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METAL TREATMENT

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The present invention relates to the treatment of metal surfaces, particularly for improving the characteristics for cold working.

Among the objects of the present invention is the provision of novel metal treatments, and treating baths that are particularly simple to use and highly effective.

Additional objects of the present invention include the provision of coated metal that is readily cold formed and/or painted.

The above as well as further objects of the present invention will be more clearly understood from the following description of several of its exemplifications.

According to the present invention a very effective coating composition consists essentially of a hydrophilic organic compound having from 12 to 30 carbon atoms in a connected group, about 0 to 90% by weight of a substantially non-volatile organic metal lubricant, about 1% to 15% water by weight and 2.5 to 25% by weight of an acid selected from the class consisting of phosphoric and phosphorous acids, said water and said acid being dissolved in the organic material, and the preparation being a stable single phase liquid at a temperature at least as low as 80° C.

The hydrophilic material can be an amide of fatty acids and/or resin acids, the amide being substituted either on the amine group or elsewhere with hydrophilic radicals of the class consisting of hydroxy, methoxy, ethoxy, amine and imine radicals, and there being a total of at least three of said hydrophilic radicals per 12 to 30 carbon group. Amines of compounds having the above carbon chains are also suitable. Where the hydrophilic radicals are amines or imines, best results are obtained if they are unsubstituted or if substituted, at least one of the substituents has a carbon chain no more than four carbons in length. Preferred amides are those formed by condensing in substantially equimolar proportions fatty acids having twelve to twenty-two carbon atoms per molecule, and polyalkylene polyamines of alkyl groups having no more than four carbon atoms per group. Such amides can also be made by reacting the above polyalkylene polyamines with esters of the above acids. Glycerine tri-fatty acid esters, represented by the natural fats and oils, readily react by heating a mixture of the reactants at 210 to 220° F., to form the amides and glycerine. If the quantity of amine used is less than that required to completely convert the fat to the amides, then glycerine mono- and di-fatty acid esters are formed along with the amide. These mono- and di-esters act as hydrophilic additives and assist in securing homogeneous compositions. Methyl, ethyl and other low alkyl esters of fatty acids also react in the desired manner.

A feature of the present invention is that the above preparations are quite stable. They can for example

be kept at temperatures as high as 200° F. without appreciable loss by volatilization or chemical change. When the preparation is applied to the surface of reactive metal, such as iron, it will react with the surface of the metal to form an adherent layer of a metal phosphate complex which in combination with the balance of the applied mixture, makes an exceedingly effective and tightly bonded lubricant coating. Both the water and the phosphoric acid are dissolved in the remaining material of the mixture and there is accordingly no tendency for an aqueous component to settle out on standing. Furthermore, because of its dissolved condition, the water does not evaporate very readily from the mixture. Similar mixtures in which water is present as a separate phase or as a continuous phase, show much higher water vapor pressures and undergo rapid water loss, particularly at elevated temperatures. In addition, contact of the metal with a two-phase system causes the phosphate formation to take place in a spotty manner, whereas a single-phase system provides uniform distribution of the reactive ingredients over the entire surface being treated, thus resulting in a uniform deposition of the metal phosphate complex.

A minimum of 1% water should be used as pointed out above, since without this water the phosphoric acid in the formulation does not attack the metal. At least about 5% phosphoric acid is preferably present when only 1% of water is used, since the phosphating of the metal is a little slow otherwise. At about 4% or more water content the metal attack is quite rapid over the entire range of said concentrations. A 4% or larger water content is more readily obtained if the coating preparation includes such coupling agents as an alkylene glycol, an alkylene glycol ether and/or a fatty acid. From 2 to 15% of an alkylene glycol or alkylene glycol ether having a chain of from 3 to 8 carbon atoms per molecule is quite effective, as is from 2 to 15% fatty acid. Some of these alkylene glycol ethers are quite volatile and are accordingly not preferred in high temperature applications. Also these ethers as well as the glycols themselves are not very good metal lubricants and reduce the lubricating effect of the formulation unless kept down to not over about 10% in concentration. It should be noted that the amides described above are in themselves very good metal lubricants.

