UNITED STATES PATENT OFFICE.

ALFRED WOHL, OF CHARLOTTENBURG, GERMANY.

PROCESS OF RECOVERING PROTOXID OF LEAD FROM WASTE PRODUCTS.

SPECIFICATION forming part of Letters Patent No. 601,299, dated March 29, 1898.

Application filed February 1, 1897. Serial No. 621,557. (No specimens.) Patented in Germany May 29, 1895, No. 90,307; in France September 3, 1895, No. 250,022; in Belgium November 16, 1895, No. 118,387; in England November 29, 1895, No. 22,859, and in Austria November 14, 1896, No. 4,577.

To all whom it may concern:

Be it known that I, ALFRED WOHL, doctor of philosophy, a subject of the King of Prussia, Emperor of Germany, residing at Charlottenburg, near Berlin, in the Kingdom of Prussia, German Empire, have invented a new and useful Improved Process of Recovering Protoxid of Lead from Waste Products, (for which I have obtained a patent in Germany, No. 90,307, bearing date May 29, 1895; in France, No. 250,022, bearing date September 3, 1895; in Belgium, No. 118,387, bearing date November 16, 1895; in Great Britain, No. 22,859, bearing date November 29, 1895, and in Austria, No. 4,577, bearing date November 14, 1896;) and I do hereby declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

The present invention relates to the recovering of lead protoxid from waste products containing lead carbonate and organic lead salts, especially from the residue obtained in the carbonation of lead saccharate obtained by treating molasses and other impure sugar solutions with lead protoxid; and it consists in carrying out the burning of said material in two phases—that is to say, first at a temperature below the melting-point of lead and then at a higher temperature, as hereinafter fully stated, whereby I am enabled to recover all the lead from said material in the form of pure yellow lead protoxid ready for reuse as a most efficient sugar-extracting agent for molasses.

In a prior application, filed December 21, 1895, Serial No. 572,894, I have described a process for extracting the sugar contained in molasses and other like impure sugar solutions by the agency of lead protoxid. According to this process the concentrated molasses, &c., is mixed with an excess of lead protoxid, preferably with yellow lead protoxid, which is by far more active for the purpose in view than the red protoxid. The mixture is allowed to stand until a viscous mass has formed, which is then washed with water. The washed mass consists of saccharate of lead and organic lead salts, the quantity of the latter of which depends upon the greater or lesser alkalinity of the sugar solution treated. It is thinned with water, or preferably with a sugar solution, and then subjected to carbonation in order to decompose the lead saccharate. This carbonation is carried out by introducing carbonic-acid gas into the thinned mass at a temperature not exceeding 60° to 70° centigrade, care being taken that the contact between the carbonic acid and the mass is as intimate as possible. The introduction of carbonic acid is discontinued as soon as the polarization of the liquor ceases to augment. Under these conditions the residue of the carbonation step consists, essentially, of an intimate mixture of basic lead carbonate with the organic lead salts present in the mass.

It is obvious that the process of extracting sugar from molasses and the like depends materially upon the recovering of lead without losses and in a form suitable for immediate reuse—that is to say, in the form of yellow protoxid. This I obtain by my process.

It is well known that lead protoxid, as well as minium, can be obtained from carbonate of lead by burning the latter in the presence of air; but it has not heretofore been known that organic lead salts can be reduced to pure lead protoxid by burning. In all of the books of chemical analysis it is said that by burning organic lead salts a mixture of lead protoxid and metallic lead is obtained which has to be separated into its constituents to enable the quantity of lead present in the salt to be determined. The same occurs when the residue referred to is burned in the same way as the burning of lead carbonate is carried out. It results in a greenish-colored mixture of lead protoxid with metallic lead, and it is impossible to convert this mixture into pure yellow protoxid. Now I have discovered that this failure can be efficiently avoided by carrying out the burning in two phases under conditions as will now be described.

The precipitate is heated for a somewhat lengthy period of time while being subjected to the action of a current of air. The temperature is slowly and gently raised, however, so as to be maintained below the melt-

ing-point of lead. The mass will first assume a black color, owing to the formation of suboxid of lead (Pb_2O) and some metallic lead in a finely-divided state, both of which being then gradually converted into protoxid of lead. When the black coloring has disappeared, the temperature is at once raised up to about 600° centigrade, whereby the yellow modification of lead protoxid is formed. I prefer to cut off the supply of air during the final calcination in order to prevent conversion of lead protoxid into a higher oxid at those parts of the furnace that are insufficiently hot. Obviously this higher oxid would upon being further heated yield up again the oxygen by the absorption of which it has been produced, and thus be reduced to protoxid; but this reduction requires the action of a higher temperature and a large period of time, which will be wholly avoided by conducting the final calcination in the absence of air.

For carrying out the improved process the precipitate may be compressed in a partly-dried state into solid blocks (in the shape of bricks, lengths of cylinders, &c.) before burning. In consequence of the expulsion of water and carbonic acid these blocks will become sufficiently porous to be capable of being burned throughout in the presence of air without falling to pieces.

Where the burning operation has not been properly conducted and greater or less quantities of a higher lead oxid have formed, the same are unavailable in the formation of lead saccharate. They need not on this account, however, be separated from the protoxid, but may be allowed to pass through the saccharate-forming and carbonating stage, and when the burning of the precipitate obtained in the latter stage is then conducted in the proper manner they will be reduced to protoxid, giving up their surplus of oxygen, even at a moderate temperature, to the organic substance present, so that in this case proportional less air or no air at all need be admitted.

The alumina, the silicic acid, and the oxid (sesquioxid) of iron present in the precipitate may be rendered innocuous by mixing the washed precipitate with finely-divided magnesia or carbonate of magnesia (say about two, three, or more per cent. of MgO of the quantity of protoxid of lead) and drying the mixture previous to calcination. On calcining the mixture the said impurities, which otherwise would have a destructive effect upon the walls of the furnace, become wholly converted into harmless magnesium compounds. An action similar to that of magnesia is exercised by baryta, strontia, and lime and their carbonates.

What I claim, and desire to secure by Letters Patent of the United States, is—

1. The process for recovering lead protoxid fit for extracting sugar from molasses and other impure sugar solutions by burning the precipitate obtained by the carbonation of lead saccharate and other waste products containing lead carbonate and organic lead salts, which consists in carrying out the burning in two phases, that is to say, in first gently heating the material in the presence of air up to a temperature below the melting-point of lead until the black color has disappeared, and then at once raising the temperature to a dark-red heat, substantially as and for the purpose specified.

2. The process for recovering lead protoxid fit for extracting sugar from molasses and other impure sugar solutions by burning the precipitate obtained by the carbonation of lead saccharate and other waste products containing lead carbonate and organic lead salts, which consists in mixing the said material with magnesia or its described equivalent, gently heating the mixture in the presence of air up to a temperature below the melting-point of lead until the black color has disappeared, and then at once raising the temperature to a dark-red heat, substantially as and for the purpose specified.

3. The process for recovering lead protoxid fit for extracting sugar from molasses and other impure sugar solutions by burning the precipitate obtained by the carbonation of lead saccharate and other waste products containing lead carbonate and organic lead salts, which consists in carrying out the burning in two phases, that is to say, in first gently heating the material in the presence of air up to a temperature below the melting-point of lead until the black color has disappeared, and then at once raising the temperature to a dark-red heat and shutting out the air, substantially as and for the purpose specified.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

ALFRED WOHL.

Witnesses:
HENRY HASPER,
W. HAUPT.