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VITREOUS ENAMELING STEEL AND METHOD OF MAKING SAME

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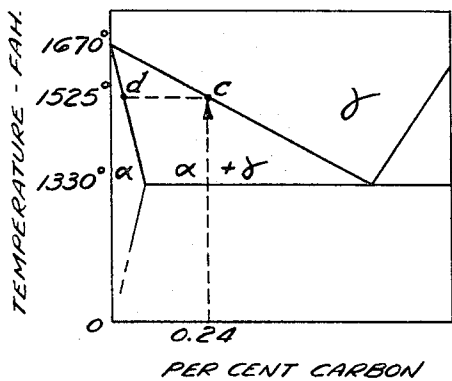


Fig. 1

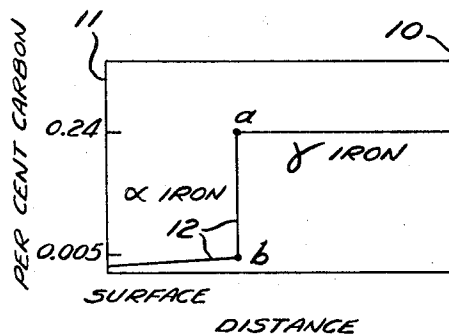


Fig. 2

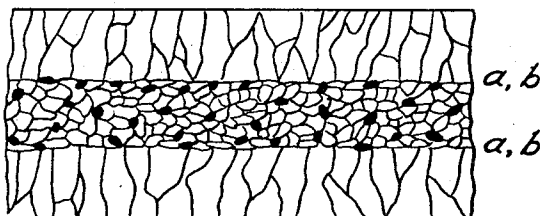


Fig. 3



Fig. 4

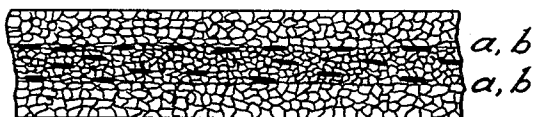


Fig. 5

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VITREOUS ENAMELING STEEL AND METHOD OF MAKING SAME

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ABSTRACT OF THE DISCLOSURE

A method of producing steel sheets for vitreous enameling in which a low carbon steel sheet is subjected to two-phase gamma-alpha decarburization whereby outer zones of alpha-iron are produced having a carbon content of not more than about .006% and extending inwardly from about 25% to about 37% with the sheet thickness, the center zone of the sheet remaining substantially unchanged, and then subjecting the sheet to cold reduction followed by sub-critical annealing.

This invention relates to a new and improved sheet steel for vitreous enameling and method of making same, and more specifically to a sheet steel suitable for single coat or direct white vitreous enameling that does not exhibit the serious loss in strength after forming and enameling that is exhibited by presently available direct white enameling sheet steels.

The suitability of a steel for one coat or direct white enameling is judged primarily by its ability to accept an enamel coat that is free of visible blemishes or defects and this suitability is known to be dependent upon such processing variables as chemical composition, hot rolling practice, cold rolling practice, and annealing practice. Correlations among these variables and freedom from observable defects in overlying enamel coats have long been sought.

The visible defects in enamel coats that are caused by evolved gases may be classified into two categories, namely, (1) delayed or low-temperature defects, such as fish scales, shiners, pop-offs, and bloats, and (2) high-temperature defects, such as blisters, pinholes, pits, black specks, and copperheads. The delayed defects appear after the enameled steel has been fired, occurring during the cooling after the glass has become rigid, or even long after the steel-enamel unit has been cooled to room temperature. The source of this trouble is known to be hydrogen dissolved or trapped in the steel which is liberated in the steel-enamel elevated temperature reaction and subsequently precipitated at the steel-enamel interface with resulting rupturing of the enamel glass.

The high temperature defects, on the other hand, are formed during the time of firing and result from a gas induced boiling of the enamel, the so called "primary boiling" phenomenon. It is generally agreed that the evolution of the carbon oxides, CO and CO₂, during the first firing of the enamel causes primary boiling, and that these carbon oxides are formed by oxidation of the carbon in or adjacent to the sheet steel surfaces.

Sheet steels (the term "sheet" being used inclusively herein to refer to thin steel either in elongated strip or separate flat sheet form) in widespread use for many decades in the enameling trade for the two coat practice are principally low metalloid rimmed steel (commonly referred to as enameling iron, enameling steel, or ingot iron and specifically produced for vitreous enameling applications) and rimmed cold rolled steel, a general purpose low carbon sheet with inclusion free surfaces produced for general usage in the stamping and forming trades and diverted to enameling usage because of its non-

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premium price. In certain drawing operations where neither the "low metalloid" or "rimmed" steels possess sufficient ductility, aluminum killed low carbon cold rolled steel is substituted by the enameling shop.

