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3,097,118 PROCESS AND PRODUCT FOR REMOVING RUST AND COATING MATERIALS

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No Drawing. Filed Nov. 9, 1959, Ser. No. 851,542
3 Claims. (Cl. 148—6.15)

My invention relates to a new and useful improvement in a process and product for removing and preventing rust, and has for its object the provision of a means for protecting metals particularly of the ferrous variety against corrosion and removal of rust therefrom when formed.

Another object of the invention is the provision of a process whereby the metal to be treated is immersed in a composition consisting of rust removing material and rust inhibiting material so that when the metal is removed from the immersion, it will be free from rust and the rust inhibiting compound will cling to the surface of the metal and serve as a rust inhibiting coating thereon.

Another object of the invention is the provision of a metal treating composition consisting of a mixture of a compound of rust removing material and a compound of rust inhibiting material.

Another object of the invention is the provision of a composition of this type in which when the metal is immersed "gassing" is reduced to a minimum.

Other objects will appear hereinafter.

It will be apparent from the description given that variations and modifications may be made from the exact detail of the structure illustrated without departing from the invention, and it is intended that the present disclosure shall be considered to be but the preferred embodiment.

The common method of protection of metals of the ferrous variety against corrosion involves various steps. The surface must be thoroughly cleaned from all oil and grease and all rust must be removed or inactivated prior to the application of protective coatings such as paints, varnishes, enamels, lacquers, etc. The effective life of such coatings is materially reduced when applied over metals which have not been properly prepared, particularly where rust and corrosive scale have not been removed.

Rust under the present method is usually removed by mechanical or chemical means. Mechanically it may be accomplished by such methods as wire brushing, sand or shot blasting, scraping, the use of abrasive wheels, abrasive paper, steel wool, etc. By chemical methods it is customary to apply acids, notably the mineral acids such as phosphoric, sulfuric or hydrochloric, either individually or mixed, and frequently salts and/or other modifying agents are added. The present invention is primarily concerned with the chemical methods of rust removal, the objective being the development of simpler and more convenient procedures, and to extend the processes to include the deposition of an impervious film to provide longer protection of the base metal after treating.

Ferrous metals that have been treated with such acids as sulfuric, hydrochloric, nitric, etc., tend to rust again soon after the acid has spent itself or been rinsed off. There are special rinses to delay this secondary rusting, such as chromic acid, solutions of chromium trioxide, in conjunction with dilute phosphoric acid. While these methods are quite effective in rust removal they do not provide permanent protection against subsequent rusting unless followed by the application of paint, varnish, oil or similar continuous films.

The use of phosphoric acid and phosphates commonly referred to as "phosphating" differs from most mineral

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acid compounds in that not only is rust removed but simultaneously an adherent film of mineral salts is formed on the metal which extends the period of immunity toward rusting, frequently to several months of inside storage prior to painting. This added protection, however, in many cases is not sufficient, particularly where there is high humidity or where the treated article must be stored outside, unpainted, for a considerable length of time.

The protective cycle provided by phosphating will depend to an appreciable degree upon the composition of the treated metal. And, whether one of the special rinses will be required is likewise determined largely by the type of metal involved.

It is obvious that the decorative processing of ferrous metals in many instances is time consuming and expensive, and any simplification or economic improvement without sacrifice of quality is highly desirable.

An immediate approach to such improvement would be the incorporation of rust removing ingredients to the paint material itself prior to application. There are many adverse factors which in the past have made it quite impossible to mix such components into a useful, homogeneous product. Since the primitive advent of protective coatings the predominating "paint materials" have been of the organic-solvent type, ordinarily immiscible with water in any appreciable amount. Conversely, the conventional rust removers are water soluble and usually supplied in aqueous solution, and consequently are incompatible with organic solvent type paints. Therefore such a mixture will be either too dilute to serve as a rust remover, or its film forming properties will be deteriorated below the range of practical usefulness.

In recent years the water emulsion type of protective finishes has been progressively assuming increased popularity, and there is sound reason for this transition. They do not contain volatile, flammable organic solvents, and thus the extremely dangerous fire hazard always associated with lacquers, shellac, oil varnishes and paints, is absent. As a result industrial insurance rates where paint operations are employed, are materially lowered. The absence of toxic vapors is particularly advantageous from the standpoint of personnel.

Since the organic thinners are volatile, and therefore lost as the paint film dries, their use is an expensive medium of application. The contrasting merit of using water as thinner stresses the importance and desirability of extensive exploitation of emulsion paints. While they offer many features of excellent superiority, they have one adverse property of deep concern. Containing upwards of fifty percent water, and more, they invariably induce rusting when applied directly to ferrous metals. If this defect could be corrected the emulsion paints could be successfully used on water wet metal, which is quite impossible with the organic solvent type of finish.

