Nov. 30, 1948. J. C. ECKEL ET AL 2,455,331

METHOD OF ENAMELING

Filed Oct. 24, 1944

Fig. 1.

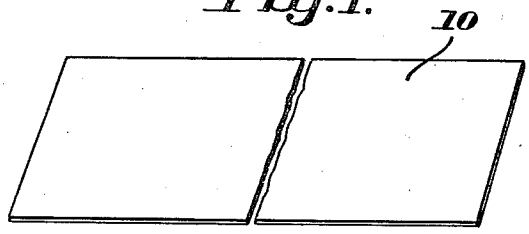



Fig. 2.

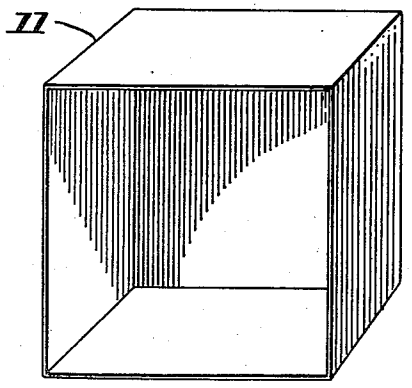



Fig. 3.

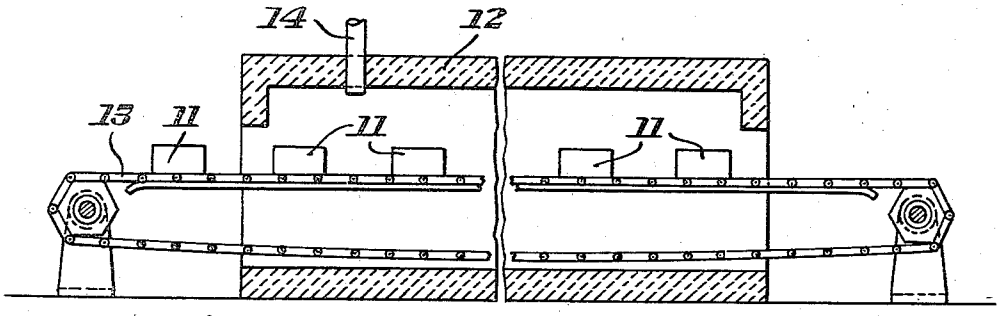



Fig. 4.

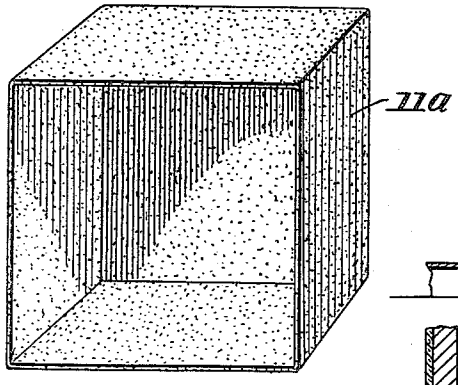



Fig. 5.

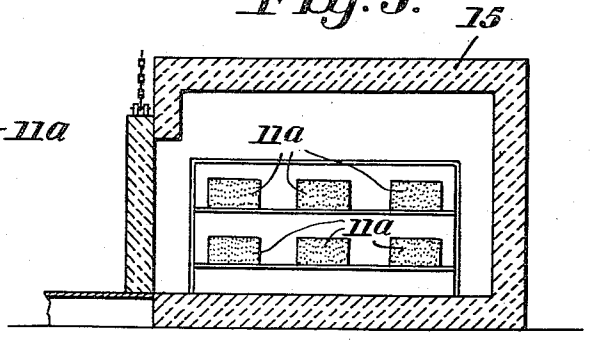
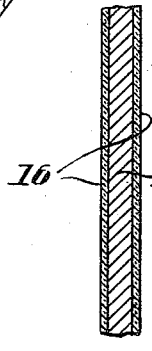



Fig. 6.

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# UNITED STATES PATENT OFFICE

2,455,331

## METHOD OF ENAMELING

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4 Claims. (Cl. 117—53)

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This invention relates to the art of enameling and, in particular, to the coating of iron or steel articles with a finish layer of enamel, particularly white or light-colored vitreous enamel, applied directly thereto without the application of a dark ground coat as required by the previous enameling practice.

