A composition and method for providing a wear-resistant and fuel-saving coating on metals, particularly metal surfaces within internal combustion engines. A source of ammonium ions, an alkali metal in an aqueous medium, and the coating metal to be applied to the surface are combined to produce an electrolyte solution comprising a complex ion mixture. The electrolyte solution can be used to deposit the coating metal on conductive substrates. The coating metal may comprise phosphorus, sulfur, carbon, bismuth, boron, silicon, and combinations thereof. The electrolyte solution can be dehydrated in a hydrocarbon medium, thus providing novel materials for use as lubricating oil additives and as fuel additives. These new surfaces may significantly reduce coefficient of friction, smooth the flame front, reduce corrosion, enhance fuel economy, and reduce hydrocarbon emissions when used in internal combustion engines.
SAMPLE IN OUTER TUBE WITH ACETONE-d6 IN INNER TUBE

Fig. 1

DBX 1038 IN OUTER TUBE WITH ACETONE-d6 IN INNER TUBE

Fig. 2
**Fig. 4**

**Fig. 5**
Fig. 6

Fig. 7
Fig. 9

Fig. 10
Fig. 13

Fig. 14
Fig. 15
COMPLEX MIXTURES OF IONS AND PROCESSES FOR DEPOSITION

CROSS-REFERENCE TO RELATED APPLICATIONS


STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

0002. Not Applicable.

BACKGROUND OF THE INVENTION

0003. 1. Technical Field of the Invention

0004. The present invention relates to the field of aqueous solutions including mixtures of inorganic and organic ions, their preparation, and applications. More particularly, the present invention relates to compositions and methods for the preparation of performance enhancing surfaces that can comprise a phosphorous, sulfur, carbon, boron, or bismuth surface conversion that can prolong metal parts, including metal parts of internal combustion engines. The new conversion surfaces improve fuel consumption and decrease hydrocarbon pollutants using complex aqueous mixtures of ions.

0005. 2. Description of the Related Art

0006. The successful deposition of silicon has long been sought in the plating art. For example, U.S. Pat. No. 4,029,747 to Merkl, entitled “Method Of Preparing Inorganic And Polymeric Complexes And Products So Produced” describes purportedly new compositions and methods of manufacture for multi-metal amides. Merkl describes these complexes as suitable for “the production of soaps and detergents” and “for plating of one or more of the various metals of groups I-VIII of periodic table on various substrates.”

0007. A characteristic of the Merkl inorganic polymeric complexes with respect to plating is that through the use of these complexes it is purportedly possible to plate certain metals which have not been previously capable of plating, for example, to the refractory metals such as titanium, tantalum, and niobium, as well as to silicon. While silicon has been previously reported as being deposited by vacuum deposition and sputtering techniques, there appears to be no record of the successful plating of silicon metal, according to Merkl.

0008. Merkl describes several experiments wherein silicon is put into solution with an ammonium hydroxide, an alkalai metal hydroxide, and a non-alkali metal. Several analytical methods described in the Merkl patent show that nitrogen can be stabilized in an alkaline medium. Merkl describes a process that requires an endothermic phase and an exothermic phase in order to make the polymeric complexes. Merkl teaches that if the reaction is not as described, then silicates will form and cannot be reversed rendering the resulting product useless for polymeric purposes. As will be demonstrated, this is no longer true in accordance with the present invention.

0009. Silicon is an abundant, brittle, nonmetallic element that is found in sand, clay, bauxite, granite and many other minerals. Silicon chemicals were first developed in the 1860’s and have since found wide uses in many industrial applications as sodium silicate, potassium silicate, ferrosilicon and high purity silicon. Sodium and potassium silicates are used as desiccants, components of detergents, fire retardants, in cements, and as additives in steel manufacturing to harden the steel. See, generally, Silicon Chemistry: From the Atom to Extended Systems”, P. Jutzi and U. Schubert (eds.) (2003) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, ISBN 3-527-30647-1.

0010. U.S. Pat. No. 4,634,540 to Ropp, describes several methods of making sodium and/or potassium silicates by reacting silicon rocks with an alkali metal hydroxide. Ammonium ions were not used in the Ropp reactions.

0011. Many attempts have been made in the past to improve the surface properties of metals in order to widen their applications. For example, U.S. Pat. No. 4,533,606 to Teng et al. describes methods and aqueous compositions said to be suitable for electrodepositing co-deposits of zinc, silicon, and phosphorus on metal substrates. However, only co-deposits including phosphorus and zinc with silicon are described, and the electro deposition requires substantial time.

0012. U.S. Pat. Nos. 5,084,263 and 5,310,419 to McCoy et al., describe more rapid electroplating with “inorganic polymeric water complexes” of many metals, however, silicon is not among them. U.S. Pat. No. 5,540,788 to Defalco et al. describes forming an iron-phosphate conversion surface in situ, in internal combustion engines. However, the methods described by both McCoy et al. and Defalco at al. require the use of strongly acidic components in their preparation.

0013. Silicon nitrides were developed in the 1960s and 70s in attempts to develop fully dense, high strength ceramics as replacements for steel, particularly in internal combustion engines. Studies on silicon nitrides showed high temperature properties for retaining high strength and oxidation resistance. Silicon nitrides come in at least three categories, namely: 1) reaction bonded silicon nitride; 2) hot pressed silicon nitride; and 3) sintered silicon nitrides. The sintered silicon nitrides have higher density and are more widely used than the other two processes. The important properties of silicon nitride surfaces include: good density, high-temperature strength, superior thermal shock resistance, excellent wear resistance, good fracture toughness, prevention of mechanical fatigue and creep, good oxidation resistance, and enhanced lubricity.

0014. However, the difficulty of the manufacturing processes has kept this material from becoming a major product in the replacement of metals for many applications. The manufacture of silicon nitride ceramic bodies can be relatively complex. For example, U.S. Pat. No. 6,784,131 to Komatsu et al. describes a silicon nitride sintered body constituting a wear resistant member that is produced by at least the following steps: mixing a predetermined amount of a sintering assistant agent, a required additive, such as an organic binder, and a compound of Al, Mg, AlN, Ti or the like, to a fine powder of silicon nitride, which has a predetermined fine average grain size and contains a very small amount of oxygen; molding into a compact having a
predetermined shape via molding methods such as single-axial pressing method, the die-pressing method or the doctor-blade method, rubber-pressing method, CIP (cold isostatic pressing) or the like. Multiple heating steps to remove the additives and binders, sintering at high temperature under vacuum, and high temperature curing, follow the molding steps.

[0015] While the method of manufacture has several drawbacks, silicon nitrides have nevertheless found uses in components of internal combustion engines such as glow plugs for quicker start-up, pre-combustion chambers for lower emissions, and in turbochargers for reduced lag and emissions control. Wider use of silicon nitrides can only be achieved by better manufacturing procedures that will drive down costs and make parts competitive. Accordingly, the ability to deposit silicon nitride surfaces on metals using an aqueous solution would be of tremendous commercial value to the automotive industry; not to mention the aerospace industry and others.

[0016] The search for methods of improving fuel economy and reducing toxic emissions has been the driving force behind the development of silicon nitride coatings for small parts for internal combustion engines. Recently, automobile regulations such as regulations regarding fuel consumption and exhaust emissions have become more and more severe. The reasons behind this are well known, and include environmental problems such as acid rain, and the like, and policies for the protection of finite global hydrocarbon resources out of concerns for depletion of petroleum energy and minimization of greenhouse gases. As a countermeasure, reducing fuel consumption is, at least arguably, the most cost-effective solution, at present.

[0017] Many of the approaches of materials science that have historically been available for increasing efficiency and improving performance are also being constrained, however. For example, as described by U.S. Pat. No. 6,784,143 to Locke et al., the need for less toxic emissions from exhaust gases is becoming more demanding, mainly because of environmental problems such as the emission of pollutants such as hydrocarbons, carbon monoxide and nitrogen oxides. Catalytic converters in the exhaust systems of automobiles have been used for some time now to reduce the emission of pollutants. Such converters generally use a combination of catalytic metals, such as platinum or variations thereof and metal oxides, and are installed in the exhaust streams, e.g., the exhaust pipes of automobiles to convert the toxic gases to non-toxic gases. Phosphorus components, such as the decomposition products of the wear-reducing additive zinc dithiophosphate, an effective anti-wear oil additive, are believed to poison the catalyst in these converters. Also, it is likely that sulfur compounds poison the catalyst components used in reduction of nitrogen oxides. Notwithstanding the above, Locke still requires significant, though reduced, concentrations of phosphorus and sulfur.

