

SPECIFICATION

Phosphate Coating Compositions and Processes

Before subjecting a metal surface to a forming or working operation such as drawing or forging it is common to apply to the surface a lubricant coating generally of organic lubricating agents such as waxes and soaps. It is common to provide a phosphate conversion coating beneath the lubricant coating.

Conventionally the phosphate coating is first formed; the surface is then rinsed, and then the lubricant coating is applied. Instead of applying the coatings by this two step operation it is also known to provide them by a one step procedure in which the phosphate coating and the lubricant coating are formed by application of a single coating composition to the metal surface.

Typical one step methods for forming a combined phosphate and lubricant coating on metal surfaces are described in US Patent Specifications Nos. 2,840,498, 2,850,418 and 3,525,651, and in British Patent Specification No. 1,421,386 and British Patent Application 7937579.

It will be seen from these specifications that it is known to provide the composite coating by contacting the metal surface with an acidic composition containing the conversion coating constituent, i.e. phosphate ions, and emulsified lubricant. The combined coating is formed by contacting the metal surface with the composition and drying the surface.

It has often been proposed that sperm oil should be included in such compositions but in practice this is generally not satisfactory. Instead such compositions generally contain glyceryl monostearate which is present primarily as an emulsifying agent although it may also contribute to the lubricant properties. Although coatings formed using such compositions are reasonably satisfactory the film obtained after drying is not always as dry as would be desired.

Also for optimum results it is necessary to monitor the composition fairly carefully. For instance the thermal stability of some compositions may be such that when the compositions are heated to elevated temperatures for prolonged times the emulsion may break down, partially at least. This may result at least in part from hydrolysis of some of the constituents. Whatever its cause its effect is shown by the presence of an oily layer floating on the surface of the bath.

Another problem with such compositions is that there may be a tendency for the iron content of the composition to build up during use to such an extent that organic constituents in the bath start to agglomerate, the emulsion thus again breaking down.

Another problem with such compositions is that unless care is taken in the drying of the metal surfaces there may be a tendency for rusting of the surfaces to occur during drying.

By the invention we provide new compositions which have, inter alia, the advantage of minimising or overcoming at least one of these problems. Preferred compositions minimise or overcome at least two of the problems, and most preferably all the problems.

An acidic composition according to the invention for forming a phosphate and lubricant coating on a metal surface, optionally after dilution of the composition in water, comprises phosphate ions, emulsified lubricant water, and emulsifying agent selected from oxazoline waxes and N-tallow poly(propylene amine) and mixtures thereof and having a pH at which phosphate coating formation occurs without substantial pickling of the surface.

Such a composition has the advantage that it is capable of giving a dryer coating than many of the prior art compositions.

In another aspect of the invention oxazoline wax is used as part or all of the emulsifying agent. The presence of oxazoline emulsifying agent has been found to impart surprising thermal stability to the emulsified solution, particularly when heated for extended periods of time above 160°F at such temperatures, under the acidic conditions in the solution the organic lubricant additives tend to hydrolyse and demulsify, resulting in a floating oily layer, but the oxazoline emulsifying agent by itself or in combination with supplemental emulsifying agents, especially N-tallow poly(propyleneamine), imparts an unexpected increase in thermal stability to the emulsion at these high temperatures.

According to another aspect of the invention the compositions include a corrosion inhibitor selected from a specific class of organic corrosion inhibiting agents present in an amount sufficient to inhibit corrosion during drying. The corrosion inhibitor is a salt of a C₇₋₁₈ carboxylic acid and an aliphatic amine containing up to 12 carbon atoms. The corrosion inhibitor not only inhibits or prevents rust but also tends to improve stability of the emulsion.

According to another aspect of the invention the composition includes a chelating agent which preferably is ethylene diamine tetraacetic acid or a partial or tetra alkali metal or ammonium salt thereof. The chelating agent tends to increase the stability of the emulsion and, very unexpectedly, inhibits rust or other corrosion and, when the bath contains other corrosion inhibitors, such as those discussed above gives synergistic improvement in corrosion inhibition.

The preferred compositions of the invention contain both corrosion inhibitor and chelating agent.

An acidic coating composition containing phosphate, lubricant and the described emulsifying agent or agents and which has become demulsified due to the presence of dissolved iron may be rejuvenated by adding to the composition the described chelating agent and agitating the composition to restore the emulsion and coating efficiency of the composition.