The coating preparation of the present invention can accordingly be very effectively used as a bath in which metal articles are immersed, removed and then subjected to the desired cold working operations. The bath will remain substantially uniform in composition and effectiveness, even though it is kept at a temperature as high as 200° F. for periods of a day or more. The reaction of the metal with the phosphoric acid is generally sufficiently complete in about one or two minutes, but the dwell of metal in the bath can be made short enough so that the principal result is to cause the coating preparation to coat the immersed surface. After the immersed articles are removed, the desired coating is obtained upon standing a minute or so to permit the phosphoric acid to develop the desired amount of metal phosphate complex. The period of immersion in the bath, or the contact time with application rolls, brush, spray, etc., need not be more than a few seconds or less, since the applied film carries the reactive ingredients which form the metal phosphate complex coating. If, however, an extremely difficult operation is to be performed, a longer period in the treating bath will result in the formation of a heavier metal phosphate complex coating.

A preferred formulation of the coating preparation of the present invention is as follows, all percentages being by weight:

Example I

49.6% partial fatty amide formed by heating 152 parts of tallow (free fatty acid, 3% maximum) together with 13 parts of diethylene triamine at 210° F.–220° F. for three hours.
3.3% oleic acid.
7.4% water.
10.1% orthophosphoric acid, 75% commercial grade.
3.3% paraffin wax, melting point 124–126° F.
4.0% hexylene glycol.
9.3% methyl ester of pigskin oil fatty acids.
13.0% mineral oil, 100 Saybolt Universal seconds at 100° F.

100.0%

The above ingredients are very readily blended in the liquid state to form a single phase liquid of fairly low viscosity.

Other examples of composition of the present invention are as follows (all proportions are by weight):

Example II

30.0% lard oil.
25.0% fatty amide prepared by heating one mole of oleic acid (282 parts) together with one mole of diethanolamine (105 parts) until the acidity (as oleic acid) is less than 5%.
7.0% orthophosphoric acid, 85% commercial grade.
1.0% water.
6.0% oleic acid.
6.0% hexylene glycol.
25.0% paraffinic mineral oil, 225 Saybolt Universal seconds at 210° F.

100.0%

Example III

20.0% fatty amide prepared by reacting 284 parts of stearic acid with 105 parts diethanolamine at 300° F. until the acidity (as stearic acid) is less than 5%.
50.0% paraffinic mineral oil (100 Saybolt Universal seconds at 100° F.).
10.0% oleic acid.
10.0% hexylene glycol.
8.0% orthophosphoric acid, 75%.
2.0% water.

100.0%

This composition is a clear liquid above about 100° F., and a pasty solid at room temperature (70°–80° F.). As much as 6 additional parts of water can be added to accelerate coating formation and still maintain the single phase composition.

Example IV

19.4% fatty amide (as in Example III).
29.1% No. 1 lard oil.
24.3% paraffinic mineral oil (100 Saybolt Universal seconds at 100° F.).
9.7% oleic acid.
9.7% hexylene glycol.
6.8% orthophosphoric acid, 85%.
1.0% water.

100.0%

This composition is a clear liquid above about 115° F., and a pasty solid at room temperature (70° F.–80° F.).

Example V

48.1% fatty amide prepared by reacting 282 parts of oleic acid with 105 parts of diethanolamine at 300° F. to 310° F. until the acidity (as oleic acid) is less than 5%.
38.5% No. 1 lard oil.
9.6% orthophosphoric acid, 75%.
3.8% water.

100.0%

This composition is a clear viscous liquid at room temperature (70° F.–80° F.), becoming more fluid with increasing temperature.