It has proved impossible prior to our invention, to enamel metal articles with a finish layer of enamel by applying a single coat of frit directly to the base metal and firing it, because of the development of bubbles, pits or specks in the surface of the enamel. Although numerous attempts have been made to overcome the defects mentioned, none of them so far as we are aware has been successful. Niedringhaus Patent 200,626, granted in 1878, discloses a method of expelling the carbon from the base metal before coating with frit, by heating it to a white heat in the presence of lime, but this method has not achieved any commercial acceptance, so far as we are aware, probably because the treatment described does not eliminate the iron carbide in the surface of the metal. Kautz Patent 2,099,340, granted more than half a century later than the Niedringhaus et al. patent, describes the production of a surface layer of substantially pure iron on the formed article by oxidizing it and then reducing the oxide. This process, however, has not been successful. We believe that the defect of the process is that it produces a coarse surface which traps the hydrates contained in the frit, preventing the elimination of the water of crystallization therefrom in the drying, with the result that water vapor is evolved on firing which is injurious to the surface of the enamel.

Badger et al. (Ceramic Industry, July, 1937, p. 41) observed that the removal of part of the surface carbon from a piece of high-carbon steel (drill rod, presumably about 1% carbon) permitted it to be successfully coated with "ordinary ground coat enamel" after it was heated in a hydrogen atmosphere to a temperature from 800 degrees to 850 degrees C., but they did not deal at all with the problem of applying finish enamels such as the white enamel used for refrigerators, bathroom fixtures and the like, and their disclosure did not enable the industry to adopt the direct application of commercial coats of finish enamels.

The practice in the art has therefore been to apply a ground coat of the cobalt-oxide type [the "ordinary ground coat enamel" of Badger et al.], before applying the finish coat of enamel, usually a white or light-colored enamel. This practice

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involves greater processing time, labor and material cost than would be required for applying a single coat of finish enamel directly to the base metal, but there has been no other process satisfactory to the trade at large for achieving the desired results.

We have discovered a novel method of applying directly to the base metal a single coat of finish enamel and fusing it thereon without the occurrence of pits or specks therein, and by which, despite the entire absence of a ground coat, a finished product may be made superior to that obtained by present practices, with minimum rejections. The product exhibits an improved adherence of the enamel to the base metal and less likelihood of chipping of the enamel because of the reduced thickness thereof. It also has a higher gloss. The absence of surface defects eliminates the loss involved in the downgrading and rejection of ware made by existing practice, which is necessary because of the occurrence of such defects in a portion, at least, of the ware.

In a preferred practice, we form a sheet or plate of low-carbon steel or iron enameling stock, i. e., steel (either open-hearth, Bessemer or electric-furnace steel) containing from .010% to .25% carbon (although usually not over 0.10% carbon) into the shape of the desired finished article. We then clean the article, and give it an acid pickle and a nickel-sulphate dip. We then eliminate carbon from the surfaces of the formed article by heating it to a temperature of 1100 degrees F. or above in a decarburizing atmosphere and maintaining it at such temperature for a substantial period, i. e., from five to thirty minutes. After cooling the article substantially to atmospheric temperature, we apply directly to the base metal a layer of finish coat vitreous enamel frit and heat the article thus coated to a temperature sufficient to cause fusion of the frit and formation of a smooth continuous enamel layer.

A complete understanding of the preferred practice of our invention may be optained from the following detailed description which refers to the accompanying drawings illustrating the several steps of the method. In the drawings,

Figures 1 through 5 show the successive steps of the process and an exemplary article as it appears in the various stages of manufacture; and

Figure 6 is a partial section to an enlarged scale through a portion of the article enameled by our invention.

Referring in detail to the drawings, we carry

out our method upon articles formed from any suitable enameling stock, e. g., low-carbon steel or iron sheets or plates having from .010% to .25% carbon. Figure 1 shows such a sheet designated 10, in the "as-rolled" condition. The sheet is of appropriate gauge, depending on the nature of the article to be formed therefrom. The sheet is formed into the shape of the desired finished article by known methods of drawing, bending, etc., together with such welding as may be required. Figure 2 illustrates an article 11 formed from the sheet 10*a*, specifically the food compartment of a mechanical refrigerator. We next clean the article to remove grease used as a lubricant in forming, and perspiration spots resulting from the necessary manual handling, and subject it to an acid pickle and a nickel-sulphate dip, in the known manner, rinsing the article after each operation.

