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METHOD OF ENAMELING STEEL

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ABSTRACT OF THE DISCLOSURE

Manufacture of vitreous enameled steel articles from steel containing less than .01% carbon and 0.02 to 0.10% phosphorus, including cold forming articles from such steel, pickling in dilute acid and enameling the articles so formed.

This application is a division of my copending application Ser. No. 289,397, filed June 20, 1963, now abanboned.

This invention relates to improvements in the production of porcelain enameled articles.

Heretofore the grades of sheet steel most widely used in the production of porcelain enameled articles have been (a) for ordinary wares, low carbon (.04–.10 carbon) rimmed steel and (b) for more critical applications, a lower carbon (.01–.03 carbon) low metalloid steel often termed "enameling iron." With either stock, the conventional enameling procedure includes forming the sheet to finished shape, cleaning, pickling and otherwise preparing the surfaces of the formed article and the application of two coats of enamel, the first termed the "ground" or "blue coat" and the second, the "color" or "finish coat."

To reduce enameling costs, there has been a continued effort to eliminate the ground coat from the above sequence. However, past attempts to apply the finish coat directly to the steel resulted in the development of surface defects in the coating. Although it was known that these defects were caused by the evolution of carbon-oxide gases from the steel during the firing of the enamel and could be avoided by fully decarburizing the steel stock prior to the application of the enamel, no commercially feasible method for such decarburization existed until the recent development of practical equipment for loose-coiling of steel strip. The latter has made possible the modification of box-annealing now known as "open-coil" annealing, wherein, by reason of the fact that the annealing atmosphere has free access to all surfaces of the steel coil, the chemical analysis of the steel can be modified within practical time intervals and in equipment of practical size. The changes in steel composition which can be effected by open-coil annealing are controlled by controlling the analysis of the annealing gas, the time and temperature in the annealing operation. Application of the open-coil technique using a decarburizing gas in the annealing of rimmed steel provides enameling stock characterized by a carbon content of less than 0.008%. This stock has been termed "direct-on" enameling steel since, due to the low carbon content, a single coat defect-free enamel coating can be produced thereon.

The compositions of conventional enameling stocks are tabulated below:

TABLE I

	C	Mn	P(max.)	S(max.)	Si(max.)	Al (max.) (total)	Fe[1]
Rimmed steel	0.04/0.10	0.20/0.50	0.012	0.035	0.02	0.015	Bal.
Enameling iron	0.01/0.03	0.05/0.20	0.010	0.035	0.02	0.015	Bal.
Direct-on	0.001/0.008	0.15/0.60	0.012	0.035	0.02	0.015	Bal.

[1] May include residual amounts of other elements such as copper, nickel, chromium, molybdenum and tin which do not affect the properties.

While the above conventional direct-on steel possesses excellent enameling properties, it suffers from a serious limitation; its extremely low carbon content renders it, when slightly strained or cold worked, extremely susceptible to abnormal grain growth at the temperatures encountered in firing of the enamel coating. The result is that any formed areas of the enameled article are extremely weak and therefore easily deformed during subsequent handling or use. As a consequence, the areas of use of this material have been limited.

It is an object of the present invention to provide an improved direct-on enameling steel which possesses a higher yield strength after cold working and heating to enameling temperatures than that afforded by conventional "direct-on" stock.

Another serious limitation of the conventional direct-on enameling steel is, it pickles too slowly. The pickling prior to enameling is a critical operation in the enameling procedure; experience in the trade has shown that a definite degree of etch is essential if good coating adherence is to be achieved. In the case of the "direct-on" application of the "finish" coat of enamel, i.e. the enameling system in which the use of a ground coat is eliminated, it has been found in the enameling industry that a minimum of 2 grams of iron per square foot of steel surface must be removed to properly prepare the surface. The pickling time required to remove this quantity of iron from the currently available "direct-on" steel has proven to be between 15 and 30 minutes; in contrast, the pickling times for preparing steels for application of ground-coat enamels is between 3 and a maximum of 10 minutes. This increased pickling time makes the use of the present "direct-on" steel economically unattractive to enamelers.

Accordingly, it is another object of the invention to provide a direct-on stock which will pickle more rapidly and to accomplish this without serious impairment of either forming or enameling characteristics.

The accomplishment of the aforementioned and other objects will be apparent from the following specification.

In my search for solutions to the above problems, I have discovered that the pickling rate of low metalloid steels containing carbon up to about 0.008%, is approximately tripled, when phosphorus in excess of about 0.02% is added thereto. The effect of phosphorus in this regard is illustrated in the following tabulation:

TABLE II

Steel	P	Weight loss, g./ft.^{2} 10 min.
A	0.008	1.43
B	0.034	4.35
C	0.050	4.14
D	0.099	8.84
E	0.14	9.3

The above tests steels all contained carbon less than 0.005% together with manganese, sulphur, silicon and other residual elements in the amounts normally present in enameling stock. Steel A is typical of the conventional direct-on enameling steel. The tabulated weight-losses are specific to pickling the steels for 10 minutes in an 8% sulphuric acid solution at approximately 155° F. It will be noted that the pickling rate or effectiveness rises sharply with increasing phosphorus up to about 0.10% but that further increase is relatively ineffective. In applying this

discovery, I have found that, under the pickling conditions normally encountered in commercial enameling operations, a phosphorus content of about 0.06% allows removal of the desired minimum of 2 grams of iron per square foot of steel surface in from 3 to 5 minutes. Such pickling times compare favorably with those used in preparing the rimmed and the enameling-iron grades of stock.

