

## UNITED STATES PATENT OFFICE

2,125,632

## PROCESS FOR THE PRODUCTION OF LEAD GLAZES

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No Drawing. Application August 22, 1936, Serial  
No. 97,441. In Switzerland August 26, 1935

7 Claims. (Cl. 106—36.2)

This invention relates to a process for the production of lead glaze, or "glazing", which renders it possible to produce such "glazes" of excellent quality using initial materials which so far have been considered as waste substances.

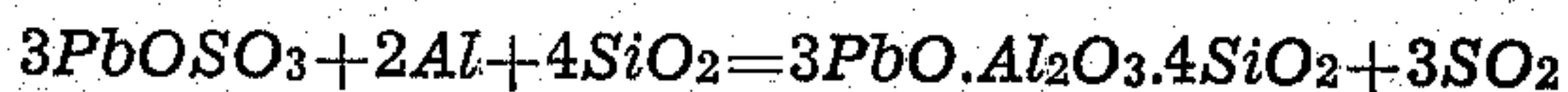
Hitherto the lead has been, in most cases, introduced into lead "glazing" preparations in the form of "litharge" or "red oxide of lead", ( $Pb_3O_4$ ) (minium); sometimes also as "white lead" or "ceruse", a lead preparation with a substantial content of basic lead carbonate, based on the presupposition that it is necessary for the production of satisfactory "glazes" to use the initial materials in an accurately defined chemical form, or degree of oxidation respectively.

It has also already been suggested to use waste materials of different kinds with a lead content for "glazing" purposes; however, these experiments proved successful only if sulphate free initial materials were used. When using initial materials containing lead with more or less sulphate content, insurmountable difficulties have so far arisen, because the elimination of these sulphates, the existence of which, as is well known, causes the finished "glaze" to become dull, was hardly possible by economical means. On the other hand just such substances containing lead sulphate are cheaply available in large quantities, and as waste or as intermediate products in the treatment of lead ore.

The difficulties presented by the use of such substances containing sulphate are eliminated by the process according to the invention. This success is attained by combining the initial materials containing the lead sulphate in the composition or preparation to be "fritted" with ingredients which decompose and reduce the sulphates during the "fritting", said material forming simultaneously components of the "glaze". As a reducing means introduced into the preparation to be "fritted", beside the substances containing lead sulphate, powdery metals which are to be finely distributed in the preparation to be fritted, such as lead proper, or aluminum, are used. These substances are introduced into the preparation to be "fritted" either singly, or several simultaneously, or respectively in the form of a mixture, depending on the  $SO_3$  already formed by the decomposition of the sulphate, or on the oxygen available accordingly, and according to the following equation:



and



In the presence of silicic acid, the metals decompose and reduce the sulphate which then, just as the oxidized reducing agent itself is converted into lead silicate, or, in case of using, for instance, aluminum as the reducing agent, to lead-aluminum silicate. Instead of the metals, metal compounds may be used also, which are decomposed and oxidized by a reaction with the ingredients of the preparation to be "fritted", and the acid residue of which escapes from the preparation, while the metal is also combined with the "glaze" after being oxidized by the resulting  $SO_3$ .

As an initial material containing lead sulphate, lead slime is preferably to be employed, which is deposited in the casings of "storage-batteries" as they are used up; of course, other materials containing lead sulphate may also be used, such as "roasted" lead ores.

These substances, more particularly the "lead slime", besides lead sulphate also contain a substantial percentage of lead oxide, the presence of which neither hinders nor interferes with the process, but is, on the other hand, actually desirable.

Again it proved to be very economical to use as a reducing agent a waste material rather than pure metal dust, or pure material respectively. A material of this kind, which is entirely suitable and available in large quantities, is the lead dust which occurs in the grinding of lead in "drum-mills" for the purposes of the storage battery industry, and which is partially oxidized, but at the same time to such an extent that it is not suitable for being employed in the production of the plate-filling paste. The content of lead oxide, which on the one hand is detrimental to the proper purpose of the dust if exceeding certain well defined limits, is on the other hand advantageous to the new process. It is merely necessary to consider on the one hand the sulphate content of the "lead slime", and on the other hand, the content of metallic lead in this ground material in rating the percentages to be used.

"Lead ash", (oxide of lead), such as obtained in the melting, refining, or like treatments of metallic lead as a waste material, may be used after grinding as a decomposing agent with the same success, and in the same manner.

Practically the new process is realized in such a way that the above mentioned ingredients and the other substances of the "glazing" preparation are mixed with one another in the corresponding percentages and then "fritted". Under certain



circumstances it is also possible to use the mixture of the ingredients without "fritting", after the requisite grinding as a "raw glaze"; in which case, the mutual reaction of the ingredients takes place on ceramic body.

5 Taking as an example lead slime as an initial material 60% of which consists of  $\text{PbSO}_4$ , a lead "glaze" can be made therefrom having the chemical structure of a lead mono-silicate having as its  
10 formula:

1  $\text{PbO} \cdot \text{SiO}_2$ , starting from:  
30% lead slime (from storage battery).  
82% sand, and  
15 62% ground and partially oxidized lead dust containing  
20% metallic lead.

The application of the new process is not limited to the manufacture of lead "glazes", but lead  
20 glass, enamel, and the like may also be produced by the same process.

Of course, if using partially oxidized lead dust, one can produce it especially for the purpose of the process according to the invention,  
25 instead of using waste material.

I claim:—

1. A process for producing lead "glazes" comprising the introduction of the lead into the preparation to be fritted in the form of a lead-sulphate-containing substance, and the reduction  
30 of all of the sulphate during the fritting by means of a powdery metal which is combined with the "glaze".

2. A process for producing lead "glazes" comprising the introduction of the lead into the com-  
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position to be fritted in the form of "lead slime" of the kind is deposited in the casings of storage-battery cells while in use, and the reduction of the sulphate contained in the "lead slime" during the fritting by means of a powdery metal which is combined with the "glaze", the proportions of lead slime and of the powdery metal used being such that all of the sulphate is converted finally into lead silicates by reaction with the silica present in the mixture.

3. A process as claimed in claim 1, characterized in that lead dust is used as a reducing agent.

4. A process as claimed in claim 1, characterized in that aluminum dust is used as a reducing agent.

5. A process as claimed in claim 1, comprising the use of initial ingredients containing lead oxide.

6. A process for producing lead glaze, comprising the introduction of the lead into the preparation to be fritted in the form of a lead-sulphate-containing substance, and the decomposition of the lead-sulphate during the fritting by partially oxidized lead dust, such as is obtained when grinding lead in drum mills in the presence of air, the proportion of lead sulphate and the reducing metal used being such that all of the sulphate is converted finally into lead silicates by reaction with the silica present in the mixture.

7. A process as claimed in claim 1, comprising the use of a mixture of metallic lead and lead oxides, such as are formed as a by-product in the melting process of lead, as a reducing agent.

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