It is, of course, apparent that the above rust removers and emulsion paints have at least one common factor, namely the aqueous phase. This common property suggests the feasibility of incorporating the two compounds into a stable, homogeneous product capable of retaining the individual characteristics of the two compounds and thus serve as a rust remover-inhibitor, and also have the capacity of depositing a normal paint film for prolonged protection. In effect, a paint material would be produced which could be successfully applied over rusted metal, wet or dry, in one operation. It must be observed however, that a search for such an optimum combination is confined within definite limitations. The simple presence of the common aqueous phase is no assurance that the introduction of the acidic rust remover will not disrupt the emulsion equilibrium by altering, for example, the hydrogen ion concentration, one of the vital

factors upon which that equilibrium sometimes depends.

Among the more prominent representatives of the fixed vehicles employed in paint emulsions are such resinous bodies as the polyethylenes, the polyvinyl acetates and chlorides, styrenated butadienes, latex, and the acrylics such as methyl methacrylate. Many members of these groups, and others, were studied in the search for a suitable combination to fulfill the requirements and many of them fell short in one respect or another. The polyvinyls as a whole gave very good indications and some excellent products were formulated with their use. And some members of the other groups have qualities that warrant further consideration. However, it was found that especially the polyacrylic acid esters, at the present stage of development, show some margin of superiority and are being given prior consideration, while concurrently work is continued with the other resins.

The acrylic esters when mixed with phosphoric rust remover have the unique property of accelerating the rate of rust removal, a highly desirable contribution to the product. It is not unusual for moderate rust to be removed in only two minutes immersion, at room temperature, while ordinarily considerably more time would be required. Gassing is held at a minimum, which is also a point of superiority.

The combination may be used with or without pigmentation. In the absence of pigments or dyes the resulting film is water white and transparent. Soluble dyes yield colored transparent films, and pigmented, opaque films have been successfully made in white, red, brown, gray and black, with and without inerts. By orthodox adjustment of the pigment-fixed vehicle ratio these colors have been produced with light reflectivity varying from high gloss enamels to conventional flats.

The actual formula is extremely flexible since the major ingredients are compatible in all proportions. In practice, the formula will vary between wide limits and is governed by the type of metal being processed, the nature and degree of rust or corrosion, the method of application, and required properties of the final film.

A representative formula of a rust remover, which may be termed composition "A," is as follows:

	Parts by weight
Phosphoric acid.....	1650
Iron phosphate.....	18
Zinc chromate.....	52
Manganese sulfate.....	46
Water	2763

A film forming composition which may be referred to as composition "B" is as follows:

Polyacrylic acid ester water emulsion, 50% total solids

In use, the two components, that is compound A and compound B are thoroughly mixed together and the metal to be treated is immersed into the mixture so obtained. Compound A will immediately set to work to remove the rust from the metal, the larger pieces of rust being deposited in the bottom of the tank or container in which the mixture is deposited, and the smaller pieces of rust going into solution. As the rust is removed, a phosphating process of the metal begins, which continues for some time to build a film of phosphates or mineral salts on deposit. This film is porous and does not protect against moisture penetration or subsequent rusting. When the metal is withdrawn from the tank from which it is immersed, the metal will be wet with the film forming component which penetrates the film. As the water in compound A and the water of compound B evaporate, compound B will form a protective film on the metal to prevent further rust. It is thus seen that the rust inhibitor is deposited immediately upon the removal of rust from the metal so that a substantially indefinite life period of protection is obtained.

The rust treating and film forming components, that

is compound A and compound B are miscible in all proportions. Their ratios can therefore be adjusted between infinitely wide limits, from a mixture on the one extreme comprised almost entirely of the rust treating component, to a mixture at the other extreme which is almost entirely film former. The practical significance of this optional range is apparent, since the application requirements will likewise vary widely, between corresponding limits. For example, on machine parts where dimensional tolerances must be held at a minimum, particularly where the machine is operating in a relatively dry atmosphere, the optimum mixture would be predominately the rust inhibiting solution, with only a very small amount of film former. Conversely, where fresh rolled or cast stock is being treated, which is already free of rust, the preferred mixture would be principally the film former, with only enough rust inhibitor present to prevent rust formation by the water in the emulsion phase, and at the same time improve adhesion of the final film to the base metal.

