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COMPOSITIONS FOR SIMULTANEOUSLY PHOSPHATING AND LUBRICATING FERROUS METALS

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This invention relates to the phosphate coating of ferrous metals. It deals with compositions and processes suitable for applying simultaneously phosphate coatings providing corrosion resistance and enamel adhesion and lubricant coatings providing lubrication for subsequent forming operations, such as drawing.

The phosphating of ferrous metals is a well-known art to provide, for such metals, a coating which will resist the corrosive action of the atmosphere and will provide a base to which enamel coatings, organic in nature, will adhere strongly.

A great proportion of the sheet metal used for industrial purposes, e.g., automobiles, domestic appliances, etc., is treated by some sort of an aqueous phosphating bath. Such treatment has been responsible for the high quality enamelled finishes characteristic of present-day products.

Many articles of ferrous metals are shaped by a drawing process in which the gauge of the metal is reduced or changed by forcing it between hardened steel dies. During such an operation it is necessary that the surface of the metal be protected from the die to prevent seizure or galling or to reduce the power required to perform the drawing operation.

Many lubricants are available for use in the drawing of metals. They may be hydrocarbon oils of various types, alone, or compounded with fatty oils, acids or sulfurized oils. They are applied from aqueous or non-aqueous systems.

The simultaneous application of a phosphate coating and a lubricant coating has been attempted in the past with slight success. One of the oldest procedures involves the emulsification of oily or fatty materials in aqueous systems containing phosphating ingredients. Such multiphase systems are usually unstable and many times produce poor phosphate coatings. A second process involves the use of organic solvents to prepare baths which will coat with both phosphate and lubricant.

Other attempts have been made to modify phosphating baths with organic additives of various kinds. In these cases results have been disappointing sometimes because of poor lubricity obtained with the additives used, sometimes because of insufficient compatibility in the phosphate bath and sometimes because a poor phosphate film is deposited resulting from interference by the organic additive.

It is an object of the present invention to provide a bath by which a ferrous metal surface may be coated simultaneously with a phosphate coating and a lubricant coating.

A further object of this invention is to provide a composition which is stable on storage and which by dilution with water provides a stable bath for applying a phosphate-lubricant coating.

Another object of this invention is to provide an aqueous bath which is transparent, having the ingredients in solution, and from which phosphate-lubricant coatings may be applied to ferrous surfaces.

A still further object of the invention is to provide a stable liquid composition which may be added to a phosphating bath in order that both a phosphate film and a lubricant film may be deposited simultaneously on a ferrous metal surface.

Unusual features of the present invention reside in the fact that a single composition of good storage stability can be readily diluted with water to obtain a bath containing the appropriate concentrations of materials to apply simultaneously a coating of a metal phosphate and a lubricant. The lubricant has high lubricity so that drawing operations of considerable area change can be accomplished. A further unusual feature is that after the drawing of the metal the lubricant can be removed readily leaving a phosphate film which is of excellent structure and density for service as an undercoat for paints, lacquers, and enamels.

According to our invention the phosphate-lubricant coating is applied to the metal surface from a bath containing the following materials:

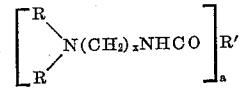
(1) Phosphoric acid
(2) Alkali metal phosphate
(3) A tertiary amino-alkyl amide of a fatty acid
(4) Water
(5) Viscosity controlling agent.

It is apparent that such a bath is in some respects similar to a phosphating bath which provides only a phosphate coating. Thus, it contains phosphoric acid and alkali metal phosphates, and after a short time of contact with the ferrous surface, probably iron phosphate. However, the bath contains an amino-amide of a structure discussed below which is present in solution as its salt. It is these compounds in the bath which provide a lubricant-film which does not impair the phosphate film deposited simultaneously. In fact, these amides make it possible to accomplish the object of this invention, producing phosphate-lubricant films of extraordinary utility.