The suitability of the three grades of sheet steel product, the "low metalloid," the "rimmed," and the "aluminum killed," for single coat or direct white enameling has been thoroughly tested over the years and each product is found deficient in one or more respects. It is to be understood that direct white enamel coats are appreciably more sensitive to the development of defects than are the two coat enamel systems, and that suitability for two coat enameling provides little, if any, indication of suitability for direct white enameling.

During single coat or direct white enamel firing of the three grades of sheet steel in common use for two coat enameling, namely, the low metalloid, the rimmed, and the aluminum killed, all exhibit the enamel bubbling action, commonly referred to as primary boiling, that is caused by the evolution of gases from the steel. That this primary boiling may be reduced to unobjectionable intensity, with a consequent elimination of the associated enamel defects, by removing carbon from the steel sheet during steel processing has been referred to previously both in the technical and patent literature. For example, the J. C. Eckel et al. Patent No. 2,455,331 of Nov. 30, 1948 describes the surface decarburization by wet hydrogen annealing of formed sheet steel articles preceding the application of a light colored finish coat of porcelain enamel. The articles are in substantially their final shape at the time of annealing. The superficial surface decarburizing treatment proposed by Eckel et al. has not yielded a satisfactory direct white enameling steel despite diligent, prolonged, and exhaustive testing programs, both laboratory and commercial; and the use of continuous annealing techniques in steel mill processing to obtain superficial decarburization also proved to be unsuitable for the production of non-primary boiling direct white enameling sheet steels.

The need for more thorough decarburization than that obtainable by box or continuous annealing was met by the development of the "open coil" annealing technique that is described in the Lee Wilson et al. Patent No. 3,114,539 dated Dec. 17, 1963. In comparison with box or continuous annealing, the open coil process permits exposure of the whole steel surface of a coil of strip steel to an annealing environment for whatever lengthy time period is required to complete the desired gas-metal interactions. The open coil process is highly efficient for uniformly decarburizing steel sheet and thereby providing steel suitable for direct white porcelain enameling. This sheet product, which exhibits a minimum tendency for hydrogen and primary boiling defect formation, is the normal rimmed steel decarburized throughout its thickness by open coil annealing.

A rimmed steel, of typical analysis as follows:

Carbon	-----percent---	0.05-0.10
Manganese	-----do---	0.12-0.45
Phosphorus	-----percent maximum---	0.010
Sulphur	-----do---	0.025
Silicon	-----do---	0.010
Copper	-----do---	0.10
Iron	-----do---	Balance

is processed by producing a hot rolled strip or band on a continuous hot strip mill, pickling, cold reducing the hot band to the desired thickness, open-coil decarburizing at 1300° F. to reduce carbon uniformly throughout full sheet thickness to 0.005% max., and then temper rolling if desired. The decarburizing atmosphere may be hydrogen, hydrogen-nitrogen or DEOX type gas moistened with wa-

ter at the annealing temperature to obtain an environment oxidizing to carbon but non-oxidizing to iron.

Typical tensile properties and hardness of such a through decarburized open coil of steel strip annealed product are:

Tensile strength	-----p.s.i.---	42,000
Yield strength	-----p.s.i.---	28,000
Elongation in 2 inches	-----percent---	40
Hardness, Rockwell B	-----	35-42

Although exhibiting freedom from both elevated temperature and delayed type defects in overlying direct white enamel coats, such through-decarburized rimmed steel exhibits a major deficiency that has markedly detracted from its acceptance as a commercially useful product. This deficiency is the serious loss in strength that occurs as a result of grain growth during enamel firing in the range 1350° to 1550° F. Grain growth occurs in those areas of the basis material that have been strained during sheet metal forming operations. Areas strained in the range 5 to 15% are particularly susceptible to critical grain growth during the enamel firing operation and grain sizes of ASTM No. 1 to 3 are commonly exhibited by such sections. A drop in yield strength occurs in such critically strained areas. Invariably, areas of critical strain are encountered in the press forming of any object, and vitreous enamel fired over these areas is subject to spalling, particularly during assembly operations where the weakened metal readily stretches or yields.

Several approaches to solving the problem of loss of strength have been investigated by steel producers, but without success. The desired product, i.e., a direct white enameled sheet with a minimum yield strength in the range 22,000 to 25,000 pounds per square inch after enamel firing, regardless of the amount of prestraining, had not been developed prior to the present invention and accordingly it is an object of our invention to provide a sheet steel product, and method of making same, that will exhibit the desirable direct white enameling characteristics of through decarburized rimmed steel and that will, at the same time, exhibit after forming and enamel firing, a yield strength in the range common to normal non-decarburized low carbon rimmed steel.