[0018] Thus, there is clear automotive industry pressure towards reducing the phosphorus and sulfur content in fuel and lubricating oil additive compositions for emissions considerations rather than in increasing them for wear-reduction purposes. Reducing the phosphorus concentrations can, obviously, be readily accomplished by reducing the allowable amount of zinc dithiophosphate that can be used in the oil composition, but this comes at the expense of diminishing the anti-wear and anti-oxidant properties of the oil (and fuel) composition. As is well known in the art, engine manufacturers have already experienced substantial difficulties with premature engine failures as a result of changing fuel and oil specifications to reduce the concentration of known anti-wear components (notably sulfur).

[0019] Accordingly, a process providing for the electroless in situ deposition of silicon and nitrogen on the wearing surfaces of metals, including but not limited to metals in the internal combustion would be both a breakthrough in engine technology and of substantial commercial importance.

BRIEF SUMMARY OF SOME OF THE PREFERRED EMBODIMENTS

[0020] It is thus an object of the present invention to overcome the deficiencies of the prior art and thereby to provide unique and new uses for a chemical composition of silicon, silicon/nitrogen/alkali, or silicon/nitrogen bimetallic metal.

[0021] In some embodiments, there is provided a composition and method for providing a wear-resistant and fuel-saving coating on metals, particularly metal surfaces within internal combustion engines. In one preferred embodiment, a source of ammonium ions, an alkali metal in an aqueous medium, and a coating metal to be applied to the surface are combined to produce an electrolyte solution comprising a complex ion mixture. In other embodiments, the electrolyte solution can be used to deposit the coating metal on conductive substrates. In some preferred embodiments, the coating metal may comprise phosphorus, sulfur, carbon, bismuth, boron, silicon, and combinations thereof. In other preferred embodiments, the electrolyte solution may be dehydrated in a hydrocarbon medium, thus providing novel materials for use as lubricating oil additives and as fuel additives. In other preferred embodiments these new surfaces may significantly reduce coefficient of friction, smooth the flame front, reduce corrosion, enhance fuel economy, and/or reduce hydrocarbon emissions when used in internal combustion engines.

[0022] As will be described in detail below, we have found that when sodium and/or potassium silicate are dissolved in water and ammonium hydroxide is placed in the aqueous solution, and then an alkali metal hydroxide, including without limitation potassium hydroxide and sodium hydroxide, is added into the aqueous solution, which is then heated, that new complex mixtures of ions are formed, which we postulate may include silicon complexes. The temperature may preferably be raised rapidly by heating to above 180° F. The reaction may preferably be allowed to go through its own further exotherm, and produce a clear viscous solution with a pH of 14 and a Specific Gravity of 1.1. A panel of 1010 steel immersed in the solution for 30 seconds then formed a visible film on the metal that was extremely slippery. The immersed panel and an untreated panel were then immersed in a solution of 3% sodium chloride for three days, extracted, and allowed to dry. There was visible red corrosion on the untreated panel and no corrosion on the treated panel, indicating the new surface imparted superior corrosion resistance. As will be recognized by those skilled in the art, other silicates may of course be used without departing from the scope of the present invention including,
without limitation, metasilicates (inosilicates), cyclosilicates, orthosilicates (nesosilicates), and silicates produced by reacting other silicate minerals, although sodium and potassium silicates are currently most preferred.

[0023] The Merkl patent discussed above recites at col. 10, 11, 57-64: "On the other hand, if the feed of the alkali hydroxide is too slow, and as result, there is insufficient NH₃ group formation and hydrogen release, the eroded non-alkaline metal tends to bind with the metal in the form of a salt, such as sodium silicate. When this occurs, it does not appear possible to reverse the reaction to achieve the product of the desired complexes." Accordingly, Merkl teaches that an alkali metal silicate cannot be used to form inorganic polymeric complexes. Merkl does not postulate the ability to form new polymeric complexes using sodium or potassium silicates.

[0024] Example 1 of Merkl describes a low purity silicon/potassium/ammonia reaction. The reaction phase is described with an endothermic phase that lasted for six hours and then an exothermic reaction that lasted for 45 minutes. Using the same elements as described in the Merkl Example, a low purity ferrosilicon of 98.5% silicon and 1.5% iron was reacted with ammonium hydroxide and potassium hydroxide and water. The solution was heated to above 180°F and exhibited an exotherm within 20 minutes. No endothermic reaction was involved. The solution continued on its own exotherm for several minutes and then stopped. A viscous, clear solution with a specific gravity of 1.2 resulted. After cooling down, a panel of 1010 steel was immersed in the solution and a clear, tenacious, thin film was formed on the panel. The surface formed was very slippery. The panel was then left in the open, humid air of Houston, Tex. for thirty days and no red corrosion was visible. Accordingly, the requirement of Merkl for an endothermic reaction appears to be unnecessary with the present invention.

[0025] We experimented further with the postulated silicon complexes described herein to determine if the complexes could be used as a lubricating oil additive and/or as a fuel additive. The complexes, as will be described in more detail later, were dehydrated in a lubricating oil by heating the oil until all the water content had been removed and the oil became clear and bright. At a certain elevated temperature, the chemical salts present in the complex precipitated out of the oil solution. A simple test was devised to determine if there was any active ingredient remaining in the oil solution. A panel of 1010 steel was immersed for one minute in the oil solution. The panel was extracted from the oil solution, wiped dry, and a noticeable, thin, bright film was present on the surface of the panel, which is taken as an indication that the active ingredient was still available for deposition on a conductive substrate from a hydrocarbon solution. There are no prior references of which the inventors are aware claiming to make silicon soluble in a hydrocarbon solution, much less using the complexes for deposition of silicon/nitrogen or silicon/nitrogen bimetallic surfaces, to conductive substrates in internal combustion engines.

[0026] The inventive oil solutions were also tested in small two-cycle engines to determine if the silicon would aid in improving fuel economy of two-cycle engines. Surprisingly, as detailed below, these tests showed a positive trend in improving fuel economy and reducing emissions from two-cycle engines.

[0027] One of the preferred embodiments of the present invention comprises solubilizing silicon/nitrogen and silicon/nitrogen bimetallic complexes in hydrocarbons and alcohols, and using the hydrocarbons to carry the active silicon/nitrogen to the surface of conductive substrates in the combustion chamber while the engine is running. This provides a new, easy, and non-obvious method of forming a thin silicon/nitrogen film on metal surfaces in engines, gearboxes, differentials, etc. by an inexpensive process.

[0028] Hydrogen is postulated as having an effect on the activity level experienced in these postulated silicon complexes. According to Merkl at col. 21, 11, 14-19, "In a further study using mass spectroscopy it has been observed that nitrogen and atomic hydrogen are released by the inorganic polymeric complex. The atomic hydrogen appears to be released all the way from room temperature through 1550°C. The nitrogen is released at 875°C. As will be detailed later, in accordance with the present invention, hydrogen preferably has an effect on the fuel economy of the hydrocarbons.

[0029] As discussed above, Ropp describes methods of making sodium and/or potassium silicates but does not describe use of ammonium ions. Ropp (at col. 2, 163—col.3, 1. 40) describes extensively the release of hydrogen gas from the silicate composition as follows: "The formation of this complex Si(OH)₆ allows an exchange of hydrogen atoms and electrons between the silicon particle surface and the trapped oil to hydrogenate certain oil components to produce gaseous products and to thin the oil. The soluble silicate thereby produced has a definite effect on oil viscosity as well as affecting the direction of modification of certain oil components ... The oil modification agent is negatively charged silicon particle surfaces in a basic medium ... The negatively charged hydroxyl ion transfers its charge to the semi-conducting silicon surface of the particle and attaches itself thereto. When two or more hydroxyl ions are attached to the silicon surface, hydrogen gas is produced."

