

UNITED STATES PATENT OFFICE

2,495,836

ENAMELWARE

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No Drawing. Original application October 15, 1945, Serial No. 622,491. Divided and this application October 17, 1949, Serial No. 124,263

4 Claims. (Cl. 117—129)

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This application is a division of our copending application Ser. No. 622,491, filed October 15, 1945, which is a continuation-in-part of our application Ser. No. 501,326, filed September 4, 1943, now abandoned.

The present invention relates to vitreous enamel-coated steel articles and to non-aging alloys particularly suited for producing cold-stamped, pressed or spun shapes to be coated with vitreous enamel.

Heretofore, vitreous enamel-coated steel articles have been preferably made from rimming steels since it has been found that the use of such steels as base stock tends to eliminate many of the defects which arise as an incident to fusing the enamel coating upon the stock. These defects are generally known as blistering, specking and reboiling.

Furthermore, enamels were applied by the employment of one or more "ground coats" upon which was superposed the finish coat. The ground coat was generally rich in certain metal oxides which give a dark color to the enamel and which absorbed the so-called "reboiling" defects. The finish coat, generally white or pastel colored, could then be applied and a light-colored or white enameled article produced which was considered commercially free of blemishes.

Many attempts have been made to produce single-coated enameled articles of high quality in white and light shades but without success.

It is an object of the invention to provide a procedure for the manufacture of vitreous enamel-coated steel articles containing one coat of white or light-colored enamel that is relatively free of blistering, specking, and reboiling defects, etc., by producing a steel stock wherein the carbon, nitrogen and oxygen are totally combined with a metal other than iron.

It is also an object of the present invention to provide an alloy steel stock eminently suitable for the production of cold-formed shapes or articles enameled with a single coat of light-colored enamel.

Another object of the invention is to provide a non-aging steel wherein titanium, in the form of ferro titanium or some other alloy, is employed as an agent for combining with the carbon of the steel melt, in order to control reboiling defects which arise in enameling.

It is also an object of the invention to permit the employment of steels of the "ingot iron" type as a reliable stock for enameling purposes wherein impurities that disturb the fusion of an enamel coating during firing are absent.

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In accordance with the present invention, low-carbon steel, or "ingot iron," as it is sometimes called, may be produced which is reliably non-aging in all conditions of heat treatment, which steel can be rolled and cold-worked to produce the required forms or shapes to be enameled. Steel of this type is made by incorporating titanium in the steel in an amount sufficient to combine with all the carbon present, or somewhat in excess of this amount, but insufficient to produce titanium alloys which cannot be cold-worked without straining or fracturing. The amount of titanium required to combine with the carbon to form titanium carbide is approximately four times the amount of carbon in the steel. However, to account for usual losses incident to practical operation, addition to the melted steel of 4.5 to 5 times as much titanium as carbon has been found to be advisable. Generally, the titanium content of the finished steel is below 1% as incorporation of titanium in quantities greater than this merely increases the expense of the operation without obtaining compensating or attendant advantages. In general, the steel stock should be a relatively low-carbon steel in which the carbon is not in excess of about 0.15%. The steel will, of course, contain the usual and permissible ingredients such as manganese, phosphorus, silicon, sulphur, and the like, the manganese as is usual not being much greater than 0.60%, while the remaining ingredients, other than iron, are usually not over 0.100% each.

Titanium, as is well known, is a strong deoxidizer and consequently combines with the oxide content of the bath as well as with the nitrogen and carbon thereof. Our present information leads us to believe that sulphur and phosphorus are also probably largely combined with the titanium in steels containing the proper amount of titanium. In consequence, steel which has been treated in accordance with the present invention contains not only no carbon left in combination with iron, but is also thoroughly deoxidized, and practically all of the nitrogen, too, is combined with the titanium in a relatively inactive form. Furthermore, owing to the absence of carbon uncombined with titanium in this steel, and the well known resistance of such steel to hydrogen attack, enameling defects due to hydrogen absorbed in pickling, as well as those due to the other gaseous impurities in steel, would be avoided by the use of stock produced as specified above. It is unnecessary, therefore, to employ a ground coat between the steel base and a finish white coat as the latter can be applied

directly to the base, the cause of reboiling defects having been controlled in the manufacture of the steel.

The steel or ingot iron produced in accordance with the present invention and containing carbon not substantially in excess of 0.15% and containing at least 4.5 times as much titanium as carbon is free from any kind of strain-aging, possesses exceptionally high ductility and shows no definite or sudden yield point when stressed above the amount required for the occurrence of plastic deformation.

The steel or ingot iron of the present invention in sheet form can be cold-drawn more severely than low titanium steels, that is to say, steels containing insufficient titanium to combine with all the carbon, without tearing or wrinkling, and possesses qualities making this stock a superior base for vitreous enameling. When employing the steel or ingot iron of the present invention as a base stock, single enamel coatings of various kinds, including standard white cover-coats, can be fused to the metal surface without the necessity of employing the usual ground-coat. The resultant enamel coat is not blistered or specked, but possesses exceptionally high gloss free from blistering, reboiling, or other defects.

