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VITREOUS ENAMEL OPACIFIER

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In the production of enamels and the like heretofore, it has been customary to employ tin oxide as a mill addition opacifier. Tin however is in limited supply; and an opacifier compound very generally available and offering an extended range of use and capable of withstanding possible abuse in firing time, is accordingly a desideratum in the art and of particular importance.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

In accordance with our invention, a composition is made up comprising oxides of antimony and of such element as titanium or zirconium, and of a base-forming element in the divalent or trivalent condition. Antimony may be provided directly as the pentoxide, Sb_2O_5, or, more usually as Sb_2O_3 or Sb_2O_4 with an oxidizing agent such as to oxidize it to the pentavalent form. The titanium or zirconium is added as the oxide or in a form to yield available oxide. The other metal oxide component is advantageously of zinc, or beryllium, calcium, tin, barium, strontium, magnesium, aluminum, cerium, and where coloration is not objectionable or is wanted, manganese, lead, copper, and the like. A part of the divalent or trivalent element may be substituted by an alkali metal, as sodium, potassium, lithium, somewhat less desirably. Taking a composition of zinc oxide, antimony oxide and titanium oxide for instance, beyond the general optimum proportion too high a ZnO content decreases the opacity, too high a TiO_2 content tends to run to a yellowish coloration, and too high a Sb_2O_5 content tends to lower the opacity. In general, the best range of proportions involves 10 to 35 per cent for ZnO, 30 to 55 per cent for Sb_2O_5, and 25–50 per cent for TiO_2. A particularly desirable proportion is represented by the compound $2ZnO.Sb_2O_5.3TiO_2$, or 22.4 per cent ZnO, 44.5 per cent Sb_2O_5, and 33.1 per cent TiO_2. Other notably good compounds also are for instance

$2BeO.Sb_2O_5.3TiO_2$, $2CaO.Sb_2O_5.3TiO_2$, $2SnO_2.Sb_2O_5.3TiO_2$.

Again, as illustrative of mixed base compounds are noted for instance,

$CaO.ZnO.Sb_2O_5.3TiO_2$,

and as illustrative of partial replacement of a divalent metal by an alkali metal, for instance

$Na_2O.ZnO.Sb_2O_5.3TiO_2$.

Use of zirconium oxide may be illustrated for instance as

$2ZnO.Sb_2O_5.3ZrO_2$.

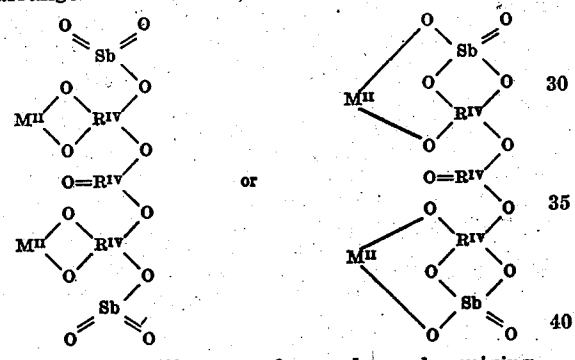
Both titanium and zirconium can be used together where desired, as for instance

$2ZnO.Sb_2O_5.2TiO_2.ZrO_2$.

These compounds are of the general formula

$2M^{II}O.3R^{IV}O_2.Sb_2O_5$

in which R represents titanium or zirconium, and M represents the other element. While the details have not been worked out and the matter is merely of theoretical interest rather than of any bearing on the present case, structurally there is reason for believing that the internal arrangement in such compounds may be



The composition may be made up by mixing the calculated amounts of Sb_2O_3 or Sb_2O_4 and TiO_2 to a paste with for instance a solution of $Zn(NO_3)_2$ calculated to give 2ZnO, and the paste may be dried, ground, and fired for several hours at about 1000° C. Antimony pentoxide, Sb_2O_5, may be used of course also in a dry mix with the other oxides, as ZnO, and TiO_2, in the desired proportions.