[0030] The Merkl patent teaches, by using mass spectrometry analytic techniques, that Atomic Hydrogen is released from a silicon/ammonium/alkali metal complex throughout a significant temperature range from ambient up to 1550°C. Ropp teaches that hydrogen obtained from an alkali silicate solution modifies unrefined hydrocarbons. We postulate in accordance with the present invention that the hydrogen available in our silicate compositions will act as a hydrogenation catalyst on refined fuels in the combustion chamber. The breaking up of larger hydrocarbon molecules into smaller gaseous molecules will have an effect on improving the combustion properties of refined fuels such as diesel and gasoline. It is further postulated that the hydrogenation of the refined hydrocarbon will give a percussive effect to the combustion process. It was well established that tetraethyl lead imparted a percussive effect to the combustion process and resulted in better burn characteristics and better fuel economy.

[0031] We have found that there is a stable electric charge in our water based silicon complexes. It is well known in the literature that free electrons cannot exist for more than $10^{-6}$
seconds in water. It is postulated that the silicon acts as a clathrate to hold the atomic hydrogen and the electrons separately and apart in a shell and allows for further chemical reactions under the right conditions. A process for stabilizing atomic hydrogen and solvated electrons in water would have wide implications in the world of chemistry and lead to many new chemical applications.

Clay is one of the most abundant minerals on earth. Clay has multiple uses because of its unique properties for hydrating in the presence of fresh water. Clay is primarily an aluminum silicate complex with minor impurities. Clays are used in zeolites as the first stage in the refinery process for cleaning and treating crude oils and catalysis. Clays are charged particles and in the presence of fresh water will “swell” and form a solid wall to allow water, oils and hazardous materials to be contained in clay pits. The swelling of clays presents major problems in oil drilling operations by slowing down the rate of penetration by the drilling rigs into the earth. Clays are also responsible for “tight sands”. Tight sands are heavily packed with various clays, with bentonite being one of the most common clays encountered in oil and gas reservoirs. The presence of clays in many reservoirs prevents the use of water flood techniques for enhanced oil recovery. As a result, many billions of barrels of crude oil are considered unrecoverable because of the swelling clays. As an example, the Department of Energy estimates that over 10 billion barrels of light gravity crude are still in the Venango sandstones, a formation that spreads across Pennsylvania, West Virginia, Ohio, and under Lake Erie into Ontario, Canada. These formations are very shallow, ranging in depth from 200 to 1200 feet, but because of the fresh water these formations have only yielded 5% of the total oil in place. An inexpensive method of breaking up the clays present in these shallow formations could lead to the ability to water flood these reservoirs, adding billions of barrels of recoverable oil to the nation’s supply and help achieve energy independence.

Because the silicon compositions of the present invention are water-soluble across a wide pH range, we decided to test whether montmorillonite (Na,Ca)4(Si,Al)2O5(OH)2.nH2O hydrated sodium calcium aluminum magnesium silicate hydroxide) a clay commonly called “gumbo”, could be delaminated in fresh water using the silicon compositions prepared in accordance with the present invention. Surprisingly, the gumbo fell apart into constituent particles in fresh water. Accordingly, the present invention thus provides a novel process for delaminating clays, including montmorillonite clays. This discovery should lead to much improved enhanced oil recovery techniques and uses in tight gas sands, opening up permeability and porosity in those formations, particularly as montmorillonite is the major component of bentonite, which is used in drilling muds. Likewise, improved breaking of bauxite—the clay-like material comprising aluminum ore—into its constituents may reduce the high costs of processing aluminum.

In other preferred embodiments, the present invention also includes a mold and mildew treatment and prevention method. Mold and mildew create huge problems, particularly in the humid areas of the United States and around the world. Mold in housing is believed to be a leading cause of asthma and other pulmonary disease. The silicon composition in the water phase in accordance with the present invention was used to spray a concrete stone 18”x18”x2” that had an extensive growth of mildew. The mildew was destroyed in less than 30 minutes and the silicon formed a surface on the concrete that remained mildew free after 60 days.

Black mold had grown on several windows in an apartment and was causing allergic reactions. The silicate composition of the present invention was used to spray the aluminum panels where the mold was attaching. The mold was wiped off and the surface of the aluminum panels was rubbed with the silicon composition. After 90 days there was no re-growth of the mold, indicating a very long-term application for prevention of mold in households.

In other preferred embodiments, the present invention includes a concrete sealing method. A piece of concrete was immersed in the silicon composition and then was placed in a glass Mason jar containing 18 API gravity crude oil. Oil is tenacious on concrete and cannot be readily removed even with steam cleaning. Surprisingly, when the treated concrete piece was extracted from the oil and dropped into a nason jar containing only fresh water, the oil immediately released from the concrete and floated to the top of the water with no visible residue on or in the concrete piece. A coating that seals concrete and makes the surface oleo-phobic would have commercial uses.

In other preferred embodiments, the tenacious, lubricating surface produced on metals in accordance with the silicon/nitrogen composition of the present invention indicated that an application would be to the cutting edges of knives, razor blades, saws, etc., for extending the life of the edge. A stainless steel razor blade sold under the Walgreen’s label was used as a test piece. A drop of the siliccon solution was wiped onto the blade surface. It was immediately apparent that the blade had much more lubricity and that shave was much smoother and comfortable. These blades have a life of about 5 shaves before being discarded. The treated blade shaved smoothly for 30 days and then was treated again and the life of the edge was extended for another 30 days. Thus an inexpensive, easy to apply coating for razor blades, and all other sharp edges such as saws, knives and medical instruments has been discovered.

Similarly, two kitchen knives made of 410 stainless steel were used for a test. One knife was coated with the silicon/nitrogen complex and the other knife was untreated. A butane torch was then held against the untreated knife and the metal became cherry red in one minute. When cooled the surface had turned a bluish color indicating that the high heat had affected the properties of the stainless steel. The treated knife was subjected to the same procedure and the metal did not turn to a cherry red for several minutes. The knife was allowed to cool down there was no visible change in the color of the stainless steel. Stainless steel is considered to be an inert material and extremely difficult to have a surface applied either electrolytically or by electroplating. Accordingly, the present invention also includes preferred embodiments comprising new methods of enhancing the properties of stainless steel.

The ability to form a thin silicon nitrogen coating on medical instruments could lead to savings in the nation’s ongoing attempts to rein in medical costs. Bacterial contamination in the metal interstices of medical instruments requires an extensive cleaning operation in an autoclave to
destroy the bacterial contaminants. The silicon nitride composition forms a thin coating on metal surfaces and into the metal interstices, filling up the holes and preventing bacteria from residing in the metal. This property should lead to a less costly method of sterilization of operating room tools.

[0040] Other preferred embodiments of the present invention include ice release treatment compositions and methods. Two 3\texttimes 3\texttimes \frac{1}{8} panels of 6061T6 aluminum were used. One was coated with a thin film of the silicon/nitrogen composition in accordance with Example 2A (below) of the present invention, while the other panel was left untreated. The silicon/nitrogen coating was identified by EDAX (Energy Dispersive X-Ray Analysis). The two panels then had a thick water film formed on the surfaces and were placed in a freezer at \(-18^\circ\) C. (0\(^\circ\) F). After one hour the panels were extracted from the freezer and the frozen surfaces subjected to a light bend test. The panel with the silicon/nitrogen surface immediately released the ice in a cracked almost monolithic sheet; the untreated panel would not release the ice sheet by cracking; the ice was melted off the surface of the aluminum substrate. The aviation industry spends much time and money in deicing airplane wings with a toxic chemical, ethylene glycol. A process that would prevent the water from attaching to the aluminum and forming adhesive ice crystals would be of commercial value and also to ease environmental problems caused by the deicing chemicals.

