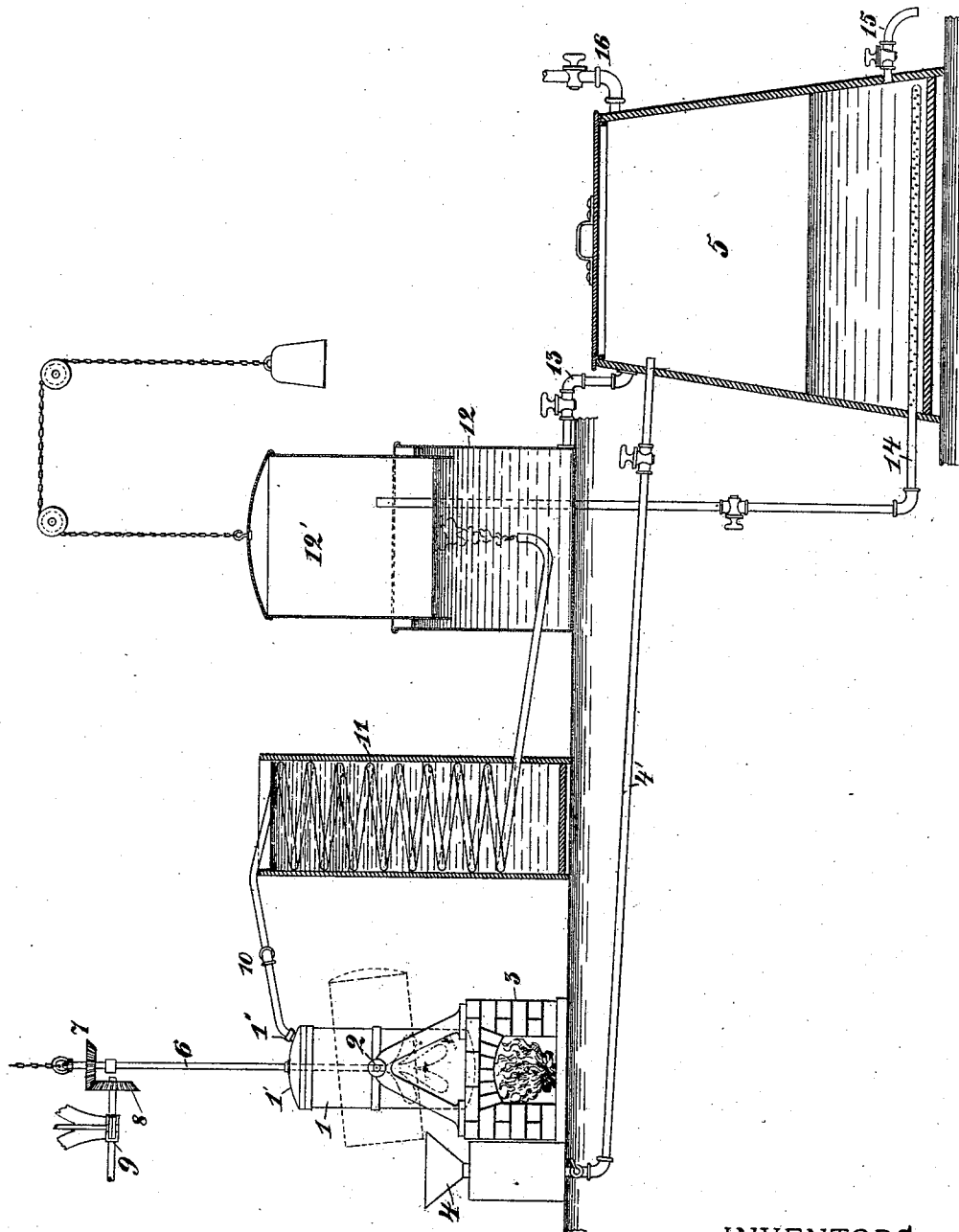


(No Model.)

