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ENAMELED ARTICLES

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This application is a continuation-in-part of my copending application Serial No. 597,603, filed June 4, 1945.

This invention relates to light-colored enameled steel articles and more particularly to a means of eliminating the use of the customary dark-colored ground coat in enameling articles of this character.

In order to obtain on a steel or iron article a smooth uniformly adhering coat of light-colored porcelain or vitreous enamel, it has been the practice in the enameling trade for many years to apply or fuse to the steel article a dark-colored ground coat containing an oxide such as cobalt oxide, nickel oxide or manganese oxide. Over the dark-colored ground coat one or more finishing or cover coats of the desired light-colored enamel were then applied and separately fused. In most instances, because of the inherent dark color of the ground coat, it has been considered necessary to employ several cover coats of light-colored enamel in order to achieve a satisfactory light-colored finish. By the term "light-colored" I mean white or pastel shades.

The conventional ground coat is dark or blue-black in color and is usually fused to the steel base at temperatures of the order of from about 1580° F. to about 1600° F. The dark color of the ground coat is due to the presence of the cobalt, nickel or manganese oxides which possess the property of promoting adherence of the cover coats to the steel base. The cover coats are separately fused over the ground coat at temperatures which may range from about 1500° F. to about 1600° F., dependent upon the composition and properties of the enamel. The cover coats may, of course, be of any color but most of the two or three coat articles, for example, parts of stoves or refrigerators, are finished in white or pastel shades.

The purpose of the dark-colored ground coat is twofold: (1) to secure satisfactory adherence of the cover coats, and (2) to eliminate or minimize in the finished article such objectionable surface defects as blistering, pitting, black-specking, and fish-scaling.

According to widely accepted theory, the adherence of vitreous enamel to steel is accomplished through an iron oxide layer or film formed on the steel surface and under the enamel coating. Apparently the iron oxide dissolves in both the steel and enamel at enamel fusing temperatures. This iron oxide may begin to form

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as soon as the enamel is applied to the steel surface because of the moisture in the enamel. However, the quantity of iron oxide so formed on plain carbon steel is not sufficient for satisfactory uniform adherence. Cobalt oxide has long been known to promote porcelain or vitreous enamel adherence and it is believed that this property is due to its relative unstability, i. e., it releases its oxygen comparatively easily, particularly at enameling temperatures and when in the presence of some element or compound which will unite with oxygen to form a more stable oxide, which in this case is iron. When the cobalt has given up its oxygen to the steel at enamel fusing temperatures, it then combines with oxygen from the atmosphere and is ready again to furnish oxygen to the steel. The cobalt therefore serves as an oxygen carrier or, in effect, as a catalyst. Nickel and manganese oxides are known to behave in a similar manner. In accordance with the foregoing explanation, it will be evident that the ground coat constitutes the medium whereby satisfactory bond obtention is realized between the steel base and the finish or cover coats of enamel.

It has also been established that one of the principal causes of surface defects in enameled articles, particularly blistering, pitting, and black-specking, is the formation and evolution of gaseous carbon products which are released from the steel base during firing of the enamel coats. These gaseous carbon products apparently result from the reaction of the carbon in the steel with metallic oxides in the enamel or with hydrogen which is sometimes formed at enameling temperatures by the reduction of water contained in the enamel. The surface defect known as fish-scaling is considered to be the result of hydrogen escaping from the enameled metal upon cooling from enameling temperatures to room temperature. The hydrogen which may be formed during enameling dissolves to a substantial extent in the steel at elevated temperatures, and as the enameled metal cools, a super-saturated condition exists with the result that free hydrogen is released from solution in the steel. The hydrogen thus released tends to create excessive pressures under the enamel coating which force the enamel off the steel in fish-scale shaped pieces. The application of a ground coat to the base steel tends to trap the various gaseous products which may form and thereby minimizes the magnitude and frequency of surface defects of the type described.

