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PROCESS FOR PRODUCING ENAMELED
IRON ARTICLES

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It has been the custom in the manufacture of enameled iron articles to put primarily on the iron a ground glaze containing cobalt oxide or cobalt and nickel oxide and cover this ground glaze with a covering glaze. As the ground glazes have a dark or even a black colour it has been necessary especially when the manufacture of white enameled articles was intended to put two or more coatings on top of the ground glaze in order to completely cover the black or dark ground.

Consequently it has been the endeavour of the industry to produce light or even white ground glazes on the iron which would necessitate one covering glaze only, or to put directly on the iron a glaze which would be white straight-away or would have at any rate a light colour. These experiments have not yielded satisfactory results up to the present time, chiefly for the reason that the ordinary opacifying agents such as antimony oxide, alkali metal antimoniate, zinc oxide, zirconium oxide and the like are not resistant to the higher temperatures which are required for firing the ground glaze. In consequence of the high temperatures necessary the opacifying effect is liable to disappear.

If one tries to produce a light or a white ground by means of the known opacifying agents on the iron articles a further disadvantage can be noticed which consists in spots making their appearance of greater or smaller size which some times are scarcely visible in the ground after it has been fired in. In these spots the iron is either not covered at all or only incompletely. If such ground glazes are coated subsequently with the covering glaze the latter bursts off easily in the respective places. This disadvantage is especially bad when larger articles are glazed as it is particularly difficult to fire large articles uniformly.

By my present invention all the drawbacks and disadvantages are avoided by using for the ground glaze opacifying agents which contain on the one hand zinc oxide and/or zirconium oxide and on the other hand antimony oxide. By using this combination of opacifying agents I obtain ground glazes which adhere firmly to the iron which are well opacified and which have the especially great advantage of the covering glaze when properly fired adhering extremely well to the ground glaze.

According to my invention, for instance, zinc antimoniate or zirconium antimoniate may be used each separately or in mixture with other suitable substances. The antimonates are ad-

vantageously prepared by heating a mixture of the components, for instance, antimony oxide and zinc oxide, or of substances which are capable of being converted into these oxides during the heating process. The components may be utilized in the quantities necessary for the formation of the antimonates, but there might be one or the other in excess. The heating process is advantageously carried out whilst the mass is agitated, for instance, by stirring or in a revolving drum.

Further experiments have shown that the heating of the mixture is effected with advantage in presence of substances which do not participate in the reaction. Especially suitable for this purpose are aluminum compounds such as aluminum oxide or substances containing the same such as clay, bauxite, cryolite, feldspar or the like. Such additions act as heat adsorbent and distributing agent when the ground enamel is fired. In consequence the heat resistance of the opacifying agent is increased. Furthermore, by the addition of such substances the product obtainable by heating the components of the opacifier may be prepared in a form, especially favorable for its application, for instance, in a pulverulent or crumbly state.

According to a further form of carrying my invention into effect, the heating process is carried out in presence of oxidizing substances. As such, for instance, nitric acid or nitrates, especially alkali metal nitrates come into consideration. By the application of alkali metal nitrates one is capable of introducing alkalis into the opacifying agents. This is sometimes desirable.

I was able to ascertain that not only the antimonates of zinc oxide or zirconium oxide are opacifiers for ground enamels which are especially resistant against the firing, but also that the same applies to the mixture of the components after it has been subjected to a process of highly heating or firing. Consequently by heating a mixture of zinc oxide and/or zirconium oxide with antimony oxide, to which substances such as clay, alkali metal nitrate or both may be added, can be converted by heating into an opacifier of excellent effect without the heating process being carried out at such a heat that the zinc oxide or the zirconium oxide respectively are converted completely or to a large extent into the corresponding antimonate. Therefore, a heated mixture of, for instance, zinc oxide and antimony oxide which contain in addition, for instance, aluminum oxide and/or saltpeter and which contain as the case may be zinc antimonate-formed

by the heating process represents an opacifying agent for ground enamels of excellent efficiency.

The heating temperature and the duration of the heating process depends on the composition of the starting mixture and the product desired. If a far reaching conversion of the components into antimonate is aimed at, a higher heating temperature is taken and the heating process is prolonged, if necessary. It was found generally that temperatures between 800° centigrade and 1300° centigrade are suitable, but I have been able to produce opacifiers for ground enamels beyond these limits.

The proportions of zinc oxide and/or zirconium oxide, on the one hand, to antimony oxide, on the other hand, may be chosen in such a manner that the quantities correspond to those theoretically necessary for the formation of antimonates. Both components, for instance, zinc oxide or antimony oxide may be in excess.

Opacifiers obtainable according to my invention have the great advantage that with their aid opacified enamels may be melted on the iron directly. Glazes thus produced show a good appearance to the ground and a light coloration. It is therefore not necessary to fall back upon the hitherto customary dark ground glazes produced with the aid of cobalt oxide or the like.

By applying a single coat of white glaze one is able to produce white enamel articles which fulfill even the highest requirements.