E. WALLER & C. A. SNIFFIN.
METHOD OF MAKING WHITE LEAD.

No. 471,780.

Patented Mar. 29, 1892.



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UNITED STATES PATENT OFFICE.

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METHOD OF MAKING WHITE LEAD.

SPECIFICATION forming part of Letters Patent No. 471,780, dated March 29, 1892.

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To all whom it may concern:

Be it known that we, ELWYN WALLER and CHARLES A. SNIFFIN, both citizens of the United States, and residents of the city, county, and State of New York, have invented certain Improvements in Methods of Making White Lead, of which the following is a specification.

This invention relates to the production of white lead for use as a pigment directly from the "carbonate" ore, an impure cerussite, such as is found in the vicinity of Leadville, Colorado, and various other places in the western part of the United States.

We have discovered that when the native carbonate ore is heated to ebullition with a solution containing either acetic acid or lead acetate the ore will yield more or less of the lead it contains to the solution, and if the proportion of acetic acid or lead acetate be sufficient and the period of heating be adequately prolonged the whole of the lead contained in the carbonate of the ore treated will be taken up and dissolved in the solution. When neutral lead acetate is used basic acetates of lead go into the solution, and when acetic acid is used neutral or basic acetate of lead are formed, according to the proportion of real acetic acid used and the amount of same, which may be allowed to boil away. When neutral lead acetate is used, or when we use less acetic acid than will suffice to form a neutral lead acetate with the lead present in the quantity of ore treated, basic acetates of lead are formed in the solution and only mere traces of the other constituents of the ore are dissolved. When carbon dioxide is added to or passed into the solution of basic lead acetates thus produced, a precipitate of lead carbonate, combined with more or less lead hydrate, is produced, affording amorphous lead hydrocarbonate if suitable conditions are maintained. This lead hydrocarbonate is the "white lead" of commerce used extensively as a pigment. After the treatment with carbon dioxide neutral lead acetate remains in the solution, and this solution may be employed in the treatment of a fresh portion of the ore, thus effecting an economy in the acetic acid employed, which is used over and over again, and the carbon dioxide evolved in the treatment of the ore primarily is or may be collected and employed in the after precipitation of the lead hydrocarbonate,

whereby an important economy in the production of this gas is effected.

In respect of the ratio of acetic acid or lead acetate to be used to the amount of lead present in the carbonate of the ore treated, it should be borne in mind that where the proportion of acetic acid is too small there is a liability of producing highly basic lead acetates which are less soluble in water than the less highly basic acetates, and therefore render the process less advantageous on account of the necessity of handling larger quantities of the solution. We will hereinafter give the proportions we have employed with good results. We do not, however, limit ourselves to these proportions.

Having thus stated in a general way the principles upon which our manufacture is based, we will now proceed to set forth more definitely how it may be carried out in practice.

The carbonate ore should be first ground or pulverized so finely that it will pass through a sieve having forty, fifty, or sixty meshes to the linear inch. The finer it is ground the more rapid and satisfactory will be the operation. An analysis should then be made of a fair average portion of the ore to determine the percentage of lead present, as this percentage varies greatly in ores from different localities. A convenient amount or charge of the ground ore is then placed in a vessel arranged over a furnace or adapted to be otherwise heated. The volume of the charge will be governed by the percentage of lead contained in the ore. Water to the amount of about fifteen or twenty times the weight of lead in the charge is now added, and to this added for the first charge real acetic acid in the proportion of about one-fifth the weight of the lead in the charge, or, more exactly, six hundred and twenty-one parts of lead to one hundred and twenty parts of acetic acid. The amount of water contained in the acetic acid added, if ordinary commercial acid be used, should be reckoned in the calculation as a part of the water in the charge. By real acetic acid is here meant the anhydrous or actual acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) as distinguished from commercial acetic acid, which is a mixture of acetic acid and water. If neutral lead acetate be used, the amount, by weight, of the acetate should be nearly equal to the lead present, or, more exactly, three hundred and seventy-nine

parts of crystallized neutral lead acetate to four hundred and fourteen parts of metallic lead present in the charge. These proportions are not liable to produce a basic acetate higher than the tri-basic when the process is carried out as described; but if any departure be made from these proportions we prefer to increase the amount of acetic acid or the solution of neutral acetate.