However, the use of the ground coat does not completely eliminate surface defects of the above type and the enameling trade has long been faced with the annoying problem of rejecting and reprocessing a substantial proportion of the enameled ware output. Nevertheless, the ground coat technique has been universally employed in the enameling trade for many years since it has long been considered to be the only commercially satisfactory means of securing the desired degree of bond obtention of the cover coats and, at the same time, at least minimizing the occurrence of surface defects and thereby reducing the percentage of enameled articles which must be rejected or reprocessed. In addition, it has been found that the use of a ground coat introduces another type of surface defect known as reboiling. In other words, during the firing of the outer cover coats, the underlying and previously applied ground coat has a tendency to soften and boil thereby disturbing the adherence and smooth appearance of the cover coats. In order to overcome the reboiling problem, it has been necessary to choose enamel compositions for the cover coats which can be fired at temperatures appreciably lower than the softening temperature of the ground coat.

For the past twenty years or more extensive efforts have been made and considerable experimentation carried out by ceramic engineers and others skilled in the enameling arts with the object in view of obtaining a light-colored enameled steel article which is free of undesirable surface defects without the necessity of using the conventional dark-colored ground coat. Moreover, it has been the hope of these investigators that the elimination of the dark-colored ground coat would thereby permit the production of enameled steel articles with only a single light-colored coat of enamel thereby greatly reducing production costs both from the point of view of materials used and the elimination of one or more process steps. It has been found that articles having only a single coat of enamel are highly resistant to chipping and crazing of the enamel surface as compared with multi-coated articles having two or three or even a greater number of cover coats. Certain of the prior art workers have attempted to solve the problem by devising special compositions for the enamel frit or by employing particular techniques in the preparation of the enamel slip. Others in the prior art have resorted to nickel flash or nickel dip techniques for the purpose of improving bond obtention. However, none of these proposals has provided a satisfactory solution to the problem of surface defects in enameled articles, and the enameling trade has consistently employed the conventional dark-colored ground coat even when special enamel compositions or nickeling techniques have also been used.

Accordingly, the principal object of my invention is to provide light-colored enameled steel articles which can be prepared without the use of the conventional dark-colored ground coat and with only a single light-colored enamel coat, which articles are substantially free of objectionable surface defects.

Broadly, I accomplish this object by utilizing a killed steel base having alloyed therewith a sufficient quantity of zirconium, columbium, or vanadium to chemically combine with and stabilize the carbon present in the steel. These metals possess the common chemical character-

istic of forming relatively stable carbides. By thus tying-up or stabilizing the carbon content of the steel, the formation of gaseous carbon products is inhibited with the result that surface defects of the type hereinbefore described are eliminated.

It is important in the practice of my invention that a killed or substantially completely deoxidized steel be employed. Deoxidation may be accomplished by the use of well known deoxidizing agents such as aluminum, titanium, and the like. If the base steel contains oxygen to any appreciable extent, the zirconium, columbium, or vanadium added as an alloying and carbon stabilizing constituent will tend to react preferentially with the oxygen content of the steel and thereby fail to react completely with the carbon. The steels employed in my invention should have carbon contents as low as consistent with good steelmaking practice since it will be obvious that the lower the carbon content the less alloying metal will be required. In general, the carbon content of the steel should not be in excess of about 0.15%. In addition to carbon and the alloying metal, the steels may contain the usual amounts of the other common ingredients such as manganese, phosphorus, sulfur, and silicon.

The killed steel may be rolled into strips, sheets, or plates and the desired articles formed therefrom by methods well known in the art. The steel articles are then cleaned by any desired method which will insure a proper surface for adherence of the enamel coat, and a light-colored enamel is then applied directly to the steel base and fused thereto by firing at an appropriate temperature. As hereinafter described in greater detail, the present invention is directed particularly to the use of a light-colored enamel containing an adherence-promoting oxide selected from the group consisting of the oxides of antimony, molybdenum, and arsenic. Preferably, the adherence-promoting oxide is incorporated as part of the enamel frit.