A process according to the invention for forming a phosphate and lubricant coating on a metal surface comprises contacting a clean metal surface with one of the described compositions, for instance by immersion, flooding, or spraying, for a period of time sufficient to effect formation of the desired thickness of conversion coating and lubricant coating. Generally the time is from 1 to 20 minutes. The coating composition may be applied at temperatures of from 26 to 94°C, preferably 49 to 71°C. The surfaces are then dried to effect substantially complete evaporation of water from the coating, the drying preferably being at temperatures of 121 to 176°C, for instance in a hot circulating air oven.

The solution preferably contains from about 0.2% to about 15% phosphate ions, from about 0.3% to about 16% of emulsified organic lubricant, about 0.1% to about 10% of the emulsifier, water and, if present up to about 5% of the organic corrosion inhibitor agent, and if present from about 0.25 to about 3% of the chelating agent. In accordance with the preferred practice, the phosphate ion concentration ranges from 0.2 to 6%, preferably 1.5% to 6%, the lubricant agent ranges from the 0.5% to 4%, any corrosion inhibitor ranges from 0.5% to 1.5% and any chelating agent ranges from 0.5% to 2% by weight. However if chelating agent is being used to regenerate a bath the amount added may be up to 5%.

Phosphate ion concentrations of less than about 0.2% are generally unsatisfactory because of the excessive time required to form a phosphate coating of the requisite weight while concentrations in excess of about 15% are undesirable because of the tendency of such higher concentrations to cause instability of the emulsion under some circumstances.

The lubricant additive can be employed in amounts of 0.3% to about 16% since amounts less than about 0.3% are undesirable because of insufficient lubricity of the coating for some metal forming operations while amounts in excess of about 16% are unsatisfactory because of the excessive viscosity of the operating bath.

The emulsifying agent should be employed in the amount necessary to emulsify the lubricant constituent present and will vary in the disclosed range in consideration of the concentration of lubricant present.

The corrosion inhibitor, if present, is employed in the operating bath up to about 5%. Amounts of the corrosion inhibitor in excess of about 5% are undesirable because no significant improvement in corrosion inhibition is obtained over that obtained at concentrations of 5% or less and such excessive concentrations contribute toward instability. Amounts of corrosion inhibitor less than about 0.1% are undesirable because they tend not to give a significant advantage.

The composition may additionally contain as optional constituents activating ions of any of the types conventionally employed in phosphate conversion coating solutions and which are

compatible with the other components of the solutions. Of the various activating ions suitable for use, heavy metal cations such as zinc or iron can be employed in amounts sufficient to promote the formation of a phosphate coating to amounts below that at which undesirable bath instability occurs, with amounts of about 0.1% to about 0.2% being typical.

The operating bath may further include compatible pH adjusters to provide the desired pH of the operating bath. Usually, the phosphate ion concentration is controlled so as to provide the satisfactory pH obviating the need for pH adjusting agents.

The operating bath may range in acidity from a lower pH value at which excessive acid pickling begins to occur to an upper pH value at which insufficient bath reactivity begins to occur preventing formation of a satisfactory coating. Usually, a pH ranging from about 2.4 to about 3.4 is satisfactory while a pH of from about 2.8 to about 3.1 is preferred.

The phosphate ion constituent of the bath can be suitably introduced in the form of a concentrated phosphoric acid. Zinc may be suitably introduced as zinc oxide in a concentration of from about 0.1 to about 1% zinc. Preferably, the phosphoric acid and zinc oxide may be precombined to form a zinc acid phosphate which may then be used to supply both zinc and phosphate constituents. The presence of the heavy metal zinc cation is preferred particularly in the preparation of a fresh bath to activate the composition. During use of the coating bath, dissolution of iron from the metal surface occurs further providing iron cations in the coating bath. A portion of the metal cation activators are removed as a result of dragout and are replenished by dissolution of iron from the metal surface as well as by periodic replenishment of the coating bath with a concentrate containing such activators, if desired.

In addition to the heavy metal cations, the bath and concentrate may further contain conventional accelerators and activators as well as pH adjusters of the types and in the concentrations conventionally employed which are compatible with and do not adversely affect the stability of the emulsion. Generally, the inclusion of such supplemental additives is not necessary to achieve satisfactory coating results.

The lubricant constituent of the bath preferably comprises an organic emulsifiable carboxylic acid/or alcohol containing from 8 to 40 carbon atoms as well as esters, mono and polyamine and/or mono and polyalkyl (C_1-C_{14}) amine salts as well as mixtures thereof. The lubricant constituent may be of a saturated or unsaturated form and of a natural or synthetic origin.