[0041] Silicates have been widely used as flame-retardants since their discovery in the 1860s. The property of silicates of swelling in the presence of a flame and providing an insulating barrier is well established. However, the use of silicates for flame retardation has been limited in the conventional art, as they do not attach tenaciously to the surfaces of wood, cloth, or steel. It is thus another preferred embodiment of the present invention to provide flame-retardant compositions and methods suitable for solving the related problems in the conventional art. A sample of old, dried lumber was immersed in a silicate solution in accordance with the present invention and allowed to dry. It was then immersed in water, extracted, and allowed to dry. A butane torch was used to hold a flame front on the surface of the dried lumber. The flame was held against the wood for five minutes and only a slight charring effect was noticeable. At no time did the timber support a flame. We postulate that not only would the silicate composition flameproof the wood, but also act as a surface to prevent formation of mold and mildew and possible termite infestation. Two panels of 12 gauge 1010 steel were used to test the efficacy of preferred embodiments of the invention including methods to impede heat transfer. One panel was immersed in the silicate composition for one minute and then extracted. The other panel was untreated. A butane torch was used to heat the metals to “cherry red”. The panels were held by hand and the flame applied to the panels. The untreated panel reached cherry red condition is less than a minute and transferred the heat down the length of the panel and became too hot to hold. The treated panel took approximately twice as long to reach a cherry red condition but the heat transfer was significantly impeded. The silicate flowed up and impeded heat transfer to the metal substrate. The panel could be held for several minutes before heat finally made the steel to hot too handle. The ability of the silicon compositions to form a thin tenacious film on metals that impedes heat transfer into the basic metal has broad uses in several commercial areas. For example, steel pillars treated with silicon compositions in accordance with the present invention could possibly impede enough heat transfer sufficiently to increase the period of time they can withstand buckling and collapse.

[0042] Ethanol is an alcohol that is the product of fermentation of organic matter. Ethanol is used as an additive to fuels to improve the cleaner burning of fuels to reduce emissions. In some countries such as Brazil, ethanol has been used solely as a renewable energy source. Ethanol is also mandated in the U.S. as one of the additives for oxygenating fuels. The use of ethanol has wide political and environmental support. A major barrier to the further use of ethanol however, is that it is highly corrosive to metals. A process that would reduce the corrosive activity of ethanol would find a very large market in the U.S. and around the world. Accordingly, it is another preferred embodiment of the present invention to provide compositions and methods to reduce the corrosivity of ethanol to metal surfaces. This embodiment has been demonstrated by placing 100 grams of ethanol in a glass beaker. Five grams of the silicon composition in accordance with an embodiment of the present invention as described in Example 1A (below), was then added to the ethanol. There was an immediate settling of salts from the solution and the materials appeared to be incompatible. The ethanol was decanted from the salts into a separate beaker. A 1010 steel panel was immersed in the ethanol solution for one minute and then extracted. A thin, tenacious film had formed on the steel panel. The panel was left in the open air in the humid Houston, Tex. climate for thirty days. No corrosion was visible on that coated part of the panel. Surprisingly, the active ingredient in the silicon composition was apparently solubilized in the alcohol and maintained its electrochemical activity, which allowed for deposition on a metal substrate using ethanol. Ethanol is sufficiently corrosive that it is transported in stainless steel trucks and pipelines. The corrosive properties of ethanol preclude its wider use as an oxygenating agent for fuels. A product that could be added to ethanol to inhibit corrosion would thus be of substantial commercial value.

[0043] Accordingly, in some preferred embodiments, the present invention provides that ammonium hydroxide is added to a solution of sodium silicate, to which potassium hydroxide is added.

[0044] In other preferred embodiments, ammonium hydroxide is added to a solution of sodium silicate to which potassium hydroxide is then added.

[0045] In other preferred embodiments, the above processes may be varied by maintaining the temperature of the resulting reaction mixture above 180\(^\circ\) F. for a predetermined period of time. By way of illustration and not limitation, said predetermined period of time may preferably be ten minutes or more, in some preferred embodiments.

[0046] In other preferred embodiments, ammonium hydroxide is added to a solution of sodium silicate, to which potassium hydroxide or sodium hydroxide is added, and the resulting liquid is dehydrated in a light mineral oil, and any resulting solids are removed by decantation.

[0047] In other preferred embodiments, ammonium hydroxide is added to a solution of potassium silicate, to which potassium hydroxide and/or sodium hydroxide is added, and the resulting liquid is dehydrated in a light mineral oil, and any resulting solids are removed by decantation.
In other preferred embodiments, ammonium hydroxide is added to a solution of sodium or potassium silicate, to which potassium hydroxide and/or sodium hydroxide is added, to produce an aqueous solution of ion mixtures, and the resulting liquid is dehydrated in a light mineral oil, and any resulting solids are removed by decantation. The resulting liquid is then added to the crankcase (as an oil additive) or combustion chamber (as a 4-cycle fuel additive or as a 2-cycle fuel or oil additive) of a 2-cycle or 4-cycle engine.

In other preferred embodiments, ammonium hydroxide is added to a solution of sodium or potassium silicate, to which potassium hydroxide and/or sodium hydroxide is added, to produce an aqueous solution of ion mixtures, and the resulting liquid is dehydrated in a light mineral oil, and any resulting solids are removed by decantation.

In other preferred embodiments, ammonium hydroxide is added to a solution of sodium or potassium silicate, to which potassium hydroxide and/or sodium hydroxide is added, to produce an aqueous solution of ion mixtures, and the resulting liquid is dehydrated in a light mineral oil, and any resulting solids are removed by decantation, and the resulting liquid is added to either the lubricating oil or fuel of an internal combustion engine.

In other preferred embodiments, ammonium hydroxide is added to a solution of sodium or potassium silicate, to which potassium hydroxide and/or sodium hydroxide is added, to produce an aqueous solution of ion mixtures, and the resulting liquid is dehydrated in a light mineral oil, and any resulting solids are removed by decantation, and the resulting liquid is added to either the lubricating oil or fuel of a gasoline internal combustion engine.

In other preferred embodiments, ammonium hydroxide is added to a solution of sodium or potassium silicate, to which potassium hydroxide and/or sodium hydroxide is added, to produce an aqueous solution of ion mixtures, and the resulting liquid is dehydrated in a light mineral oil, and any resulting solids are removed by decantation, and the resulting liquid is added to either the lubricating oil or fuel of a diesel engine.

In other preferred embodiments, a thin adherent layer comprising silicon and nitrogen is electrolessly applied to metal wear surfaces by application of a precursor prepared by the combination of the aqueous ion solution resulting from the mixture of sodium or potassium silicate with ammonium hydroxide and an alkali metal hydroxide to produce an aqueous inorganic complex, with a light oil at a temperature sufficient for dehydration, followed by incorporation of the complex into either lubricating oil or fuel.

In other preferred embodiments, an additive to lubricating oils that significantly decreases the coefficient of friction is applied according to means described by the present invention.

Other preferred embodiments comprise a fuel additive for introduction of a complex to accomplish the deposition of a silicon-nitrogen surface on internal wear parts of an internal combustion engine. Other related preferred embodiments comprise a lubricating oil additive for introduction of a complex to accomplish the deposition of a silicon-nitrogen surface on internal wear parts of an internal combustion engine.

Other preferred embodiments include an additive for ethanol with improved corrosion resistance.

Other preferred embodiments include addition of the above compositions and use of the above methods to provide compositions for applications to the delamination of clays, particularly montmorillonite clays related to the recovery of petroleum hydrocarbons.

Still other preferred embodiments include processes and materials for inhibiting corrosion, mildew, mold, heat, and fire, thus extending the life of objects thus endangered, as well as providing for their improvement.

It is well understood in the chemical arts that ammonia, in the presence of an alkali metal, can produce a volatile compound (i.e., sodium azide). The ammonia is expelled from aqueous solutions by the presence of alkali metal in the solution. Therefore, the ability to complex ammonia in highly alkaline solutions with pH approaching 14 would create novel chemicals complexes with a wide range of commercial uses. Surprisingly, it has now been found that when ammonium/alkaline metal is reacted with selected elements, the ammonium remained in solution at a pH above 12. The complexes formed exhibit unusual electrochemical properties, such as forming new surfaces on metal substrates without the use of applied external electro motive force.

Accordingly, it is an object of the present invention to provide unique and new alkaline chemical complexes of ions comprising, in some embodiments, a mixture of salts.

