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(54) **METHOD AND COMPOSITION FOR  
CREATION OF CONVERSION SURFACE**

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(57) **ABSTRACT**

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The present invention relates generally to the field of metal conversion surfaces, in particular, the creation of a phosphate-metal chemisorbed layer for iron and aluminum parts as well as to other metal substrates capable of forming a conversion surface. A phosphorus-containing solution is brought into contact with the metal components such that a conversion surface is formed.

## METHOD AND COMPOSITION FOR CREATION OF CONVERSION SURFACE

### RELATED APPLICATIONS

[0001] This patent application claims priority to U.S. Provisional Patent Application Serial No. 60/443,995 filed on Jan. 31, 2003, and U.S. Provisional Patent Application Serial No. 60/480,672 filed on Jun. 23, 2003, which are incorporated by reference in their entirety.

### TECHNICAL FIELD OF THE INVENTION

[0002] The present invention relates generally to the field of metal conversion surfaces, in particular, the creation of a phosphate-metal chemisorbed layer for iron and aluminum parts as well as to other metal substrates capable of forming a conversion surface.

### BACKGROUND OF THE INVENTION

[0003] The creation of an iron-phosphate conversion surface is known to create a surface that exhibits high dry lubricity, among other benefits. Creation of the iron-phosphate conversion surface on an iron part or piece of equipment traditionally is accomplished through a phosphatizing bath process. This bath also typically includes the element of zinc in order to optimize the process of deposition of the phosphate onto the surface of the item of interest. While the use of a bath process is practical for coating particular types of parts or pieces, i.e. large items where the surface is otherwise exposed to the elements, the bath process requires that the parts to be treated be disassembled in order to receive the coating.

[0004] U.S. Pat. No. 5,540,788 issued to DeFalco teaches a process for creating an iron-phosphorus surface through the formation of a conversion surface on iron substrates by delivering the phosphatizing compound in a lubricating fluid. This method includes the formation of a conversion surface to create the iron/phosphate surface onto completed machinery engines. The composition can be introduced through the lubricating oil into a running engine. The composition disclosed includes a source of phosphoric acid, an alkali metal hydroxide and a source of reactive NH<sub>2</sub> groups. Notably, the source of the reactive NH<sub>2</sub> groups produces the reactive NH<sub>2</sub> groups as a result of the highly exothermic reaction that is described. Testing indicates that the same compounds that act as a source of reactive NH<sub>2</sub> groups in the above reaction do not produce reactive NH<sub>2</sub> groups under different physical conditions since they follow a different reaction path. The reactive NH<sub>2</sub> groups produced in the DeFalco patent are best described as phosphamids. This specific chemistry results from the highly exothermic reaction described in the DeFalco patent. It is also noted that the physical conditions of having a high pH results in the production of free ammonia. When the phosphamids circulate with the lubrication medium in the engine, a phosphate-iron conversion surface specific to this composition was created.

[0005] Various forms of phosphate-containing substances have been used to create the desired conversion surface on iron as well as non-ferrous metals, each resulting in a specific surface with unique characteristics. Most efforts have focused on the deposition of the phosphorus-containing coating on iron substrates and include the use of zinc. It

would be advantageous to create a cost-effective composition that, when contacted with a metal substrate or part, would create a phosphate-metal conversion surface. It would be advantageous if this composition were useful for the conversion of iron surface. It would be advantageous if this composition were useful for the conversion of non-ferrous surfaces capable of forming a conversion surface. It would be particularly advantageous if this composition were useful for the conversion of aluminum surfaces, including aluminum alloys. It would be advantageous to create a conversion surface that is resistant to corrosion and that has a high coefficient of lubricity even when dry. It would be advantageous to include a method of delivering this composition to the parts to be converted without disassembly of the pieces to be coated.

[0006] In addition to ferrous components, efforts to create improved non-ferrous components, in particular aluminum components, are numerous. Such efforts to create improved aluminum components, such as 2-cycle engines commonly found in snow mobiles, lawn mowers, weed-trimmers, mopeds, outboard motors, ATVs, dirt bikes, chain saws and the like, have typically focused on the composition of the aluminum alloy as opposed to the creation of a conversion surface. For example, a distinct silicon-aluminum alloy composition is disclosed in U.S. Pat. No. 6,419,769. Similarly, rare earth elements have been added to aluminum alloys for strength, such as the composition discussed in U.S. Pat. No. 5,284,532.

[0007] Two-cycle engines, because of the typical applications, are often used sporadically. For example, snow mobiles are shut down during off-season. This leads to additional difficulties related to condensation and resulting corrosion. Corrosion inhibitors are often added to avoid this type of difficulty.