Example VI

15.1% fatty amide prepared by reacting 284 parts of stearic acid with 105 parts diethanolamine at 300° F. until the acidity (as stearic acid) is less than 5%.
8.6% palm oil.
51.3% paraffinic mineral oil, 100 Saybolt Universal seconds at 100° F.
6.1% orthophosphoric acid, 85%.
3.4% water.
7.8% hexylene glycol.
7.7% oleic acid.

100.0%

This composition is a clear liquid at a temperature above about 95° F. and a pasty solid at room temperature (70° F.–80° F.).

Example VII

30.0% raw linseed oil partial amide prepared by heating 100 parts of raw linseed oil with 8.4 parts of diethylene triamine at 200° F. for 3 hours.
40.0% raw linseed oil.
10.0% oleic acid.
10.0% hexylene glycol.
7.1% orthophosphoric acid, 85%.
2.9% water.

100.0%

This composition is a clear liquid. Addition of small quantities (0.1% to 0.5%) of dryer (such as cobalt linoleate) will accelerate the hardening of the deposited film.

Example VIII

72.7% fatty amide prepared by reacting 282 parts of oleic acid with 105 parts of diethanolamine at 300° F. to 310° F. until the acidity (as oleic acid) is less than 5%.
17.7% orthophosphoric acid, 85%.
7.3% hexylene glycol.
2.3% water.

100.0%

This composition is a clear liquid at room temperature.

Example IX

33.9% fatty amide prepared by reacting 284 parts of stearic acid with 105 parts diethanolamine at 300° F. until the acidity (as stearic acid) is less than 5%.
30.3% No. 1 lard oil.
8.1% oleic acid.
8.4% phosphorous acid, 70%.
11.2% water.

100.0%

Example X

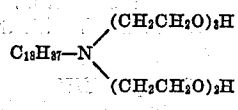
28.6% raw linseed oil partial amide prepared by heating 100 parts of raw linseed oil with 8.4 parts of diethylene triamine at 200° F. for 3 hours.
42.8% castor oil.
12.6% orthophosphoric acid, 85%.
14.3% hexylene glycol.
1.7% water.

100.0%

This composition is a clear liquid at room temperature.

Example XI

20.4% Ethomeen 18/15 (Armour and Co.) which has the composition



where the $C_{18}H_{37}$ is n-stearyl
44.0% paraffinic mineral oil (100 Saybolt Universal seconds at 100° F.).
10.6% orthophosphoric acid, 75%.
2.0% water.
10.2% oleic acid.
12.8% hexylene glycol.

100.0%

This composition is a clear liquid at room temperature.

The important ingredients of the above compositions of Examples I to XI are the fatty amide or amine, either of which makes a good lubricant carrier, a good lubricant by itself, is miscible with the other lubricants, and makes possible the solution of water and phosphoric acid in the mixture without separation. Any oil such as mineral oil, or fatty oils such as tallow, lard oil, palm oil, palm kernel oil, mustard seed oil and peanut oil can be used as a supplemental lubricant, and sharply reduce the frictional resistance to surface forming operations. Drying or semi-drying oils such as linseed oil, tung oil and soya bean oil may be used in the lubricant portion to obtain relatively hard, dry, tenacious films such as may be desired for extremely severe cold working operations. Rosin amine such as that prepared by hydrogenating the nitrile of rosin (abietic acid) is also a good supplemental lubricant.

The hydrophilic amide can be formed of any fatty acid and/or resin acid. The group of 12 to 30 carbon atoms can be in one unbranched chain, as in the fatty acids, or in fused rings, as in a resin acid such as abietic acid. They can also be in branched chains as in betaethyl decanoic acid, or in combinations of chains and rings as in alphanaphthyl acetic acid. It appears that the acid should have a strongly lyophilic character which it does not develop unless the appropriate number of carbon atoms are linked directly to each other as a group. Linkages by way of oxygen, sulfur, nitrogen, or the like are not effective for this purpose. These acids can be saturated or unsaturated, as for example stearic acid, oleic acid, palmitic acid, linoleic acid, fully hydrogenated pimaric acid and even omegacarboxy stearic acid. The most desirable commercial acids are those containing 16 or 18 carbon atoms. The preferred compositions have 10 to 40% of the polyalkylene polyamine reaction products of these acids with 30 to 80% of an organic oily lubricant, 4 to 15% water and 5 to 20% phosphoric acid, all percentages being by weight.