Opacifiers according to my invention are advantageously added to the slip on the mill together with other additions. The opacifiers may be added partly to the enamel slip before milling and then fired and may be partly added to the mill. Generally it was found to be advantageous to add it completely or as to its major part to the mill.

The quantity of the opacifier to be added can vary in relatively large limits. Sometimes additions of 1% and more are sufficient; in general the quantities to be added are between 2 and 10% and advantageously between 3 and 5%.

In accordance to a further manner of carrying my invention into effect barium compounds are made to participate in the formation of the glaze. Particularly suitable are compounds of barium which react with silica such as, for instance, barium oxide, barium carbonate, barium hydrate, barium antimonate, barium borate and the like. Barium compounds are added generally in quantities from 3 to 10% but these quantities may be exceeded as far as 20%. The addition of barium compounds favors the formation of the glass and facilitates the coating and the adherence of the covering glaze on top of the ground glaze in as much as by means of barium compounds the expansion coefficient of the ground glaze may be made to coincide with the expansion coefficient with the covering glaze. A further advantage is that by the simultaneous use of barium compounds a smooth and durable unobjectionable coating can be melted on the iron at such temperatures also which according to the general experiences were not sufficient for firing a satisfactory ground glaze. This offers a great advantage in as much as the opacity is much better when lower firing temperatures are employed than when the firing takes place at higher temperatures. Therefore, by the addition of barium compounds the ground may be fired at lower temperatures and the opacity effect is favored thereby.

The barium compounds may be added when the

batch is prepared or to the mill, for instance, together with the opacity agent for the ground glaze or also partly to the batch and partly to the mill.

The favorable action of the barium compounds may be improved by using in addition zinc oxide or zirconium oxide or both when added to the batch or to the mill or in both directions. In the place of the special addition of zinc oxide or zirconium oxide the opacifying agent may be prepared in such a way that the opacifier when finished contains uncombined zinc oxide or/and zirconium oxide in such quantities that by interaction with the barium compounds the above mentioned effects are obtained.

The preparation of the white ground agent may be illustrated by the following example:

50 parts by weight of antimony oxide, 13 parts zinc oxide, 13 parts ammonium nitrate and 24 parts clay are thoroughly mixed and fired in a muffle or open flame furnace, for instance, in a revolving tube to 700-800° centigrade whilst agitating the pulverulent mixture. The heating process may be discontinued when the generation of steam ceases. In the place of ammonium nitrate another oxidizing agent such as, for instance, sodium nitrate may be used.

Also, for instance, antimony oxide may be combined with the quantity necessary for the formation of antimonate, of zinc oxide or zirconium oxide or a mixture of zinc oxide and zirconium oxide in the presence of an oxidizing agent such as, for instance, a nitrate and a substance containing aluminum, such as, for instance, clay, in the above described manner.

Instead of taking the starting mixture as stated above the following mixtures may be heated to suitable temperatures and thus worked into white ground agents.

(1) 70 parts by weight of antimony oxide, 30 parts by weight zirconium oxide, 25 parts by weight ammonium nitrate and 10 parts by weight clay.

(2) 20 parts by weight antimony oxide, 43 parts by weight zinc oxide, 13 parts by weight sodium nitrate and 24 parts by weight clay.

The heated product is obtained as a rule in a more or less fritted or sintered form. It may consist, for instance, of particles fritted together from the single components, more or less great fractions of the conversion products between zinc oxide and antimony oxide and/or zirconium oxide and antimony oxide, namely antimonate of zinc and/or antimonate of zirconium being present.

The working conditions, for instance, the composition of the mixtures, the temperatures and the duration of the heating process may be chosen in such a way that the conversion of the components into antimonates is achieved to a greater or lesser extent, for instance, by the application of higher heating temperatures the formation of the antimonate is favored.

After cooling the heated products are comminuted to a fine powder and applied in this form.

The white ground agent prepared in accordance to my invention may be applied in conjunction with the ordinary ground glazes. It is advisable to find out by some preliminary trials which of the white ground agents prepared according to the present invention is best suited for the ground glaze in question. Also it is possible to adapt the composition of the ground glaze in such a way to the white ground agent that when applied together they are best suited to each other.

For the execution of the process, for instance, ground glazes of the following composition come in consideration:

		Parts by weight
5	(1)	
	1. Borax	24
	2. Feldspar	35
	3. Quartz	18
	4. Soda	8
10	5. Cryolite	6
	6. Fluorspar	3
	7. Saltpeter	3
	8. Antimony oxide	3
	9. Zinc oxide	3
15	10. Barium carbonate	3
	(2)	
	1. Cryolite	7
	2. Feldspar	9
	3. Soda	9
	4. Fluorspar	6
20	5. Manganese dioxide	0.5
	6. Quartz	7
	7. Borax	22
	8. Clay	3
	9. Zinc oxide	3
25	10. Glass powder containing boric acid	27
	11. Antimony oxide	4

These glazes contain already certain quantities of opacifiers, for instance, zinc oxide and antimony oxide. This has the special advantage that one can manage with a smaller quantity of the white ground agent to be added to the mill. By this procedure a smooth melt and a good adherence of the ground glaze to the iron and of the covering glaze to the ground glaze is ensured. I have been able to do without any preliminary opacity in the glaze but in this case greater quantities of the white ground agent had to be added to the mill.