[0008] Aluminum alloy engines include a lubricating oil for lubricity of the engine. The lubricating oil is selected for high film strength to minimize wear. This prevents metal-to-metal contact and provides protection against piston scuffing. When temperatures of operation are high, two-cycle motors lose power and torque. The aluminum pistons expand from heat and cause an increase in friction. Various proprietary lubricating oils have been introduced into the market place to improve performance at high operating temperatures. The ASTM D-4863 two-cycle motor lubricity test measures torque output at 350° C. (662° F.) and is a benchmark for performance.

[0009] The field of lubricant technology is characterized by a never-ending search for improved lubricants and additives. Additives, essential for satisfactory performance of lubricants for all manner of modern engines, serve many roles, including those of providing detergency, antioxidant properties, and suspension of contaminants. In an effort to improve lubricity, various synthetic oils and various additives have been investigated. Numerous combinations of synthetic esters have been measured for increased lubricity. Further additives have also been proposed to reduce wear. One example is U.S. Pat. No. 6,242,394 disclosing a two-stroke cycle lubricant. U.S. Pat. No. 6,172,013 discloses lubricating oil compositions having enhanced friction coefficient and wear properties through the use of additives of molybdenum and diesters of aliphatic or aromatic dicarboxylic acids. Adducts of glyoxylic acids and phenols are

known. For example, U.S. Pat. No. 5,281,346, Adams, discloses a two-cycle engine lubricant comprising alkali or alkaline earth metal salts of carboxylic aromatic acids.

[0010] Various forms of phosphate-containing substances have been investigated to create the desired lubricant or surface, each phosphate-containing substance resulting in a specific surface composition with unique characteristics. Most efforts have focused on the deposition of the phosphorus-containing coating on iron substrates and include the use of zinc. It would be advantageous to create a cost-effective composition that would create a phosphate-metal conversion surface on a non-ferrous surface. It would be advantageous to create a phosphate-metal conversion surface on an aluminum alloy engine. It would be advantageous if this conversion surface could be created on the engine or part while in operation. It would be advantageous to create a conversion surface on the aluminum alloy engine that would improve dry lubricity, efficiency, strength and/or emission control. It would be advantageous to include a method of delivering this composition to the parts to be converted without disassembly of the pieces to be coated. It would be advantageous to create a composition and method that does not require zinc.

#### SUMMARY OF THE INVENTION

[0011] The present invention includes compositions and methods useful for the creation of phosphorus-containing conversion surfaces on metal components. The composition of the invention is useful to create a thin layer on metal surfaces.

[0012] The invention includes a phosphorus-containing solution containing  $[Y]H_2PO_4$ ,  $[Y]_2HPO_4$ , and water or other solvent as components of an intermediate solution, where Y is a cation.  $[Y]H_2PO_4$ ,  $[Y]_2HPO_4$  as well as other salts discussed herein are also called salt components. The cationic portion of the salt components can be any cation, with potassium being a preferred cation. In this case, the preferred components would be  $KH_2PO_4$ ,  $K_2HPO_4$ , and water. The intermediate solution is mixed with a carrier fluid. The carrier fluid is any fluid that is operable to maintain the salts in at least a partially dispersed state within the carrier fluid. Water or other solvents used in the intermediate solution are then largely driven off such that the salts remain in at least a partially dispersed and/or partially dissolved state in the carrier fluid to create the phosphorus-containing solution. The resulting phosphorus-containing solution is operable to create a phosphate-metal layer on a metal substrate when the phosphorus-containing solution is placed in contact with the metal substrate.

[0013] A group of preferred cations for the salts are the alkali metals or Group 1A elements. While orthophosphoric acids have been described, the invention also includes pyrophosphoric acids, which are the condensed analogs and therefore derivatives of and equivalent to orthophosphoric acid. It is noted that, through the process to condense the orthophosphoric acid to pyrophosphoric acids, the  $PO_4^{3-}$  become  $P_2O_7^{2-}$  or other condensed phosphates. Therefore,  $[Y]H_2PO_4$ ,  $[Y]_2HPO_4$  and  $[NH_4]_2HPO_4$  are precursors to pyrophosphoric acids. The use of the pyrophosphoric form is therefore encompassed within the definition of the orthophosphate form, which can be expressed as  $[Y]H_2PO_4$ ,  $[Y]_2HPO_4$  and  $[NH_4]_2HPO_4$  and in similar form.

[0014] Advantageously, the phosphorus-containing solution is essentially free of zinc. While some amount of zinc can exist in the solution, for example, when it is present in raw materials, zinc is not added or present in a quantity beneficial for plating. Thus, the phosphorus-containing solution is considered essentially free of zinc. Beneficially, the solution is also substantially free of halogens.

