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ENAMELWARE MAKING

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3 Claims. (Cl. 91-73)

This invention relates to the production of enamelware, and, specifically, to the production of enamelware of crinkle finish, as described in the application of William J. Baldwin for Letters Patent of the United States, Serial No. 267,523, filed April 12, 1939.

According to the teaching of the application alluded to, the crinkle finish will develop if, and only if, in the firing operation, the molten glass upon the surface of the metal article contains a fluoride, together with an antimony compound of trivalent character, and if the furnace atmosphere be of oxidizing character. Under such circumstances a skin apparently forms upon the air interface of the molten layer of coating, and in the cooling and solidification of the layer the underlying body of glass (it would seem) contracts slightly, with the effect of causing the skin to wrinkle and the wrinkles to organize themselves into groups radiating from centres that seem to be determined by chance. The minutely waved surface, in the formation of which order and chance are combined, under the light of day relieves monotony of appearance and imposes upon an otherwise plane surface a pattern that closely resembles the surface pattern of galvanized iron. The appearance is pleasing. This surface finish has been called "crinkle finish."

In the specification of the earlier application named it has been said that coloring matter may be included in the composition of the coating; that, if coloring matter be present, it may not be itself a compound of reducing nature; for, if it is, the desired crinkle finish will not develop. And the inference is suggested, that the skin that forms upon the air interface of the molten layer of coating may be formed by oxidation.

A typical pigment of reducing nature is cadmium sulpho-selenide. It is widely used in the enameling industry to produce a clear and brilliant red color. If cadmium sulpho-selenide be present as pigment in the coating, although antimony trioxide in excess together with a fluoride be present, still the crinkle finish will not develop. This failure I impute to the activity of the selenide in taking up oxygen, and so preventing the formation of the skin of the hypothesis.

My present invention lies in a procedure that enables me to use pigments of reducing nature, and still to gain the crinkle finish. I resort to the expedient of overspraying. I form the frit and prepare and apply the slip in usual manner, including the desired pigment; and I prepare an

overspray material that includes in its composition a fluoride together with an antimony compound of trivalent character and that, when it has been fused and solidified, is transparent or translucent. I apply the overspray to the outspread layer of pigmented coating (the layer may or may not have been preliminarily dried and baked), and I then fire the whole in an oxidizing atmosphere. In the firing, the overspray seals the pigment from the access of air, the skin forms, and in the cooling the crinkle finish develops.

The overspray compounded according to the formula given in the Baldwin application alluded to above may be as follows:

	Parts
Dehydrated borax ($\text{Na}_2\text{B}_4\text{O}_7$)	15.4
Soda ash (Na_2CO_3)	6.5
Silica (SiO_2)	23.8
Feldspar ($\text{NaK.OAl}_2\text{O}_3.6\text{SiO}_2$)	33.2
Cryolite (Na_3AlF_6)	10.5
Fluorspar (CaF_2)	4.3
Antimony trioxide (Sb_2O_3)	8.5
Nitrate of soda (NaNO_3)	3.2

In the smelting, while there is a small loss in total weight, there is no loss in the weights of the cryolite and the antimony trioxide constituents; and it will be found that in the frit these two constituents will continue—cryolite, substantially 10.5%, and antimony trioxide, substantially 8.5%.

By varying the degree of translucency of the overspray the intensity of color may be varied, and by including in the overspray other pigment (having no reducing effect) I may modify the color of the product.

In the ensuing claims I shall use the term clear enamel in the sense that is familiar in the industry, definitive of material which, sprayed upon and fired upon the otherwise prepared article, will afford a surface layer that is light-transmitting.

While it is true that in the enameling industry of today the only pigment of reducing nature in general use, other than cadmium sulpho-selenide is cadmium sulphide (a pigment that gives an intense yellow color to the ware), the invention is pertinent, in that case and in any other case as well, in which a pigment of reducing nature is employed.

It remains only to say that the industry knows how to develop within the molten substance of glass from other cadmium and selenium com-

pounds the particular pigments that I have named; and it will be understood that I mean to include in the field of practice of my invention such production of pigment.

5 I claim as my invention:

1. The method herein described of producing an article of enamelware of crinkle finish which consists in spreading upon the surface of the article to be enameled a vitreous coating that
10 includes a pigment of reducing nature, overspraying such coating with a coating of milled clear enamel that carries, in association with a fluoride, an antimony compound of trivalent character, firing in an oxidizing atmosphere, and
15 cooling.

2. The method herein described of producing an article of enamelware of crinkle finish which consists in spreading upon the surface of the

article to be enameled a vitreous coating that includes as a pigment cadmium sulpho-selenide, overspraying such coating with a coating of milled clear enamel that carries, in association with a fluoride, an antimony compound of trivalent character, firing in an oxidizing atmosphere, and cooling.

3. The method herein described of producing an article of enamelware of crinkle finish which consists in spreading upon the surface of the
10 article to be enameled a vitreous coating that includes as a pigment cadmium sulphide, overspraying such coating with a coating of milled clear enamel that carries, in association with a fluoride, an antimony compound of trivalent
15 character, firing in an oxidizing atmosphere, and cooling.

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