Other objects of our invention will become apparent from the following description, reference being had to the accompanying drawings in which:

FIGURE 1 is a partial iron-iron carbide equilibrium diagram illustrating the decarburization reaction which occurs in carrying out our process.

FIGURE 2 is a chart showing the carbon content of a cross section of a steel sheet, from the center to one outer surface thereof, that has been processed in accordance with our invention.

FIGURE 3 illustrates the micro-structure of the cross section of a steel sheet in accordance with our invention after two phase gamma-alpha decarburization has been completed.

FIGURE 4 is a cross sectional view similar to FIGURE 3 but illustrating the micro-structure of the sheet after it has been cold rolled to the final thickness.

FIGURE 5 is a cross sectional view similar to FIGURES 3 and 4 but illustrating the micro-structure of the sheet illustrated in FIGURE 4 after it has been subjected to sub-critical annealing and temper rolling.

The sheet steel product of this invention is attained by the practice of a two phase decarburization (from the gamma-iron to the alpha-iron condition) as is illustrated in FIGURES 1 and 2. In this procedure a coil of strip steel, suitably opened so that all surfaces thereof are exposed to the treating atmosphere, is heated in an enclosed furnace chamber or retort by a circulating gaseous atmosphere to the minimum temperature at which the structure of the steel is substantially entirely gamma-iron. The particular temperature required is dictated by the chemical composition of the steel, and for the non-alloyed

plain carbon steels, is dependent on the carbon and manganese content. Thus, as illustrated in FIGURE 1, for a plain carbon steel having a carbon content of 0.24%, a temperature of 1525° F. provides the required temperature environment wherein the structure of the steel is a solid solution of carbon in gamma-iron.

After the opened coil of 0.24% carbon steel has been heated to the gamma-iron field, as indicated at point *c* in FIGURE 1, a decarburization reaction is initiated by the introduction of water vapor into the furnace atmosphere to obtain a partial pressure of oxygen that is oxidizing to carbon but not to iron. As carbon is removed from the gamma-iron sheet, initially from the surface and then subsequently from the sub-surface thereof, the outer zones which have lost carbon, undergo a micro-structural change from the gamma-iron to the alpha-iron crystal structure. This change is indicated in FIGURE 1 by the line *c-d*.

As the decarburization reaction proceeds, the alpha-iron crystals or grains grow inwardly from both outer surfaces of the sheet replacing the previously existing original gamma-iron crystals or grains. At any instant during the decarburizing annealing step, the gamma-iron and the alpha-iron phases, or structures, or crystals, co-exist in equilibrium at the moving decarburization front which is illustrated by line *a-b* in FIGURE 2.

In FIGURE 2 the right hand vertical dot and dash line 10 represents the center of the cross section of the sheet and the left hand vertical line 11 represents one outer surface of the sheet. The line 12 charts the carbon content of the steel against the distance inwardly from the outer surface toward the center, and it will be seen that, under the conditions of FIGURE 2, decarburization from the original .24% carbon down to less than .005% carbon has proceeded from the outer surface 11 inwardly a little less than one-half of the distance to the center 10 of the cross section of the sheet, or a little less than one-fourth the thickness of the sheet. The vertical portion of line 12 (FIGURE 2) between the essentially carbon free outer alpha-iron zone and the high carbon gamma-iron inner center zone or core, moves inwardly from the surface of the sheet during this decarburizing treatment at a calculable rate as the carbon is removed from the sheet by outward lattice diffusion and subsequent oxidation at the sheet surface. It will be understood that a similar and substantially equal decarburization will simultaneously occur from the other surface of the sheet inwardly toward the center to produce a similar substantially carbon free outer alpha-iron zone on the other side of the sheet.

This two phase gamma-alpha decarburization procedure is continued until a cross sectional micro structure of the sheet as illustrated in FIGURE 3 is obtained. The sharp demarcation line or boundary between the decarburized outer zones and the high carbon inner ferrite-carbide zone or core is characteristic of our gamma-alpha decarburizing practice which allows center core carbon to be retained at its original value while the surfaces, and the sub-surface zones for a predetermined degree inwardly, are rendered substantially carbon free.

After completion of the above described decarburization the coil of steel is cold reduced to the required final thickness, the micro structure of the cross section of the so cold reduced sheet being shown in FIGURE 4. Relief of the cold rolling stresses is then preferably effected by a sub-critical anneal in the temperature range of 1150° F. to 1275° F. The resulting stress relieved product may then be temper rolled to meet specific forming requirements and the cross sectional micro structure of the fully processed sheet is illustrated in FIGURE 5. It will be noted that the demarcation lines *a*, *b*, between the outer zones and the center zone remain clearly defined in the sheet under the three conditions illustrated in FIGURES 3, 4 and 5.

