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UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING LEAD SALTS.

SPECIFICATION forming part of Letters Patent No. 754,667, dated March 15, 1904.

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To all whom it may concern:

Be it known that I, WALTER MILLS, a subject of the King of Great Britain, residing in London, England, have invented certain new and useful Improvements in Processes of Making Lead Salts, of which the following is a specification.

This invention relates to the manufacture of certain salts of lead by simpler and more economical methods than those at present in use, and the preparation of such salts is based upon the discovery that not only metallic lead but certain ores of lead (especially galena and cerusite) are attacked and dissolved by hydrofluosilicic acid when that acid is sufficiently concentrated, and particularly when the concentrated acid is heated. The silicofluorid of lead thus formed serves as a starting-point for the preparation of various lead salts by a few simpler and easily-performed reactions, a few of which are hereinafter referred to.

I find in practice that the warm acid begins to attack and dissolve the lead-carrying substances when the specific gravity of the acid is about 1.80.

In carrying out the present process with ore I prefer to use the same in a crushed and finely-ground condition. The acid and the lead or lead-carrying compound are permitted to react in a pan or other receptacle, and the reaction is assisted by the aid of heat, which is usually continued until the mass becomes substantially dry. If galena or metallic lead is used, it is immaterial whether it be added to the acid or the acid to it; but if ore, such as cerusite or an oxygen-carrying compound, be used it is necessary to add the same to the acid—that is, to have the acid in excess—as otherwise silicates are formed. In case scrap lead is used the action of the acid is somewhat accelerated by blowing air through the mixture. Warm water may then be added and an aqueous solution of silicofluorid of lead formed, which after being filtered is ready for use.

Nitrate of lead may be readily obtained from the solution of silicofluorid by adding to the latter nitrate of calcium, potassium, or sodium either in liquid solution or in fine powder. The silicofluorids of the respective metals are precipitated, while nitrate of lead remains in solution. The aqueous solution of this nitrate of lead may be employed for the preparation of fluorid of lead by adding to the solution fluorid of ammonium, calcium, potassium, or sodium. It is best to use the fluorids of ammonium and potassium in aqueous solution and to heat all the solutions before mixing them to a temperature of about 80° centigrade; otherwise double salts in a more or less hydrated condition are frequently formed and precipitated. In the event that the double salt is formed the same may be resolved by washing it with water at about 100° centigrade. Moreover, the fluorids of calcium and sodium being practically insoluble in water I prefer to grind them to a fine powder and assist the action by heating the solution of nitrate of lead or the powdered fluorid, or both, to about 100° centigrade before mixing them together. After the precipitation of fluorid of lead has fallen the nitrate of the element whereof the fluorid has been employed remains in solution. This nitrate may be used to add to the silicofluorid of lead, as previously described, for preparing the nitrate of that material. Although I have stated that fluorid of ammonium may be used for the preparation of fluorid of lead, it is not altogether desirable under all circumstances to use the same, since the silicofluorid of ammonium is soluble in water.

For the preparation of sulfate of lead from the lead-nitrate solution sulfuric acid may be added thereto, whereupon reaction takes place, as indicated by the equation

$$Pb(NO_3)_2 + H_2SO_4 = 2HNO_3 + PbSO_4.$$

If a cold dilute solution of sulfuric acid is used, a brilliant white precipitate of sulfate of lead in an exceedingly-fine state of division is formed. This is valuable as a pigment, unalterable by exposure to the atmosphere or salt water. After separation from the nitric acid and washing and drying it may be mixed with oil for that purpose in the usual manner. Sulfate of lead being slightly soluble in concentrated nitric acid, the solutions employed

should not be too strong. It is advantageous also to keep the sulfuric acid in excess when mixing the fluids and to have that acid in slight excess at the close of the operation. Practically all the sulfate of lead can thus be removed from aqueous nitric acid of a specific gravity of about 1.2.

Various salts of sulfuric acid may be used instead of the acid itself for the preparation of the sulfate. Thus moistened ground gypsum may be employed in accordance with the equation

$$Pb(NO_3)_2+CaSO_4=Ca(NO_3)_2+PbSO_4.$$

Basic carbonate of lead may also be prepared from the aqueous solution of nitrate of lead. Any suitable form of carbonate may be used for producing the reaction—such, for instance, as finely-divided chalk. By varying the specific gravity of the solution of nitrate of lead before adding the calcium carbonate basic carbonate of lead of almost any composition may be obtained from a substance the percentage composition of which corresponds almost precisely with the formula

$$2PbCO_3.Pb(HO)_2$$

down to a salt which is almost free from combined hydrate of lead, the general rule being that the more dilute the solution of the nitrate the more basic is the carbonate that is produced and the greater the quantity of carbonic anhydrid that is expelled from the solution. This reaction is assisted by heating the calcium carbonate or other carbonate before adding it to the solution of nitrate of lead.

Having described my invention, I claim—

1. That method of making salts of lead which consists in dissolving lead-carrying substances in hydrofluosilicic acid to form silicofluorid of lead, and in then reacting upon such silicofluorid with a nitrate to form nitrate of lead.

2. That method of making salts of lead which consists in dissolving lead-carrying substances in hydrofluosilicic acid to form silicofluorid of lead; in then acting upon such silicofluorid with a nitrate to form nitrate of lead; and in then reacting upon such nitrate with the proper reagent to form the salt desired.

3. That method of making salts of lead which consists in heating a mixture of a lead-carrying substance and concentrated hydrofluosilicic acid and thereby forming silicofluorid of lead; in then acting upon such silicofluorid with a nitrate to form nitrate of lead; and in then reacting upon such silicofluorid with a proper reagent to form the lead salt desired.

Signed at Nos. 9 to 15 Murray street, New York, N. Y., this 23d day of May, 1903.

WALTER MILLS.

Witnesses:
FRED. J. DOLE,
JOHN O. SEIFERT.