[0015] Another preferred embodiment of the phosphorus-containing solution includes the addition of  $[NR_4]_2HPO_4$  to the intermediate solution of  $[Y]H_2PO_4$ ,  $[Y]_2HPO_4$ , and water or other solvent. R in  $[NR_4]$  can be an alkyl group, hydrogen, or combinations of both. Thus, this encompasses ammonium as well as amine phosphates. When the solution is prepared using ammonium compounds or amine compounds, the nitrogen in the solution is essentially all in the form of ammonium or amine ions. There is at most a negligible amount of free ammonia such that the solution is substantially ammonia free.

[0016] Yet another embodiment includes the addition of  $[X]C_2H_3O_2$  where  $C_2H_3O_2^-$  ion is an acetate group such that the intermediate solution contains at least  $[Y]H_2PO_4$ ,  $[Y]_2HPO_4$ ,  $[X]C_2H_3O_2$  and water or other solvent. Preferred embodiments include X as  $NH_4$  or K or other Group 1A elements.  $[NR_4]_2HPO_4$ , where R hydrogen, alkyl group or a combination of both, can also be added to this mixture. This intermediate solution is combined with the carrier fluid and the water or other solvent is largely removed to create the phosphorus-containing solution. Preferably the solvent, such as alcohols, have sufficient volatility to allow for removal from the intermediate solution mixed with carrier fluid through the addition of heat, although this is not a required characteristic. When the phosphorus-containing solution is prepared using ammonium compounds, ammonium compounds being defined as those compounds containing  $NH_x$  groups, the nitrogen in the phosphorus-containing solution is essentially all in the form of ammonium ions. Amine ions are also encompassed herein. There is at most a negligible amount of free ammonia. Furthermore, the mixture is advantageously created without the production of excessive amounts of heat, i.e., no highly exothermic reaction is performed.

[0017] In a preferred embodiment, the phosphorus-containing solution has a pH between about 6.0 and 8.0.

[0018] The phosphorus-containing solution of the invention can be used in various types of environments, such as aqueous or hydrophilic environments. In the case of a hydrophilic environment, it is advantageous to include a carrier fluid and a dispersant to promote dispersion in the carrier fluid. The carrier fluid can be a lubricating fluid that is to be placed in contact with the metal parts or metal substrate or, in a preferred embodiment, the carrier fluid is a separate hydrophilic fluid that is highly miscible with lubricating fluid, such as a motor oil. One characteristic of the carrier fluid is that the salts of the phosphorus-containing solution are at least partially soluble in the carrier fluid.

[0019] In certain circumstances, the carrier fluid is a quantity of a target fluid, such as the lubricating fluid. The target fluid is the fluid that is identified as the majority fluid that is intended to bring the phosphorus-containing solution into contact with the metal to be treated. The phosphorus-containing solution can be dispersed through the target fluid

through the use of physical mixing, such as a high speed shear mixer, or other means. In such instances, the target fluid acts as the carrier fluid.

[0020] The current invention includes a process for creating a conversion surface on a metal part or metal substrate in a system using the phosphorus-containing solution. The system can be as simple as a metal part operable to be brought into contact with the phosphorus-containing solution or it can be a complex series of parts, such as in an engine, where the phosphorus-containing solution is brought into contact with at least part of the system. Where the part is at least partially in contact with the phosphorus-containing solution or target fluid containing the phosphorus-containing solution, the phosphate-metal layer surface is created resulting in a converted metal substrate have the phosphate-metal layer or conversion surface on surfaces of the metal substrate contacted by the phosphorus-containing solution. The amount of phosphorus-containing solution used is the amount effective to create the conversion surface. Preferred embodiments of the target fluid that is contacting the part include a lubricating fluid or a phosphating bath. The conversion surface that is created as a result of this process has characteristics and composition specific to the metal contained in the metal part and to the phosphorus-containing solution. When the metal part includes iron, a phosphate-iron surface is created on the surface of the iron. When the metal part includes aluminum, an aluminum-phosphate surface is created. When the metal contains nickel, a phosphate-nickel surface is created. Similar results are observed with chromium and molybdenum.

[0021] In addition to being useful for ferrous metal components, the present invention includes compositions and methods useful for the creation of phosphorus-containing conversion surfaces on non-ferrous components, such as aluminum two cycle engines. The composition of the invention is useful to create a thin layer on metal surfaces.