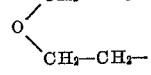
The amino-amides of our invention have been referred to above as tertiary amino-alkyl amides of fatty acids. The expression "fatty acid" as used herein is intended to include an acid which occurs as a glyceride in a vegetable, animal, or fish fat or oil and which contains 8 to 22 carbon atoms and may be saturated or unsaturated and also the polymers of unsaturated fatty acids, i.e., dimeric and trimeric acids, containing multiples of 8 to 22 carbons.

The tertiary amino groups preferred for the purposes of the invention are those containing dimethylamino, diethylamino, and morpholino groups. The alkyl group substituted on the amide nitrogen may be either ethyl or propyl.

The thus broadly defined amino-amides may also be represented by the formula



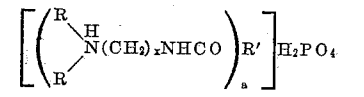
wherein R is selected from the group consisting of CH_3—, C_2H_5— and



x is an integer from 2 to 3; R′ is a radical selected from the group consisting of monovalent aliphatic radicals having the composition C_nH_{2n+1}—, C_nH_{2n-1}—, C_nH_{2n-3}— wherein n is an integer from 7 to 21, divalent radicals having the composition $C_{34}H_{66}$= and $C_{34}H_{62}$= and trivalent radicals having the composition $C_{51}H_{99}$≡ and $C_{51}H_{93}$≡, and a is an integer from 1 to 3 but not greater than the valence of R′.

When dissolved in the phosphating bath the amino-

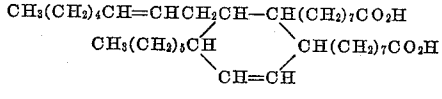
amide is probably present as a phosphate salt whose formula may be written as follows:



thus describing an amino-amide as defined above combined with an equivalent amount of phosphoric acid.

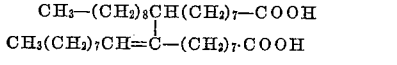
In the preparation of our amino-amides it is possible to react the amine with the acid or with simple derivatives thereof such as esters, acid halides or anhydrides. Many of the useful acids are derived from naturally occurring fats and oils or the oils or fats themselves may be used. In reacting the amine and the acid substantially equivalent amounts of amine and acid are condensed, the reaction taking place between the primary amine group and the carboxyl group. The reaction is carried out by simply heating or in some cases by the use of an azeotroping material such as benzene, toluene, xylene or some other inert solvent which helps to remove water from the reaction. There is an advantage in the use of esters in the reaction with the amine in that the reaction product includes the alcohol formed by aminolysis. There are a number of fatty acids and their derivatives which are useful in preparing amino-amides of our invention. We may use the various fatty acids from tallow or palm oil. We may use commercial stearic acid or blends containing it. Such acids as caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, and behenic are useful. Unsaturated acids such as oleic, linoleic, and ricinoleic may also be used. It is immaterial whether these acids are obtained from natural sources or by synthetic processes. Hydroxyl-containing acids as ricinoleic and hydroxy stearic acid may be employed. Polybasic acids formed by the polymerization of unsaturated fatty acids such as those prepared from linoleic acid may be used.

Such polymers are mixtures of dimers and trimers whose structure has not been definitely established. The dimer acid contains a total of 36 carbon atoms; a likely structure has been suggested:



Whatever the exact structure between the carboxyl groups the composition of this portion of the molecule is $C_{34}H_{62}$. Similarly, the trimer acid has three carboxyl groups attached to a carbon skeleton with 51 carbon atoms and 93 hydrogen atoms. A typical commercial acid is available from Emery Industries, Inc. under the designation Empol 1022. This product is said to contain 75 percent dimer and 22 percent trimer and 3 percent of the monomeric acid. Another polymeric acid which is useful is sold under the name of VR–1 Acids supplied by Rohm and Haas Company. These acids are still residues obtained in the manufacture of sebacic acid and consist largely of dimer and trimers of unsaturated C_{18} acids, as described in U.S. Patent 2,880,095 March 31, 1959.

Other polymeric acids, such as those obtained from oleic acid by the action of catalysts such as BF_3, may be used. A suggested formula for a dimer of oleic acid is as follows:



The divalent radical in such a structure has the formula $C_{34}H_{66}=$; the trivalent radical in the trimer would be $C_{51}H_{99}\equiv$.