If desired, the steel article may be subjected to a nickeling process, by methods well known in the art, whereby to deposit upon the steel a nickel film which has the effect of assisting bond obtention and also of lowering the requisite firing temperature for light-colored enamels of the above-mentioned type. Such a nickel deposit may comprise from about .02 gram to about .08 gram of nickel per square foot of surface although greater amounts may also be used, if desired. The use of a nickel treatment prior to the application of the enamel coat to the steel article permits the firing temperature of the enamel coat to be reduced by as much as 40° F. to 50° F. below the usual firing temperature required for enamels of this type. Thus, in the case where it is desired to employ the nickeling pretreatment, the steel base comprises the nickeled steel article, and the light-colored enamel coat is applied directly to the base without the conventional dark-colored ground coat.

As mentioned above, the alloying metal, i. e. zirconium, columbium, or vanadium, is employed in sufficient quantity to combine chemically with the carbon content of the particular steel being used. On the basis of experimental investigation, it has been determined that in the case of zirconium and columbium the weight ratio of alloying metal to carbon should be within the range of from about 7:1 to about 15:1. In the case of vanadium, the weight ratio of vanadium to car-

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bon should be within the range of from about 8:1 to about 18:1. The upper limits on the amounts of alloying metal are determined primarily by economic considerations, but for all practical purposes the above-indicated maximum quantities will suffice. Furthermore, by the use of the alloying metal in the above amounts, sufficient zirconium, columbium, or vanadium is provided to compensate for the usual process losses in excess of the stoichiometric quantities required, and also such amounts will be sufficient to combine with any free hydrogen which may be formed incidentally during firing of the enamel coatings as previously described.

I have found by extended experiments that there is an excellent correlation between the amount of alloying metal needed to eliminate surface defects during subsequent enameling and the amount necessary to eliminate the yield point of the steel as indicated by the conventional stress-strain curves. Accordingly, the yield point test affords a highly convenient physical technique for determining the appropriate amount of alloying metal for stabilizing the carbon content of any given steel. Thus, in order to practice my invention, the amount of alloying metal to be added to a given quantity of steel may be ascertained by either of two methods:

(1) The carbon content of the steel may be determined quantitatively by chemical or metallurgical methods and the quantity of alloying metal then calculated by selecting a weight ratio of alloying metal to carbon within the ranges disclosed above; or

(2) A series of sample steels may be prepared containing different known quantities of alloying metal and the samples then tested for yield point by conventional test methods. The samples in which the yield point has been substantially eliminated contain sufficient alloying metal to stabilize the carbon content and consequently any steel of corresponding composition will enamel satisfactorily without the conventional ground coat.

It will thus be seen that in practicing my invention the quantity of alloying metal to be added to a batch of steel in any given instance may be determined in advance by either purely chemical or by essentially physical methods.

Although the advantages of enameling steels containing zirconium, columbium or vanadium in the amounts herein disclosed are obtained with a wide variety of enamel compositions, my invention is particularly directed to the use of light-colored enamel compositions containing as part of the frit an adherence-promoting oxide selected from the group consisting of the oxides of antimony, molybdenum, and arsenic. Thus, the invention contemplates the use of a steel base containing any of the aforementioned alloying metals (zirconium, columbium, vanadium) in combination with an enamel coat containing any of the previously mentioned adherence-promoting oxides (antimony, molybdenum, and arsenic oxides).

In order to further illustrate the invention, the following specific examples are presented, but it will be understood that the scope of the invention is by no means limited to the details of these examples.

EXAMPLE I

A zirconium steel having a weight ratio of zirconium to carbon of 7.7:1 was enameled directly, i. e. without an intervening ground coat,

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using a white enamel containing antimony oxide as the adherence-promoting oxide.

