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PROCESS FOR ENAMELING METALS

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This invention relates to the protective or decorative coating of metals and their alloys, and more particularly to novel methods and means for promoting the adhesion or bonding of vitreous enamels to the surfaces of such metals or alloys.

In applying a hard, vitreous ceramic or enamel coating to a metal such as steel, copper, aluminum, silver, etc., or various metal alloys, difficulty is experienced in obtaining a tenaciously adherent, satisfactory bond between the surface of the metal or alloy and the enamel. If bonding is lacking, objectionable scaling, chipping, water-spalling and similar defects characterizing poor adhesion result to defeat the objects and purposes of the coating operation. The procurance of desired bonding or adherence is especially difficult in the vitreous coating of light metals such as aluminum and its alloys, and the lack thereof will disadvantageously result in objectionable "water-spalling" when the coated product is exposed to moisture.

To minimize or overcome this difficulty and provide a firm bond between the metal or alloy surface and ceramic, such surface, prior to the enameling, is usually pretreated with a special ground coat. For instance, in producing enameled sheet iron or sheet metal, a cobalt blue ground coat or a flash coat of nickel is applied, but these treatments require the use of compositions and methods of application which must be carefully controlled and within relatively narrow limits.

It is among the objects of this invention to overcome these and other disadvantages attendant prior metal coating operations, especially in coating metals and their alloys with vitreous enamels. A particular object is to provide an improved vitreous-enamel-coated metal product possessing relatively high resistance to or complete freedom from the defects alluded to occurring from poor bonding or adhesion, and to provide novel methods and means for achieving that object. It is an additional, specific object of the invention to provide an effective means for pretreating a metal surface, especially of steel and aluminum, whereby the subsequent vitreous enameling thereof will readily afford production of an enamel-coated product satisfactorily free from the defects alluded to. Other objects and advantages of the invention will be apparent from the ensuing description of my invention.

These and other objects are attained in this invention which comprises promoting desired adhesion of an enamel frit to a surface of a metal or its alloys by forming, prior to the enameling operation, a relatively thin film of a fourth group metal oxide on said surface through hydrolysis of a fourth group metal ester, especially of titanium and zirconium.

In a more specific and preferred embodiment, the invention comprises bonding a vitreous enamel in secured relationship to a steel, aluminum, or aluminum-rich alloy metal surface by pretreating said surface with a coating of a relatively dilute, organic solvent solution of an ester of titanic acid corresponding to the formula $Ti(OR)_4$, wherein R is an alkyl radical containing from

1–8 carbon atoms, drying and hardening the coating thereon to a clear, thin, transparent and flexible film by evaporating the organic solvent and hydrolyzing the titanate ester, and then coating the pretreated surface with a vitreous enamel.

In the practice of the invention, the surface of a stamped, cut, or otherwise suitably fabricated iron, steel, aluminum, or like metal or alloy specimen to be enameled is first conventionally cleaned by subjecting it, for example, to physical or chemical solution treatment to provide the smooth, clean metal surface necessary for the enameling operation. Thereafter, in accordance with my invention, the surface is suitably coated, as by dipping, immersion, spraying, brushing, etc., with a relatively thin layer or film of a dilute solution of a titanium ester dissolved in a volatile, anhydrous organic solvent, such as ethanol, cyclohexane, mineral spirits, benzene, toluene, xylene, etc. Such ester preferably comprises one prepared by reacting titanium tetrachloride with a lower alkyl monohydroxy alcohol containing, say, from 2–8 carbon atoms, such as butanol, propanol, etc., under anhydrous conditions and in the presence of ammonia or like neutralizing agent. The amount of ester in such solution can range, preferably, from about 2–15% by weight. The layer or coating of dissolved titanate ester thus applied is then dried and hardened to a closely adhering, thin film on the surface to be enameled, as by (1) evaporation of the solvent, and (2) hydrolysis of the ester through air drying or under controlled conditions of temperature and humidity simulating normal atmospheric conditions, e. g., those adapted to induce gradual evaporation of the organic solvent from the solution and slow hydrolysis in situ of the ester by reason of moisture contact from the drying atmosphere so that a film of hydrolyzed oxide, such as hydrous titanium oxide, forms on said surface and, following heat curing, promotes and enhances adhesion of the enamel frit to said surface during the sintering operation.