In some embodiments, a complex combination (Y)H(NH_3)_4HPO_4 including ammonium phosphate is provided, wherein Y can be any cation with potassium being a preferred cation. In other embodiments, a complex combination (Y)NH_3(NH_2)S including ammonium sulfide is provided, wherein Y can be any cation with sodium being a preferred cation. In other embodiments, a complex combination (Y)NH_3(C_2H_5NO_2) including ammonium acetate is provided, wherein Y can be any cation. In other embodiments, a complex combination (Y)CH_3NO_3 including ammonium bicarbonate is provided, wherein Y can be any cation. In other embodiments, a complex combination (Y)NH_2SO_4(B(NH_3))_x is provided. In other embodiments, a complex combination (Y)NH_2Si_4 is provided.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

FIG. 1 is a ^29Si NMR spectrum of an aqueous solution comprising a complex mixture of ions in accordance with the present invention.

FIG. 2 is a ^29Si NMR spectrum of an aqueous solution comprising a complex mixture of ions in accordance with the present invention.

FIG. 3 is a summary scan XPS spectrum of a steel panel treated with an aqueous solution comprising a complex mixture of ions in accordance with the present invention.

FIG. 4 is a high-resolution XPS spectrum of the Si2p peak of a steel panel treated with an aqueous solution comprising a complex mixture of ions in accordance with the present invention.
FIG. 5 is a high-resolution XPS spectrum of the N1s peak of a steel panel treated with an aqueous solution comprising a complex mixture of ions in accordance with the present invention.

FIG. 6 is an EDAX spectrum of a steel panel treated with an aqueous solution comprising a complex mixture of ions including in accordance with the present invention.

FIG. 7 is an EDAX spectrum of an aluminum panel treated with an aqueous solution comprising a complex mixture of ions in accordance with the present invention.

FIG. 8 is a summary scan XPS spectrum of a steel panel treated with an aqueous solution comprising a complex mixture of ions in accordance with the present invention.

FIG. 9 is a high-resolution XPS spectrum of the Si2p peak of a steel panel treated with an aqueous solution comprising a complex mixture of ions in accordance with the present invention.

FIG. 10 is a high-resolution XPS spectrum of the N1s peak of a steel panel treated with an aqueous solution comprising a complex mixture of ions in accordance with the present invention.

FIG. 11 is an EDAX spectrum of a steel panel treated with an aqueous solution comprising a complex mixture of ions including silicon and tungsten in accordance with the present invention.

FIG. 12 is an EDAX spectrum treated with an oil-based solution comprising silicon in accordance with the present invention.

FIG. 13 is an EDAX spectrum of a steel panel treated with an aqueous solution of complex ions including silicon and molybdenum in accordance with the present invention.

FIG. 14 is an EDAX spectrum of a steel panel treated with a solution made with ferrosilicon in accordance with the present invention.

FIG. 15 is an EDAX spectrum treated with an oil-based solution comprising silicon in accordance with the present invention.

EXAMPLES

Composition 1

Example 1A

The following equipment was used in experiments described below: 4000 ml Kimax beaker; Thermolyne Cimarec 2 with magnetic mixer; Acculab V600 scale with a 0.1 gram readability; and Accurius 100°-400° F. thermometer.

A solution comprising a complex mixture of ions was prepared by the steps of adding the following reagents to the beaker: 200 ml water; 50 grams of sodium silicate (solid); 25 grams of ammonium hydroxide (29° Baume); 50 grams of potassium hydroxide (flakes).

A slight ammonia odor was detectable. The solution was forced into exotherm by heating while stirring. The temperature was maintained above 180° F. for 10 minutes and then turned off. The solution continued its exotherm for several more minutes and then was allowed to cool down. The solution was examined by liquid-phase 29Si NMR (Nuclear Magnetic Resonance) Spectroscopy, which identified SiO₄ as illustrated by the spectrum of FIG. 1.

Example 1B

A solution comprising a complex mixture of ions was produced in accordance with Example 1A except that sodium hydroxide was substituted for potassium hydroxide. The solution was examined by liquid-phase 29Si NMR (Nuclear Magnetic Resonance) Spectroscopy, which identified SiO₄ as illustrated by the spectrum of FIG. 2.

Example 2A

A 1010 steel coupon was immersed in the solution comprising a complex mixture of ions prepared in accordance with Example 1A when the temperature was below 140° F. with no external electromotive force required. A visible, tenacious film formed on the steel panel. The panel was examined by XPS (X-Ray Photoelectron Spectroscopy) and the presence of silicon and nitrogen on the surface of the panel was detected, as illustrated by FIG. 3 (summary scan spectrum), FIG. 4 (high-resolution spectrum of Si2p peak), and FIG. 5 (high-resolution spectrum of N1s peak). Another steel panel immersed in this solution was analyzed via EDAX with the results illustrated in the spectrum of FIG. 6. An aluminum panel immersed in this solution was analyzed via EDAX with the results illustrated in the spectrum of FIG. 7.

1 Table 4 provides semi-quantitative, ZAF-corrected and normalized EDAX results (atomic-%).

Example 2B

A 1010 steel coupon was immersed in the solution comprising a complex mixture of ions prepared in accordance with Example 1B when the temperature was below 140° F. with no external electromotive force required. A visible, tenacious film formed on the steel panel. The panel was examined by XPS and the presence of silicon and nitrogen on the surface of the panel was detected, as illustrated by FIG. 8 (summary scan spectrum), FIG. 9.
Example 3

In each of two glass beakers, 70 grams of montmorillonite clay was immersed in 100 grams of fresh water. In one beaker 5 ml of the solution comprising a complex mixture of ions prepared in accordance with Example 1A was added to the fresh water. Both beakers were observed closely. In the beaker to which the inventive solution had been added, the clay slowly began to delaminate and fall to the bottom of the beaker as finely divided particles. In the other beaker there was no visible delamination of the clay. After 24 hours the clay in treated beaker had been completely separated into constituent elements. In the other beaker, the clay was still intact and there was a slight indication of the clay swelling.

Example 4

Preparation of “Con1”

600 grams of Penreco® Drakeol® 5 was added to a glass beaker with 120 grams of the solution comprising a complex mixture of ions prepared in accordance with Example 1A. The heater was turned on with continuous stirring. The temperature of the mixture was raised above 265°F and boiled at that temperature for 20 minutes, at which time salts formed and precipitated from the solution to the bottom of the beaker. The oil phase was bright and clear. This solution will hereinafter be referred to as “Con1”.

Example 5

Preparation of “Additive 1”

5 grams of Con1, prepared in accordance with the procedure described in Example 4, was mixed with 100 grams of Drakeol® 5 and stirred. The resulting solution will hereinafter be referred to as “Additive 1”. 10 ml of the Additive 1 was mixed into 200 ml of diesel fuel. The Additive 1 was completely miscible in the diesel fuel.

Example 6

4 grams of Additive 1 and 225 grams of unleaded gasoline were mixed in a beaker. The Additive 1 was miscible in the gasoline.

Two-Cycle Engine Tests

The mixture prepared in accordance with Example 6 was used in experiments for testing on two-cycle engines to measure fuel economy and “do no harm”. The engine chosen for the test procedure was a Homelite two-cycle leaf blower with a 30 cc engine. The need to turn the blower at high rpm places a load on the small engine. The engine is run in the 7200 rpm range with a constant load at all times. Two-cycle engines, which typically use a mixture of fuel to oil at a 50:1 ratio, are difficult to lubricate and are not fuel-efficient. The two-cycle lubricants currently being widely used to lubricate and protect against engine damage contain a large amount of “bright stock”, a heavy fraction in oils that is very toxic and polluting. A two-cycle engine of this type, if not properly lubricated, will typically seize up within 20 minutes or less. It would thus not be expected that a lubricant made with a silicon-containing component would provide protection for a two-cycle engine against seizure and failure.

