METHOD OF ENAMELING STEEL

Michael Kotyk, Durham, N.C., assignor to United States Steel Corporation, a corporation of Delaware


Invent. C, C23g 1/02; C23d 5/02, 3/00

U.S. Cl. 29—257

2 Claims

ABSTRACT OF THE DISCLOSURE

Manufacture of vitreous enameled steel articles from steel containing less than .01% carbon and .02 to .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 abandoned.

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 "enameled 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 gas 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-collar 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 .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>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>Rimmed steel</td>
</tr>
<tr>
<td>Direct-on</td>
</tr>
</tbody>
</table>

The above tests steels all contained carbon less than .0005% 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 picking the steels for 10 minutes in an 8% sulphuric acid solution at approximately 155° F. It will be noted that the picking rate or effectiveness rises sharply with increasing phosphorus up to about .010% 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 steel.

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.

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:

<table>
<thead>
<tr>
<th>Steel</th>
<th>Phos., percent</th>
<th>Yield strength, p.s.i.</th>
<th>Tensile strength, p.s.i.</th>
<th>Elong. in 2&quot;, percent</th>
<th>Hardness, Rockwell B</th>
<th>Swift cup</th>
<th>Minimum yield strength after enameling firing, 5 min. at 1,450-1,500° F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.068</td>
<td>30,700</td>
<td>44,500</td>
<td>41.0</td>
<td>46</td>
<td>2.3</td>
<td>21,100</td>
</tr>
<tr>
<td>B</td>
<td>0.084</td>
<td>31,300</td>
<td>47,300</td>
<td>40.0</td>
<td>46</td>
<td>2.3</td>
<td>18,500</td>
</tr>
<tr>
<td>C</td>
<td>0.050</td>
<td>21,600</td>
<td>45,500</td>
<td>39.4</td>
<td>50</td>
<td>2.2</td>
<td>17,600</td>
</tr>
<tr>
<td>D</td>
<td>0.009</td>
<td>21,100</td>
<td>51,250</td>
<td>34.2</td>
<td>50</td>
<td>2.2</td>
<td>20,000</td>
</tr>
<tr>
<td>E</td>
<td>0.14</td>
<td>36,700</td>
<td>50,600</td>
<td>33.0</td>
<td>50</td>
<td>1.1</td>
<td>23,600</td>
</tr>
</tbody>
</table>

*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. 206 and April 1957, p. 207.

Specimens critically strained 2 to 12% to simulate cold forming prior to enamel firing.

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 enamelled steel articles comprising obtaining steel stock containing 0.01% to 0.008% carbon, at least 15% manganese, up to 0.15% aluminum, 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, and then heating the coated articles to vitrify the coating.

2. A method of making vitreous enamelled steel articles comprising obtaining steel stock containing .006% maximum carbon, .15 to .45% manganese up to .015% aluminum and .03 to .06% 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.

References Cited

UNITED STATES PATENTS

2,109,271 2/1938 Krause 75—123 X
2,639,264 5/1953 Chester 117—53 X
2,677,624 5/1954 Eckel et al. 117—53
2,956,906 10/1960 Blickwede et al. 117—129 10
3,193,417 7/1965 Kopchak 117—129 X
3,244,565 4/1966 Mayer 148—12

OTHER REFERENCES


RALPH S. KENDALL, Primary Examiner.

U.S. Cl. X.R.

117—53, 129; 148—31, 16