If the enamel to be applied contains a substantial quantity of a white or light-colored substitute for cobalt oxide, we believe the nickel-sulphate dip may be eliminated. Compounds of the cerium group have been mentioned as a suitable substitute (German Patent 282,348). Other elements whose compounds are mentioned in the literature for use in promoting the adherence of white or light-colored enamels are antimony (Tetrick, Journal of the American Ceramic Society, p. 349, 1934), zirconium (Anon., Bureau of Standards, Technical News Bulletin No. 122, p. 10, 1927) and molybdenum (Kautz, Journal of the American Ceramic Society, p. 283, 1940). The nickel dip is necessary to improve the adherence of many white or colored enamel compositions (Andrews, "Enamels" book, p. 177, 1935). Cobalt solutions have been used in a similar manner (Anon., Journal of the American Ceramic Society, Abstracts, p. 519, 1928). Tetrick, in the article cited, also discusses the value of chemical etching treatments of the base metal in improving enamel adherence. Hot acid gases may be used to etch the metal surface in a manner to improve enamel adherence generally (Turin, Iron Age, p. 70, 1944). Etching should be done prior to the decarburizing operation. We believe that the most successful enamels for our process will be those which have good adherence due to the enamel composition and that complete reliance should not be placed on surface treatments such as nickel dipping and etching in order to obtain adherence as such surface treatments appear to give less satisfactory results in commercial practice.

We then heat the article to a temperature of about 1100 degrees F. or above, and preferably in the neighborhood of 1400 degrees F., in a decarburizing atmosphere, and hold it at such temperature for a substantial period, say from five to thirty minutes. Figure 3 shows one mode of performing this part of the process. A continuous or tunnel-type furnace 12 is provided with a conveyor 13 for moving formed articles progressively therethrough. The furnace is provided with appropriate heating means to maintain the temperature at around 1400 degrees F. and the speed of the conveyor is so adjusted with reference to the length of the furnace that each article will be within the heating zone of the furnace for the period of time indicated, i. e., from five to thirty minutes.

A decarburizing atmosphere is supplied to the interior of the furnace, through a conduit 14, for example. The composition of the gas may vary widely but it should include free hydrogen and free water vapor in such amounts as to inhibit oxidation of the metal of the articles being processed. Gas of the following composition has proved satisfactory: 5% $CO_2$, 10% CO, 12% $H_2$, water vapor corresponding to a dew point of about 85 degrees F., and the balance substantially nitrogen. This composition of gas for the atmosphere of the furnace 12 is similar to what is known as bright-annealing gas but has a somewhat higher water-vapor content.



The furnace 12 may conveniently have a heating-up zone, a soaking zone and a cooling zone. The above-mentioned atmosphere is preferably maintained in each zone. Thus the articles are protected against atmospheric oxidation until they have been cooled. The cooling zone should be so constructed and arranged as to reduce the temperature of the articles gradually to a final value not greatly in excess of that of the atmosphere, unless a certain amount of oxide scale is deliberately produced on the articles by removing them from the furnace at temperatures somewhat above atmospheric in order to provide the oxidation necessary when the articles are subsequently fired in a neutral atmosphere as is done in certain special enameling practices.

The dipping of the article in nickel sulphate may follow the decarburizing treatment just described instead of preceding it. It is important, however, that the pickling be done before the decarburizing operation.

After the articles have been processed as above described, they are sprayed or otherwise coated with a frit appropriate for forming a finish layer of vitreous enamel, usually white or light-colored containing an opacifier. This frit is applied directly to the surface of the processed articles. Figure 4 shows one of the articles at 11*a* having a coating of frit thereon.

The frit-coated articles are next fired in the known manner by placing them in a conventional enameling furnace such as indicated at 15 in Figure 5. In this process, the ware is heated to a temperature of about 1500 degrees F., i. e., slightly above the fusion point of the frit. On removal from the furnace the ware is cooled in air, according to the usual practice in the enameling art. The enamel layer thus formed on the ware is smooth and continuous, unmarred by defects, such as pits or specks. Figure 6 illustrates to enlarged scale the layer of finish enamel 16 applied directly to the base metal 17 and bonded therewith.

It will be apparent from the foregoing that our invention is characterized by important advantages over the previous practice of enameling. The ability to apply a finish layer of enamel directly to the base metal without the formation of defects in the surface saves the substantial cost and processing time involved in applying the ground coat which has heretofore been necessary. The preliminary processing of the formed articles according to our invention is relatively inexpensive and may be carried out by continuous, straight-line apparatus without impairing the efficiency or production rate of an enameling plant.