The analysis of the steel was as follows (the balance being iron):

	Weight per cent
Carbon	.06
Manganese	.41
Sulfur	.015
Phosphorus	.013
Silicon	.91
Aluminum	.06
Zirconium	.46

Specimens of this steel were hot-rolled to one-quarter inch plates and samples were cut for enameling. The specimens were cleaned thoroughly, pickled, dried, and then enameled. The enamel frit had the following composition:

	Weight per cent
Sb ₂ O ₅	6.45
SiO ₂	42.22
Al ₂ O ₃	1.80
AlF ₃	10.00
CaF ₂	7.15
ZnO	3.15
Na ₂ O	12.11
K ₂ O	2.35
B ₂ O ₃	14.48
Undetermined portion	0.29

The enamel slip was prepared by combining the following mill additions:

Frit (having above analysis)	grams	3,400
Clay	do	238
Commercial opacifier	do	68
Sodium nitrite	do	4.25
Water	cc	1,400

The composition of the commercial opacifier referred to above was as follows: ZrO₂ 79.21%, SiO₂ 14.20%, Na₂O 2.23%, K₂O .25%, CaO 2.09%, Fe₂O₃ 1.03%, Al₂O₃ .63%, and undetermined portion 0.45%.

The enamel was applied to the surface of the steel samples by spraying, the thickness of the sprayed coating varying from .006 inch to .010 inch. The sprayed enamel coating was dried and fired for approximately six minutes at about 1560° F.

The samples resulting from this treatment were free of blisters, black-specks, pin-holes, and fish-scaling, and the enamel had an excellent bond, i. e. a high degree of adherence to the steel surface.

EXAMPLE II

Following substantially the same procedure as described above in connection with Example I, a zirconium-containing steel having a zirconium to carbon ratio of approximately 9.6:1 was enameled with a somewhat similar white enamel containing antimony oxide as the adherence-promoting oxide.

The analysis of the steel was as follows (remainder being iron plus sulfur, phosphorus, and other impurities in the usual amounts):

	Weight per cent
Carbon	.05
Manganese	.21
Silicon	1.62
Aluminum	.026
Zirconium	.48

The composition of the enamel frit was substantially as follows:

	Weight Percent
SiO ₂	41.90
Al ₂ O ₃	7.87
CaO	5.10
ZnO	3.15
Sb ₂ O ₅	6.45
Na ₂ O	18.03
K ₂ O	2.48
Undetermined portion (comprising principally fluorides and boric oxide)	15.02

An enamel slip was prepared using the above frit and other mill additions in substantially the same proportions as disclosed in connection with Example I. The enamel coating was applied directly to the steel without the use of an intervening ground coat. Excellent adherence was obtained with no objectionable surface defects.

EXAMPLE III

In place of the zirconium-containing steels such as those described in Examples I and II, my invention also contemplates the use of steels containing columbium in similar amounts. Typical steel compositions which I have found will enamel satisfactorily without the use of an intervening ground coat are as follows:

Sample No.	1	2	3
Carbon (weight percent).....	.05	.07	.09
Manganese.....	.28	.32	.34
Phosphorus.....	.011	.011	.013
Sulfur.....	.026	.028	.017
Silicon.....	.04	.06	.07
Columbium.....	.37	.61	1.20
Aluminum.....	.011	.034	.015
Cb/C (weight ratio).....	7.4	8.7	13.4

Any of the light-colored enamels containing antimony, molybdenum, or arsenic oxides as part of the frit may be employed successfully with steels of the above character.

EXAMPLE IV

In addition to the zirconium- and columbium-containing steels, the invention also embraces the use of vanadium-containing steels of which the following steel analyses are typical of those which have been found to enamel satisfactorily with only a single light-colored enamel coat applied directly to the steel base:

Sample No.	4	5	6	7	8
Carbon (weight percent).....	.05	.10	.04	.05	.04
Manganese.....	.28	.35	.28	.25	.27
Phosphorus.....	.007	.012	.007	.007	.008
Sulfur.....	.032	.032	.031	.028	0.27
Silicon.....	.015	.20	.015	.020	.015
Vanadium.....	.40	1.17	.52	.78	.68
Aluminum.....	.032	.061	.014	.027	.035
V/C (weight ratio).....	8.0	11.7	13.0	15.6	17.0

The foregoing steels may be enameled successfully without the use of a ground coat by means of any of the light-colored enamels herein disclosed containing antimony, molybdenum or arsenic oxides as part of the frit.

