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VITREOUS ENAMELING

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This invention relates to vitreous enameling and is a continuation-in-part application of my copending application S. N. 349,566 filed April 17, 1953, now abandoned. More particularly this invention concerns an improved metallic base for vitreous enamels, a method for providing a vitreous enamel coating on such metallic bases and an enameled metal article produced thereby. Vitreous enamels of conventional types are well known to be fragile, subject to cracking and chipping and generally incapable of withstanding shock and impact forces. Deformation of enameled metal usually results in rupture of the enamel and particularly is this true when the deformation is relatively severe. It has long been desired to overcome these disadvantages of enamel coatings.

In the past, many unsuccessful attempts have been made to provide a metallic surface with a finish layer of vitreous enamel by applying only a single coat of frit directly to the base metal and firing it. In attempting to provide such a one-step single-layer, vitreous enamel coating, various special alloy compositions and metal preparation treatments have been proposed including numerous methods for expelling carbon from the base metal, the provision of electrodeposited or thermally deposited layered pure metallic coatings on the base metal, oxide coatings on the base metal, and the use of acidic etches, etc. Customary commercial practice has usually involved the use of specially manufactured, relatively expensive, low carbon content enameling iron, and the sequential steps of preliminary metal cleaning, immersion in aqueous nickel or cobalt containing salt solutions, provision of a ground coat of enamel usually containing nickel and cobalt compounds, and the application of one or more vitreous enamel coats with proper firing for each coat. None of the proposed metal conditioning treatments have afforded sufficient increase in adherence to be accepted commercially, and the commercial practice of using a nickel or cobalt flash coating leaves much to be desired both because of the expense involved and the periodic scarcity of both nickel and cobalt.

The principal object of this invention is to provide a new base stock which has improved receptivity for a vitreous enamel coating.

Another important object is to provide an easily-controlled method of preparing metal surfaces, particularly ordinary carbon steel surfaces, to receive vitreous enamel coatings.

A further object of the invention is to provide a new and improved vitreous enameled article which is characterized by unusually good adherence of the enamel coating to the base metal and increased resistance of the enamel coating to impact, torsion and deformation forces.

An additional object is to provide a process which is inexpensive and which eliminates the necessity for the use of nickel and cobalt and utilizes only normally plentifully available materials.

Other objects and advantages will appear upon considering the following detailed description in its entirety.

U. S. Patent 2,076,869 suggests that enamel frit may be deposited over a layer of metallic phosphate and fired if the phosphate coating is protected from the air when temperatures of about 1000° F. and above are attained. Phosphate coatings which are subject to decomposition into a loose powdery material in air at temperatures between 500° F. and about 1000° F. are said to be, after decomposition, of no further use as a rust preventative or as an undercoating for enamel.

In accordance with the present invention, it has now been unexpectedly found that certain phosphate-containing coatings convert metallic surfaces including ordinary carbon steel into new and improved base stock for vitreous enamels.

The present invention is based on the discovery that a combination coating containing phosphate and oxide, and mostly oxide, is surprisingly effective as a base for vitreous enamel. The presence of the phosphate portion of the coating sufficiently alters the normal characteristics of the oxide coating so that greatly improved adhesion of the enamel to the metal surface is obtained. Such coatings, while at present of greatest commercial usefulness on ferrous surfaces, may also be provided on other metal substrates such as the alloy steels and titanium. Broadly stated, the method of this invention comprises the steps of forming a metallic phosphate coating on the metal surface, the coating having a weight of metallic phosphate not exceeding about 580 milligrams per square foot, or about 212 milligrams per square foot of PO_4 and heating the phosphate coating in an oxidizing atmosphere to form a combination phosphate-oxide coating on the metal surface. A metal surface having thereon a phosphate coating, the PO_4 portion of which does not exceed about 212 milligrams per square foot in weight, which has been heated in an oxidizing atmosphere until the oxide portion of the coating constitutes the preponderant portion of the total coating is the improved base stock of this invention.