Further advantages reside in the fact that the enamel layer applied by our invention has excellent adherence to the base metal. In addition, the removal of surface carbides appears to improve the resistance of the ware to sagging under the temperature of the enameling furnace. Warping of the ware is also reduced or eliminated. This appears to result from the relief of warping stress

afforded by the heating of the ware for eliminating carbides from the surface thereof. A further advantage is that the total thickness of enamel applied by our method is less than that applied in the prior practice. As a result, ware enameled by our method is more resistant to chipping than that previously made. It also has a higher gloss. While the invention has been described with reference to the use of low-carbon steel as a base metal, it is also applicable to low-metalloid steel and open-hearth iron.

We believe that the superior results obtained by practicing our method may be explained as follows, although we do not limit ourselves to this particular theory: The frit for forming a finish enamel such as the white or light-colored enamels used in bathroom fixtures, refrigerators, stoves, and the like, must include an opacifier. A typical formula is the following:

| | Parts | Percentage |
|---|---|---|
| Feldspar | 31.5 | 33.5 |
| Borax | 24.4 | 25.9 |
| Quartz | 19.0 | 20.1 |
| Soda ash | 4.1 | 4.4 |
| Soda nitre | 3.5 | 3.7 |
| Fluorspar | 11.7 | 12.4 |
| | 94.2 | 100.0 |

For use, this frit is milled with about 6% clay, an opacifier, such as zirconium oxide type, in amount to produce desired opacity (generally 6 to 8%) and the necessary amount of water. Frits of this type when fused will not "wet" and bond themselves properly to the base except in the presence of oxygen, free or combined. The milled frit is generally applied in a liquid vehicle over the surface of the article prior to heating and consequently is in the form of a dull porous coating when applied. The frit is a glass and has no fixed melting point, but as the temperature is increased it does ultimately soften to the extent that the particles coalesce. Until this coalescence occurs, the layer of frit is porous and the oxygen in the furnace atmosphere can penetrate through to the base. If this base is naked iron or steel, gases form. If these gases escape through the coalesced frit of finish enamel, they leave pits or other defects. If they do not escape, they form bubbles or blisters.

In the ordinary enameling processes now in vogue, the ground-coat enamel is essentially a cobalt-oxide glass. A typical formula is the following:

| | Parts | Percentage |
|---|---|---|
| Feldspar | 30.9 | 31.5 |
| Borax | 30.4 | 31.0 |
| Quartz | 20.0 | 20.4 |
| Soda ash | 6.4 | 6.5 |
| Soda nitrate | 4.2 | 4.3 |
| Fluorspar | 4.8 | 4.9 |
| Cobalt oxide | 0.4 | 0.4 |
| Manganese dioxide | 1.0 | 1.0 |
| | 98.1 | 100.0 |

For use, this frit is milled with about 6% clay. Such frit is relatively quite fluid and has a low surface tension when fused by heating to usual enameling temperatures. We believe that the gases escape readily through this fluid ground coat and that any pits thus formed disappear as the enamel thereafter levels itself off. On the other hand, finish enamels have a high viscosity because of the presence of the opacifier, and if pits



form therein, the enamel will not level itself off to the extent necessary to give a commercial finish. If the finish enamel is applied over a ground-coat enamel, there is no reaction as, for example, between the steel and the furnace atmosphere, which cause gases to evolve, since the steel base is walled off by a continuous and unbroken layer of ground-coat enamel. We believe that the reactions which result in gas formation in these circumstances are complex and that the composition of the gases may vary considerably under different conditions. We believe, however, that they are always at least in part carbon monoxide.

The iron or steel principally used in the enameling industry varies in carbon content from .010% to 0.25%. The lower figure is about the minimum obtainable by current steel-making processes in extensive use and producing metal in the form desired for fabrication. The particular carbon content specified will depend upon a number of factors such as the complexity of the articles and the corresponding difficulties of forming it, the stiffness desired in the final product, etc. We believe that even in the softest enameling iron or steel there is a substantial amount of carbon at or near the surface in the form of iron carbide with which the oxygen from the furnace atmosphere will react to form carbon monoxide. In our process the treatment of the articles in the furnace 12 removes gas-forming compounds such as iron carbide from the surfaces of the articles as well as inwardly of the surfaces to a predetermined depth, depending on the extent of the processing, the minimum objective being, in any case, to leave no carbides or other gas-forming constituents at or near the surface which would react with the furnace atmosphere penetrating through the porous frit during firing.