Up to 50% of the lubricant present may be N-tallow-1,3-propanediamine dioleate which possesses good film forming properties and acts as a boundary lubricant. This lubricant additive also possesses emulsifying properties and has

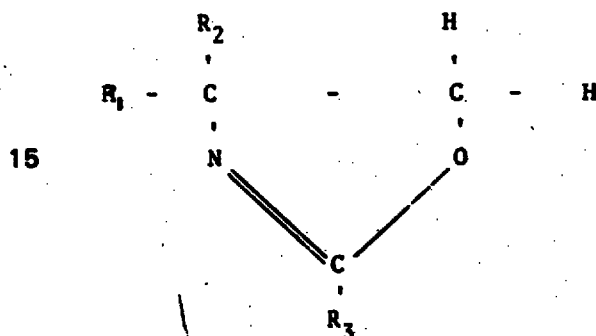
cationic activity further contributing to the provision of a substantially stable emulsion.

- When the solution contains N-tallow polypropylene amine, the material used should be one that has from 1 to 5 propyleneamine groups of a composition corresponding to the following structural formula:



- wherein R is tallow and n is 1 to 5 and mixtures thereof. Preferred materials are those known as N-tallow polypropylene tetramines.

When the solution contains oxazoline waxes as emulsifying agent the materials chosen generally have the formula:



- wherein R_1 , R_2 and R_3 are the same or different and are selected from the group consisting of esters, alcohols, carboxylic acids, and hydrocarbons containing 1 to 36 carbon atoms and R_2 may also be H.

- Examples of such oxazoline compounds in accordance with the foregoing structural formula which are effective and commercially available are sold under the brand designation Wax TS 254, Wax TS 254 A, Wax TS 254 AA, Wax TS 970, Alkaterge E and Alkaterge T from NP Division of IMC Chemical Group, Inc. of Hillside, Illinois.

- When the solution contains a corrosion inhibitor this preferably is a salt of a C_7 - C_{18} carboxylic acid and an aliphatic amine containing up to C_{12} . Preferably it is a salt of an alkanolamine, the salts of octanoic acid with triethanolamine or of stearic acid with triethanolamine being preferred. A corrosion inhibitor of the foregoing type reported to contain 40% triethanolamine octanoate suitable for use in accordance with the present invention is available under the brand designation Synkad 303, which is available from Kell Chemical Division of Ferro Corporation, Indiana, U.S.A., in the form of a solution having a viscosity of 230 SUS, at 37°C, a specific gravity of 1.07 g/ml at 25°C. This commercial corrosion inhibiting agent contains about 30% volatiles and a preferred form designated as Synkad 303 HT of increased concentration is preferably employed. The corrosion inhibiting effect of the described salts on the preferred metal surfaces, namely ferrous surfaces, is surprising in view of the fact that alternative oil soluble corrosion inhibitors have

- been unsatisfactory in similar one step coating solutions since they tend to be ineffective in preventing rusting until such time as substantially all the water phase has been evaporated, and by this time undesirable rusting may often have occurred. Corrosion inhibitors such as amides and imidazolines have also been ineffective at the low operating pH of the solutions or have been found to cause emulsion instability or to inhibit the formation of a satisfactory conversion coating on the metal surface.

- When chelating agent is included the agent is preferably EDTA or a partial or tetra alkali metal and ammonium salt thereof. Other materials may be used, for instance nitrilo triacetic acid or its salts. The chelating agent is used in amounts of about 0.25% up to amounts below that at which emulsion instability of the bath occurs which will vary depending on the types and concentrations of the other constituents present. Usually, concentrations of the chelating agent of up to about 3% by weight can be employed while concentrations of about 0.5 to about 2% are preferred.

- The use of the chelating agent not only enhances the stability of the emulsion even when iron concentrations in the bath attain levels of about 0.2% and greater, but unexpectedly, the chelating agent also imparts corrosion inhibiting properties to the bath in the absence of other corrosion inhibiting agents. Surprisingly, the rust inhibiting action of the optional corrosion inhibiting agent is synergistically enhanced by the inclusion of the chelating agent. Because excessive concentrations of either the corrosion inhibiting agent and the chelating agent cannot be used due to the adverse effects on bath stability, the synergism between these two agents enables the use of compatible concentrations of each constituent attaining a corrosion inhibiting effect unattainable by the use of either agent by itself.

- It has been further discovered in accordance with the present invention, that an operating bath which has become unstable due to the increase in iron concentration as a result of use can be rejuvenated and restored to stability with agitation by the addition of a controlled effective amount of the chelating agent. It has also been observed in some instances that the inclusion of the chelating agent of the present invention appears to increase the rate of drying of the metal surfaces during the drying stage thereby providing still further benefits by the savings achieved in time and energy.