The acids are condensed with amines as pointed out above, and the condensation is carried out so that the product contains at least 3 hydrophilic radicals per molecule. This appears to be essential in order to have the desired amount of water dissolved in the coating preparation. Amines suitable for condensation in accordance

with the present invention include in addition to those of the above example, triethylenetetramine; dipropylene triamine; tri(hydroxy methyl) methylamine; 2-methyl-2-amino-1,3-propandiol; 2-propyl-2-amino-1,3-propandiol; N-hydroxyethyl ethylenediamine, N-hydroxyethyl diethylenetriamine; N,N,N'-trihydroxyethyl ethylenediamine; dibutanolamine; diisopropanolamine; tetraethylene pentamine; phenyl diethanolamine; N-(2-hydroxypropyl) ethylenediamine; and triglycolamine

$(H_2NC_2H_4OC_2H_4OC_2H_4NH_2)$

The Ethomeen of Example XI is not as effective a water carrier as the amides. Relatively large proportions of fatty acid and glycol or glycol ether are needed in formulations relying on such a carrier.

Similar materials such as polyethoxylated fatty alcohols (alcohols prepared by reducing esters of C_{18} acids with sodium and methyl isobutyl carbinol), as for example that formed by condensing one mole of alcohols corresponding to tallow fatty acids, with 6 moles of ethylene oxide, will also provide mixtures that dissolve the appropriate amount of water but such mixtures will not be as stable as the fatty acid amides and undergo deterioration at temperatures of 60° C. or higher. In general, a chain of alkoxy groups is equivalent to half as many separate alkoxy groups in providing hydrophilic qualities.

As in Example I, the coating preparations of the present invention can contain an appreciable amount, up to 20% of paraffin or fat that is solid at 80° F. Hydrogenated fat or oil, or petroleum, natural or synthetic waxes can be so used. In addition, low viscosity additives, such as the methyl ester of Example I, help to lower the viscosity, and to thereby facilitate the application of the coating. Relatively low viscosity mineral oil can be used for the same reason. It is also preferred that about half the lubricant be fatty material as against hydrocarbon lubricant.

The amount of phosphoric acid as specified above, refers to the total phosphoric acid. Where the preparation includes basic groups such as amine and amide radicals in the fatty amine or amide, some of the phosphoric acid will be bound up by salt formation. The bound-up portion does not contribute any amount of free phosphoric acid and will in general not cause any significant phosphate-forming reaction with the metal if the water content is less than about 4%. However, the amine-phosphate generally undergoes some hydrolysis, particularly where the coating mixture has a water content in the high end of the range. The phosphoric acid so released by this hydrolysis will not produce coatings of sufficient magnitude to be of practical importance, and can accordingly be neglected. Metaphosphoric acid and pyrophosphoric acid can be used instead of orthophosphoric acid, but they gradually combine with some of the water in the bath during this conversion. This bound-up water is not effective in contributing any of the desired final water content. However, most commercial grades of phosphoric acid contain some water which should be taken into account in the formulation. Phosphorous acid can be substituted for part or all of the phosphoric acid in these compositions.

Best results are obtained with the above coating preparations when applied in an amount of at least about 400 milligrams per square foot of metal surface. Such an application will cause, with iron, aluminum, zinc or similar metals, development of at least about 40 milligrams per square foot of metal phosphate complex which provides a tenacious bonding medium for the organic portion of the composition. If the metal surface is subjected to a degreasing operation, such as exposure to vapors of condensing trichlorethylene, most, but not all of the organic coating is removed, the remainder being the solvent insoluble metal phosphate complex which contains some of the organic material. This bound-up residual organic material cannot be entirely removed by solvent

degreasing; the complex phosphate must first be decomposed chemically to release the organic material. Degreased coatings of 40 to as much as 2500 milligrams per square foot are highly effective for even severe cold working and also give good corrosion resistance. Furthermore, the degreased surface, before or after working, can be directly painted without removal of any of the coating. In fact, the residual coating causes paint to adhere better and gives the metal more corrosion resistance.