The ester-treated, oxide-coated metal is then enameled in a conventional manner with an enameling composition adapted to provide a hard, smooth, glossy, durable protective or decorating coating, either white, clear or colored. The type of composition used in the enameling will depend upon the metal or alloy to be coated and should consist of one adapted to be fired at a temperature below that at which the metal or alloy is deleteriously affected, e. g., will deform or lose tensile strength during the enameling. Thus, in the vitreous coating of cast iron and steel, recourse to enameling firing and maturing temperatures of the order of about 650–900° C. can be had, while with aluminum and high strength aluminum-rich (at least 80% aluminum) alloys, enameling temperatures of a lower order, e. g., not to exceed about 600° C., and preferably from between 480° C. and 580° C., are used to avoid any adverse effects due to metal or alloy melting at higher temperatures.

Enameling compositions of requisite type are well known and are made up of refractories such as quartz, feldspar, clay, rutile; fluxes, such as borax, soda ash, lead, lithium, cryloite, fluorspar; opacifiers, such as tin oxide, antimony oxide, zirconium oxide, titanium oxide; coloring agents, such as cobalt oxide, copper oxide, iron oxide, nickel oxide, chrome oxide; floating agents, such as clays and gums; and various electrolytes including borax, soda ash, magnesium carbonate, sodium silicate, magnesium sulfate, etc. Specific types of useful sheet iron or steel cover enamel compositions include those referred to at pages 178–188 of the publication "Enamels" by A. I. Andrews, first edition (1935). Useful vitreous coatings for light metals such as aluminum and aluminum-rich alloys include those made up of the following composition:

10 to 18 mole percent PbO
38 to 65 mole percent SiO_2
5 to 12 mole percent Li_2O, at least one of the group consisting of Na_2O and K_2O in amounts as follows:
Up to 22 mole percent Na_2O
Up to 20 mole percent K_2O, and
From traces to 20 mole percent TiO_2
the total alkali metal oxide content

$$(Li_2O+Na_2O+K_2O)$$

of the enamel being between 25 and 36 mole percent, and the ratio of the sum of said silica content and twice the said titanium oxide content of the enamel to the total alkali metal oxide content of the enamel being between 1.8 and 3.0, all of said oxides being melted into the enamel composition.

After application of the enamel to the surface, the composition is fired in a suitable furnace in order to fuse the powdered enamel to a continuous glassy coating. Firing temperatures used should be high enough to melt the particular enamel being applied but insufficiently high to injure the metal or alloy. Such firing should be effected in a furnace free of sulfate or chloride or other objectionable fumes the presence of which might impair desired gloss. As indicated, the particular temperature employed will depend upon the particular metal or alloy being coated and the enamel composition itself, and in the firing operation it is necessary only to maintain the coated specimen at the selected temperature for a few minutes in order to permit the enamel to fuse completely to a uniform, adherent vitreous layer. Obviously, and if desired, several coats of enamel can be applied.

The enameled products of this invention will advantageously contain an adherent, vitreous enamel highly resistant to thermal shock or mechanical flexing. Advantageously, the coated aluminum or aluminum alloy products of the invention can be subjected to considerable mechanical abuse without danger of spalling or cracking off of the vitreous coating.

To a clearer understanding of the invention, the following specific examples are given. These are merely illustrative and are not to be regarded as in limitation of the invention:

Example I

An isopropyl titanate solution comprising 2.0% by weight of the ester and 98.0% by weight of hexane, was prepared by dissolving the titanate at room temperature in the solvent. The resulting solution was then sprayed onto the previously cleaned, smooth dry surface of aluminum alloy sheet stock composed of aluminum alloy 61 (containing, by weight, 0.25% copper, 0.6% silicon, 1.0% magnesium, and 0.25% chromium). The resulting coating was then air dried for 10 minutes at a high relative humidity of about 50% and then heat-cured at 200° C. for about 15 minutes. A thin film of hydrolyzed titanium oxide formed over said surface. The coated sheet was then dipped into a water slurry of an enamel consisting by weight of 38.1% PbO, 25.3% SiO_2, 2.2% Li_2O, 10.2% Na_2O, 8.3% K_2O, 8.7% TiO_2, 2.9% Sb_2O_3, and 4.3% B_2O_3. To the water slurry is also added 3% of boric acid and 0.5% of potassium chromate, based on the weight of the water in the slurry for the purpose of obtaining better enameling. The liquid and solid contents of the slurry are mixed in such proportions that the sheet, after dipping in the slurry and draining, will contain between 15 and 30 grams (based on dry weight of enamel) per square foot for each coating; several enamel coatings, which may contain pigments or opacifying agents, with separate firings being applied if desired. The enamel is fired at a temperature between 480° C. and 515° C.