- A working bath of the solution may be prepared employing a concentrated solution of the constituents within the permissible upper concentration limits which is suitable after dilution with water to form an operating bath of the desired lower concentration. While such a concentrated solution can itself be employed as the operating bath in some situations, the relatively high viscosity of such concentrates makes it desirable to dilute them with water to

produce an operating bath within the preferred concentration ranges as hereinbefore set forth.

- 5 A concentrate suitable for further dilution with water can be conveniently prepared by mixing the lubricating agent and emulsifying agent and heating the mixture to form a molten mass. A hot aqueous solution is prepared containing the phosphate ions and supplemental optional aqueous soluble constituents to which the molten organic mixture is slowly added in the presence of vigorous agitation effecting a dispersion of the organic phase into globules forming an emulsion. The aqueous phosphate solution is preferably heated within a range of about 71 up to about 15 94°C and maintained within that range during the addition of the organic mixture. The resultant emulsified concentrate is thereafter cooled. The emulsifying agent can instead be added directly to the heated aqueous phosphate solution.
- 20 whereafter the molten lubricant additive is added in the presence of agitation.

- The resultant concentrate can be directly employed or can be further diluted with water to prepare an operating bath by the addition of appropriate quantities of water to provide the 25 desired final concentration. The resultant bath is preferably heated to an elevated temperature during use to increase the activity and formation of the phosphate conversion coating. The emulsified particles of lubricant in the concentrate 30 may solidify depending on their specific melting point during the cooling of the concentrate. Such solid particles nevertheless remain dispersed in the aqueous phase. Upon subsequent heating of the coating bath, certain of the particles 35 depending upon their melting point may again become molten. The specific form of the particles as liquid globules or solid particles is immaterial to the formation of a satisfactory lubricant coating on the metal surfaces.
- 40

- The operating bath can be employed at temperatures ranging from ambient temperature up to about 94°C with temperatures of from about 49 to about 71°C being particularly 45 satisfactory. The coating bath composition can be applied to the metal surface by flooding, immersion, spraying, and the like, so as to provide intimate contact therebetween. The duration of the contact time will vary depending upon the 50 composition of the coating composition, the concentration thereof, the temperature of application, and the desired coating weight required in consideration of the severity of the metal forming operations to which the articles are 55 to be subjected. Ordinarily, contact times employing an immersion technique of from about one minute up to about twenty minutes is satisfactory. The coating formed comprises a phosphate coating having lubricant particles 60 included therein or deposited thereon.

- The coated article at the conclusion of the contact time is subjected to a drying stage prior to metal forming. The drying step can be 65 accomplished at temperatures ranging from ambient temperature up to about 176°C with

temperatures of from about 121°C to about 176°C being preferred due to the accelerated drying rate obtained. During the drying step at elevated temperature, the lubricant particles may 70 coalesce into a film. Such coalescence, however, is not important in achieving satisfactory lubricant coatings in that solid particles dispersed in or on the phosphate coating also provide for satisfactory lubricity during subsequent metal 75 working operations.

- The metal articles prior to the coating operation are subjected, if necessary, to conventional precleaning treatments to remove contaminating substances and scale from the 80 surfaces thereof providing for a clean surface.

The following are some examples of the invention.

Example 1

- A concentrate is prepared containing 2.6% zinc 85 acid phosphate (14% zinc, 48% PO_4), 5.6% phosphoric acid (75%), 2.0% N-tallow polypropylene tetramine emulsifying agent, commercially available under the brand name Jet Amine Tet from Jetco Chemicals, Inc. of Texas; 90 and as a lubricating agent, a mixture of high molecular weight constituents present in an amount based on the total concentrate of 2.9% stearic acid (95% C_{18}), 2.5% of partially oxidized high molecular weight acids, esters and alcohols 95 commercially available under the brand name Alox 600 from Alox Corporation and 2.0% N-tallow, 1,3 propanediamine dioleate, commercially available under the brand name Duomeen TDO from Armac Chemicals Div. of 100 Akzona Incorporated of Chicago, Illinois, and the remainder water. The concentrate is employed to make up an operating bath by dilution with water at a ratio of one volume concentrate for one volume water. The resultant operating bath is 105 heated to a temperature of 76°C.