It is a further feature of the present invention that the metal treated with the above preparation can have a surface that is prepared in any way. For example, ferrous surfaces can be either sand blasted, shot blasted, pickled or either hot or cold rolled, and in addition can have light surface films of oil and/or rust. Sand blasted surfaces seem to be the most active and form the desired metal phosphate layer most rapidly. Shot blasted surfaces are somewhat slower to react. Pickled surfaces and ordinary cold-rolled surfaces may take longer than blasted surfaces. The presence of thin films of oil such as palm oil or mineral oil, ordinarily applied to bare metal in order to prevent prompt corrosion, does not significantly interfere with the practice of the present invention. The coating preparation appears to dissolve in or through an oil layer quite rapidly and the development of the phosphate coating is not appreciably prolonged.

In addition to the above, the coating preparation will also work very effectively with a metal surface that is covered with some oxide or even scale. Heavy scale or thick oxide film is only partially converted to phosphate, but the partially converted material is suitable for working operations. A cold rolled steel or even a pickled steel need not be completely free of rust for the purpose of the present invention, and will be suitable for direct application of the coating preparation without any preliminary treatment.

The coating preparation can be applied by dipping, flooding, brushing, rolling or even spraying. After the application the coated metal can be permitted to stand as long as desired. One convenient way of practicing the invention is to roller coat metal sheets with the coating preparation and then to stack them on top of each other. Sufficient coating preparation will remain between the individual sheets in the stack to give the desired lubrication after the phosphate layer has developed.

Detailed specific examples of the use of the coating preparation of the invention are as follows:

Example XII

Tube drawing.—SAE 1015 steel tubing with an outside diameter of 0.875" and a wall thickness of 0.058" was pickled in 20% sulphuric acid by weight for approximately 5 minutes. It was rinsed to remove the residual pickle acid and air-dried.

The tubing was then submerged in the coating preparation of Example II and maintained at a temperature of 135° F. for 5 minutes. The tubes were removed from the coating bath, allowed to drain, and then drawn to an outside diameter of 0.705" and a wall thickness of 0.040". This represents a reduction of 44.2% and is the maximum usually attempted on this type steel.

There was no difficulty in drawing and no scratches on the tubes or dies resulted. The finish was excellent. The prior art treatment usually used for such drawing is the separate application of a phosphate coating after pickling, followed by rinsing, and then dipping into a super-fatted soap type lubricant.

Example XIII

Bar drawing.—SAE 1015 round steel bars approximately 2 inches in diameter and 50 feet long were pickled in 20% by weight sulphuric acid and rinsed. These bars developed a slight rust coat prior to the application of the coating preparation, but this rust did not interfere with the drawing operations which were conducted. The coating preparation of Example I was heated to 140° F. and brushed on the bars. After about 1 hour interval, these bars were given a reduction of 1/16 inch diameter which is considered a heavy reduction in bar drawing.

The drawing was conducted without any difficulty and there was a noticeable improvement in finish over that produced by the prior art treatment which is to apply to heavy lime coating after pickling, and then lubricate with an oil circulated at the draw bench.

Following the procedure of Example IV, bars of SAE 4340 steel 2¾ inches in diameter and hexagonal bars of SAE 1144 steel were drawn without any difficulty using the standard reductions employed with the conventional lime coating and oil application. In all cases, there was a decided improvement in finish with the treatment of the present invention.