Furthermore, I have found it advantageous to add certain components of the ground glaze such as, for instance, quartz, soda carbonate, boric acid, aluminum oxide and the like in a fused state, for example, as glass. Thereby the formation of the white ground glaze is favorably influenced. I have given sub (2) a recipe by which this part of the invention is illustrated: a considerable part of the frit consists of glass powder. In practice waste glass and debris may be used for the production of the ground glazes as this material is very cheap.

Recipe (1) contains in addition barium carbonate which favors the formation of glass. Barium compounds may also be added to recipe (2) in quantities of, for instance, 2 parts barium carbonate and is fused with the other components. The presence of barium compounds not only improves the formation of the glaze but also makes it possible to abbreviate the time of firing which is of great importance for the firing of the ground as it has been found that the best ground is obtained by high but short firing.

As has been mentioned previously it is best to add the white ground agent to the mill or partly to the mill and to fuse the other part with the batch, for instance, in such a manner that 5% are fused with the batch and 2% are added to the mill. In general the mode of applying the opacifier the quantity to be used and the like depend on the composition of the glaze, the degree of the opacity desired, the method of the firing process, the quality of the firing furnace and other working conditions.

The ground glazes, for instance, of the kind mentioned above are favorably added to the mill

in conjunction with Vallendar clay and such substances, as sodium carbonate or magnesium carbonate in addition to the required quantity of white ground agent and subsequently ground, for instance, to medium fineness. To glaze (1), for instance, 8% of an enamel clay, such as Vallendar clay and 5% magnesium carbonate and 3% white ground agent are added, whilst to glaze (2) 7% Vallendar clay, 0.5% soda and 3% of the white ground agent are given.

The aqueous suspension prepared with the mill product is put onto the previously cleaned articles in the ordinary way and after drying it is fired at ground heat, for example at about 850° centigrade.

What I claim is:

1. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises melting a mixture of oxide of antimony and of oxide of zinc to produce a fritted product, incorporating said fritted product in a raw glaze, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

2. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises melting a mixture of oxide of antimony and of oxide of zinc in the presence of an oxidizing agent to produce a fritted product, incorporating said fritted product in a raw glaze, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

3. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises melting a mixture of oxide of antimony and of oxide of zinc in the presence of a nitrate to produce a fritted product, incorporating said fritted product in a raw glaze, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

4. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises melting a mixture of oxide of antimony and of oxide of zinc in the presence of an alkali nitrate to produce a fritted product, incorporating said fritted product in a raw glaze, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

5. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises pre-igniting a mixture of oxide of antimony and of oxide of zinc in the presence of a heat absorbent and distributing agent of the group consisting of clay, feldspar, bauxite, cryolite and aluminum oxide to form a fritted product, incorporating said fritted product in a raw glaze, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

6. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises pre-igniting a mixture of oxide of antimony and of oxide of zinc to produce a fritted product, incorporating said fritted product in a raw glaze containing a barium compound, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

7. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises pre-igniting a mixture of oxide of antimony and of oxide of zinc to pro-

duce a fritted product, incorporating said fritted product in a raw glaze containing a substance of the group consisting of cryolite, and sodium fluosilicate, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

8. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises pre-igniting a mixture of oxide of antimony and of oxide of zinc to produce a fritted product, incorporating up to about 10% of said fritted product in a raw glaze, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

9. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises pre-igniting a mixture of oxide of antimony and of oxide of zinc to produce a fritted product, incorporating about 3% to about 5% of said fritted product in a raw glaze, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

10. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises pre-igniting a mixture of oxide of antimony and of oxide of zinc to produce a fritted product, incorporating about 1% of said fritted product in a raw glaze, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

11. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises pre-igniting a mixture of

oxide of antimony and of an oxide of zinc to produce a fritted product, incorporating said fritted product in a raw glaze containing up to about 20% of barium, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

12. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises pre-igniting a mixture of oxide of antimony and of oxide of zinc to produce a fritted product, incorporating said fritted product in a raw glaze containing up to about 3% to about 10% of barium, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

13. In the process of directly enameling iron articles with a light colored glaze, the improvement which comprises pre-igniting a mixture of oxide of antimony and of oxide of zinc at a temperature of about 800° C. to about 1300° C. to produce a fritted product, incorporating said fritted product in a raw glaze, and applying the raw glaze containing said fritted mixture directly to the surface of the iron article to be enameled.

14. In the process of directly enameling iron articles with a white glaze, the improvement which comprises pre-igniting a mixture of oxide of antimony and of an oxide of zinc to produce a fritted product, incorporating said fritted product in a white glaze, and applying a single coat of said white glaze containing said fritted mixture directly to the surface of the iron article to be subjected to heat, whereby a white enamel article may be produced.

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