Fatty esters such as methyl stearate, methyl laurate, and ethyl myristate may be used in the formation of our tertiary amino-alkyl amides.

It is not necessary that the amino-amide used in our invention be a compound of high purity. We may use

the reaction mixture obtained from the dimethylaminoalkyl amine and a glyceride. In this case the amino-amide contains glycerine. It is also possible that we may use a slight excess of the amine in carrying out the reaction. Under these conditions the amino-amide may contain some free primary amine. However, it is preferable to keep the amount of free primary amine small. When naturally occurring fats or oils are used, or acids prepared therefrom, mixtures of amides are obtained.

The amino-amides used in our phosphating-lubricating compositions are usually present in those compositions as salts. Usually this is the phosphate because the amino-amide may be added to the phosphoric acid solution of the phosphating bath. However, it is possible to add sufficient sulfuric acid to neutralize the tertiary amine group of the amino-amide and apply the coatings of our invention from a bath containing both phosphate and sulfate ions. It is of interest to note that hydrochloric or nitric acids cannot be used for this purpose.

In formulating compositions of our invention there must always be used an amount of acid equivalent to the tertiary amine group present in the amino-amide. Therefore, it is always necessary that there be additional acid provided to take care of that required for the normal phosphating process.

Further, in formulating compositions of our invention, it is necessary to combine the phosphoric acid and the alkali metal phosphate in the proportions which are usually used to give phosphating conditions. Although we prefer to use a pyrophosphate, we may use polyphosphates, e.g., potassium tripolyphosphate or sodium hexa metaphosphate. Alternatively, we may form the alkali metal phosphate in the bath by adding a base such as NaOH or KOH to neutralize sufficient phosphoric acid to give phosphating conditions. The amount of amino-amide required for satisfactory lubricity depends upon the forming operation for which the lubricant is being used. It is possible to get lubrication of considerable degree with as little as 1% of the amino-amide present in the composition. When 3% or more of the amino-amide is used, films of high lubricity are obtained. It is possible to use compositions with as high a concentration of amino-amide as 30% of the total weight of solution for the application of a combination phosphate-lubricant film to a ferrous metal.

In most cases the compositions of our invention are viscous, dark-colored or amber-colored solutions. They may range from clear transparency to solutions which contain some turbidity. Viscosity and turbidity may be controlled somewhat by the amount of viscosity controlling agent used in the formulation. Butyl "Cellosolve" (2-n-butoxyethanol) or such other agents usually known as coupling agents are employed. Such compounds as butyl "Carbitol," [2-(2-n-butoxy)ethanol] diethylene glycol, higher alkoxyethanols or other hydroxyl-containing polyethoxy materials may be used for the purpose of controlling viscosity of these compositions. The percentage of coupling agents will be in the range of 2 to 15 percent.

The application of the phosphate-lubricant film is best carried out by immersing the ferrous metal in a bath which is kept at a temperature of between 150 to 200° F. A temperature of 180° F. has been found to be a most satisfactory operating temperature. The weight of the coating which may be applied depends upon the temperature and the time for which the metal is exposed to the bath. As the temperature increases or as the time of contact increases the coating weight becomes heavier. Times of one to five minutes are practical.

In general, the variables in the application of the phosphate-lubricant coating are those which apply to phosphating operations in general. The pH of the phosphating lubricating bath lies between 2 and 4. The preferred range is 2.7 to 3.5. If desired so-called accelera-

tors may be added, such as chlorates or nitrates, or an activator such as a copper salt may be introduced.

A number of embodiments of our invention are described below; at this point an experiment is described which shows the behavior of an amino-amide of a type which does not perform satisfactorily.

An imidazoline-amide was prepared by condensing one-half mole (141 g.) of tallow fatty acids with a quarter mole of diethylene triamine (26 g.), heating in toluene to remove water of reaction. Approximately 14 g. of water were obtained. The product, after removal of toluene by distillation, was a reddish oil.