Example XIV

Forming.—Coils of low carbon steel (SAE 1010) approximately 20 inches wide and 0.071 inch thick were shot blasted in order to remove mill scale which was present as a heavy surface layer. The coating preparation of Example I was applied to the shot blasted surface by roller coating at the rate of 2.8 pounds per ton of steel or approximately 1 pound for 580 square feet of steel surface. After application of the coating preparation, the steel was formed into conduit boxes of various sizes and shapes. Forming of the boxes was accomplished without any difficulty whatsoever with extremely low breakage and with a punch life of over 400,000 pieces per punch. The punch life with prior art lubricants on the same steel surface had averaged less than 100,000 pieces per punch.

After forming, the residual film from the coating preparation was removed by alkali cleaning and the boxes were then galvanized without any difficulty.

Example XV

Forming.—The coating preparation of Example I was heated to 140° F. and applied, using transfer roller coating, to both surfaces of hot rolled and freshly pickled SAE 1010 steel 28 inches wide and 0.075 inch thick. The metal was coiled immediately after coating. The metal temperature was 145° F. at the point of application and cooled to room temperature after a period of 10 hours.

These coils of metal were rolled on a 5-stand tandem mill, as normally employed in the cold rolling of tin plate, and the rolling was carried out the day following the application of the coating preparation. The average mill loads obtained with the coating preparation on the metal are given below as compared to prior art practice:

Roll Stand	The Coating Preparation of Example I	Synthetic Palm Oil (Prior Art)
	Amps.	*Amps.*
#1	110	110
#2	1,790	1,980
#3	2,030	2,200
#4	1,900	1,970
#5	2,060	2,160

It will be noticed that a definite reduction in load was obtained. During the above operation, the steel was rolled down to a finish gauge of 0.011" and was then alkali cleaned. Annealing and electrolytic plating with tin followed and the tin plate produced was of normal quality.

Example XVI

Paint bonding.—Panels of SAE 1040 steel, cold rolled, were immersed in the coating preparation of Example II for one minute at a temperature of 140° F. These were removed and allowed to stand for several hours. The

panels were then degreased for one hour in trichlorethylene vapors.

These panels were then spray painted using a urea and melamine modified alkyd baking enamel (Pratt and Lambert #0358), thickness 0.7 to 1.0 mil, baked for 10 minutes at 350° F. After drying they were subjected to a 15 day salt spray test using a salt solution of 20% concentration.

Conventional phosphate type paint bonding chemicals were employed on similar panels painted and exposed to the salt spray at the same time. The paint bonding ability of the coating preparation was at least equal to the conventional type phosphate coating in all cases.

Example XVII

Deep drawing.—The blanks used were of deep drawing quality low carbon steel (SAE 1020), octagon shape, 32⅞" x 30" x 0.062". The blanks had a film of rust preventive palm oil on the surface, which was not removed. The coating preparation of Example I was applied with cloth rolls, at room temperature.

Within two minutes of application, the blanks were drawn in a 400 ton press into a gasoline pump dome measuring about 10¼" deep, 21" long, 13½" wide, with an average wall thickness of 0.049". The dome had rounded corners and an oval shaped bottom.

Several hundred domes were drawn with the coating and the lubricant removed by alkali cleaning. No difficulties were encountered and the operation was entirely satisfactory. In order to obtain equally satisfactory drawing, the prior art practice is to clean the slushing oil from the steel, rinse, apply zinc phosphate coating, rinse, apply soap-borax type dry film lubricant, and dry carefully in order to remove all of the moisture from the soap borax film. In this case the single application of the coating preparation of the present invention replaces a six-step process.

The coating preparation of the present invention can be used with any metal that reacts with phosphoric acid. Low alloy steels, that is steels containing less than 5% of other alloying metals, are suitable, including low carbon steels, such as SAE 1010, SAE X1040; high carbon steels, such as SAE 1095; molybdenum steels, such as SAE 4150; chromium steels, such as SAE 5140; chromium vanadium steels, such as SAE 6145; nickel-chromium steels, including SAE 3220; tungsten steels, such as SAE 7260; and silicon-manganese steels, such as SAE 9255. Coatings can also be formed on aluminum and other non-ferrous metals which react with phosphoric acid. Metals which do not react with phosphoric acid, such as stainless steels, can also be lubricated since the coating preparation will function in the same manner as normal boundary lubricants in these cases.