The improved base stock of this invention may be employed as the base stock for the conventional two-coat vitreous enamel finishes or may be used as the base stock for a single layer vitreous enamel finish. While improved adhesion is obtained in connection with the conventional two-coat vitreous enamels, the greatest advantage is gained when the improved base stock of this invention is covered by a single layer vitreous enamel coating. An article fabricated with the improved base stock of this invention having a single layer vitreous enamel coating has greater adhesion, resistance to impact, torsion and deformation forces than the two-coat enamels over the same improved base stock and the method of forming such an article reduces the number of processing steps and quantity of enamel frit required, to about one-half of that required in the two-coat enamel procedures.

In forming the phosphate coating, an aqueous dihydrogen phosphate solution may be employed. The type of phosphate solution employed is not critical and the solution may be either a conventional type such as zinc or manganese phosphate or iron phosphate producing phosphates such as sodium, potassium or ammonium phosphates. A relatively thin, fine-grained, adherent phosphate coating is best for the purposes of this invention and it is now well known that oxidizing agents greatly assist the formation of such coatings and may be employed, and it is to be understood that the phosphate solutions may be operated with or without oxidizing agents. Oxidizing agents which are suitable and typical for use with zinc or manganese phosphates include materials containing the nitrate, nitrite, chlorate, and bromate radicals as well as organic nitro compounds and peroxides. When alkali metal phosphate solutions are employed, suitable oxidizing agents include, for example, chlorate, bromate, nitrite, or sulfite radicals and organic nitro compounds such as meta nitrobenzene sulfonate. Somewhat lighter weight coatings, which are fine-grained and especially adherent, are obtained from the use of alkali metal or "non-coating" phosphates than are obtained from the use of the "coating" phosphates. Moreover the conditions of operation of the alkali metal phosphate solutions to produce the desired coatings for the purposes of this invention are less exact and may be controlled with relatively greater ease than the coating phosphate solutions, and for these reasons, the formation of the phosphate coating by the use of alkali phosphate solutions is preferred. It is to be understood, however, that as long as the PO_4 portion of the phosphate coating produced does not exceed about 212 milligrams per square foot of the metal surface, the benefits of the invention are obtained irrespective of the particular type of phosphate coating.

The weight of the PO_4 portion of the total phosphate-oxide coating has been found to exert a strong influence on the vitreous enamel coating, and while the PO_4 portion of the metallic phosphate coating can be as high as the critical maximum previously indicated, i. e. 212 milligrams per square foot, for best adherence the PO_4 portion preferably should not exceed about 40 milligrams per square foot. When the PO_4 portion of the metallic phosphate coating exceeds about 40 milligrams per square foot, the adherence of the vitreous enamel coating is not as high as when the PO_4 portion has a weight in the range of 1 to 40 milligrams per square foot. When the PO_4 portion is less than about 1 milligram per square foot, no significant increase in adherence and quality of the vitreous enamel coating is obtained. More preferred phosphate coatings have PO_4 portion-weights in the range of 10 to 35 milligrams per square foot. The very best adherence of the vitreous enamel coating generally is obtained when the PO_4 portion of the metallic phosphate coating has a weight in the range of 20–25 milligrams per square foot. The metallic phosphate coating weight and the weight of the PO_4 portion of the coating as these weights are given throughout the specification were determined respectively by gravimetric and colorimetric determination procedures briefly described as follows:

The metallic phosphate coating weight is determined by weighing the coated panels, stripping the coating completely from the panels with a 20% chromic acid solution at 180° to 200° F. The time of treatment with the chromic acid solution will vary but generally 3 minutes has been found to be sufficient. In any event, the treatment with the chromic acid solution is continued until the coatings are completely removed from the panels. The panels are then dried and weighed and the loss in weight of each panel is the weight of the metallic phosphate coating.

For determining the weight of the PO_4 portion of the coating, the coated panels are leached in 5% sodium hydroxide solution. In the usual case immersion in the sodium hydroxide solution for 20 minutes at room temperature is satisfactory. The PO_4 portion-weight is then determined colormetrically by the molybdato-vanadate method which is conventional and understood by those skilled in this art.

