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PROCESS FOR MAKING WHITE CLOUDED ENAMEL

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6 Claims. (Cl. 106—40)

This application is a divisional application of application Serial Number 97,286, filed August 21, 1936.

This invention relates to a process for making white clouded enamel, more particularly iron enamel, by gas clouding, the white clouding being brought about by development of small gas bubbles from substances which decompose at the burning-in temperature, which substances are added to the enamel composition on the mill instead of the usual solid white clouding agents.

The present invention depends upon the discovery that by means of certain metal oxides or compounds thereof, such as more particularly oxides of iron, antimony, cerium, uranium, arsenic or mixtures containing these oxides, the whiteness value of the gas clouding can be very considerably enhanced, whence a decolourising effect may be allied to gas clouding means which have a colouring effect (for example may give rise to the formation of substances having a colouring action, such as carbon compounds having a colouring effect), obviously in consequence of the better burning brought about by their oxidising effect at the burning-in temperature.

The process according to the invention consists in this that metal oxides, such as antimony oxide, uranium oxide, cerium oxide, iron oxide, arsenic oxide, or compounds of these oxides with other metal oxides, are introduced into the enamel independently of the fact whether the compound added as gas clouding agent contains one of these oxides or not, the introduction of these oxides into the enamel however being made in such small quantities that in the enamel the oxide is contained only in a quantity such that any clouding that may be attributable to the oxide itself is without influence, but nevertheless in a quantity sufficient for the oxide to enhance the whiteness value.

Processes for making white clouded enamel are already known in which the clouding action of the solid substances usual as clouding agents for enamel, such as for example the oxides of tin, zirconium, antimony or the like, is strengthened by addition in the mill of substances which produce their effect by gas clouding. Processes are also known in which compounds or complexes of the metals of the white clouding agents group, which split off gases even in the slip at the burning-in temperature, are added to the enamel on the mill in quantities which are so small that the solid residue can bring about no clouding effects, whilst on the other hand the volatile portion suffices owing to the development of small gas bubbles to impart a white clouding as a result of these bubbles.

In these known processes the quantity of metal oxide for example stands in a definite ratio to the quantity of gas clouding agent or of the decomposable portion which is active as gas clouding agent and the quantity to be added as clouding agent depends on the quantity of the gas clouding agent introduced with the oxide, as a result of which a correct adjustment to the whiteness value of the enamel, at which the present invention aims, is not possible. In these known processes the effect may arise that either too little metal oxide is introduced into the enamel with correct addition of clouding agent, or too much clouding agent must be added with correct addition of metal oxide.

In the process according to the present invention the action of these oxides and compounds is an action which is quite different in nature from that of a clouding action. The action of these oxides appears irrespective of whether these oxides or compounds are added to the enamel on the mill or are fused with the raw substances forming the enamel. The action also already appears with such small quantities that any clouding effect attributable to these oxides themselves can be ignored. How different this action is from a clouding action is apparent from the fact that oxides which are not capable of effecting a clouding at all, such as for example iron oxide and uranium oxide, are just as well suited for the process according to the invention as for example antimony oxide and the like.

The effect at which the invention aims already appears with a content of the said oxides and compounds of these oxides in the enamel amounting to far below 1%, an increase of this content above 1% bringing with it no further advantages as regards the action at which the invention aims. Preferably an addition is made in such a small quantity that, independently of the fact whether the compounds added as gas clouding agent contain one of these oxides or not, the total quantity of these oxides does not

exceed 1%, and advantageously lies below 1%.

The action of these substances is obviously to be attributed to this that in the quantities in which they exert their effect in the process according to the invention they are without injurious auxiliary effect on the slip or a constituent of the slip.

Not only however are the oxides of antimony, uranium, iron, cerium and arsenic, all of which are capable of forming several oxidation stages, suitable for carrying out the process according to the invention, that is to say for introduction into the enamel, but also mixtures containing such oxides and also compounds of these oxides may be used, more particularly their compounds with other oxides, e. g. antimoniates or the like.

The process according to the invention is particularly suitable for those methods of making white clouded enamel in which gas clouding agents are used in conjunction with enamel frits, which in the slip possess larger colloidal portions than normal enamel frits. For example the colloidal properties or the colloidal portions of an enamel frit, that is to say the fritted raw mixture of the enamel charge, can be enhanced during normal grinding on normal enamel mills by variation of the composition of the enamel charge, for example by raising the fluorine content in normal enamel compositions. Normal enamel compositions or charges contain approximately 5% fluorine with a proportion between alkali and boric acid of 1½ parts alkali to one part boric acid. By raising the fluorine content to approximately double the amount, that is to say to about 10–12% fluorine for example, frits in a colloid-like state with a normal ratio of alkali to boric acid may be obtained, the fluorine however preferably being introduced in the form of alkali fluosilicate, such as for example sodium fluosilicate.

Examples

1	Grams
Enamel mass	1,000
Water	500
Methylene blue	0.25
Cerium oxide	2
Clay	100

are ground up on the mill and thereupon applied in the usual manner and burnt in.

2	Grams
Enamel mass	1,000
Water	500
Methylene blue	0.25
Cerium fluoride	5
Clay	100

are ground up on the mill and thereupon applied in the usual manner and burnt in.

In these examples a frit particularly suitable for gas cloudings, and in fact a fluorine-rich frit of highly colloidal properties was used as enamel frit, in which the fluorine content originates from alkali fluorides or alkali silicofluorides. However, the invention of course is not limited to such frits.

The additions forming the subject of the invention may be added to the enamel frit or to the enamel slip not only on the mill but also ready previously to a constituent of the enamel slip, or may also be fused together with the raw substances forming the enamel.

What I claim is:

1. In a method of producing a gas clouded viterous enamel, the step of incorporating in the enamel batch a compound containing cerium in an amount less than 1% of the enamel.

2. A process as claimed in claim 1 in which said compound also contains oxygen.

3. In a process of producing a gas clouded viterous enamel from a frit, in which the frit is produced by melting together and grinding a mixture of materials, the step of adding to the frit materials before melting a compound containing cerium in an amount less than 1% of the enamel.

4. In a method of producing a gas clouded viterous enamel the step of adding to the enamel slip a compound containing cerium in an amount less than 1% of the enamel.

5. An article of manufacture comprising a metal article having thereon a coating of gas clouded viterous enamel containing cerium in a quantity less than 1% of the enamel.

6. An article as claimed in claim 5 in which said compound also contains oxygen.

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