EXAMPLE V

In Examples I and II, typical antimony-containing enamel compositions were given. In place of such antimony enamels, molybdenum trioxide enamels may also be employed with equally satisfactory results. The following is a

typical molybdenum oxide enamel frit analysis and a slip composition using this frit:

Frit	Weight Percent
Sodium oxide, Na ₂ O	12.04
Potassium oxide, K ₂ O	3.58
Barium oxide, BaO	23.40
Alumina, Al ₂ O ₃	3.83
Boric oxide, B ₂ O ₃	8.87
Silica, SiO ₂	30.33
Antimony oxide, Sb ₂ O ₃	2.90
Calcium fluoride, CaF ₂	9.95
Molybdenum oxide, MoO ₃	5.10
	100.00

Mill additions

	Parts
Frit	100.00
Clay	6.00
Sodium nitrite	0.25
Opacifier	4.00
Water	45.00

Other typical molybdenum oxide enamels which may be employed are as follows, the ingredients being given on the basis of the smelter batch percentage used in producing the frit:

Ingredient	Smelter Batch, Weight Per Cent			
Borax (hydrous).....	19.0	20.0	26.6	26.5
Feldspar.....	16.6	11.5	22.2	19.3
Quartz.....	13.1	17.4	10.6	12.6
Soda Ash.....	6.3	8.7	1.8	3.0
Sodium nitrate.....	7.3	3.5	4.6	4.1
Fluorspar.....	7.8	6.4	4.1	4.9
Cryolite.....		4.4	4.0	3.5
Calc spar.....				
Barium carbonate.....	23.6	20.3	19.5	17.2
Zinc oxide.....		1.6		1.4
Molybdc oxide.....	4.0	4.4	5.4	4.1
Antimony trioxide.....	2.3	1.8	1.2	2.0
Titanium dioxide.....				1.4
	100.0	100.0	100.0	100.0

EXAMPLE VI

In place of the molybdenum oxide and antimony oxide enamels hereinbefore disclosed, arsenic oxide-containing enamels may also be employed in practicing the invention. A typical arsenic oxide enamel frit and a typical slip composition are as follows:

Frit	Weight Percent
Sodium oxide, Na ₂ O	17.73
Potassium oxide, K ₂ O	4.80
Alumina, Al ₂ O ₃	5.20
Boric oxide, B ₂ O ₃	23.60
Silica, SiO ₂	38.22
Arsenic oxide, As ₂ O ₃	2.42
Calcium fluoride, CaF ₂	8.03
	100.00

Mill additions

	Parts
Frit	100.00
Clay	7.00
Opacifier	3.00
Calcined clay	10.00
Water	47.00

Other typical arsenic-containing enamel frits which may be used are as follows, the ingredients

being reported on the basis of the smelter batch percentages employed in forming the frits:

Ingredient:			
Feldspar	4.0	1.1	1.1
Borax	29.0	30.7	26.6
Quartz	4.7	1.7	3.8
Soda ash	4.2	2.4	1.7
Soda nitre	2.0	2.0	2.4
Pearl ash	2.0	2.8	2.0
Potash nitre	41.9	2.1	2.8
Red lead	---	---	---
Cryolite	---	6.7	---
Arsenic oxide	5.1	4.6	4.6
Tin oxide	9.1	---	---
White lead	---	54.7	51.5
	---	---	58.4
	100.0	100.0	100.0

It will be seen that my invention provides a means of eliminating the conventional dark-colored ground coat from enameled steel articles. This result is accomplished by the combination of a particular steel base with a preferred class of light-colored enamels. The presence of zirconium, columbium, or vanadium in the disclosed amounts results in substantially complete chemical combination of the carbon present in the steel to form stable carbides, and in addition, any free hydrogen formed during enameling may react with the alloying metal to form the corresponding hydride. Thus, the formation and release of gaseous products during the enameling step is avoided and the cause of such surface defects as blistering, pitting, black-specking and fish-scaling is eliminated.