- The heated bath may be used for coating steel work pieces. For instance cold rolled steel unpolished panels of a size 3"x4" are cleaned by immersion for a period of five minutes in an 110 aqueous cleaning solution at a temperature of 82°C whereafter the panels are water rinsed for one minute. The panels are thereafter immersed in the operating bath for a period of ten minutes and then dried.

- 115 In one process, upon extraction from the bath, a pair of the wet coated panels are placed in face to face overlying relationship in a horizontal position and are placed in an oven at 80°C for a period of one hour. After the one hour drying phase, the facing surfaces of the test panels are 120 examined for rust. An inspection of the test specimens reveals an area of about 10 to 20% of red rust on the two facing surfaces but a good coating on the surfaces that had been dried 125 quicker.

If the heated bath is employed for processing steel work pieces during prolonged use of the bath there is a tendency for the concentration of iron dissolved from the processed work pieces to

increase attaining a level of about 0.2% by weight. An inspection of the bath indicates that the organic constituents in the bath start to agglomerate forming larger particles which eventually demulsify.

Example 2

A concentrate and operating bath similar to that of Example 1 is prepared with the exception that 2% by weight of a chelating agent comprising tetrasodiummethylenediaminetetraacetate is added to the concentrate producing a net 1% by weight concentration in the operating bath. The operating bath is employed for processing steel work pieces in a manner as described in Example 1 and it is observed that when the dissolved iron concentration approaches a concentration in the operating bath of about 0.2%, no agglomeration of the organic constituents is evident and no demulsification of the bath occurs.

Example 3

An operating bath of a composition similar to that described in Example 1, but further including about 1% by weight of a rust inhibiting agent comprising Synkad 303 containing triethanolamine octanoate is employed in a trial production run for applying a lubricant coating to steel tubing to facilitate subsequent drawing. After a prolonged trial run, the iron concentration in the operating bath increases as a result of dissolving iron from the tubes being processed. Agglomeration and demulsification of the bath is also evidenced. The lubricant coating produced on the tubes processed in the aged bath provides less than desirable drawing characteristics and also produce rusting of the tube bundles at their points of contact during the drying stage of the tubes, evidencing a loss of effectiveness of the rust inhibiting agent. The addition of 1% by weight of tetrasodiummethylenediaminetetraacetate to the operating bath is in the presence of agitation effects a rejuvenation of the bath as evidenced by improved drawing characteristics of the processed steel tubing and the substantial elimination of rusting of the tubes during the drying stage. The rejuvenated bath containing the chelating agent also exhibits surprising increase in the rate of drying of the tubing during the drying state.

Example 4

A laboratory sample of the aged and demulsified operating bath as described in Example 3 is subjected to agitation by stirring at room temperature. Upon cessation of agitation, the bath sample again separates rapidly. The addition of an equivalent of 1% by weight of tetrasodiummethylenediaminetetraacetate to the bath sample with stirring effects a remulsification of the test sample. Upon cessation of stirring, the bath sample remains emulsified without significant separation for a period of about 48 hours.

Example 5

Two laboratory batch operating baths are prepared designated Sample A, corresponding to the composition Example 1 and Sample B of similar composition but also containing an equivalent of 1% by weight of tetrasodiummethylenediaminetetraacetate. Samples A and B are heated to 150°F and are artificially aged by sequentially immersing 20 steel wool pads (000 grade steel wool each weighing 30-grams), for one hour each. Sample A, comprising the control devoid of any chelating agent undergoes demulsification due to the high dissolved iron concentration. In contrast, Sample B prepared in accordance with the practice of the present invention, remains as a uniform stable emulsion.

Example 6

Fresh laboratory batch operating baths without artificial aging corresponding to Samples A and B of Example 5 are prepared for comparison purposes. Cold rolled steel unpolished panels of a size 3" x 4" are cleaned by immersion for a period of five minutes in an aqueous cleaning solution at a temperature of 180°F whereafter the panels are water rinsed for one minute. The panels are thereafter immersed in Sample Bath A and Sample Bath B, heated to a temperature of about 71 to about 76°C for a period of ten minutes. Upon extraction from each bath, a pair of the wet coated panels are placed in face to face overlying relationship in a horizontal position and are placed in an oven at 80°C for a period of one hour. After the one hour drying stage, the facing surfaces of the test panels are examined for rust. An inspection of the test panels treated in Sample A reveals an area of about 30% of rust on the two facing surfaces. An inspection of the test panels treated in Sample B reveals an area of rust of less than about 2% on the two facing surfaces.