After firing and cooling, the enamel-coated structure is gouged through the enamel coating to expose a six-inch raw edge and is then placed for 96 hours in a 5% aqueous solution of ammonium chloride. The coated structure showed high resistance to water-spalling on subjection to this accelerated spalling test. It also exhibited excellent adherence characteristics when the coated product was subjected to deformation.

Example II

A butyl titanate solution comprising 1.5% by weight of the ester and 98.5% by weight of hexane was prepared by dissolving the titanate at room temperature in the solvent. The solution thus obtained was sprayed onto the previously cleaned, dry, smooth surface of sheeted steel containing a .14% carbon content. The resulting coating was then dried at a relative humidity of about 35% for 24 hours and heat cured at 250° C. for 15 minutes to form a thin, adherent film of titanium oxide on such surface. The thus-surface-treated metal was then enameled with a vitreous enamel frit consisting of a slip having the following composition:

	Percent
Feldspar	19.3
Borax	27.6
Quartz	21.7
Soda ash	4.1
Soda nitre	2.7
Fluorspar	6.2
Cryolite	9.5
Zinc oxide	4.8
Antimony oxide	4.1

The enamel was fired at a temperature between 800–850° C. for 30 minutes. The coated product was found to be resistant to thermal shock by withstanding high temperatures and repeated heating and cooling without deterioration.

Example III

A xylene solution containing ½ mole of isopropyl zirconate per litre was applied to a clean, dry, smooth surface of a good enameling steel specimen of the type referred to in Example II. The zirconate-coated metal was then air dried for one-half hour at a relative humidity of 25% and a temperature of 25° C. At the end of this period, the film then appearing dry, the temperature was raised to 200° C. and curing of the film was effected at this temperature for twenty minutes. This resulted in the formation on the metal surface of a closely adhering, insoluble zirconium oxide film. The resulting product was then enameled in the same manner as that described in Example II to obtain an equivalent improved vitreous coated product.

Example IV

The surfaces of a sheeted carbon steel specimen were thoroughly cleaned with fine abrasive, rinsed with water, and dried. The specimen was then coated with a tetrapropyl titanate solution comprising 2% by weight of the ester and 98% by weight of hexane. The coated specimen was then baked at 200° C. in a humid atmosphere until the specimen became coated with the desired hydrolyzed, heat-cured oxide film. Thereafter, it was coated with a standard pigmented cover frit and fired at about 810° C. for a period of 3 minutes, the raw batch mix having the following composition:

Silica sand	2.82
Dehydrated borax	17.96
Feldspar	24.75
Zircon sand	19.14
Sodium nitrate	1.11
Fluorspar	4.49
Sodium fluosilicate	16.15
Bone ash	5.26
Aluminum hydrate	4.87
Zinc oxide	2.65
Titanium dioxide	0.80

The coated product exhibited excellent adherence and was free from blistering and pin holes. On subjecting the enameled product to a standard impact test by dropping a 1" steel ball thereon from a height of 3 feet, no penetration of the enamel film took place.

Example V

A butyl titanate solution consisting of 2.5% by weight of butyl titanate and 97.5% by weight of hexane was prepared by dissolving the titanate at room temperature in the solvent. This solution was then sprayed onto a previously cleaned, smooth, dry surface of the same type aluminum alloy sheet stock referred to in Example I. The resulting coating was then air dried as in Example I to provide the covering film of titanium oxide. The coated surface was then immersed in a solution of 20% sodium chromate in water at 60° C. for 5 minutes and on removal therefrom was rinsed, dried and baked at 540° C. for 7 minutes. After cooling, it was sprayed with a slip of the vitreous enamel coating employed in Example I, and then fired for 7 minutes at 540° C. and cooled.

On subjecting the coated product to a standard spall test by immersion in 5% ammonium chloride, no failures were observed. Furthermore, upon heating the coated product to 500° C., immediately quenching in water, and bending the product into a U shape of approximately ¼" radius, no failures occurred as a result of such quenching and bending tests.

While described in its application to certain specific, preferred embodiments, the invention is not limited thereto. Many variations thereof can be resorted to without departing from its underlying spirit and scope. Thus, while specific titanate ester solutions and esters have been mentioned as employable, other titanium esters and solutions thereof as well as other metal esters can be utilized. In general, organic solutions containing from about .1–.5 mole of the ester per liter of solution can be employed. Preferably, and to obtain optimum results hereunder, ester concentrations ranging from .2–.5 mole per liter of solution are used.