The following example is given merely as illustrative of the present invention and is not to be deemed limitative thereof as the scope of the invention is comprehended within the claims appended hereto.

A 200 ton heat of very low-carbon steel was made in a basic open-hearth furnace according to the usual practice for effervescing or rimming sheet steel. The carbon content was estimated as 0.04% before the heat was tapped from the furnace. In the ladle a small addition of aluminum was made, but this was not sufficient to kill the steel which produced very good rimming ingots. One ingot was killed with 175 lbs. of a finely crushed alloy containing about 65% titanium and 11% aluminum, added to the steel while the 24,000 lb. ingot was being poured. Another ingot was treated with a smaller amount of titanium using ferro titanium containing 40% titanium. The first ingot was found by analysis to contain 0.04% carbon, 0.35% manganese, 0.009% phosphorus, 0.03% sulphur, 0.01% silicon, 0.06% nickel, 0.02% chromium, 0.07% copper, 0.01% tin, 0.01% molybdenum, 0.01% aluminum, and 0.38% titanium. The steel was worked by usual commercial methods into the desired shape for enameling, in this instance into cold-finished sheets about 0.04 inch thick, and different samples of the product showed by analysis 0.041 to 0.048% carbon, and 0.308 to 0.395% titanium. All this steel, therefore, contained more than enough titanium to meet the practical requirement of at least 4.5 times the carbon content, the practical upper limit of this ratio being about 30 to 1.

Tests of this titanium sheet steel showed the following average properties, after straining by temper-rolling 1% and aging about 5 weeks:

No definite yield point.
Yield strength, 0.5% offset, 37,075 lbs. per sq. in.
Tensile strength, 51,075 lbs. per sq. in.
Elongation in 2 in., 32.2%
Rockwell B hardness, 51
Boulger-Dahle cup-drawing index, 11-27% to 100%

The Boulger-Dahle cup-drawing index was recently proposed by those authors, in a paper

presented before the A. S. T. M., as a measure of drawability. The value reported means that round flat blanks of this steel as large as $2\frac{1}{2}$ in. in diameter could be cold-drawn into standard cups of 1 in. inside diameter with 27% unbroken in the case of one sample sheet of this steel, or with no failures in the case of another sheet. These values indicate excellent cold-drawing properties for cold-rolled and aged sheet steel. A difficult cowl-top stamping for an automotive truck was also made successfully with this titanium steel although cracks and wrinkles were prevalent when the same stamping was made with a steel containing a titanium carbon ratio of 3.7:1 and therefore insufficient titanium to combine with all the carbon.

The microstructure of the sheets made from the above heat was distinctive in that no trace of iron carbide in any form, such as pearlite or cementite, could be found in the steel at 500 diameters magnification, the phases present being only ferrite, titanium carbide (or carbonitride), and the usual non-metallic inclusions such as sulphides, alumina, etc., in insignificant amounts.

Samples of the same steel sheets were enameled with various types of vitreous enamel coatings, and improved results compared to ordinary steels were found. In order to secure results which would not be influenced by the usual sand blasting or pickling practice the stock was washed free of any oil or grease with tri-sodium-phosphate solution. Four different types of vitreous enamel, including a white cover-coat not designed to be used without the usual ground-coat, were applied by spray-coating and firing. Two types of sheet steel were used, identical in chemical composition and physical form, except that one contained 0.3 to 0.4% titanium which was more than 4.5 times the carbon content, and the other contained only about 0.14% titanium or less than 4 times as much titanium as carbon. The stock containing .3 to .4% titanium showed better enameling behavior with all enamels by this comparison and in the case of the white cover-coat did not develop the usual specking and blistering which resulted when used on ordinary steel without the usual grip-coat. The improvement in enameling quality is undoubtedly due to the absence, in this titanium steel, of any particles of iron carbide (as well as of oxide or nitride in reactive form) which could react with a component of the enamel to form carbonaceous or other gases when the enamel is fused.

The formation of compounds in the steel which are stable at the enameling temperatures, by virtue of the added titanium as described above, makes possible the direct application to the metal of conventional cover-coat enamels or one coat vitreous enamel finishes for various purposes. In the case of the cover-coat enamels, this procedure avoids the use of the usual dark-colored ground or grip-coat. Since one function of such a ground or grip-coat, however, was to insure a proper bonding of the enamel with the metal base it may be desirable to promote the bonding of the cover-coat by one or more of the following methods. Such bonding methods may include:

1. Nickel flash-coating on the steel following the pickling process. The steel is immersed for five minutes at 160°-180° F. in a solution consisting of two ounces of nickel sulfate and $\frac{1}{4}$ ounce boric acid per gal. producing a coating of 0.05 to 0.1 gram per square foot. This solution is best maintained at a pH of about 4.0 and

should be followed by a rinse with a similar pH and then a neutralizing bath.