This oil was incorporated into a phosphoric acid-phosphate composition as follows: 3 grams tetrasodium pyrophosphate, 47 grams water, and 15 grams 75% phosphoric acid were mixed and then 30 grams of the imidazoline-amide prepared above were added. Five grams of butyl Cellosolve were added and the mixture diluted with water (9 water: 1 mixture). The diluted mixture was used to treat cleaned mild steel panels. The bath temperature was 180° F. and the panels were immersed for three minutes and then dried. There was no phosphate coating apparent on inspection.

The practice of our invention is illustrated first by the preparation of a number of tertiary aminoalkyl amides. Following these are examples of the preparation of phosphating-lubricating baths and illustrations of the process of coating ferrous metals with these novel compositions.

PREPARATION A

Dimethylaminopropyl amine (86.0 g., 0.84 mole), capric acid (129.0 g., 0.75 mole), and toluene (50 cc.) were refluxed together using a water trap beneath the condenser. Water collected measured 13.5 ml. The toluene was stripped off leaving a light brown oily residue of amino-amide, whose acid number was 3.0.

PREPARATION B

The dimethylaminopropyl amide of caprylic acid was prepared similarly by refluxing in toluene, 86 g. (0.84 mole) of dimethylaminopropyl amine and 108 g. (0.75 mole) caprylic acid until 20 ml. of water had been removed. The product, after removal of toluene, was an oil and had an acid number of 12.0.

PREPARATION C

A mixture of 142 g. (0.5 mole) of hydrogenated tallow fatty acid and 51 g. (0.5 mole) of dimethylaminopropyl amine was heated to 315–325° F. in a glass system and the water of reaction removed by distillation. The product was a brown, wax-like material whose acid number was 20.

PREPARATION D

Tallow fatty acids (64 g., 0.23 mole) and dimethylaminoethyl amine (20.5 g., 0.23 mole) were heated in refluxing toluene while the water of reaction was taken off in a trap. Five and four-tenths milliliters of water were collected. The product, obtained by stripping off the toluene, was a soft wax.

PREPARATION E

A polymerized linoleic acid containing a large proportion of the dimeric acid (149 g.) was heated with 63.8 g. of dimethylaminopropyl amine in toluene (50 ml.). After half-hour reflux, water was azeotropically distilled until 10 ml. were removed. The toluene was stripped off; the amide remained as a viscous brown oil with an acid number of 8.0.

PREPARATION F

The mixture of polybasic acids designated VR–1 acids (15.2 g.) and 51.0 g. dimethylaminopropyl amine were refluxed with toluene (50 ml.) for half-hour. A water trap was then placed in the system and water taken off until 12.4 ml. were collected. The toluene was then stripped off, leaving a dark viscous oil. The product was used as described below.

PREPARATION G

One hundred and ninety-five grams of a mixture of oils composed of used cooking oils reclaimed by filtering and heating to remove moisture and easily volatile materials, were heated with 77.2 g. of diethylaminoethyl amine at 356° F. for two hours. The product was a semi-solid brown wax.

PREPARATION H

Castor oil fatty acids (135 g.) and 46 g. of dimethylaminopropyl amine were heated until an acid number of 20 was obtained.

PREPARATION I

Oleic acid (L. T. Red Oil) (142 g.) and 51 g. of dimethylaminopropyl amine were heated under conditions such that water of reaction was evaporated (320–375° F.) until the acid number was reduced to 16.

PREPARATION J

Dimethylaminopropyl amine (112 g.) was heated with pelargonic acid (160 g.) in an open system for removal of water of reaction. The temperature was raised from 320 to 375° F.; the acid value was reduced to 20. The residue was a dark oil.

PREPARATION K

Dimethylaminopropyl amine (51 g.) was mixed with glyceryl trioleate (147 g.) and the mixture stirred and heated at 356° F. for three hours. The product was a reddish oil.

PREPARATION L

Seventy-five parts of refined tall oil fatty acids were mixed with 25 parts of dimethylaminopropyl amine. The mixture was heated at about 320° F. with water of reaction being allowed to escape until titration with acid showed the primary amine group to have reacted. The product was a dark red-brown oil containing some solids probably derived from the rosin acids present in the starting material.