After a phosphate coating of the above described type is formed, the coated article is ready to be oxidized. The step of firing in an oxidizing atmosphere the article having on its surface a phosphate coating, is considered to be of extreme importance to the success of the invention. It has been found that the formation of a heat-induced oxide in the presence of the phosphate on the metal surface results in a combination blue-black oxide-phosphate coating which is necessary in order to obtain the benefits of the invention and whose characteristics will be hereinafter described. By "heat induced" is meant simply that the oxide portion of the coating is formed as the result of the application of heat in the presence of air or other oxidizing atmosphere including oxygen, water, etc., to the phosphate coating in contradistinction to oxides such as rust. The oxide may be formed by a variety of procedures so long as the formation of oxides other than heat induced blue-black oxides are avoided. One procedure found to be suitable comprises the steps of rinsing the phosphate coating in cold water after its removal from the phosphate coating solution, and immediately after the cold water rinse, introducing the coated article while still wet into a furnace provided with an oxidizing atmosphere at a temperature above about 1100° F. Somewhat inferior adhesion has been obtained when a hot water rinse was employed following the phosphate coating step, and similarly it was found to be undesirable to allow the rinsed coated article to dry at room temperature prior to the introduction into the furnace. It is desirable to remove all traces of the rinse water from the coated surface immediately, in the event the article cannot be deposited into a furnace while still in the wet condition. The removal of this excess water may be accomplished, for example, by employing a strong air blast or flash drying or by immersion of the rinsed, coated article directly in any of a variety of water absorbing organic solvents such as ketones, alcohols, glycols including acetone, isobutyl alcohol, ethyl ether or ethylene glycol, etc. Under certain circumstances a rinsing step prior to firing in an oxidizing atmosphere is not necessary. It has been found that phosphate coatings on metal surfaces produced from aqueous phosphoric acid solutions comprising about 0.5% to 2% phosphoric acid by weight and from ammonium phosphate solutions comprising about 0.5% to 1.5% ammonium dihydrogen phosphate by weight need not be subjected to a water rinsing step but may be introduced directly into a furnace provided with an oxidizing atmosphere.

The amount of heat-induced, blue-black oxide coating which is formed on the surface of the phosphate coated article to form the base stock of the present invention is dependent upon the temperature employed, the time the article is maintained at the elevated temperature and the nature of the oxidizing atmosphere which is provided. As both the time and temperature are increased, the proportion of heat-induced oxide coating which is formed also increases. Similarly, as the oxygen content of the oxidizing atmosphere is increased, the proportion of oxide formed at any particular time and temperature is increased. It will be apparent to those skilled in the art that the desired combination blue-black oxide-phosphate coating may be obtained under a variety of particular conditions by varying one or more of the three controlling variables. Irrespective of the particular operating conditions which are chosen, the total coating on the surface of the article to be enameled, including both the phosphate and the heat-induced blue-black oxide portions, should for best adherence, have a weight in the range of 0.4 gram/sq. ft. to 42 grams/sq. ft. The total phosphate-oxide coating weight is determined by stripping coated panels with a formaldehyde-hydrochloric acid mixture and the loss in weight of each panel is the weight of the total phosphate-oxide coating. Of this total coating, the phosphate portion is relatively small and as indicated previously, the PO_4 portion of the metallic phosphate coating should lie in the range of 1 to 212 milligrams per square foot.