Example 7

The operating bath as described in Example 1 is modified in accordance with the practice of the present invention by the addition of $\frac{1}{2}$ gram per litre of a corrosion inhibiting agent consisting of triethanolamine octanoate produced by the neutralisation reaction between $\frac{1}{2}$ gram triethanolamine and $\frac{1}{2}$ gram octanoic acid and a second set of panels is processed in the same manner as previously described. An examination of the facing surfaces of the panels after a period of one hour drying in the oven reveals substantially no rust on the facing surfaces. A series of supplemental panels processed under the same processing cycle as hereinabove described employing the bath composition of the present invention reveals substantially no rusting on the facing surfaces with the areas of the opposed faces exhibiting zero up to 2% rust.

Example 8

An operating bath is prepared employing the concentrate as described in Example 1, devoid of

any corrosion inhibiting agent. The operating bath is prepared by adding 60 gallons of the concentrate to 340 galls of water and thereafter heating the bath to 71°C.

- 5 A bundle of about 250 type 5048 alloy tubes having a diameter of 0.5", a wall thickness of 0.019" and a length of 12' are precleaned by subjecting them to a ten minute immersion in a 10% sulphuric acid pickling solution, followed by
10 a one minute cold water rinse and a second one minute cold water rinse. The cleaned tubes in a bundle are thereafter subjected to two dips in the operating bath, each for a duration of two minutes whereafter they are drawn and placed in a tube dryer at a temperature of 162°C for a period of
15 two hours. An inspection of the tubes at the completion of the drying cycle reveals the formation of rust along the contacting surfaces of the adjacent tubes.

20 Example 9

- The operating bath as described in Example 8 is modified in accordance with the present invention by adding about seven gallons of the triethanolamine octanoate corrosion inhibiting
25 agent in the form of ten gallons of Synkad 303 (70%) whereafter subsequent bundles of tubes were processed employing the cycle as hereinabove described. An inspection of the tubes after the drying cycle employing the operating
30 bath of the present invention shows no signs of rust. The foregoing operating bath is employed for processing several thousand tubes over a period of three weeks with no signs of rust on the tubes treated or instability of the operating bath.

35 Example 10

- A concentrate is prepared containing 43.9 g of an aqueous solution containing 10% by weight zinc and 34.4% by weight phosphate ions, 65.5 g of 75% phosphoric acid, 825.6 g water, 25 g of
40 Alox 600 (as defined in Example 1), 29 g of stearic acid (95% C₁₈), and 40 g of N-tallow polypropylene tetramine emulsifying agent (Jet Amine TET). The concentrate is diluted with 75% by volume water and 28 g of a corrosion
45 inhibiting agent consisting of triethanolamine octanoate are added.

- The operating bath provides satisfactory lubricant coatings without any significant rusting on the coated parts. The operating bath is
50 subjected to an accelerated thermal stability test by heating to 71°C without agitation for a period of eight days and remains stable incurring only minimal hydrolysis of the organic constituents.

Example 11

- 55 A series of operating baths is prepared of a composition corresponding to that of Example 7 with the exception that the 2% N-tallow 1,3 propanediamine dioleate is omitted and a corresponding amount of an oxazoline compound
60 is substituted in the concentrate for the purpose of providing improved thermal stability to the operating bath. The series of baths comprises

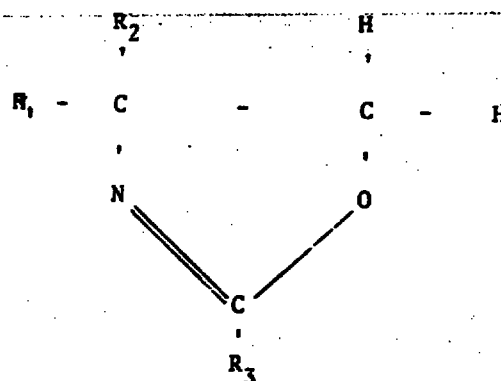
- bath A containing Wax TS-254, bath B containing Wax TS—254AA, bath C containing Wax TS—
65 970, bath D containing Alkaterge E, and bath E containing Alkaterge T. The baths A—E and a sample of the bath of Example 2 are subjected to accelerated thermal stability tests by heating them without agitation to a temperature of 71°C
70 and maintaining them at that temperature. The bath of Example 7 comprising the control is observed at the end of two days to have a thick oily layer floating on the top surface evidencing hydrolysis of the organic constituents therein and
75 a loss of stability. In comparison, baths A—E remained stable under these same conditions for at least 4 days.