Because of the absence of significant amounts of volatile ingredients, there is very little fire hazard involved in the use of the above formulations even at high temperatures. The use of supplemental thinners or solvents is not desirable for this reason and also because these dilute the lubricating effectiveness. The dilution of the formulations of Example X with an equal weight of kerosene will for example give significantly reduced lubricity, although ¾ hour standing of iron coated with this preparation will raise the lubricity back to a value approaching that of the undiluted preparation.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed:

1. A metal coating preparation consisting essentially of a hydrophilic organic compound having from 12 to 30 carbon atoms in a connected group, up to 90% by weight of substantially non-volatile organic metal lubricant, about 1% to 15% water by weight, and 2.5 to 25% by weight of an acid selected from the class consisting of phosphoric and phosphorous acids, said water and said acid being dissolved in the organic material, and the preparation being a stable single phase liquid at a temperature at least as low as 80° C.

2. The combination of claim 1 in which the hydrophilic compound is selected from the class consisting of amines and amides that are substituted with hydrophilic radicals of the class consisting of hydroxy, methoxy, ethoxy, amine and imine radicals, and there being a total of at least three hydrophilic radicals per 12 to 30 carbon group.

3. The combination of claim 1 in which the hydrophilic compound is the amide formed by condensing in substantially equimolar proportions fatty acids and polyalkylene polyamines of alkyl groups having no more than four carbon atoms per group.

4. The combination of claim 3 in which the preparation also contains from 2 to 15% fatty acid and from 2 to 15% of a member of the group consisting of alkylene glycols and ethers of alkylene glycols, said member having a chain of from three to eight carbon atoms per molecule.

5. The combination of claim 1 in which the preparation also contains from 2 to 20% paraffin wax.

6. A metal coating preparation consisting essentially of

10 to 40% by weight of the equimolar reaction product of a fatty acid having 14 to 20 carbon atoms per molecule with a polyethylene polyamine

30 to 80% by weight of an organic lubricant oil having a chain of at least 12 connected carbon atoms

4 to 15% water by weight, and

5 to 20% phosphoric acid by weight,

the water and acid being dissolved in the remaining ingredients.

7. The composition of claim 6 in which about half the lubricant oil is a fatty oil.

8. A metal having its surface covered with a layer of the composition of claim 1, said layer weighing at least 400 milligrams per square foot of surface that it covers.

9. A ferrous metal having its surface covered with a layer of the composition of claim 6, said layer weighing at least 400 milligrams per square foot of surface that it covers.

10. The method of applying a coating to a metal that reacts with phosphoric acid to form an insoluble phosphate coating which method is characterized by the step of contacting the metal surface with the composition of claim 1 for a period long enough to cause the composition to react with the metal and form an adherent layer which after solvent degreasing weighs at least 40 milligrams per square foot.

11. The method of claim 10 in which the contacted metal surface is a sand blasted ferrous surface.

12. The method of claim 10 in which the contacted metal surface is shot blasted ferrous surface.

13. The method of claim 10 in which the contacted metal surface is a pickled ferrous surface.

14. The method of claim 10 in which the contacted metal surface is rolled ferrous surface.

15. The method of claim 14 in which the contacted metal surface is a cold worked one.

16. The method of claim 14 in which the contacted metal surface is a hot worked one.

17. The method of preparing cold worked metal objects, said method being characterized by the steps of providing the metal precursor, coating it with the composition of claim 1 to form on its surface a lubricant coating suitable for cold working, degreasing the coated metal, and cold working the degreased material.

18. The method of claim 17 in which the coated sur-

face is a ferrous surface and after cold working is directly painted over the degreased coating.

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