The vessel containing the charge may be of enameled iron or other suitable material, and the charge should not fill it more than about one-third full. It should have a close-fitting cover and be provided with a rotating mechanical stirrer and an outlet for the carbon dioxide which leads through a condenser to a gas-holder. After the vessel is charged and the stirrer set in operation, heat is applied and the temperature raised until the contents boil gently or simmer. This heat should be maintained for from four to six hours continuously.

The stirrer is not absolutely essential; but it is useful, because, unless the heat be very carefully regulated, the contents of the vessel are apt to boil over. As low a heat as possible consistent with the necessity of keeping the mass gently simmering is best. At the end of from four to six hours about one-half of the water should have boiled away. The actual length of time required for maintaining the heat in any given case will depend somewhat upon the purity of the ore, the management of the heat, and similar conditions. When the period of boiling shall have terminated, the charge is allowed time to settle.

The water driven off as vapor from the charge and the carbon dioxide which is driven off with it are passed through a coil or condenser, which should be kept as cold as possible in order that the water of condensation may absorb as much of the carbon dioxide as possible, and this water, as well as the free carbon dioxide, is led from the condenser into a closed vessel or, better, a gas-holder, where it is stored. Pipes from this holder lead the carbonated water and the free carbon dioxide into a precipitating tank or vessel, the liquid flowing into the tank in any manner desired and the gas entering below the level of the said liquid. The charge in the boiling-vessel, as soon as the heat is withdrawn, settles rapidly, leaving only a few finely-divided particles of the residuum in suspension. To obtain perfectly-pure white lead, these particles should be removed by passing the supernatant solution in the vessel (now containing basic lead acetates) through a filter. While still hot, it is led to the tank containing the carbonated water and carbon dioxide passed through the mixture, when a reaction takes place and the lead is precipitated in the form of amorphous lead hydrocarbonate or white lead.

We have discovered that when a solution of basic lead acetate is quite dilute, or when precipitation is induced at once by mingling the

solution containing basic lead acetate with water containing carbon dioxide in solution and more carbon dioxide be passed into the solution, a precipitate of amorphous lead hydrocarbonate is obtained, and the uncombined carbon dioxide arising from the precipitating-vessel may be conveyed to a gas-holder for further use.

The amount of carbon dioxide set free from the ore treated should be more than sufficient for the precipitation of the lead hydrocarbonate in the tank, since lead is present in the ore as a neutral carbonate, (PbCO_3) containing forty-four parts of carbon dioxide to two hundred and seven parts of metallic lead, whereas the white lead of commerce contains from twenty-seven and a half to thirty-six and two-thirds parts of carbon dioxide to two hundred and seven parts of lead. The more common proportion is twenty-nine and one-third parts carbon dioxide to two hundred and seven parts metallic lead. However, as some carbon dioxide may be lost by leakage it may be necessary to manufacture a portion of that required by some one of the well-known methods. If a large excess of carbon dioxide be employed the precipitate tends to become crystalline, and consequently deficient in covering power or "body" when used as a pigment. Hence it is advisable to stop the introduction of the carbon dioxide when the solution in the tank (which will be milky) shows a tendency to clear up rapidly. After precipitation time is allowed for the solution to become clear, when it is drawn off from the tank for use with another charge. The precipitate is removed, washed, and dried in the usual manner.

Our object in using carbonated water or water charged with carbon dioxide in the precipitating-tank and passing carbon dioxide in a gaseous form through the solution in said tank is to avoid crystallization and render the precipitate amorphous.

The residual ore from the treatment may retain some lead in the form of basic acetate probably in a more basic form than the tri-basic, and the amount will be larger if the solution be allowed to cool in contact with it. If desired, practically all of this basic acetate may be recovered by boiling the residue in water.