Example 7

The fuel was prepared using standard two-cycle oil at a fuel:oil mix ratio of 50:1. Two control runs were made with a new engine; each run using 225 grams of gasoline mixed with 4.5 grams of standard two-cycle oil. A “baseline” control run length (i.e., time to fuel exhaustion) was determined by averaging the lengths of the two runs, which resulted in a baseline of 29 minutes, 45 seconds. A one-pint volume of treated two-cycle oil was then prepared that contained 5% (by weight) of Con1, which had been prepared in accordance with Example 4. Four identical test runs were then performed; each using 225 grams of gasoline mixed with 4.5 grams of the treated two-cycle oil, running the test engine until it shut down for lack of fuel. The time to fuel exhaustion was measured in each of the four tests. Results from the four runs were as shown below in Table 1:

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (min, sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>29 minutes, 45 seconds</td>
</tr>
<tr>
<td>1</td>
<td>34 minutes, 40 seconds</td>
</tr>
<tr>
<td>2</td>
<td>36 minutes, 18 seconds</td>
</tr>
<tr>
<td>3</td>
<td>32 minutes, 0 seconds</td>
</tr>
<tr>
<td>4</td>
<td>32 minutes, 15 seconds</td>
</tr>
</tbody>
</table>

The average of the four test runs (using the Con1 as an additive) was 33 minutes and 13 seconds compared with control runs (baseline—no additive) of 29 minutes and 45 seconds or a decrease in fuel usage for identical runs. There was also a noticeable reduction in particulate emissions with the test mixtures prepared using the Con1 additive. The engine did not seize and, in fact, appeared to run smoother with the test mixtures prepared using Con1. This test demonstrated that the Con1 additive improved fuel economy and reduced emissions, and did not harm the engine.

Example 8

300 grams of methyl ester (Soy Methyl Ester, Columbus Food, Chicago, Ill.) were placed in a beaker to which 15 grams of the solution comprising a complex mixture of ions prepared in accordance with Example 1A was added. The solution was heated to above 200° F, began to foam, and on cooling formed soap. This example mixture was deemed not to be a candidate as a fuel or lubricant additive.

Example 9

5 grams of Con1 was added to 100 grams of methyl ester, in which it was completely miscible. The resulting mixture was used as a fuel additive at a rate of approximately 1 ounce of fuel additive mixture to 10 gallons of automotive gasoline or diesel fuel.

Example 10

0.1 grams ammonia paratungstate (solid) was added to 40 grams of the complex mixture of ions produced
in accordance with Example 1A with stirring until the solid dissolved. A 1010 steel panel was then immersed in the resulting solution and extracted after 1 minute. A visible thin, tenacious, adherent film had formed on the metal substrate. The panel surface was examined by EDAX and the results that were obtained are illustrated by the spectrum shown in FIG. 11. The presence of tungsten and silicon was detected on the surface of the metal.

The above-described solution of ammonia para-tungstate was then dehydrated with Drakel® 5 using the general procedure described in Example 4, by heating to above 300° F. with stirring until salts formed and precipitated to the bottom of the glass beaker. A 1010 steel panel was inserted in the resulting solution while the temperature was about 180° F. and a visible, thin film was present on the panel. This panel was then analyzed by EDAX. The results that were obtained are illustrated by the spectrum provided at FIG. 12. The presence of tungsten and silicon was detected on the surface.

Example 11

0.1 grams of ammonia molybdate (solid) was added to 40 grams of the complex mixture of ions produced in accordance with Example 1A, with stirring until the solid dissolved. A 1010 steel panel was then immersed in the resulting solution and extracted after 1 minute. A visible, thin, tenacious, adherent surface had formed on the metal. The panel surface was then analyzed by EDAX. The results are illustrated by the spectrum provided at FIG. 13. Silicon and molybdenum were detected on the metal surface.

The electroless deposition of tungsten and molybdenum from aqueous solutions is another novel characteristic of the present invention. The conventional art teaches that such deposition is not possible. For example, the conventional text by Frederick A. Lowenheim, “Electroplating: Fundamentals of Surface Finishing” (1977) McGraw-Hill Book Company (TX), ASIN 070388369 (pg. 141) teaches that “from the standpoint of their electrode potentials, it should be possible to electroplate such metals as tungsten and molybdenum from aqueous solutions with a pH of about 5. Nevertheless (in spite of claims in the literature) these metals cannot be deposited in pure form from aqueous solutions”. Therefore, the electroless deposition of tungsten and molybdenum, together with other refractory metals, from aqueous solutions is new in the art. Silicon/refractory metal surfaces would find wide fields of commercial use in, for example, protection of metal surfaces, reducing coefficients of friction, inhibiting corrosion, hardening metals and, as previously described, could impart high heat resistance. Other specific areas of potential usage include as fuel additives for jet turbine engines in aircraft in addition to ground use turbine applications. A thermal barrier could easily be formed by the methods of the present invention for use on components designed for hostile environmental conditions, such as super-alloy turbines and the combustor and augmentor components of gas turbine engines. The silicon-nitrogen could diffuse into the surface of the jet turbine components and form a heat resistant (and potentially reflective) coating. There is no method known today for coating jet turbine engine components that does not involve taking the engine apart and either replacing components or applying metallizing sprays. The methods currently used obviously place a heavy financial burden on turbine owners because of both the downtime and the replacement costs for parts and materials.

Another commercial use segment of significant potential value is burners for industrial combustion systems, such as gas-fired furnaces for heat-treating and low-NOx industrial pyrolysis furnaces. The combustion of natural gas generates substantial quantities of nitrogen oxides and much time and money has been spent on improving natural gas burner designs to lower their NOx emissions. The new low NOx burners will reduce NOx emissions for periods of time, but it is expected that metals in natural gas in the parts per billion range will slowly build up on the nozzles of the burners and affect flow patterns to increase NOx emissions. A heat resistant coating on industrial burners would significantly extend the useful life of the burners with continued low NOx emissions. Such a further advantage of potentially permitting the use of less expensive burner materials. The thin coating of the silicon nitride, for example, could improve the flow characteristics of combustion gases giving further benefits in terms of burner design options for lowering NOx emissions and improving burner performance.

Four—Cycle Engine Tests

Example 12

For the tests of this Example, a 2000 model year Lincoln Town Car with a 4.6-liter engine and an automatic transmission was used. A base line fuel consumption figure was first established by running the vehicle for over 300 miles at about 72 MPH continuously with regular unleaded fuel. The resulting baseline average fuel consumption was 22.4 MPG. The fuel tank was then refilled using the additive in accordance with the present invention as described above in Example 9 (one ounce of fuel additive per 10 gallons of Diamond Shamrock brand regular unleaded fuel). The test car was then driven over approximately the same highway at about the same speed (72 MPH) and at generally the same ambient conditions. The onboard computer indicated that the car achieved 25.9 MPG with the additive-treated fuel. This amounts to a decrease in fuel usage of 3.5 gallons per tank, or a 15.6% improvement in fuel economy.

Example 13

A 1991 Ford F150 pickup with a 4.9 L engine, a standard five speed manual transmission, and 325,000 miles of usage, which had an established baseline of 15.5 MPG using regular unleaded fuel, was tested using Additive 1 prepared in accordance with the procedure described above in Example 5. using 1 ounce of Additive 1 per 10 gallons regular unleaded fuel. Under test conditions similar to those described above with respect to Example 12, this test vehicle obtained a fuel usage of 19.67 MPG, which is a fuel economy benefit of 26.9%.

Example 14

A 1998 Chevrolet CK3500 4x4 with a 6.5-L diesel engine with 184,165 miles was used as a test vehicle. A baseline mileage was established at 14.7 MPG. One test run was then made with the test vehicle to establish a baseline. Three test runs were then made using Additive 1 in standard on road automotive diesel fuel. The ratio of addition was 1 ounce of Additive 1 to 10 gallons of diesel fuel. The results were as follows in Table 2:

[0100] A 1998 Chevrolet CK3500 4x4 with a 6.5-L diesel engine with 184,165 miles was used as a test vehicle. A baseline mileage was established at 14.7 MPG. One test run was then made with the test vehicle to establish a baseline. Three test runs were then made using Additive 1 in standard on road automotive diesel fuel. The ratio of addition was 1 ounce of Additive 1 to 10 gallons of diesel fuel. The results were as follows in Table 2:
TABLE 2

<table>
<thead>
<tr>
<th>Tank</th>
<th>Fuel Consumption (MPG)</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.9</td>
<td>+8.2%</td>
</tr>
<tr>
<td>2</td>
<td>16.8</td>
<td>+14.7</td>
</tr>
<tr>
<td>3</td>
<td>17.0</td>
<td>+15.6</td>
</tr>
</tbody>
</table>

[0102] As noted in Table 3, the base line fuel consumption (with no Additive 1) was 4.075 gallons per hour, as compared to the test fuel consumption of 3.634 gallons per hour using Additive 1 as described above. This amounts to a reduction in fuel consumption of approximately 9.24%.