PREPARATION M

The preceding preparation was repeated using a refined tall oil which contained not more than 1% rosin acid, sold under the name of Crofatol. This product was a dark red-brown oil containing less solids than in Preparation L.

PREPARATION N

One mole (142 g.) of N-aminopropylmorpholine and one mole (284 g.) of stearic acid (Wilmar 80) were mixed with 100 ml. of xylene. The mixture was stirred and refluxed under a water trap until 20 ml. of water were collected. The xylene was stripped off, leaving a waxy solid having an acid number of 9.2.

PREPARATION O

Seventy-five parts of an oil such as that used in Preparation G were heated with 25 parts of dimethylaminopropyl amine at approximately 320° F. until the titration of amine indicated that conversion to amide was essentially complete. The product was a brown oil which set to a paste on cooling.

Compositions were made using these preparations by combining them with phosphates and phosphoric acid using the following quantities and procedures:

	Parts by weight
Tetrasodium pyrophosphate	3
Water	47
Phosphoric acid (75%)	15
Product of Preparations A to N	30
2-n-butoxyethanol	5

A solution of the tetrasodium pyrophosphate in water was first made and the phosphoric acid added. Then the tertiary aminoalkyl amide (Preparations A to N) was added with stirring and addition of 2-n-butoxyethanol. The compositions so obtained were clear to hazy liquids. They were usable directly to apply a lubricant-phosphate film or could be diluted with water (using up to 10 parts of water to one part of the solution) to obtain baths suitable for simultaneously phosphating and lubricating.

Examples 1–14

The compositions made by the above procedure were used in a 10% dilution at 180° F. to apply a phosphate-lubricant film on ferrous metal. These baths had a pH of 3.0±0.2. Test panels of mild steel were cleaned by treatment with cleaners and organic solvents and rinsed. They were then immersed in the treating bath for three minutes. The panels were then dried overnight. The films on the strips were tested for coefficient of friction and evaluated for appearance of the phosphate coating. Results are given in Table I.

TABLE I.—PHOSPHATE-LUBRICANT FILMS ON STEEL

Example No.	Amino-Amide Prep. No.	Bath Appearance	Coefficient of Friction	Phosphate Coating
1	A	clear	0.11	excellent.
2	B	do	0.11	Do.
3	C	hazy	0.08–0.09	good.
4	D	do	0.09	excellent.
5	E	clear	0.16	Do.
6	F	do	0.14	Do.
7	G	do	0.11–0.12	Do.
8	H	do	0.11	Do.
9	I	do	0.09	Do.
10	J	do	0.11–0.12	Do.
11	K	do	0.09	good.
12	L	do	0.11	Do.
13	M	sl. hazy	0.10	Do.
14	N	slight floc	0.10	fair.

The coefficient of friction was measured by employing a modification of the Bowden-Leben apparatus (Proc. Roy. Soc., 169, 371 (1939)) for measuring boundary friction between steel surfaces under calculated pressures of 200,000–400,000 pounds per square inch.

The phosphate coating was evaluated visually after washing the lubricant from the film.

Example 15

Preparation O was made up into a phosphating-lubricating composition by combining with tetrasodium pyrophosphate, phosphoric acid, water and 2-n-butoxyethanol as described above. Concentration of the aminoamide was 30%.

This composition (1 part) was diluted with 10 parts of water and used at 175° F. to treat 15/16 inch leaded steel hexagonal bar stock. The steel was treated for five minutes after being subjected to pickling and rinsing. After the phosphate-lubricant film had dried the bars were reduced to 7/8 inch by cold drawing through a die. The operation demonstrated excellent lubricity and washing resulted in a finish with no surface discoloration.

Example 16

A series of experiments was run to test the effect of variation in total phosphoric acid in the bath. Compositions were prepared having the following proportions by weight:

Ingredient:	Parts by weight
Product of Preparation O	30
Tetra sodium pyrophosphate	3
2-n butoxyethanol	5
75% phosphoric acid	Varied 14 to 18
Water to make 100 total parts by weight.	