Tetra orthotitanates corresponding to the formula $Ti(OR)_4$ in which R is an alkyl radical containing from 2–8 carbon atoms are especially preferred for use. Examples thereof include ethyl titanate, methyl titanate, propyl titanate, isopropyl titanate, butyl titanate, amyl titanate, octyl titanate, dodecyl titanate, etc. These titanate esters can, as already noted, be prepared through reaction of $TiCl_4$ with an alkyl monohydroxy alcohol, such as ethyl, propyl (normal or iso), butyl (normal, iso, secondary, or tertiary), amyl, hexyl, heptyl, or octyl alcohols. These alcohols yield titanium esters adapted to react with moisture to provide a hydrolyzed TiO_2 film on the metal surface.

Although orthotitanate esters are preferred for use, hydrolyzable esters corresponding to the formula $Me(OR)_4$, where Me is a fourth group metal (titanium, zirconium, hafnium) and R is a hydrocarbon radical, especially an alkyl group containing from 1–12 carbon atoms, or mixtures of such esters are generally employable. Examples of such useful compounds, in addition to the titanium esters mentioned, include the corresponding esters of zirconium, thorium and hafnium, such as isopropyl zirconate, butyl zirconate, ethyl zirconate, octyl zirconate, amyl zirconate, etc.

In effecting hydrolysis of the ester, I prefer to operate under such conditions of time, temperature and humidity as are adapted to effectuate substantially complete hydrolysis. In general, room temperature conditions will be adequate to effect the contemplated drying and hydrolysis, but I also resort to an additional heat curing for a few minutes of the hydrolyzed film at temperatures ranging from about 100–500° C., depending upon the oxidation resistance characteristics of the metal being treated, in order to remove volatile solvents and effect condensation of the hydrolysate to the desired metal oxide.

If desired, and as contemplated in Example V, an aqueous alkaline solution of a chromate can be applied over the cured ester film and prior to application of the enameling composition, particularly in instances where aluminum or its alloys are being enameled. Such chromate solutions and procedures for effecting their application are disclosed in U. S. 2,544,139. These solutions may have substantially any degree of alkalinity between pH 8.0 and pH 14 and can contain any chromate, including dichromates, which is soluble in water, the alkali metal chromates being preferred for use. The chromate content may vary from 0.25% to 25%, expressed as potassium chromate. Following application of the chromate, the ester and chromate-treated product can be heat treated to temperatures between 350° C. and the heat tolerance limit of the metal or alloy, and can then be enameled in accordance with conventional procedures and with a vitreous enamel having a melting point below the temperature at which the metal or alloy will lose tensile strength.

I claim as my invention:

1. A method for bonding a vitreous enamel coating to the surface of a metal comprising prior to the application of said enamel, coating said surface with a thin film of an anhydrous solution of a metal ester selected from the group consisting of titanium esters and zirconium esters, hydrolyzing and condensing said ester on said surface, applying an enameling composition thereover, and then firing said composition at a temperature below that at which the metal will lose tensile strength.

2. A method for bonding a vitreous enamel coating to the surface of a metal comprising prior to the application of said enamel, coating said surface with a thin film of an anhydrous solution of a titanium ester, hydrolyzing and condensing the latter on said surface, applying an enameling composition thereover, and then firing said composition at a temperature below that at which the metal will lose tensile strength.

3. A method for enameling a steel surface comprising coating said surface with a .1–.5 molar solution of a titanium ester in an anhydrous organic solvent, evaporating said solvent and hydrolyzing said ester, heat curing the hydrolyzed product on said metal surface, applying a vitreous enameling composition thereover, and then firing the coated product at a temperature ranging from 650–900° C.

4. A method for enameling an aluminum surface comprising coating said surface with a .1–.5 molar solution of a titanium ester in an anhydrous organic solvent, evaporating said solvent and hydrolyzing said ester, heat curing the hydrolyzed product on said metal surface, applying a vitreous enameling composition thereover, and then firing the coated product at a temperature not to exceed 600° C.

5. A method for bonding a vitreous enamel coating to the surface of a metal comprising prior to the application of said enamel, coating said surface with a thin film of an anhydrous solution of a zirconium ester, hydrolyzing and condensing the latter on said surface, applying an enameling composition thereover, and then firing said composition at a temperature below that at which the metal will lose tensile strength.

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