It should be pointed out that even in the present practice of first firing a ground-coat enamel and then placing and firing a finish coat thereover, difficulties are sometimes encountered with what is known as "re-boiling." This defect, which is well known in the art, manifests itself by the presence of pits or bubbles in the ware, sometimes requiring down-grading or outright rejection. Re-boiling defects may occur from even minor changes, many of which are extremely difficult to locate. Re-boiling defects are entirely eliminated by our discovery because it permits the application directly to the base of a frit for a finish enamel, even though it contains substantial quantities of an opacifier. Such enamels are so viscous at enameling-furnace that any gases which might be given off by the base metal would form blisters or bubbles which, if they break, would show as pits remaining in the surface of the enamel after the gas escapes.

An important aspect of our invention is the surface treatment of the articles after they have been formed to shape. We have found that if the treatment is applied to the steel prior to fabrication, enameling defects are prone to occur in those parts of the article where the metal has been bent or die-shaped to a material extent or has been abraded as in metal finishing and even in zones where the metal has been heated to high temperature as in welding operations which may be employed in fabrication.

Although we have disclosed herein a preferred practice of our invention, it will be recognized that modifications thereof may be made within the scope of the appended claims.

We claim:

1. In a method of enameling in which an ar-

ticle is made from conventional ferrous enameling stock having a carbon content of from .010% to .25% and in which the article is approximately in its final shape, the steps including, cleaning the article with a cleaning solution and drying it to prepare the ferrous surface thereof for enameling, then heating the article to a temperature in the neighborhood of 1400 degrees F. in a decarburizing atmosphere containing free hydrogen and water vapor and effective to inhibit oxidation of and to decarburize the ferrous metal surface, maintaining the article at such temperature and in such atmosphere for a period of time between about 5 and 30 minutes until its ferrous surface has been freed from gas-forming constituents such as iron carbide, gradually cooling the article in a non-oxidizing atmosphere substantially to atmospheric temperature, applying directly to the surface of the article a layer of light-colored finish-coat vitreous enamel frit containing an opacifier, and heating the article thus coated to a temperature sufficient to convert the frit into a coat of fused enamel.

2. The method as defined by claim 1 characterized by said first-mentioned atmosphere being composed substantially of 12% hydrogen, 10% carbon monoxide, 5% carbon dioxide, water vapor corresponding to a dew point of 85 degrees F. and the balance substantially nitrogen.

3. In a method of enameling in which an article is made from conventional ferrous enameling stock having a carbon content of from .010% to .25% and in which the article is approximately in its final shape, the steps including, cleaning the article with a cleaning solution and drying it to prepare the ferrous surface thereof for enameling, then heating the article to a temperature in the neighborhood of 1400 degrees F. in a decarburizing atmosphere containing free hydrogen and water vapor and effective to inhibit oxidation of and to decarburize the ferrous metal surface, maintaining the article at such temperature and in such atmosphere for a period of time between about 5 and 30 minutes until its ferrous surface has been freed from gas-forming constituents such as iron carbide, gradually cooling the article in a non-oxidizing atmosphere substantially to atmospheric temperature, applying directly to the surface of the article a layer of vitreous enamel frit, and heating the article thus coated to a temperature sufficient to convert the frit into a coat of fused enamel.



4. In a method of enameling in which an article is made from conventional ferrous enameling stock having a carbon content of from .010% to .25% and in which the article is approximately in its final shape, the steps including, cleaning the article with a cleaning solution and drying it to prepare the ferrous surface thereof for enameling, then heating the article to a temperature between about 1100 degrees F. and about 1400 degrees F. in a decarburizing atmosphere containing free hydrogen and water vapor and effective to inhibit oxidation of and to decarburize the ferrous metal surface, maintaining the article at such temperature and in such atmosphere for a period of time between about 5 and 30 minutes until its ferrous surface has been freed from gas-forming constituents such as iron carbide, gradually cooling the article in a non-oxidizing atmosphere substantially to atmospheric temperature, applying directly to the surface of the article a layer of light-colored finish-coat vitreous enamel frit containing an opacifier, and heating the article thus coated to a temperature sufficient to convert the frit into a coat of fused enamel.

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