The following procedure has been used in the pro-

cessing, according to this invention, of a hot rolled and pickled steel. A coil of strip steel, of composition 0.24% carbon, 0.43% manganese, 0.004% phosphorus, 0.022% sulphur and remainder iron, of thickness 0.095", of width 35½", and of weight 2190 pounds, was opened to provide an effective spacing between laps of approximately 0.150" by the use of a twisted wire separator. The two phase gamma-alpha decarburizing treatment described above was carried out according to the following schedule:

- (1) Coil placed in enclosed furnace chamber.
- (2) Chamber purged with dry 8% hydrogen-92% nitrogen gas at a flow of 900 cubic feet per hour for 1 hour.
- (3) Coil heated to 900° F. by heated circulating atmosphere.
- (4) At 900° F. gas composition changed to 20% hydrogen-80% nitrogen and flow to 1500 cubic feet per hour.
- (5) Coil heated to 1525° F. by heated circulating atmosphere.
- (6) Water vapor introduced at coil temperature of 1525° F. to obtain an outlet dew point in the range +80° to +85° F., and soak for 8 hours at 1525° F.
- (7) Atmosphere dried out at 1525° F. to +20° F. dew point.
- (8) Charge cooled to 175° F. and furnace chamber opened.

After the two phase decarburizing the coil was cold-reduced from the hot rolled thickness of 0.095" to 0.036" (20 gage) and then sub-critically annealed (as an open coil) for 3 hours at 1275° F. in dry 20% hydrogen-80% nitrogen gas atmosphere.

Chemical and metallographic analysis of the sheet product produced by the above described procedure revealed that the carbon content of the center core portion of the sheet remained unaltered throughout the processing cycle, and that the high carbon center zone or core occupied substantially the desired one third central portion of the sheet thickness. Direct white enameling characteristics were excellent and a minimum yield strength, after critical straining and enamel firing, of 22,800 pounds per square inch was exhibited by the sheet product. Freedom from elevated temperature enamel defects was obtained because of the absence of carbon in surface and sub-surface zones. Freedom from room temperature or delayed type enamel defects was obtained because of the presence of a ferrite-carbide core structure within the sheet during cold reduction. Catastrophic loss in yield strength after critical straining and enamel firing, which is characteristic of presently produced through-decarburized steel sheets, was avoided because objectionable ferrite grain growth was restricted to the outer decarburized alpha-iron zones while the pearlitic center core portion retained its strength.

The following table shows the comparison between the yield strength, after critical straining and enamel firing, of direct white enameling steel sheet produced by the method disclosed herein (column A) and direct white enameling sheet produced by the conventional process of through-decarburizing at sub-critical temperatures (column B):

Strain Before Firing, percent	Yield Strength, p.s.i.	
	A	B
0	32,000	23,500
4	32,500	13,500
8	27,500	13,800
12	26,000	14,500
16	23,000	16,250
20	23,500	16,750
24	25,250	17,500

In the practice of our herein described procedure to produce our improved enameling steel, it is preferred that the two phase alpha-gamma decarburizing step be carried on for a time sufficient to decarburize the sheet inwardly from each surface thereof for a distance at least 25% of the strip thickness. It is also preferred that the decarburization be terminated when the undecarburized center core portion has a thickness of not less than about 25% of the strip thickness. Furthermore, although we have rather specifically described our procedure as applied to a particular steel of a particular carbon content, it will be understood that our improved process may be utilized for the production of enameling steel from sheet of other carbon contents and that the specific times, temperatures, gas compositions, etc. referred to herein may be modified from those specifically mentioned. Accordingly we do not wish to be limited to the specific procedures and products herein illustrated and described but claim as our invention all embodiments coming within the scope of the appended claims.

We claim:

1. The method of producing steel sheet for vitreous enameling which comprises subjecting a low carbon steel sheet having an initial carbon content of not less than of about .20% to a two-phase gamma-alpha decarburization step by heating the sheet to the minimum temperature at which the structure of the steel is substantially entirely gamma-iron, subject the sheet, while maintaining said temperature, to a decarburizing atmosphere, maintaining the sheet in said atmosphere at said temperature until outer zones of alpha-iron having a carbon content of not more than about 0.006% are produced extending inwardly on each side of the sheet for at least about 25% but not more than about 37% of the sheet thickness, and subsequently subjecting the sheet to cold reduction followed by sub-critical annealing.

2. A steel sheet for vitreous enameling produced by the process defined in claim 1.

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CHARLES N. LOVELL, Primary Examiner.