medium adsorption at 1000 to 1080 and strong adsorption at 1150 to 1260 wave numbers (8). The sample from Manufacturer No. 2 has strong sulfonate peaks in the 1000 to 1300 wave number range. The weight ratio of carboxylates to sulfonates in sample No. 2 is in the range of 4 to 1. The actual sulfonate content in this products is about 15% by total weight of product. (6)

The sample from Manufacturer No. 3 known in the industry as a "Sulfonate" has weak peaks in the sulfonate absorption range. This indicates qualitatively that this product has less sulfonate content than the "Sulfonate/Carboxylate" product from Manufacturer No. 2.

The sulfonate peaks are absent in the sample from Manufacturer No. 1 which is known to be a carboxylate product that does not contain sulfonates.

Density and Viscosity

The density of the finished product is important to the end user of the fuel additive. The vanadium in the fuel is treated at a ratio of 3 parts magnesium to 1 part vanadium, by weight. Lower density indicates that the customer receives less weight of magnesium in a volume of product yielding less cost effective treatment. When comparing products, the customer must take density into consideration in evaluating cost.

Viscosity is critical to handling the product. Low viscosity, less than 5 cSt at 40° C., can result in low lubricity and abrasion of additive injection pump. High viscosity can lead to cavitation on the suction side at low ambient temperatures with failure to treat the fuel.

Sulfonate containing products have higher densities and viscosities than carboxylate products. The density and viscosity can be controlled by varying the ratio of sulfonate and carboxylate in the product.

Water Sensitivity

During the late 1970's, General Electric Co. developed the "Certification Tank" fuel treatment concept. In this system, fuel is water washed to remove the sodium, magnesium fuel additive injected and the treated fuel sent to a certification tank. The fuel is tested for various metals and if it meets specification, it is forwarded to a treated fuel tank.

Ash-bearing fuels contain 0.5 to 1.0% water after water washing and breaking of the emulsion. Overbased magnesium compounds are metal soaps and will react

with water. As a result, after a few days or weeks, the magnesium reacted with water and settled out of the system.

Magnesium fuel additives made in the magnesium hydroxide decomposition process (No. 1 and No. 2) have been observed to react with water more quickly than material No. 3. This has been attributed to the sulfonate component in this material. Because of the low level of sulfonate in material No. 3 demonstrated above, there are other factors involved.

The manufacturing process may play an important role in water tolerance. Minute quantities of residual magnesium hydroxide may be more likely to promote soap formation than magnesium oxide or carbonate. We have found that solvents may be a factor as some result in systems that form soaps more slowly than others.

SFA has synthesized a number of products with a wide range of sulfonate to carboxylate ratios. We have observed that sulfonate containing products react more slowly with water than carboxylate only materials. However, all of these products will form soaps which will precipitate from the solution over a period of time ranging from 1 to 100 hours. We have also observed that in far more concentrated systems than would be found in an actual fuel system, gentle stirring will bring these soaps back into solution. Thus, this problem can be solved with stirring or recirculation of the fuel.

Another related observation that has been made in the field is that fuel additives made from the different processes are not compatible when mixed. This is caused by differences in density and viscosity which slow the mixing process. Mild stirring will dissolve this film and the additives are totally compatible.

Solvent Sensitivity and Appearance

Magnesium products made by the magnesium hydroxide decomposition process will sometimes have a more gray and grainy or turbid appearance than material made from the two-step magnesium oxide process. It has been reported that these products react with petroleum ether (low molecular weight aliphatic hydrocarbon solvent) to form hazy product which indicates the presence of carboxylate.

The “grainy” or “turbid” appearance of product made by decomposition of magnesium hydroxide is caused by the presence of minute quantities of magnesium hydroxide which are insoluble in aliphatic hydrocarbon solvents. Additional decomposition of remaining traces of magnesium hydroxide during the manufacturing process will produce a bright, shiny, black material which “dissolves” in aliphatic hydrocarbons without forming the grainy appearance. Varying the ratio of carboxylate to sulfonate does not affect this observation.

Even though trace levels of undecomposed magnesium hydroxide result in the “grainy” appearance of the product in bulk, in thin layers the product is transparent. This demonstrates that the remaining particles of magnesium hydroxide are in the size range of the wave length of visible light.

Inorganic Moieties and Reactivity of the Product

The magnesium is in the form of magnesium oxide, hydroxide and/or carbonate crystals, smaller than the wave length of light, $<0.4 \mu\text{m}$. Magnesium carbonate and magnesium hydroxide decompose into magnesium oxide at 350°C . Magnesium oxide then reacts with vanadium pentoxide to form higher melting vanadates.

The hypothesis has been advanced that “fresh” magnesium oxide which is formed from the carbonate is more reactive with vanadium pentoxide than “old” magnesium oxide which was formed in the manufacturing process for the overbased magnesium product.

The organic acids which stabilize the magnesium suspension burn in the flame. Magnesium hydroxide and carbonate both decompose at 350°C yielding magnesium oxide. The result is that magnesium oxide is the compound which reacts with the vanadium pentoxide in the hot air stream.

A more important factor is the particle size of the magnesium oxide. Maximum surface area will lead to more reactivity; therefore, minimal particle size is optimum. Any mechanism which yields smaller particles of magnesium oxide will make the additive more efficient. Therefore, an argument can be made that on an equal size basis, magnesium carbonate and hydroxide emulsions would be more “reactive” than magnesium oxide emulsions because they will undergo further decomposition. Therefore, grainy, turbid appearing material with some magnesium hydroxide may be more reactive than the black, shiny material which totally dissolves in petroleum ether.

Acknowledgments

The authors would like to thank John Powers of Dixie Services, Inc., Galena Park, Texas, for assistance with measuring the infrared red spectra of these products and preparing the figure for publication.

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Table I.

Properties of Oil Soluble Magnesium Compounds Used in the Manufacture of Gas Turbine Fuel Additives

Manufacturer	Baker/Petrolite	SFA international	Witco
Surfactant System	Carboxylate	Carboxylate & Sulfonate	Carboxylate & "Sulfonate"
Inorganic Compound	MgO	MgO & MgCO ₃	MgO & MgCO ₃
Mg, Wt. %	15*	20	14.2
Particulate Matter, >1 μm	<0.1%	<0.1%	<0.1%
Density, Gm./CC	1.14	1.25	1.24
Viscosity, cSt., 40° C.	20 – 50	600 – 1000	400 - 800
Contaminant Metals			
Mg/Na + K	<1000	<1000	<1000
Mg/Ca	<100	<100	<100
Mg/V	<5000	<5000	<5000
Appearance	Light Brown	Dark Brown	Amber

* The product from Manufacturer is available containing 20% Mg.