In addition, I have found that increasing the phosphorus in these extremely low carbon steel compositions significantly increases the yield strength thereof after critically straining and annealing for 5 minutes to simulate enamel firing. The effect of phosphorus in this respect is illustrated below.

TABLE III

Steel	Phos., percent	Yield strength, p.s.i.	Tensile strength, p.s.i.	Elong. in 2", percent	Hardness, Rockwell B	Swift cup [1]	Minimum yield strength after enamel firing [2] 5 min. at 1,450–1,500° F.
A	0.008	29,700	44,900	41.0	46	2.3	11,900
B	0.034	31,700	47,200	40.0	46	2.3	13,900
C	0.050	31,000	45,600	39.5	50	2.3	17,050
D	0.099	31,100	51,200	32.5	54	2.2	20,000
E	0.14	30,700	50,500	33.0	50	2.1	23,600

[1] The Swift cup test provides a measure of the formability of sheet materials, a description of the test will be found in Sheet Metal Industries, March 1957, p. 203 and April 1957, p. 257.
[2] Specimens critically strained 4 to 12% to simulate cold forming prior to enamel firing.

It will be noted that phosphorus up to about 0.10% can be added without significantly affecting the formability of these steels and that below this amount the essential increase in yield strength after cold straining and heating is obtained without detectable loss of ductility. As indicated by the mechanical test results the operating range of the phosphorus addition is between about 0.02 and 0.10% and within this range I prefer about 0.06%.

The foregoing improvements are obtained without any adverse effect on enameling characteristics, i.e. any steel falling within the following composition range possesses enameling properties equal or superior to those of the currently available direct-on stock and are substantially free of the limitations of the latter:

C	0.001/0.008
Mn	0.15/0.60
P	0.02/0.10
S(max.)	0.035
Si(max.)	0.02
Al(max.) total	0.015
Fe*	Bal.

*May include the usual residuals of other elements in amounts which do not deleteriously affect the properties.

In practicing my invention, however, I prefer to manufacture stock of the following more limited analysis: 0.006% carbon, 0.15 to 0.45% manganese, 0.03 to 0.06% phosphorus, 0.035% sulphur, 0.01% maximum silicon, 0.01% maximum total aluminum, with the balance essentially iron.

The preferred practice of my invention is outlined below

Manufacture starts with making of the steel. The heat is melted to the usual 0.10% carbon maximum low metalloid rimmed steel specification containing at least 0.15% manganese using any suitable conventional practice, but the phosphorus content of the heat is adjusted to lie in the range 0.02–0.10%, preferably to between about 0.03 and 0.06%. The heat is cast, hot rolled, continuously pickled and cold reduced to strip of ordered gauge and width, in accordance with the conventional practices used in these operations. Upon completion of the cold reduction, the strip may be alkaline cleaned to remove cold mill lubricants after which it is loose-coiled and then open-coil annealed at 1275 to 1300° F. in a decarburizing atmosphere until its carbon content is reduced to at least 0.008% and preferably to 0.006% or less. While any suitable decarburizing atmosphere may be used, I prefer an atmosphere of the following composition:

Hydrogen	percent 9
Nitrogen	do 91
Water vapor	dewpoint ° F 55–60

Following the annealing operation, the strip is recoiled, temper rolled, if desired, and sheared into cut sheets of ordered length. The resulting sheets are then cold formed into the articles of the desired shape, alkaline cleaned to remove grease and drawing lubricants, rinsed in water, and then pickled in dilute sulphuric acid (e.g. an 8% by weight aqueous solution of H_2SO_4), for up to 10 minutes to remove a minimum of 2 grams of iron per square foot of article surface. After rinsing to remove residual pickle acids, the articles are flashed with nickel, using any of the common aqueous nickel salt solutions available for this purpose. Upon completion of the preparatory steps, the articles are given a final rinse preferably in a slightly alkaline neutralizing solution, dried and subsequently coated with enamel slip. The article is next subjected to a low temperature drying operation to remove excess water from the slip and then fired in a suitable furnace for about 5 minutes at a temperature sufficient to vitrify the coating. The temperature of firing will depend upon the composition of the enamel but will generally fall in the range of 1300 to 1500° F.

Although the new stock is intended primarily for one coat enameling, it is, of course, admirably adapted to the production of quality ware by the two-coat process. In the latter case, the first coat of enamel applied after the preparatory steps will be a "ground" coat, this is fired and a second coat of slip compounded to the desired color is applied, dried and fired to produce the finished article.

While I have shown and described certain specific embodiments of my invention, it will be obvious that certain modifications therefrom can be made without departing from the scope of the appended claims.

I claim:

1. A method of making vitreous enameled steel articles comprising obtaining steel stock containing 0.001 to 0.008% carbon, at least .15% manganese, up to .015% aluminum and 0.02 to 0.10% phosphorus, cold forming said stock into articles of the desired shape, pickling said articles in dilute acid to remove at least 2 grams of iron per square foot of article surface, coating said articles with enamel slip and then heating the coated articles to vitrify the coating.

2. A method of making vitreous enameled steel articles comprising obtaining steel stock containing .006% maximum carbon, .15 to .45% manganese up to .015% aluminum and .03 to .06% phosphorous, cold forming said stock into articles of the desired shape, pickling said articles in dilute acid to remove at least 2 grams of iron

per square foot of article surface, coating said articles with enamel slip and then heating the coated articles to vitrefy the coating.

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