[0103] Further, as noted, the test engine had relatively heavy particulate emissions during startup for the baseline run, which is not atypical for a diesel engine. The engine had noticeably significant reductions in startup particulates after treatment, indicative of improvement in the combustion process.

TABLE 4

<table>
<thead>
<tr>
<th>Element</th>
<th>Ex. 2A (steel)</th>
<th>Ex. 2A (alum.)</th>
<th>Ex. 10 (aq.)</th>
<th>Ex. 10 (oil)</th>
<th>Ex. 11</th>
<th>Ex. 17</th>
<th>Ex. 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>0.378</td>
<td>80.970</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.839</td>
<td>1.475</td>
<td>1.516</td>
<td>0.346</td>
<td>0.158</td>
<td>0.315</td>
<td>0.499</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.005</td>
<td>0.098</td>
<td>0.003</td>
<td>-0.015</td>
<td>-0.009</td>
<td>0.098</td>
<td>-0.015</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.126</td>
<td>0.083</td>
<td>-0.015</td>
<td>-0.009</td>
<td>0.104</td>
<td>0.092</td>
<td>0.091</td>
</tr>
<tr>
<td>Calcium</td>
<td>—</td>
<td>0.161</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Iron</td>
<td>111.777</td>
<td>0.091</td>
<td>99.904</td>
<td>103.760</td>
<td>105.279</td>
<td>107.776</td>
<td>101.172</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>-0.016</td>
<td>—</td>
<td>-0.002</td>
<td>0.003</td>
<td>0.051</td>
<td>-0.008</td>
<td>-0.004</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.360</td>
<td>—</td>
<td>0.474</td>
<td>0.239</td>
<td>0.345</td>
<td>—</td>
<td>0.464</td>
</tr>
<tr>
<td>Tungsten</td>
<td>—</td>
<td>—</td>
<td>0.032</td>
<td>0.010</td>
<td>—</td>
<td>—</td>
<td>-0.021</td>
</tr>
<tr>
<td>Total</td>
<td>100.000</td>
<td>100.000</td>
<td>100.000</td>
<td>100.000</td>
<td>100.000</td>
<td>100.000</td>
<td>100.000</td>
</tr>
</tbody>
</table>

Example 15

[0101] For the following Example, a diesel-electric generator with a 150 KW Fiat engine was used. The Fiat engine had 13,850 hours of use prior to testing. The purpose of the test was to determine the effect if any of additives prepared in accordance with the present invention on fuel efficiency and environmental emissions. The engine typically released substantial particulates upon start-up, and generally continued visible smoking during operation. The generator was set at 33% load capacity for this test. A base line of fuel usage was determined by filling the fuel tank to the top of the tank. The diesel engine was then started, and the generator was run with a 33% load for 8 hours. The fuel tank was then refilled and the amount used to fill the tank was noted to determine fuel consumption. The fuel tank capacity was 100 gallons.

TABLE 3

<table>
<thead>
<tr>
<th>Run</th>
<th>Fuel (gal)</th>
<th>Time (hrs)</th>
<th>Fuel Consumption (gal/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>32.6</td>
<td>8</td>
<td>4.075</td>
</tr>
<tr>
<td>Test</td>
<td>83.6</td>
<td>23</td>
<td>3.634</td>
</tr>
</tbody>
</table>

Composition 2

[0104] In Merkl, a study of low purity silicon/potassium is described (see Example 1 of Merkl at column 23). As discussed above, the Merki method employed an exothermic phase that lasted 6 hours followed by an exothermic phase that lasted for 45 minutes. In accordance with certain embodiments of the present invention, a reaction scheme was employed comprising a novel variant wherein the rate of addition of the alkali metal is varied and no endothermic reaction is employed.

Example 16

[0105] This Example used 616 grams of ferrosilicon rocks containing about 75% silicon with about 25% iron, and a rock size of approximately 1 cm (about ½ inch). Other reagents included 2000 grams ammonium hydroxide (26° Baumé) and 616 grams potassium hydroxide (flakes). The ingredients were added as quickly as possible and then forced into an exothermic reaction by applying heat to the vessel. The exothermic reaction lasted for 45 minutes and a clear viscous fluid resulted. Specific gravity was then measured at 1.2. The resulting solution was decanted from the unreacted ferrosilicon rocks.

Example 17

[0106] Approximately one hour after preparation of the solution as described in Example 16, a panel of 1010 steel
was immersed in the solution for 30 seconds and then extracted. The panel was then analyzed via EDAX. The analytical results are provided in the spectrum provided at FIG. 14. Silicon was detected on the surface of the metal.

Example 18
Preparation of “Con2”
[0107] 600 grams of Drakel® 5 was placed in a 4000-ml beaker and 120 grams of a ferrosilicon solution prepared in accordance with Example 16 was added. The solution was heated with stirring. Above 300° F. salts precipitated, leaving a clear and bright solution, indicating that all the water had been removed. The heat was turned off and the temperature dropped to 180° F., at which time a panel of 1010 steel was immersed in the oil solution for 1 minute. The panel was extracted and a thin, tenacious film was observed on the metal. The panel was then analyzed via EDAX. The result is provided in the spectrum shown in FIG. 15. Silicon was detected on the metal surface, which indicates that a soluble silicon species in the oil is deposited on the metal from the oil-based solution. This solution is hereinafter referred to as “Con2”.

[0108] Con2 was added to 150 solvent neutral BP 901 base oil at a ratio of 1 gram Con2 to 20 grams solvent neutral oil, to provide make an oil and lubricant additive. Although 150 solvent neutral BP 901 base oil was used in this Example, those skilled in the art will recognize that any similar oil, such as any base oil manufactured from solvent refined paraffinic lube distillates or a US 350H group 2 oil may be used with satisfactory results.

Four—Cycle Engine Tests

Example 19
[0109] 5 grams of Con2 prepared in accordance with Example 18 was stirred into 100 grams of Drakel® 5. The resulting mixture, referred to hereinafter as “Additive 2” was placed in the fuel tank of the model year 2000 Lincoln Town Car previously referred to in the context of Example 12, at the rate of one ounce of the Additive 2 per ten gallons of regular Diamond Shamrock brand unleaded fuel. As noted with respect to Example 12, base line fuel consumption for this vehicle had previously been established at 22.4 MPG. The test vehicle was then driven 310 miles at an average speed of 72 MPH. During the first 100 miles the onboard computer registered at 24.5 MPG. For the balance of the test the onboard computer registered at 27.4 MPG, for an improvement in fuel economy of 5 MPG or 22.3%. This represents a further increase in fuel efficiency over the Example 12 results using Con1 of 3.5 mpg or 15.6%.

Example 20
[0110] In this Example, Additive 2 was tested in the Ford 150 pickup of Example 13 (now with 334,000 miles of usage) at the ratio of 1 ounce per 10 gallons of Diamond Shamrock brand regular unleaded fuel. The vehicle was then driven for 220 miles and an average of 19.37 MPG was achieved, which is similar to the result achieved in Example 13.

Additional Metal Tests

Example 21
[0111] In this Example, a stoichiometric amount of ammonium phosphate monobasic is dissolved in water. The pH of the solution is raised to 14 by the addition of an alkaline metal hydroxide. The resulting solution is then heated to above 180° F. and maintained at elevated temperature for 20 minutes or until the odor of the ammonia is no longer present. A panel of 1010 steel is then immersed in the solution for 20 seconds and a thin, tenacious film is formed on the metal. A stainless steel kitchen knife is immersed in the solution for 30 seconds, removed, and dried. A thin tenacious film formed on the stainless steel. Stainless steel is a passive metal alloy and does not accept a new surface without significant preparation in a dilute nitric acid solution followed immediately by placement in a plating bath with applied electromotive force in order to obtain a new surface. The solution contains ammonium/alkali metal/phosphorous and water. The solution is then dehydrated thermally in a hydrocarbon oil. A panel of 1010 steel was immersed in the oil solution for 30 seconds and a thin tenacious film formed on the steel panel.