[0022] One preferred embodiment includes a lubricating composition or lubricant that has a substantial amount of an oil having a lubricating viscosity. An amount of the phosphorus-containing solution is added to the oil thereby creating a lubricating composition operable to create a conversion surface upon a metal component upon being brought into contact with the metal component.

[0023] Another embodiment of the invention includes a method of forming a non-ferrous metal-phosphate conversion surface on non-ferrous metal components by contacting the non-ferrous metal component in a contact region with an active phosphorus solution to form the non-ferrous metal-phosphate conversion surface on the contact region. The contact region can be limited to a portion of the surface of the metal component or can encompass the entire metal component. The active phosphorus solution is prepared by mixing a phosphorus-containing acid with an alkali metal hydroxide salt and an ammonium/amine compound under conditions designed to create a highly exothermic reaction thereby producing the active phosphorus-solution. The ammonium/amine compound is an active compound that contains either ammonium or amine and is operable to interact in the exothermic reaction. Ammonium hydroxide and ammonia paratungstate are two examples of such compounds.

#### DETAILED DESCRIPTION

[0024] While the active phosphorus solution was disclosed as being useful to produce conversion surfaces on iron, new investigations indicate that, when carried to the surface of aluminum in an appropriate carrier, the active phosphorus solution can be used to create a conversion surface on aluminum.

[0025] While many engines are iron, 2-cycle engines tend to be made of aluminum. This invention is also useful for the creation of a conversion surface on such engines. The phosphorus-containing solution of the invention can be introduced to the engine while in use through any fluid circulating to the parts.

[0026] Aluminum-phosphate conversion surfaces are created upon contacting of the aluminum part or engine with the phosphorus-containing solution of the invention or the active phosphorus solution. With either solution, this conversion surface can be produced in bath processes or in situ. Unlike traditional electro-deposition in baths, the phosphorus-containing solution of the current invention does not utilize zinc. The phosphorus-containing solution can be delivered into contact to create the aluminum conversion surface on the aluminum part through the use of a target fluid. An example of a preferred target fluid is a lubricating oil in a two-cycle aluminum engine as part of a motorized vehicle or other equipment. The phosphorus-containing solution is combined with the lubricating oil to create a lubricating composition. The lubricating composition including the substantial amount of oil having a lubricating viscosity and an amount of the phosphorus-containing primary solution operable to create a conversion surface upon the aluminum part or metal component. Like the phosphorus-containing solution, the active phosphorus solution is also useful for creating the conversion surface on an aluminum part by contacting the active phosphorus solution to the aluminum engine, preferably delivered into contact through the use of target fluid.

[0027] For the lubricating composition, examples of amounts used in testing include amounts between about 0.01% by weight to about 0.5% by weight of phosphorus in the lubricating composition. A preferred embodiment includes 0.3% by weight of phosphorus. Increased amounts of phosphorus are effective as well. It is notable that a very cost-effective solution can be prepared with low weight percent of phosphorus.

[0028] While the phosphorus-containing solution is used to create conversion surfaces on engines for benefits derived therefrom, the process of the invention includes the creation of conversion surfaces using the phosphorus-containing solution of the invention on any metal part or metal substrate. For example, aircraft parts are often made of aluminum. The application of the conversion surface upon aircraft parts can reduce coefficients of friction. Motorboat engines, lawn mowers or other equipment that includes metal motors or metal parts benefit from the conversion surface of the invention. By creating a cost-effective manner of creating the conversion surface, application to a wide range of equipment becomes economically feasible. This process is also used with the active phosphorus solution on non-ferrous components.

[0029] The conversion surface is formed as a result of contacting the aluminum alloy of the part or component with

an amount of the phosphorus-containing solution or active phosphorus solution operable to create the conversion surface. The resulting conversion surface with use of the phosphorus-containing solution includes aluminum phosphate and aluminum oxide. The addition of the phosphorus-containing solution to an aluminum surface results in the formation of the reaction product of  $\text{AlPO}_4$ , aluminum phosphate, and  $\text{Al}_2\text{O}_3$ , aluminum oxide, as a conversion surface on the aluminum component. Test run using infrared and X-ray testing techniques confirm the existence of these species. Other aluminum species also are produced depending upon composition of an aluminum alloy of the aluminum surface and side reactions. In a preferred embodiment, acetate compounds are utilized to manipulate the pH of the solution.

#### EXAMPLE 1

[0030] One example of a preferred formulation includes the phosphorus-containing solution with the following amounts

[0031] 1.597 mols  $\text{KH}_2\text{PO}_4$

[0032] 0.693 mol  $\text{K}_2\text{HPO}_4$

[0033] 0.315 mol  $[\text{NH}_4]_2\text{HPO}_4$

[0034] and water.