It is not known for certain whether the phosphate coating remains intact during the firing step or not, but it is thought that a major portion of the phosphate coating does remain unchanged and forms an integrally bonded surface layer which is overlaid with the heat-induced oxide layer. It is known that for comparable surface areas, the presence of a phosphate coating of this invention decreases the quantity of blue-black oxide coating which is formed under comparable firing conditions. The amount of the reduction of oxide coating which is formed is relatively slight however, and the mechanism or function of the phosphate coating is not completely understood. The combination blue-black oxide-phosphate coating which is formed on the base stock in accordance with the present invention has an actual color which varies with the conditions during the subjection of the phosphate coated article to the firing step in an oxidizing atmosphere. The resultant coating is always dark but may vary in shades from slate gray through black depending upon the particular operating conditions during the firing step and upon the substrate metallic surface. As can best be determined the phosphate layer which is bonded to the metallic surface is overlaid with an integrally united iron oxide layer the composition of which is approximately 90% FeO, 2 to 3% Fe_2O_3 and balance Fe_3O_4. The composition thus given of the oxide portion of the combination oxide-phosphate coating was determined from a typical base stock formed in the practice of the invention and it is to be understood that the same is exemplary and not to be interpreted in a limiting sense. Because of the presence of the various oxides of iron together with the phosphate the combination oxide-phosphate coating characteristically has a bluish-black sheen when observed at various angles in visible light, and it is this characteristic coating which is meant to be defined more precisely by the term blue-black as used throughout the specification and in the appended claims. When the combination blue-black oxide-phosphate coating of the above-described type is formed, the evidence is clear that an unexpected increase in the adherence of an enamel coating applied thereover is obtained. Moreover, blister formation is minimized and uniformity of the subsequently applied vitreous enamel coating is increased substantially due to the presence of the combination blue-black oxide-phosphate coating on the base stock. Total coating weights in the range of 5.0 to 22.0 grams/sq. ft. give somewhat more consistent results, and the best adherence of the enamel coatings is obtained when the total coating weight is between 12 grams and 14 grams/sq. ft. of surface area. It is to be clearly understood that variations within the broad ranges of 1 to 212 mg./sq. ft. for the PO_4 portion of the metallic phosphate coating and in the range of 0.4 to 42 grams/sq. ft. for the total coating are permissible and can be independently controlled. The most desirable coatings from an overall standpoint are obtained when the weights of each are maintained within the preferred ranges above given.

Typically suitable conditions for the firing step are as follows. The temperatures suitable for use when the oxidizing atmosphere is air, vary from 1100° F. to 1900° F. At 1100° F., thirty minutes is required to produce a coating having increased adhesion for enamel, whereas at 1900° F. maintaining the article at temperature for more than about 50 seconds produced a blistered scaly coating of no value. Temperatures between about 1200° F. and 1550° F. are more practical and treatment at about 1350° F. to 1465° F. is suitable for most operations. Noticeably sharp increases in the adhesion of the vitreous enamel layer have been observed from treatment for about 5 minutes in contrast to shorter and longer times at about 1450° F.

The enamel which is applied to the improved base stock of this invention is not critical and any known vitreous enamel coating material may be employed. Suitable porcelain enamels include the alkali-aluminum-fluoborosilicate glasses which are fired in a temperature range of 1470° F. to 1560° F., and titanium-containing enamels. For the one layer enamel applications, the titanium-containing enamels have been found to be particularly suitable. Such titanium-containing enamels may be described as titanium opacified porcelain enamel comprising essentially an alkali-titanium-fluoborosilicate glass susceptible to fusion on a metal surface at a temperature in the range of 1400° F. to 1550° F. During the fusion operation, titanium dioxide is precipitated, giving a white coating of high opacity. Such vitreous enamels may optionally contain various color producing compounds, and it is to be understood colored enamels are contemplated. The enamel may

be applied in a conventional manner by either dipping or spraying the phosphate-oxide coated article and the finished article is obtained by properly firing the vitreous enamel coating.

The below examples illustrate in greater detail the present invention.

Example I

An aqueous acidic phosphate solution was prepared having a concentration of monosodium phosphate of 12.5 grams per liter and a pH of 5.2. Clean mild steel panels were immersed in separate portions of the solution for one minute at a temperature between room temperature and 160° F. and withdrawn. The panels were coated with typical appearing metallic phosphate coatings having PO_4 portion-weights between 30 and 36 milligrams per square foot. After removal from the phosphate solution, the panels were thoroughly rinsed by spraying with cold water, and while still wet were positioned in a muffle furnace, having its door partially open, at a temperature of 1350° F. and maintained therein for three minutes. Upon removal from the furnace, inspection of the panels revealed that the coatings were blue-black and relatively brittle and hard. The coatings, though not loose, were subject to disengagement by flaking when the panels were bent or deformed.