Example 22
[0112] In this Example, a stoichiometric amount of ammonium sulfate is dissolved in water. The pH of the aqueous solution is raised to above 12 and the solution is then heated to above 180° F. and held at that temperature until the odor of ammonia is no longer present. A stainless steel knife is then immersed in the solution and a thin, tenacious film is formed on the stainless steel piece. The solution contains ammonium/alkali metal/sulfur and water. The solution is then thermally dehydrated in a hydrocarbon oil. A panel of 1010 steel was immersed in the oil solution for 30 seconds and a thin tenacious film formed on the steel panel.

Example 23
[0113] In this Example, ammonium acetate is dissolved in water. The pH of the solution is then raised to above 12 and held at a temperature above 180° F. until the odor of ammonia is no longer present. The solution contains ammonium/alkali metal/carbon and water. The solution was then thermally dehydrated in a hydrocarbon oil.

Example 24
[0114] In this Example, a stoichiometric amount of ammonium borate is dissolved in water. The pH of the solution is then raised to above 12 by the addition of an alkaline metal and then heated for 20 minutes or until the odor of ammonia is no longer present. The solution contains ammonium/alkali metal/boron. A stainless steel panel is immersed in the solution and a thin, tenacious film formed on the stainless steel. The solution is then dehydrated thermally in a hydrocarbon oil. A panel of 1010 steel was immersed in the oil solution and a thin tenacious film formed on the metal.

Example 25
[0115] In this Example, 54.4 grams of bismuth BB's (small spheres) is mixed with boiling H2SO4 and water. The solution is decanted and the bismuth BB's are washed with water, dried, and then weighed. A total of 2.4 grams of
bismuth was dissolved into the solution, which had a pH below 2. The solution was raised to a pH of 8 by adding ammonium hydroxide, and the pH was further raised above 12 by the addition of potassium hydroxide. The solution was then heated to above 180° F, until the odor of ammonia was no longer present. A panel of 1010 steel was immersed in the solution and a thin, tenacious film formed on the steel panel. The solution was then thermally dehydrated in a hydrocarbon oil. A panel of 1010 steel was immersed in the oil solution for 30 seconds and a thin tenacious film formed on the steel panel.

Example 26

[0116] In this Example, ferrosilicon (75% Si) is placed in a reaction vessel. Ammonium hydroxide, an alkali metal hydroxide, and water are then placed in the reaction vessel. The vessel is then heated to 180° F, and an exothermic reaction occurs which continues until the solution is too viscous to support further reaction.

[0117] A solution of ethanol/methanol is placed in a glass beaker. A measured amount of the aqueous silicon solution is poured into the alcohol mixture. There is an immediate precipitation of salts. A panel of 1010 steel is then immersed in the solution for 30 seconds, and a thin tenacious film formed on the steel panel.

[0118] The aqueous silicon solution is then thermally dehydrated into a hydrocarbon oil and some of the silicon becomes partly soluble in the oil. The sulfur oil of Example 22 (above) is then mixed with the silicon oil and the oils are miscible. A beaker of ethanol/methanol is added to a vessel and the sulfur/silicon oil is added to the ethanol/methanol solution. A 1010 steel panel is then immersed in the sulfur/silicon oil solution for 30 seconds and then extracted. A thin tenacious film had formed on the steel panel. Ethanol is currently being touted as a method of reducing dependency on oil resources. Ethanol has limitations in the transport and handling of the solution. Ethanol is extremely corrosive; thus, any system that would allow for film forming on metals that contact ethanol would be valuable.

Example 27

[0119] Bio-diesel is also being touted as a method to reduce reliance on oil. Bio-diesel, for example, is a mixture of 80% hydrocarbon diesel fuel and 20% methyl esters. The methyl ester is derived from vegetable oils, primarily soybean oils, and is processed to remove the glycerin. The methyl ester can then be added to hydrocarbon diesel at any ratio and used for combustion purposes. The aqueous solution of Example 1A above is first thermally dehydrated in a hydrocarbon oil. The resulting solution is then added to the methyl esters and becomes completely miscible. A 1010 steel panel is immersed in the modified methyl ester for 30 seconds. A thin tenacious film is deposited on the steel substrate. Methyl esters can thus be used to bring thin tenacious films onto all the metal parts in internal combustion engines.

[0120] While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

[0121] The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modification thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, pendant processing equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term “optionally” with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

[0122] The discussion of a reference in the Description of the Related Art is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

We claim:

1. An additive for improving engine performance comprising, in aqueous solution, ammonium, an alkali metal, and a coating component selected from the group consisting of phosphorus, sulfur, carbon, bismuth, boron, silicon, and combinations thereof.
2. The additive of claim 1 further comprising a hydrocarbon oil.
3. An engine additive consisting essentially of a source of ammonium ions, a source of alkali metal ions, a coating component, and a hydrocarbon.
4. The additive of claim 3 wherein the coating component is selected from the group consisting of phosphorus, sulfur, carbon, bismuth, boron, silicon, and combinations thereof.
5. The additive of claim 3 wherein the coating component is selected from the group consisting of ammonium phosphate, ammonium sulfate, ammonium acetate, ammonium borate, metallic bismuth dissolved in sulfuric acid solution, ferrosilicon, and combinations thereof.
6. The additive of claim 3 wherein the hydrocarbon comprises an oil selected from the group consisting of solvent neutral oils, synthetic oils, mineral oils, vegetable oils, methyl esters, and combinations thereof.
7. A method for preparing an additive for improving fuel performance comprising the steps of preparing an aqueous mixture comprising ammonium, an alkali metal, and a coating component selected from the group consisting of phosphorus, sulfur, carbon, bismuth, boron, silicon, and combinations thereof, and heating the aqueous mixture.
8. The method of claim 7 further comprising dehydrating the aqueous mixture.
9. The method of claim 8 further comprising precipitating salts.

10. The method of claim 9 further comprising solubilizing in a hydrocarbon oil.

11. An aqueous composition with a pH greater than 9 and capable of solubilization in hydrocarbons for improving fuel economy, said solution being formed by combination of an alkali metal, a source of ammonium ions, and a coating component selected from the group consisting of phosphorus, sulfur, carbon, bismuth, boron, silicon, and combinations thereof.

12. The aqueous composition according to claim 11 wherein the alkali metal is sodium.

13. The aqueous composition according to claim 11 wherein the alkali metal is potassium.

14. The aqueous composition according to claim 11 wherein the source of ammonium ions is selected from the group consisting of ammonium phosphate, ammonium sulfate, ammonium acetate, ammonium borate, ammonium hydroxide, and combinations thereof.

15. The aqueous composition according to claim 11 wherein said aqueous composition is solubilized in a hydrocarbon oil selected from the group consisting of solvent neutral oils, synthetic oils, mineral oils, vegetable oils, methyl esters, and combinations thereof, such that the solubilized composition is miscible and stable in diesel fuel.

16. A method of preparing an aqueous composition comprising providing a source of ammonium ions, providing a source of alkali metal ions, providing a coating component, solubilizing said mixture in a hydrocarbon liquid to produce an additive, and applying said additive to an internal wear surface of an internal combustion engine.

17. The method of claim 16 wherein the coating component is selected from the group consisting of phosphorus, sulfur, carbon, bismuth, boron, silicon, and combinations thereof.

18. The method of claim 17 wherein the hydrocarbon liquid is selected from the group consisting of solvent neutral oils, synthetic oils, mineral oils, vegetable oils, methyl esters, and combinations thereof.

19. The method of claim 18 wherein the source of ammonium ions is selected from the group consisting of ammonium phosphate, ammonium sulfate, ammonium acetate, ammonium borate, ammonium hydroxide, and combinations thereof.

20. The method of claim 19 further comprising dehydrating the aqueous mixture and precipitating salts.

21. The method of claim 19 wherein at least one additional metal from Groups I-VIII of the Periodic Table is also solubilized in the additive.

22. The method of claim 19 further comprising electrolessly depositing a silicon surface on at least one conductive substrate.

23. The method of claim 16 wherein the internal combustion engine comprises a diesel engine.

24. The method of claim 16 wherein the internal combustion engine comprises a gasoline engine.

25. The method of claim 16 wherein the fuel consumption of the engine is improved by at least 5%.

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