[0035] In this example, the identified salts are mixed with and dissolved in an amount of water sufficient to at least partially dissolve the salts. The test shown above used 55.6 moles of water. This creates the intermediate solution, which in this case has 2.9 mole % of  $\text{KH}_2\text{PO}_4$ , 1.2 mole % of  $\text{K}_2\text{HPO}_4$ , 0.5 mol % of  $\text{K}_2\text{HPO}_4$  and 95.3 mol % of water. The intermediate solution is then mixed with the carrier fluid. The water is then driven off thermally from the mixture of the intermediate solution with the carrier fluid to produce the phosphorus-containing solution of the invention. The resulting phosphorus-containing solution of the invention is referred to as being substantially dry or water free due to the negligible amount of water remaining in the solution. Preferably, the water is driven off to a level of around 0.1 wt % of the phosphorus-containing solution. It is noted that more water can remain in the solution without changing the functionality of the phosphorus-containing solution, but 0.1 wt % has been selected as a preferred product specification.

[0036] Phosphorus-containing solutions with K or other cation between 0.16 and 16 mole % have been evaluated. Solutions outside of this range will also be effective, although with varying degrees of cost effectiveness or efficiency.

[0037] The pH of the phosphorus-containing solution can be controlled through manipulation of the ratios of components. By manipulating the ratios of the resulting  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  ions, the phosphorus-containing solution can be created in the preferred pH range of about 6.0 to about 8.0. For example, the ratio is approximately 15.8 for a pH of 6. The ratio is about 0.0158 for a pH of 8. Test results were controlled for a pH of 7, although the entire range is considered neutral and therefore preferred. Through simulation, the following amounts are anticipated to reach the indicated pH using the ratio as the only means of manipulating the pH.

pH	Salt Components, in Mole		Salt Components, in Wt	
	$\text{KH}_2\text{PO}_4$ , mole	$\text{K}_2\text{HPO}_4$ , mole	$\text{KH}_2\text{PO}_4$ , wt	$\text{K}_2\text{HPO}_4$ , wt
6.0	41.5	13	5706.25	2293.2
6.5	17.7	29	2433.75	5115.6
7.0	7.5	40	1031.25	7056
7.5	3	46.5	412.5	8202.6
8.0	1.5	48	206.25	8467.2

#### EXAMPLE 2

[0038] Preparation of the formulation includes dissolving  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$  and KAcetate salts in water. No ammonium salts are used in this example, so the final formulation will contain no ammonia.

[0039] The procedure includes adding 51 lbs of deionized water, 17.6 lbs of  $\text{KH}_2\text{PO}_4$ , 14.2 lbs of  $\text{K}_2\text{HPO}_4$  and 2.2 lbs of Kacetate in that order to two 5-gallon plastic pails. An additional 16.4 lbs of water was added thereafter. The salts were added to the water with rapid mechanical agitation and the mixture was heated after the addition of all the salts. The dissolution of the  $\text{KH}_2\text{PO}_4$  was slightly endothermic, dropping the temperature of the batch by 4 to 5 degrees C. While complete dissolution is not necessary, this experiment included heating the mixture to 40 degrees C. in order to dissolve the remaining salts. Alternately, additional water can be added if complete dissolution is desired. The pH after complete dissolution was in the target range of 7.0-7.1 so no adjustment of pH, such as, through the addition of KOH or acetic acid, was made. The resulting P value was approximately 65,000 ppm after final dilution such that no salts crystallize out of solution.

#### EXAMPLES 3-5

[0040] The following intermediate mixtures were formed and tested:

#### EXAMPLE 3

[0041]

	Components, g-mole	Formula Wt., g/g-mole	Wt. Used, g
$\text{KH}_2\text{PO}_4$	1.597	136.1	217.3
$\text{K}_2\text{HPO}_4$	1.008	174.2	175.6
KOAc	0.289	98.1	28.4
45% KOH	1.256	56.1	156.6
Water	36.2	18.0	652.2
Total =	40.3		1,230.0
EF	2.61		
1000 P, moles/L = EF	65,591		
1000 P, ppm =			

## EXAMPLE 4

[0042]

	Components, g-mole	Formula Wt., g/g-mole	Wt. Used, g
	KH <sub>2</sub> PO <sub>4</sub>	1.597	136.1
	K <sub>2</sub> HPO <sub>4</sub>	1.008	174.2
	45% KOH	1.545	56.1
	Water	35.8	18.0
Total =			1,230.0
EF	2.61		
1000 P, moles/L =			
EF	65,591		
1000 P, ppm =			

## EXAMPLE 5

[0043]