Example 12

- A series of operating baths is prepared similar
80 to Example 11 with the exception that the corrosion inhibiting agent triethanolamine octanoate is omitted from the concentrate. Similar improvements in the thermal stability of the test baths are obtained.

85 Claims

1. An acidic composition for forming a phosphate and lubricant coating on a metal surface, optionally after dilution of the composition in water, and which comprises
90 phosphate ions, emulsified lubricant, water and an emulsifying agent selected from oxazoline waxes and N-tallow polypropyleneamine and mixtures thereof, and having a pH at which phosphate coating formation occurs without
95 substantial pickling of the surface.
2. A composition according to claim 1 in which the emulsifying agent comprises an oxazoline wax.
3. A composition according to claim 2 in which
100 the oxazoline wax has the formula



- wherein R₁, R₂ and R₃ are the same or different and are selected from the group consisting of esters, alcohols, carboxylic acids and
105 hydrocarbons containing 1 to 36 carbon atoms and R₂ may also be H.

4. A composition according to any preceding claim including a corrosion inhibitor which is a salt of a C₇₋₁₈ carboxylic acid and aliphatic amine
110 containing up to C₁₂.

5. A composition according to claim 4 in which the aliphatic amine is an alkanolamine.



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any corrosion inhibiting agent. The operating bath is prepared by adding 60 gallons of the concentrate to 340 galls of water and thereafter heating the bath to 71°C.

- 5 A bundle of about 250 type 5048 alloy tubes having a diameter of 0.5", a wall thickness of 0.019" and a length of 12' are precleaned by
10 subjecting them to a ten minute immersion in a 10% sulphuric acid pickling solution, followed by a one minute cold water rinse and a second one
15 minute cold water rinse. The cleaned tubes in a bundle are thereafter subjected to two dips in the operating bath, each for a duration of two minutes whereafter they are drawn and placed in a tube
20 dryer at a temperature of 162°C for a period of two hours. An inspection of the tubes at the completion of the drying cycle reveals the formation of rust along the contacting surfaces of the adjacent tubes.

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45 inhibiting agent consisting of triethanolamine octanoate are added.

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Example 11

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60 is substituted in the concentrate for the purpose of providing improved thermal stability to the operating bath. The series of baths comprises

- bath A containing Wax TS-254, bath B containing Wax TS-254AA, bath C containing Wax TS-
65 970, bath D containing Alkaterge E, and bath E containing Alkaterge T. The baths A-E and a sample of the bath of Example 2 are subjected to accelerated thermal stability tests by heating them without agitation to a temperature of 71°C
70 and maintaining them at that temperature. The bath of Example 7 comprising the control is observed at the end of two days to have a thick oily layer floating on the top surface evidencing hydrolysis of the organic constituents therein and
75 a loss of stability. In comparison, baths A-E remained stable under these same conditions for at least 4 days.

Example 12

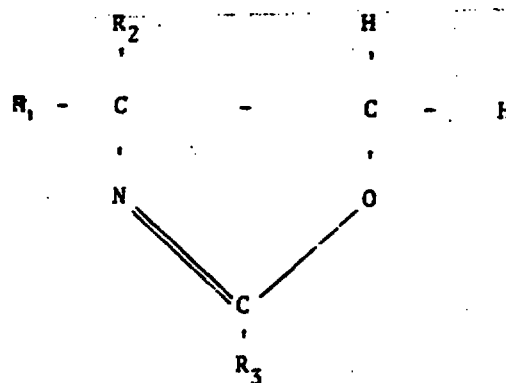
- A series of operating baths is prepared similar
80 to Example 11 with the exception that the corrosion inhibiting agent triethanolamine octanoate is omitted from the concentrate. Similar improvements in the thermal stability of the test baths are obtained.

85 Claims

1. An acidic composition for forming a phosphate and lubricant coating on a metal surface, optionally after dilution of the composition in water, and which comprises
90 phosphate ions, emulsified lubricant, water and an emulsifying agent selected from oxazoline waxes and N-tallow polypropyleneamine and mixtures thereof, and having a pH at which phosphate coating formation occurs without
95 substantial pickling of the surface.

2. A composition according to claim 1 in which the emulsifying agent comprises an oxazoline wax.

3. A composition according to claim 2 in which
100 the oxazoline wax has the formula



wherein R₁, R₂ and R₃ are the same or different and are selected from the group consisting of esters, alcohols, carboxylic acids and
105 hydrocarbons containing 1 to 36 carbon atoms and R₂ may also be H.

4. A composition according to any preceding claim including a corrosion inhibitor which is a salt of a C₇₋₁₈ carboxylic acid and aliphatic amine containing up to C₁₂.