An enamel slip was prepared as follows:

	Grams
Titanium containing frit (Neowite #20)	680.0
Clay (Micronize M-32)	20.5
Bentonite	1.7
Sodium nitrite	0.85
Sodium aluminate	0.85
Potassium carbonate	1.7
Water	353.0

To the above mix, 500 cc. of water was added and the mixture placed in a ball mill provided with porcelain balls and ground for about three hours. Grinding was usually continued until all except about ½% to 1% of the mixture passed through a 200 screen mesh.

The phosphate-oxide coated panels were sprayed with the prepared slip to uniformly cover one side of the panels. This layer averaged about 30 grams per square foot. The panels were allowed to dry, and any thin spots of the enamel were touched up before inserting them in a muffle furnace at a temperature of 1480° F. The panels were maintained in the furnace for four minutes and upon withdrawal were found to be coated with a white glossy enamel finish.

Some of the enameled panels were tested by impact, some by deformation, and others in torsion. The impact test used comprised placing the coated panel over an aperture larger than the end of a hammer and striking the enamel surface a sharp downward blow with the ball end of the hammer with sufficient force to form a depression in the panel of about 0.150 inch in depth. Other panels were tested in a standard Olsen tester using ¾ inch diameter balls and sufficient force to form an indentation having a depth of 0.150 inch. Still other panels were tested by the Porcelain Enamel Institute bump test which consists in indenting 20 gauge stock with a 1" diameter ball until the crown of the indentation is depressed 0.156" to 0.190". The panels deformed by both of these tests were, upon close examination, found to have a number of fine hair-line cracks surrounding the indentations, but there was no chipping or flaking of the coating. A plurality of angle irons having a length of 12 inches, and 1" wide leg portions coated with enamel by the above procedure, were used for torsion testing. The enameled angle irons were inserted in a twisting machine which holds one end stationary and slowly rotates the other end. No flaking of the enamel was obtained before the rotatable end had passed through an angle between 90° and about 130°.

Another series of steel panels was treated in the above phosphate solution for varying time periods to produce

PO_4 portion coating weights of 1.8 mg./sq. ft., 20 mg./sq. ft., 36 mg./sq. ft., 55 mg./sq. ft., and 139 mg./sq. ft. These panels, after firing to produce a phosphate-oxide coating, were coated with enamel as above and when tested in a comparable manner, the enamel coating was found to be adherent and to resist flaking for all coating weights.

Silicon steel reacted quite differently when treated in accordance with the present invention and did not yield a suitable base stock. Panels of steel having an analysis of approximately 0.8% silicon were treated as set forth in this example and as the panels came from the firing step the oxide-phosphate coating had a very definite red color instead of the characteristic blue-black color. After scrubbing some of the panels with emery, microscope examination showed the coating to be all red and it was concluded from this that the coating was principally Fe_2O_3. The other silicon steel panels after the same firing step, and which had the same red surface coating, were enameled as above and upon testing by the Porcelain Enamel Institute bump test as previously described, they gave an adhesion of 0%.

The two following examples illustrate the formation of entirely satisfactory vitreous enameled articles from base stock provided with phosphate coatings and then with the combination blue-black oxide-phosphate coatings without an intermediate rinsing step.

Example II

Phosphoric acid solutions having a concentration of 0.5%, 1% and 2% phosphoric acid were prepared and steel panels were immersed in each solution for a few seconds at a temperature of about 75° F. and withdrawn. After withdrawal from the phosphoric acid solutions the panels were dried at 200° F. Without any rinsing whatsoever the panels were subjected to the firing step for 6 minutes at 1465° F. to form the characteristic blue-black phosphate-oxide coating and subsequently enameled.

All of the enameled panels tested satisfactorily under the Porcelain Enamel Institute bump test described in the previous example. The total coating weight and the weight of the PO_4 portion were determined and the averages of these weights are given below. Angle irons were similarly enameled and tested in torsion as described in the previous example and the angle through which the angle irons could be rotated without flaking of the enamel is listed below as the average for five panels from each solution.