	Components, g-mole	Formula Wt., g/g-mole	Wt. Used, g
	KH <sub>2</sub> PO <sub>4</sub>	58.7	136.1
	K <sub>2</sub> HPO <sub>4</sub>	37.0	174.2
	KOAc	10.2	98.1
	45% KOH	0.0	56.1
	Water	1,698.1	18.0
Total =			30,599.6
			46,035.6

[0044] In these intermediate mixtures, KH<sub>2</sub>PO<sub>4</sub> is between 38 and 55 mole percent of the salts. K<sub>2</sub>HPO<sub>4</sub> ranged from 24 to 35 mole percent of the salts. The salts were diluted with water such that moles of phosphorus (P) per liter of the intermediate solution was approximately 2.61 moles/L. This intermediate solution was mixed with the carrier fluid. Phosphorus-containing solutions prepared with much lower concentrations of phosphorus have also been found to be effective.

[0045] 10 [0038] Example 6:

[0046] 1.597 mols KH<sub>2</sub>PO<sub>4</sub>

[0047] 0.693 mol K<sub>2</sub>HPO<sub>4</sub>

[0048] 0.315 mol [NH<sub>4</sub>]<sub>2</sub>HPO<sub>4</sub>

[0049] 0.289 mol [NH<sub>4</sub>]<sub>2</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

[0050] and water.

[0051] [NH<sub>4</sub>]<sub>2</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub> can also be referred to as [NH<sub>4</sub>]<sub>2</sub>Oac.

[0052] In a preferred embodiment, KH<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, [NH<sub>4</sub>]<sub>2</sub>HPO<sub>4</sub> and water are created into the intermediate solution that is added to refined oil carrier fluid and mixed with dispersants to create the phosphorus-containing solution. Exemplary dispersants include alkenyl succinimides or similar type of dispersants, including the previously-marketed product TFA 4690C. In a preferred embodiment, a dispersant with a total base number of from 30 to 160 on an oil-free basis is used. The phosphorus-containing solution preferably ranges from approximately 8 to 12 wt % of the intermediate solution while the refined oil carrier fluid

ranges from 88 to 92 wt % of the resulting mixture. The intermediate solution is added in at approximately 10 wt. % of the refined oil carrier fluid in a preferred embodiment. The resulting mixture is heated to drive off a significant amount of water. The resulting mixture exhibits characteristics that can be described as a colloid or an emulsion. When the intermediate mixture is mixed into a lubricating oil, an effective amount of the phosphorus in the phosphorus-containing solution can be very dilute and still remain effective. One example of a preferred embodiment is 0.3 wt % phosphorus in the intermediate solution. Upon addition to the lubricating oil, the phosphorus content can be in the range of 5-100 ppb and still be effective. Preferred range of phosphorus in the phosphorus-containing solution is 300-1250 ppm. Additional preferred range of phosphorus is 300-600 ppm. Particularly preferred range of phosphorus is 300-400 ppm. Higher amounts are also effective as shown in the previous examples.

[0053] An example of an alternate embodiment of the phosphorus-containing solution includes mixing about 2.6 molar (M) orthophosphate with alkali metal and ammonium cations, having a pH of 7 at ambient temperatures. A measured volume of this aqueous phosphorus-containing solution is suspended in an oil-dispersant mixture, most of the water removed thermally, and diluted to about 0.3 wt % P. Advantageously, the phosphorus-containing solution can be contacted to metal parts while the engine is running and without disassembly of the engine.

[0054] Laboratory tests with the phosphorus-containing solution of KH<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, [NH<sub>4</sub>]<sub>2</sub>HPO<sub>4</sub> and water as an additive show major improvements. Sodium has also been evaluated for use as a cation in this formulation. Group IA metals are preferred cations. Other cations can include organic compounds. Factors related to selection of the cation include commercial expense and/or corrosion resistance.