5. A composition according to claim 4 in which the aliphatic amine is an alkanolamine.



6. A composition according to claim 5 in which the amine is triethanolamine.
7. A composition according to claim 6 in which the corrosion inhibitor is a salt of octanoic acid and triethanolamine.
8. A composition according to claim 6 in which the corrosion inhibitor is a salt of stearic acid and triethanolamine.
9. A composition according to any preceding claim comprising a chelating agent.
10. A composition according to claim 9 in which the chelating agent comprises ethylenediaminetetraacetic acid or a partial or tetra alkali metal or ammonium salt thereof.
11. A composition according to any preceding claim containing 0.2 to 15% phosphate ion, 0.3 to 16% emulsified lubricant selected from C_8 to C_{40} carboxylic acids and alcohols including the esters, mono and polyamide salts, mono and polyalkyl (C_1 — C_{18}) amine salts thereof as well as mixtures thereof, and 0.1 to 10% of emulsifying agent and optionally 0.1 to 5% of a corrosion inhibitor which is a salt of a C_{7-18} carboxylic acid and aliphatic amine containing up to C_{12} and optionally 0.25 to 3% of a chelating agent.
12. A composition according to claim 2 or claim 3 comprising 0.2 to 6% phosphate ion, 0.3 to 16% emulsified lubricant selected from C_8 to C_{40} carboxylic acids and alcohols including the esters, mono and polyamide salts, mono and polyalkyl (C_1 — C_{18}) amine salts thereof as well as mixtures thereof and 0.1 to 10% emulsifying agent selected from oxazoline waxes and N-tallow polypropylene tetramine.
13. A composition according to any of claims 1 to 8 comprising 0.2 to 6% phosphate ion, 0.3 to 16% emulsified lubricant selected from C_8 to C_{40} carboxylic acids and alcohols including the esters, mono and polyamide salts, mono and polyalkyl (C_1 — C_{18}) amine salts thereof as well as mixtures thereof and 0.1 to 10% emulsifying agent selected from oxazoline waxes and N-tallow polypropylene tetramine and 0.1 to 5% of a corrosion inhibitor which is a salt of a C_{7-18} carboxylic acid and aliphatic amine containing up to C_{12} .
14. A composition according to any of claims 4 to 8 containing 1.5 to 6% phosphate ion, 2 to 6% of the lubricant, 0.5 to 4% of the emulsifying agent and 0.5 to 1.5% of the corrosion inhibitor.
15. A composition according to claim 1 containing 0.2 to 6% phosphate ion, 0.3 to 16% emulsified lubricant selected from C_8 to C_{40} carboxylic acids and alcohols including the esters, mono and polyamide salts, mono and polyalkyl (C_1 — C_{18}) amine salts thereof as well as mixtures thereof, 0.1 to 10% emulsifying agent selected from oxazoline waxes and N-tallow polypropylene tetramine and 0.25 to 5% of a chelating agent which comprises ethylenediaminetetraacetic acid or a partial or tetra alkali metal or ammonium salt thereof.
16. A composition according to claim 9 or claim 10 containing 1.5 to 6% phosphate ions, 2 to 6% of the lubricant, 0.5 to 4% of the emulsifier and 0.5 to 2% of the chelating agent.
17. A composition according to claim 15 or claim 16 additionally comprising 0.1 to 5% of a corrosion inhibitor comprising a salt of a C_{7-18} carboxylic acid and an aliphatic amine containing up to C_{12} .
18. A composition according to any preceding claim in which up to 50% of the lubricant is N-tallow-1,3-propanediaminedioleate.
19. A composition according to any preceding claim additionally containing zinc and/or iron ions.
20. A composition according to any preceding claim in which the major portion of the lubricant is formed of C_8 to C_{24} constituents.
21. A composition according to any preceding claim in which the pH is from 2.4 to 3.4.
22. A composition according to claim 22 in which the pH is from 2.8 to 3.1.
23. A composition according to claim 1 substantially as herein described.
24. A method of forming a phosphate and lubricant coating on a metal surface comprising contacting the surface with a composition according to any preceding claim and drying the resultant coating.
25. A method of rejuvenating a used composition according to any of claims 1 to 8 and which has become demulsified due to the presence of dissolved iron, the method comprising mixing into the composition a chelating agent.
26. A method according to claim 25 comprising mixing into the composition 0.25 to 5% of ethylenediaminetetra-acetic acid or a partial or tetra alkali metal or ammonium salt thereof.