While some of the resin emulsions used as protective film formers have an acid pH, or neutral, the majority of them are alkaline. Conversely, the rust treating compound is obviously acid. In cross-blending throughout the above wide range, therefore, the final mixtures will vary in pH value from strongly acid to alkaline, depending upon the predominating component. For example, a mixture of 99% solution A, in the preliminary discussion, and 1% emulsion B, will approximate the high acidity of "A" itself, while a mixture of 1% A and 99% B will have an alkaline pH of upwards of 11. The mixtures at these two extremes, and all intermediate ratios, are stable, where a non-pigmented formulation is employed, with all of the previously indicated resin emulsions.

Some pigments are reactive toward the relatively high acidity of the rust treating compound and consequently when they are introduced into the system the amount of this component must be reduced to insure compatibility. In general, with pigmentation, the maximum practical tolerance of the rust treating component in the mixture is double the amount of resin emulsion used, while the optimum will usually fall below this amount. The minimum quantity of solution A is determined by the requirements of any given application, extending down to the low values noted above, namely 1% or less.

Compound "A" is not confined to the specific formula as shown in the preliminary discussion. The formula components can be adjusted through wide ranges and still yield products that will very effectively act as rust remover-inhibitor. And other metal salts can be used as replacement for, or addition to those shown. This is generally recognized in the field of rust treatment. The formula shown as "A" is a good representative of the field of such compounds, and functions particularly well in the mixtures under discussion.

The emulsions in "B" are usually stocked at 45 to 55% total solids. They can be further diluted when desirable.

The following examples illustrate the wide scope of useful combinations:

Example 1

	Parts by weight
Solution "A".....	1 to 100
Emulsion "B" (at 25-60% total solids).....	1 to 100
Additional water.....	0 to 100
Wetting agent.....	0 to 15
Anti-foaming agent.....	0 to 15

Example 2

Solution "A".....	1 to 200
Emulsion "B" (at 25-60% total solids).....	60 to 200
Additional water.....	0 to 400
Wetting agent.....	0 to 40
Anti-foaming agent.....	0 to 40
Dispersing agent.....	0 to 40
Pigment	100 to 300
Inert extenders.....	0 to 300

The resins in "B" may be:

Acrylics, such as methyl methacrylate.
Vinyls, such as vinyl acetate or chloride.
Latexes, such as styrene butadiene.
Alkyds, etc.

Typical wetting agents are:

Lecithin.
Alkali polyphosphates.
Sodium di (2-ethylhexyl) sulfosuccinate.

Suitable anti-foaming agents are:

Silicones.
Tributyl phosphate.
Diethylhexyl ether.
Sulfonated castor oil.

Representative dispersing agents are:

Sodium lignosulfonate.
Polycarboxylic naphthalene sulfonate polymer.
Octyl phenol polyoxyethylene.
Polyoxyethylene sorbitan monolaurate.
Tetrasodium pyrophosphate.

Satisfactory inert extenders are:

Barytes.
Silica.
Asbestine.
Bentonite.

Pigments are:

Titanium dioxide.
Red oxide of iron.
Black oxide of iron.
Carbon black etc.

The pigments and inerts may be used individually or cross-blended in the mixtures.

In the above examples I have selected those film formers which in general are preferred, and have been extensively used for this purpose.

It will be noted that the preferred compound B which specifies acrylics, in a water emulsion, may be substituted by vinyls, such as vinyl acetate or chloride, latexes, such as styrene butadiene, alkyds, etc.

Anti-foaming agents are used for the obvious purpose.

Experience has shown that the metal when treated in the manner indicated is rust proofed over an indefinite

period of time and that a quick and economical operation is obtained.

What I claim is:

1. A composition of matter for coating and protecting metals from rust and for removing rust therefrom consisting essentially of phosphoric acid 1,650 parts by weight, iron phosphate 18 parts by weight, zinc chromate 52 parts by weight, manganese sulfate 46 parts by weight and water 2,763 parts by weight, mixed with polyacrylic acid ester water emulsion, 50% total solids.

2. A composition of matter for coating and protecting metals from rust and for removing rust therefrom consisting essentially of phosphoric acid 1,650 parts by weight, iron phosphate 18 parts by weight, zinc chromate 52 parts by weight, manganese sulfate 46 parts by weight, and water 2763 parts by weight; mixed with a polyacrylic acid ester water emulsion containing 25 to 60 percent total solids.

3. The method of coating and protecting metal from rust and for removing rust therefrom, consisting in subjecting the metal to the action of a composition of matter consisting essentially of an aqueous solution of free phosphoric acid, mixed with a polyacrylic acid ester water emulsion, the amount of said free phosphoric acid in said composition being sufficient to remove rust from said metal and to protect said metal from rust, and the amount of said polyacrylic acid ester in said composition being sufficient to form a coating on said metal.

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