[0055] Laboratory measurements have revealed the nature of the surface layer. Application of the phosphorus-containing solution to 1018 carbon steel at 180° F. was followed by a series of analytical tests. Optical microscope examination (20x) clearly reveals a fairly uniform surface layer from the application of the phosphorus-containing solution of the invention to the carbon steel. Scanning electron microscopy (SEM) of the steel surface after the application of the phosphorus-containing solution in the oil-based mixture shows a relatively smooth layer. State-of-the-art surface analytical instrumental measurements have shown that a thin surface conversion layer, ranging from 15-80 Angstroms depending upon conditions and concentrations, is formed. This layer is of variable composition and contains Fe, O, P, N, and K. The layer is believed to form from the reaction of phosphate species in the mixtures with the oxide surface of the metal (Fe), initially of about 25 Angstroms in thickness. The surface compounds resulting from this chemical reaction resulting in the conversion layer appear to range from the simple FePO<sub>4</sub> to more complex phosphates such as NH<sub>4</sub>Fe<sub>2</sub>[PO<sub>4</sub>]<sub>2</sub>, K<sub>3</sub>Fe<sub>3</sub>[PO<sub>4</sub>]<sub>4</sub> · xH<sub>2</sub>O, NH<sub>4</sub>Fe<sub>3</sub>[H<sub>2</sub>PO<sub>4</sub>]<sub>6</sub> [HPO<sub>4</sub>]<sub>2</sub> · xH<sub>2</sub>O, KFe<sub>2</sub>[HPO<sub>4</sub>]<sub>2</sub>[PO<sub>4</sub>], and related compounds, depending upon operating conditions. Coordination of the phosphate structure to the surface metal (Fe) ions in the surface layer is believed to be the origin of the stability of these surface compounds.

[0056] The diverse oils of lubricating viscosity include natural and synthetic lubricating oils and mixtures thereof.

These lubricants include crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, including automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines, and the like. They can also be used in gas engines, stationary power engines and turbines and the like. Automatic transmission fluids, transaxle lubricants, gear lubricants, metal-working lubricants, hydraulic fluids and other lubricating oil and grease compositions can also benefit from the incorporation of the compositions of the present invention.

**[0057]** A mixture of phosphoric acid, alkali metal hydroxide and a source of reactive NH<sub>2</sub> groups have been explored in U.S. Pat. No. 5,540,788, which is herein incorporated by reference. This mixture, referred to as the phosphamid mixture, has been disclosed for use in creation of an iron-phosphate conversion surface. The process to create the phosphamid mixture is through chemical reaction, not through dissolution or dissolving. The phosphamid mixture is achieved as a result of a highly exothermic reaction that leads to the creation of the phosphamid. The current active phosphorus solution as used in the creation of aluminum conversion surfaces is an improvement of the disclosure related to phosphamid and its use.

**[0058]** The phosphamid mixture continues to be useful and is the subject of further development as disclosed herein. The exothermic reaction and the production of free ammonia at elevated pHs are two characteristics of phosphamid production that, under particular circumstances, can be considered less desirable. The phosphorus-containing solution of the current invention avoids the production of free ammonia and the related issues through maintaining pH in a range of approximately 6 to 8, or maintaining the pH below the level at which ammonia is formed, as well as avoiding the results and complexity of the creation of the highly exothermic reaction.

**[0059]** Tests of the active phosphorus solution indicate that the active phosphorus solution interacts with non-ferrous metals to create conversion surfaces. An exemplary non-ferrous metal discussed above is aluminum. The active phosphorus solution creates a phosphorus-aluminum conversion surface when brought into contact with aluminum. Other non-ferrous metals capable of creating conversion surfaces also interact with the active phosphorus solution.

**[0060]** While the invention has been shown or described in only some of its forms, it should be apparent to those skilled in the art that it is not so limited, but is susceptible to various changes without departing from the scope of the invention. For example, conversion surfaces on aluminum and iron parts have been specifically discussed. Use of the phosphorus-containing solution or active phosphorus solution on other metals or metal parts is also encompassed within this invention. Alloys are also encompassed within the discussion of metals.

What is claimed is:

1. A phosphorus-containing solution comprising a mixture of salts and a carrier fluid, the salts comprising:

[Y]H<sub>2</sub>PO<sub>4</sub>; and

[y]<sub>2</sub>HPO<sub>4</sub>, where [Y] is a cation,

the carrier fluid being operable to maintain the salts within the carrier fluid in at least a partially dispersed state, the phosphorus-containing solution being operable to create a phosphate-metal layer on a metal substrate when the phosphorus-containing solution is placed in contact with the metal substrate, the phosphorus-containing solution being essentially free of zinc and the mixture to form the phosphorus-containing solution being mixed in the absence of a highly exothermic reaction.

2. The phosphorus-containing solution of claim 1 further comprising [NR<sub>4</sub>]<sub>2</sub>HPO<sub>4</sub> wherein R is selected from the group consisting of hydrogen, alkyl groups and combinations thereof.

3. The phosphorus-containing solution of claim 2 wherein substantially no free ammonia is present.

4. The phosphorus-containing solution of claim 1 further comprising [X]C<sub>2</sub>H<sub>3</sub>O<sub>2</sub> where C<sub>2</sub>H<sub>3</sub>O<sub>2</sub> is an acetate group and [α] is a cation.

5. The phosphorus-containing solution of claim 4 wherein [X] is selected from the group consisting of potassium, NH<sub>4</sub>, and combinations thereof.