Solution	Angle, degrees	Metallic Phosphate Coating Weight, mg./sq. ft.	PO_4 Portion-weight, mg./sq. ft.
0.5% phos. acid	231	38.0	9.36
1% phos. acid	160	71.2	18
2% phos. acid	100	62	22.7

Example III

Another series of steel panels was treated in a 10 point aqueous acidic phosphate coating bath having a concentration of ammonium dihydrogen phosphate of approximately 12.5 grams per liter by immersion for one minute while the temperature of the bath was maintained at about 80° F. The panels were withdrawn from the bath and the phosphate solution thereon was dried at 160° F. without any rinsing and prefired for seven minutes at 1450° F. in a muffle furnace provided with an oxidizing atmosphere. The phosphate-oxide coated panels were enameled in the manner as in Example I and upon withdrawal from the enameling furnace were found to be coated with a blister-free vitreous enamel finish. The panels were subjected to the previously described Porcelain Enamel Institute bump test and no chipping or flaking of the coating was apparent as a result thereof. Angle irons were similarly treated and used for torsion testing as already described and the average angle through which ten representative angle irons could be rotated without flaking of the enamel was 244°. The bath was aged by processing numerous other panels therethrough and improvement of the adhesion of the vitreous enamel coating was noted on panels treated in the aged bath. The angle through which the angle irons treated in the aged bath could be rotated without flaking of the enamel averaged about 290°.

Example IV

Two sets of twenty 4" x 6" panels and two sets of twenty angle irons from the same stock of mild steel were cleaned, rinsed and then processed by immersion in separate zinc dihydrogen phosphate coating baths of conventional type containing about 10 to 15 grams/liter of zinc dihydrogen phosphate and 0.3% to 0.4% ClO_3 for 20 seconds to 5 minutes at 160° F. Following immersion in the respective coating baths each set of panels and angle irons were given a ½ minute cold water rinse and a 15 second dip in distilled water and dried for 5 minutes at 200° F. Thereafter each set was subjected to a firing step in an oxidizing atmosphere at 1450° F. for 5 minutes. Certain of the panels and angle irons of each set were used for coating weight determinations and others were enameled as in Example I and tested for torsion. The metallic phosphate coating weight, the weight of the PO_4 portion and the total phosphate-oxide coating weight is given as the average of a representative number of panels from each group. The angle through which the angle irons could be rotated without flaking is given as the average of 4 samples. The term failed as used below means that flaking of the vitreous enamel coating occurred before the free end of the angle irons could be rotated through 100°.

	Coating Weights			Torsion Test
	A	B	C	
1st Set	125	507	11	129°.
	287	747	11	failed.
2nd Set	212	581	16	143°.
	263	851	16	failed.

A = PO_4 portion-weight of the coating in mg./sq. ft.
B = total phosphate coating weight in mg./sq. ft.
C = total phosphate-oxide coating weight in grams/sq. ft.

The following four examples are of suitable phosphate solutions from which phosphate coatings were formed having the respective coating weights indicated. The surfaces treated in all but the last example were mild steel. The thus coated metal surfaces in each of the examples were subsequently subjected to the firing and enameling steps as set forth in Example I and entirely satisfactory results from the Porcelain Enamel Institute bump test and torsion test were observed.

Example V

Zinc dihydrogen phosphate	grams/liter	20
Sodium chlorate	do	5
pH		2.7

Panels immersed in this solution for 10 seconds at 160° F. produced coatings having PO_4 portion-weights of about 30 mg./sq. ft.

Example VI

H_3PO_4 (75%)	grams/liter	3
Sodium 2, 4 dinitro benzene sulfonate	do	10
pH		3

Example VII

Panels immersed in 75% H_3PO_4 solution for one minute at 160° F. were provided with coatings having a weight of 8 mg. PO_4/sq. ft., and after 1½ minutes with coatings having a weight of 11 mg. PO_4/sq. ft.

Example VIII

A solution found to be particularly suitable for titanium is as follows:

	Grams
Zinc dihydrogen phosphate—$Zn(H_2PO_4)_2.2H_2O$	13.1
Sodium chlorate—$NaClO_3$	3.6
Ammonium fluoride—NH_4HF_2	4.0
Tetra-sodium ethylene diamine tetraacetate	1.0
Water to make 600 ml.	