The elimination of the conventional dark-colored ground coat offers a number of important advantages. Obviously, the process becomes more economical as a result of the saving in material and also as a result of the elimination of a process step. Moreover, the conventional ground coat is fired at a relatively high temperature whereas the cover coats are usually fired at somewhat lower temperatures. By eliminating the application of the ground coat altogether, I avoid subjecting the enameled articles to excessively high temperatures thereby minimizing sagging and warping of the articles during the firing cycle. In addition, with the dark-colored ground coat omitted, I am able to employ a relatively thin enamel coat which is much more resistant to crazing and chipping than the thick multi-coat wear of the prior art.

I claim:

1. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing alloyed therewith a metal selected from the group consisting of zirconium, columbium, and vanadium, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of alloying metal to carbon present in the steel being from about 8:1 to about 18:1 in the case of vanadium and from about 7:1 to about 15:1 in the case of zirconium and columbium, whereby to provide sufficient alloying metal to eliminate the yield point of the steel; and (2) a coat of light-colored vitreous enamel applied directly to said base and containing as part of the frit a light-colored adherence promoting oxide selected from the group consisting of the oxides of antimony, molybdenum, and arsenic.

2. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing alloyed therewith a metal selected from the group consisting of zirconium, columbium, and vanadium, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of alloying metal to carbon present

in the steel being from about 8:1 to about 18:1 in the case of vanadium and from about 7:1 to about 15:1 in the case of zirconium and columbium; and (2) a coat of light-colored vitreous enamel applied directly to said base and containing as part of the frit a light-colored adherence promoting oxide selected from the group consisting of the oxides of antimony, molybdenum, and arsenic.

3. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing vanadium alloyed therewith, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of vanadium to carbon present in the steel being from about 8:1 to about 18:1; and (2) a coat of light-colored vitreous enamel applied directly to said base and containing as part of the frit a light-colored adherence promoting oxide selected from the group consisting of the oxides of antimony, molybdenum, and arsenic.

4. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing zirconium alloyed therewith, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of zirconium to carbon present in the steel being from about 7:1 to about 15:1; and (2) a coat of light-colored vitreous enamel applied directly to said base and containing as part of the frit a light-colored adherence promoting oxide selected from the group consisting of the oxides of antimony, molybdenum, and arsenic.

5. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing columbium alloyed therewith, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of columbium to carbon present in the steel being from about 7:1 to about 15:1; and (2) a coat of light-colored vitreous enamel applied directly to said base and containing as part of the frit a light-colored adherence promoting oxide selected from the group consisting of the oxides of antimony, molybdenum, and arsenic.

6. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing alloyed therewith a metal selected from the group consisting of zirconium, columbium, and vanadium, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of alloying metal to carbon present in the steel being from about 8:1 to about 18:1 in the case of vanadium and from about 7:1 to about 15:1 in the case of zirconium and columbium; and (2) a coat of light-colored vitreous enamel applied directly to said base and containing antimony oxide as part of the frit.

7. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing alloyed therewith a metal selected from the group consisting of zirconium, columbium, and vanadium, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of alloying metal to carbon present in the steel being from about 8:1 to about 18:1 in the case of vanadium and from about 7:1 to about 15:1 in the case of zirconium and columbium; and (2) a coat of light-colored vitreous enamel applied directly to said base and containing molybdenum oxide as part of the frit.

8. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing alloyed therewith a metal selected from the group consisting of zirconium, colum-

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bium, and vanadium, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of alloying metal to carbon present in the steel being from about 8:1 to about 18:1 in the case of vanadium and from about 7:1 to about 15:1 in the case of zirconium and columbium; and (2) a coat of light-colored vitreous enamel applied directly to said base and containing arsenic oxide as part of the frit.

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