6. The phosphorus-containing solution of claim 1 wherein the pH of the phosphorus-containing solution is between about 6.0 and 8.0.

7. The phosphorus-containing solution of claim 1 wherein Y in [Y]H<sub>2</sub>PO<sub>4</sub> is potassium.

8. The phosphorus-containing solution of claim 1 wherein Y in [Y]<sub>2</sub>HPO<sub>4</sub> is potassium.

9. The phosphorus-containing solution of claim 1 wherein Y in [Y]H<sub>2</sub>PO<sub>4</sub> and [Y]<sub>2</sub>HPO<sub>4</sub> is selected from alkali metals.

10. The phosphorus-containing solution of claim 1 further comprising a dispersant.

11. The phosphorus-containing solution of claim 1 further comprising a target fluid such that the target fluid is operable to bring the phosphorus-containing solution into contact with metal.

12. The phosphorus-containing solution of claim 11 wherein the target fluid is a lubricating fluid.

13. The phosphorus-containing solution of claim 1 wherein the metal substrate comprises at least part of an engine

14. A process for creating a phosphate-metal layer on a metal substrate where the metal substrate is in at least partial contact with a target fluid, the process comprising adding an amount of the phosphorus-containing solution of claim 1 to the target fluid effective to create the phosphate-metal layer, the target fluid combined with the phosphorus-containing solution being brought into contact with the metal substrate such that the phosphate-metal layer results on the metal substrate.

15. The process of claim 14 wherein the phosphorus-containing solution further comprises [NR<sub>4</sub>]<sub>2</sub>HPO<sub>4</sub> wherein R is selected from the group consisting of hydrogen, alkyl groups and combinations thereof.

16. The process of claim 15 wherein the phosphorus-containing solution further comprises NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub> where C<sub>2</sub>H<sub>3</sub>O<sub>2</sub> is an acetate group.

17. The process of claim 16 wherein the pH of the phosphorus-containing solution is between about 6.0 and 8.0.

18. The process of claim 14 wherein the Y in [Y]H<sub>2</sub>PO<sub>4</sub> in the phosphorus-containing solution is potassium.

19. The process of claim 14 wherein the Y in [Y]<sub>2</sub>HPO<sub>4</sub> in the phosphorus-containing solution is potassium.

**20.** The process of claim 14 wherein the target fluid is selected from the group consisting of lubricating fluid or phosphating bath.

**21.** A converted metal substrate including a phosphate-metal layer created by the process of claim 14 forming a conversion surface on a metal substrate.

**22.** The converted metal substrate of claim 21 wherein the metal substrate comprises iron.

**23.** The converted metal substrate of claim 21 wherein the metal substrate comprises a non-ferrous metal.

**24.** The converted metal substrate of claim 23 wherein the non-ferrous metal is aluminum.

**25.** The converted metal substrate of claim 20 wherein the metal substrate is at least part of an engine.

**26.** A lubricating composition comprising

a substantial amount of an oil having a lubricating viscosity, and an amount of the phosphorus-containing solution of claim 1 operable to create a phosphate-metal layer upon a metal component upon being brought into contact with the metal component.

**27.** The lubricating composition of claim 26 wherein phosphorus is present in the lubricating composition in an amount of between about 300 ppm and 1250 ppm.

**28.** A method of lubricating an internal combustion engine, comprising supplying to the engine the lubricating composition of claim 26.

**29.** A method of forming a non-ferrous metal-phosphate conversion surface on a non-ferrous metal components, the method comprising the steps of:

preparing an active phosphorus solution by mixing a phosphorus-containing acid with an alkali metal hydroxide salt and an ammonium/amine compound to create an exothermic reaction thereby producing the active phosphorus-solution; and

contacting the non-ferrous metal component with the active phosphorus solution in a contact region on the non-ferrous metal component to form the non-ferrous metal-phosphate conversion surface on the contact region.

**30.** The method of claim 29 wherein the non-ferrous metal component comprises aluminum.

**31.** The method of claim 30 wherein the non-ferrous metal component comprises at least part of an engine.

**32.** The method of claim 29 wherein the active phosphorus solution is delivered into contact with the non-ferrous metal in a lubricating environment using a lubricating fluid.

**33.** A phosphate-metal layer for aluminum components, the surface comprising:

aluminum phosphate; and

aluminum oxide, the aluminum phosphate and aluminum oxide forming the phosphate-metal layer on an aluminum component, the phosphate-metal layer being formed as a result of contacting the aluminum component with an amount of a phosphorous-containing solution of claim 1 operable to create the phosphate-metal layer.

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