Application of a single enamel coating to sheets of steel of the type described herein and containing titanium in an amount more than four times the carbon, which have been thus nickel-treated, was made as follows:

A commercial vitreous enamel frit of the zirconium-opacified type was milled with 40% water, 6% enameling clay, 2% zirconium oxide opacifier, and $\frac{1}{16}$ % sodium nitrite to a fineness of 5 grams dry residue on 200 mesh screen from 100 cc. sample. The resulting enamel slip was applied in one coat at a weight of 40 grams per square foot by spraying and, after drying, was fired for four min. at 1550° F. The resulting coating was a commercially acceptable white with a reflectance of 74 plus, as determined by the Hunter reflectometer.

2. Antimony-containing enamels which are suitably compounded and applied to metal which has been hard-pickled as should result from a treatment of 15 to 20 minutes in the usual sulphuric acid pickle bath can develop a practical bond by virtue of the antimony content. The following composition is an example of such an enamel:

Dehydrated borax	20.08
Fluorspar	6.87
Zinc oxide	3.03
Potash feldspar	8.70
Cryolite	9.60
Antimonate of soda	7.41
Quartz	35.00
Potassium nitrate	2.43
Soda ash	6.88
	100.00

A frit was made by smelting down the raw batch to an opaque glass at about 2000° F. For application to the steel base of the present invention, this was milled with 6 to 7% Kentucky Ball clay #5, about 6% zirconium oxide opacifier, $\frac{1}{16}$ % sodium nitrite to a fineness of 5 gram dry residue on a 200 mesh screen from 100 cc. of sample. As before, a single coat was applied at 40 gram per square foot and fired at 1480 to 1500° F. with production of a blemish-free ivory-colored finish.

3. The use of molybdc oxide in combination with antimony compounds in the enamel may be used as a method of securing bond. The following enamel is representative:

Dehydrated borax	17.94
Soda ash	19.23
Quartz	25.43
Nitrate soda	3.45
Calcspar	9.40
Barium carbonate	3.70
Talc	7.13
Antimony oxide	2.87
Milled zircon	6.00
Potash feldspar	4.20
Molybdc oxide	.65
	100.00

The batch was smelted at 200° to 2050° F. and the frit milled with 8% Kentucky Ball clay, 6 to 8% zirconium oxide opacifier, $\frac{1}{16}$ percent sodium nitrite to the standard fineness as before. The single coat of 40 gram per square foot, fired

at 1500° F. was an excellent cream-colored blemish-free enamel.

4. The introduction of a small amount of As_2O_3 to an enamel is a well-known means of producing a bond with the metal. The following is an example of such an enamel:

Dehydrated borax	35.41
Quartz	20.30
Potash feldspar	18.90
Soda ash	10.40
Cryolite	4.73
Fluorspar	4.48
Sodium nitrate	5.08
Arsenic oxide (As_2O_3)	.70
	100.00

The frit obtained by smelting the batch at about 2100° F. was milled with 5 to 6% Kentucky Ball clay, 4-6% zirconium oxide opacifier and $1\frac{1}{2}$ % magnesium carbonate to 10 gram fineness. The enamel was applied at 40 gram per square foot to the titanium steel of the present invention and fired at 1520° F. with production of an excellent gray enamel.

In addition to the above examples of bonding, it is also possible to improve enamel adherence by the electrical deposition of a molybdenum compound on the metal, by the application of cobalt compounds to the surface of the metal, and by the introduction of vanadium to the enamel.

From the foregoing, it will be apparent that the present invention provides a suitable stock of killed and non-aging steel by the inclusion in low carbon steels, that is to say, steels containing less than about 0.15% carbon, of titanium in an amount at least 4.5 times the amount of carbon, from which metal articles can be formed or shaped by cold-working or cold-rolling, which articles can be coated with vitreous enamel coatings free from the usual defects of blistering, specking or reboiling.

What is claimed is:

1. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing titanium alloyed therewith, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of titanium to carbon present in the steel being from about 4:1 to about 30:1; and (2) a coat of light-colored vitreous enamel applied directly to said base and containing as part of the frit an 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 titanium alloyed therewith, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of titanium to carbon present in the steel being from about 4:1 to about 30:1; and (2) a coat of light-colored vitreous enamel applied directly to said base and containing antimony oxide as part of the frit.

3. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing titanium alloyed therewith, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of titanium to carbon present in the steel being from about 4:1 to about 30:1; and (2) a coat of light-colored vitreous enamel applied directly to said base and

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containing molybdenum oxide as part of the frit.

4. A light-colored enameled steel article comprising: (1) a steel base comprising a killed steel containing titanium alloyed therewith, the carbon content of said steel being not in excess of about 0.15% and the weight ratio of titanium to carbon present in the steel being from about

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4:1 to about 30:1; 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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No references cited.