In practical operation, it is especially advantageous to proceed by weighing the components in their respective proportions, and where employing zinc oxide dissolving half thereof in nitric acid, this solution serving as the wetting agent

for the slip mix of the components. By taking care to use a zinc oxide free from lead, whiteness of product is maintained. Otherwise, if lead be present, there is a tendency to yellow coloration. The slip mix may be made by grinding in a ball mill, and may then be dried, preferably at a temperature under 100° C., and be powdered, and the powder then be fired for several hours at about 1000° C. The product is a fluffy white powder. If the furnace should happen to have a reducing atmosphere, the product would run grayish. By a controlled furnace operation however, uniformly white fluffy products may be obtained.

Zinc oxide, and other oxides have long been used in enamel practice by smelting them into the frit, but it is readily apparent that combining the agents we have set forth, in the ratios shown, firing these together at suitable temperature, and employing the so-formed compound with enamels, etc., as a mill addition, is quite a different matter, and the present invention makes available an opacifier or pigment of outstanding covering power capable of very economical usage.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. A vitreous enamel white opacifying agent having the general formula

$$2M^{II}O.3R^{IV}O_2.Sb_2O_5,$$

in which R is titanium or zirconium and M is zinc, barium, calcium, beryllium, tin, strontium, magnesium, aluminum, cerium, manganese, lead, copper, or an alkali metal in partial substitution of the aforesaid metals.

2. A vitreous enamel white opacifying agent consisting of the reaction product of an oxide of antimony, and of an oxide of an element from the group consisting of titanium and zirconium, and of an oxide of another element from the group consisting of metals in divalent and trivalent condition, said oxides being present in amount sufficient to form a white fluffy powder.

3. A vitreous enamel white opacifying agent consisting of the reaction product of an oxide of antimony, and of an oxide of an element from the group consisting of titanium and zirconium, and of oxides of mixed bases from the group consisting of metals in divalent and trivalent condition, said oxides being present in amount sufficient to form a white fluffy powder.

4. A vitreous enamel white opacifying agent consisting of the reaction product of an oxide of antimony, and of an oxide of an element from the group consisting of titanium and zirconium, and of an oxide of another element from the group consisting of metals in divalent condition, said oxides being present in amount sufficient to form a white fluffy powder.

5. A vitreous enamel white opacifying agent consisting of the reaction product of an oxide of antimony, and of an oxide of an element from the group consisting of titanium and zirconium, and of an oxide of another element from the group consisting of zinc, beryllium, calcium and tin, said oxides being present in amount sufficient to form a white fluffy powder.

6. A vitreous enamel white opacifying agent consisting of the reaction product of an oxide of antimony, and of an oxide of an element from the group consisting of titanium and zirconium, and of zinc oxide, said oxides being present in amount sufficient to form a white fluffy powder.

7. A vitreous enamel white opacifying agent consisting of the reaction product of an oxide of antimony, and of an oxide of titanium, and of an oxide of another element from the group consisting of metals in divalent and trivalent condition, said oxides being present in amount sufficient to form a white fluffy powder.

8. A vitreous enamel white opacifying agent consisting of the reaction product of an oxide of antimony, and of an oxide of titanium, and of an oxide of another element from the group consisting of metals in divalent condition, said oxides being present in amount sufficient to form a white fluffy powder.

9. A vitreous enamel white opacifying agent consisting of the reaction product of an oxide of antimony, and of an oxide of titanium, and of an oxide of another element from the group consisting of zinc, beryllium, calcium and tin, said oxides being present in amount sufficient to form a white fluffy powder.

10. A vitreous enamel white opacifying agent consisting of the preformed reaction product of an oxide of antimony, and of an oxide of titanium, and of zinc oxide.

11. A vitreous enamel white opacifying agent consisting of the preformed reaction product of Sb_2O_5 30–55 per cent, TiO_2 25–50 per cent, and ZnO 10–35 per cent.

12. A vitreous enamel white opacifying agent consisting of the reaction product of Sb_2O_5 about 44.5 per cent, TiO_2 about 33.1 per cent, and ZnO about 22.4 per cent.

13. A vitreous enamel white opacifying agent consisting of

$$2ZnO.Sb_2O_5.3TiO_2.$$

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