This solution when maintained at 130° F.–140° F. produces a phosphate coating having a weight of 40 mg. PO_4/sq. ft. on titanium in about 3 minutes.

What is claimed is:

1. A vitreous enamel base stock comprising a metal having a combination blue-black phosphate-oxide coating thereon, the PO_4 portion of said coating having a weight in the range of 1 to about 212 mg./sq. ft. and the total coating having a weight in the range of 0.4 gram to 42 grams/sq. ft.

2. A vitreous enamel base stock comprising a metal having on the surface thereof a combination blue-black phosphate-oxide coating, the PO_4 portion of said coating having a weight not greater than about 212 mg./sq. ft. and the total coating having a weight in the range of 0.4 gram and 42 grams/sq. ft.

3. A vitreous enamel base stock consisting essentially of a ferrous metal having on the surface thereof a combination blue-black phosphate-oxide coating, said coating having a total weight not exceeding 42 grams/sq. ft. of surface, and the PO_4 portion of said coating having a weight not exceeding about 212 mg./sq. ft.

4. A vitreous enamel base stock comprising a metal having on the surface thereof a combination blue-black phosphate-oxide coating, said coating having a total weight in the range of 5 to 22 grams/sq. ft. and the PO_4 portion of said coating being in the range of 1 to 40 mg./sq. ft.

5. A vitreous enamel base stock comprising a metal having on the surface thereof a combination blue-black phosphate-oxide coating, said coating having a total weight in the range of 12 to 14 grams/sq. ft. and the PO_4 portion of said coating having a weight in the range of 10 to 35 mg./sq. ft.

6. A method of forming a vitreous enamel base stock which comprises the steps of forming a metallic phosphate coating on the surface of a metal, the PO_4 portion of said coating having a weight not exceeding about 212 mg./sq. ft., and heating the said phosphate coated metal in an oxidizing atmosphere at a temperature and for a time sufficient to produce on said metal a combination blue-black phosphate-oxide coating having a total weight not exceeding 42 grams/sq. ft.

7. A method of forming a vitreous enameled metallic article which comprises the steps of forming a metallic phosphate coating on a metal surface, the PO_4 portion of said coating having a weight in the range of 1 to 212 mg./sq. ft., heating the phosphate coated metal in an oxidizing atmosphere at a temperature above about 1100° F. to form a combination blue-black phosphate-oxide coating having a weight in the range of 0.4 gram to 42 grams/sq. ft., and thereafter firing a vitreous enamel on said phosphate-oxide coating.

8. A method according to claim 7 wherein said phosphate coating is formed by treating said surface with an aqueous acidic solution consisting essentially of about 0.5% to 2% phosphoric acid.

9. A method according to claim 7 wherein said phosphate coating is formed by treating said surface with an aqueous acidic solution consisting essentially of about 0.5% to 1.5% ammonium dihydrogen phosphate.

10. A method of forming a vitreous enamel base stock which comprises the steps of forming a metallic phosphate coating on a metal surface, the PO_4 portion of said coating having a weight in the range of 1 to 212 mg./sq. ft., rinsing the said coating in water, immediately removing the excess water from the said rinsed surface, and heating the said coating in an oxidizing atmosphere at a temperature above about 1100° F. until a combination blue-black phosphate-oxide coating is formed having a total weight in the range of 0.4 and 42 grams/sq. ft.

11. A vitreous enamel coated metallic article which comprises a metallic base stock having on its surface a combination blue-black phosphate-oxide coating having a total weight in the range of 0.4 and 42 grams/sq. ft. and the PO_4 portion of said coating being in the range of 1 to 212 mg./sq. ft., and at least one overlayer of a vitreous enamel.

12. A vitreous enamel coated metallic article which comprises a metallic base stock having on its surface a combination blue-black phosphate-oxide coating having a total weight in the range of 0.4 to 42 grams/sq. ft. and the PO_4 portion of said coating being in the range of 1 to 212 mg./sq. ft., and at least one overlayer of a titanium-containing vitreous enamel.

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