Clear solutions were obtained. Dilution with water (10 to 1) also gave clear solutions which were used to apply good phosphate-lubricant coatings to steel panels.

Example 17

Another series of compositions were prepared using 15 parts of 75% phosphoric acid and varying the tetra sodium pyrophosphate (TSPP) over the range of 3 to 4.5 parts.

Used in a way similar to Example 16 good phosphate-lubricant coatings were obtained.

Example 18

In order to test the effect of varying amounts of both phosphate and phosphoric acid, compositions were prepared by mixing the following ingredients: In this example the first portion of phosphoric acid was used to neutralize the amino-amide; the second portion required for phosphating was varied as indicated in Table II.

Ingredients:	Parts by weight
Product of Preparation O	30
75% phosphoric acid	10
Tetra sodium pyrophosphate	[1] Variable
75% phosphoric acid	[1] Variable
2-n-butoxyethanol	5
Water sufficient to make 100 total parts by weight.	

[1] See Table II.

After mixing, dilutions were formed using 10 parts of water to one part of the mixture. Steel panels were treated in the diluted product at 160–180° F. for one, two and three minutes. The table gives parts by weight of phosphate and phosphoric acid used in the undiluted mixture and the appearance of this mixture. Also the appearance and pH of the diluted bath are given together with the appearance of the phosphate coating.

TABLE II.—PHOSPHATING LUBRICATING BATHS

Before diluting with water (10:1)			After diluting with water (10:1)		
Pts.		Appearance	pH	Appearance	Phosphate coating
75% H_3PO_4	TSPP				
2.5	1.5	clear	3.0	clear	excellent.
3.5	3.0	do	3.3	do	Do.
5.0	3.0	do	3.0	do	Do.
7.5	4.5	sl. haze	2.8	do	good.
10	6	cloudy	2.8	do	Do.
12.5	7.5	do	2.7	do	poor.
15	9.0	do	2.7	do	good.
17.5	10.5	do	2.6	do	Do.

Example 19

In this example a composition was prepared using sufficient sulfuric acid to form a salt with the amino-amide and using phosphoric acid to obtain a phosphating bath.

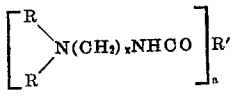
Ingredients:	Parts by weight
Product of Preparation O	30
Water	57.9
Concentrated sulfuric acid	4.17
Tetrasodium pyrophosphate	3
Phosphoric acid (75%)	5
2-n-butoxyethanol	5

This product was diluted with water (10 parts to 1 part of composition). It yielded a clear solution having a pH of 2.4. Panels were immersed at 175° F. for 3 minutes and then removed. They were found to have a good phosphate-lubricant coating.

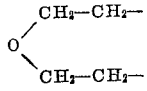
We claim:

1. An aqueous bath for the simultaneous application of a phosphate coating and a lubricant coating to ferrous metals, said bath consisting essentially of (*a*) 1 to

30 percent by weight of a tertiary amino-alkyl amide having the formula



wherein R is selected from the group consisting of CH_3—, C_2H_5— and



x is an integer from 2 to 3; R′ is a radical selected from the group consisting of monovalent aliphatic radicals having the composition C_nH_{2n+1}—, C_nH_{2n-1}—, C_nH_{2n-3}— wherein n is an integer from 7 to 21, divalent radicals having the composition $C_{34}H_{66}$= and $C_{34}H_{62}$= and trivalent radicals having the composition $C_{51}H_{99}$≡ and

$C_{51}H_{93}$≡ and a is an integer from 1 to 3 but not greater than the valence of R′, and (*b*) phosphoric acid equivalent to said amide.

2. A stable aqueous composition for the simultaneous application of a phosphate coating and a lubricant coating to ferrous metal consisting essentially by weight of (*a*) one to thirty per cent of a dimethyl amino propyl amide of a fatty acid having 8 to 22 carbon atoms, (*b*) 0.25 to 18 percent of phosphoric acid, (*c*) 0.1 to 4.5 percent tetrasodium pyrophosphate, and (*d*) 0.1 to 10 percent of 2-n-butoxyethanol.

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