In the accompanying drawing we have shown somewhat diagrammatically an apparatus adapted for carrying out our method.

1 represents the vessel or retort in which the charge is boiled or simmered for from four to six hours. This vessel is represented as mounted on trunnions 2 over a furnace 3 or any form of heating apparatus, so that it may be tilted for decanting into a filter 4, from which the solution of basic acetate flows by a pipe 4' to the precipitating-tank 5. Within the vessel 1 is a mechanical stirrer, (indicated in dotted lines,) the shaft 6 of which has on it a bevel-wheel 7, which gears with a similar wheel 8 on a power-shaft 9.

The removable cover 1' of the vessel 1 is provided with a gas and vapor outlet 1'', which is coupled by a suitable union with a jointed pipe 10, which leads the carbon dioxide and watery vapor from the vessel 1 to the condenser 11, from which the free gas and the carbonated water pass to a holder 12, provided with a counterweighted bell-cover 12'. The water remains in the holder and seals the bell, while the free gas rises in the bell. The carbonated water from the holder 12 flows into the precipitating-tank 5 by way of a cock-controlled pipe 13, and the gas from the bell 12' enters the tank below the liquid level therein by way of a pipe 14, that portion of said pipe within the tank being perforated. After the precipitation of the white lead in the tank, the remaining solution of neutral lead acetate is drawn off by a cock 15 for use with the next charge treated.

The rotary stirrer may be removed from vessel 1 by lifting it with the cover of the vessel to facilitate cleaning and the removal of the residual ore. The free carbon dioxide escapes from the tank 5 at an outlet 16.

Any other apparatus of a similar character to that illustrated may be employed.

We may say here that we use acetic acid only with the first charge treated by preference, and for the succeeding charge we employ the solution of neutral lead acetate from the precipitating-tank for admixture with the water and pulverized ore. Of course we may employ acetic acid with each charge, or a solution of the neutral lead acetate with each charge; but for economical reasons we prefer to operate as above stated. In each case the acetic acid is the active agent, whether combined in the form of the neutral acetate or not, and so far as our process or method is concerned the diluted acetic acid used with the first charge is the equivalent of the solution of neutral lead acetate used with the subsequent charges.

Having thus described our invention, we claim—

1. The herein-described method of producing a solution of a basic lead acetate from lead carbonate, which consists in heating the carbonate with water containing neutral lead acetate, substantially as set forth.

2. The herein-described method of producing lead hydrocarbonate or white lead directly from ores containing lead carbonate, which consists in heating said ores with water containing neutral lead acetate, whereby a solution of a basic lead acetate is obtained and then precipitating the lead hydrocarbonate from this solution with carbon dioxide, substantially as set forth.

3. The herein-described method of producing lead hydrocarbonate or white lead directly from ores containing lead carbonate, which consists in first heating said ores with water containing neutral lead acetate, whereby a solution of a basic lead acetate is obtained, then mixing this solution with water charged

with carbon dioxide and passing through the mixture carbon dioxide in its gaseous form, whereby lead hydrocarbonate of a highly amorphous character is precipitated, substantially as set forth.

4. The herein-described method of producing lead hydrocarbonate or white lead direct from the native lead carbonates, which consists in first mixing together the carbonate ore, water, and neutral lead acetate, then heating the mixture to ebullition and maintaining this heat until the lead in the ore has been converted into a basic acetate and the latter dissolved, then mixing the solution of basic acetate with water charged with carbon dioxide and passing through said mixture carbon dioxide in a gaseous form until the lead shall have been precipitated therefrom in the form of lead hydrocarbonate, substantially as set forth.

5. The herein-described method of producing lead hydrocarbonate from a solution of a basic lead acetate, which consists in mixing the said solution with water charged with carbon dioxide and passing through said mixture carbon dioxide in its gaseous form, whereby the lead is precipitated in the form of a hydrocarbonate, substantially as set forth.

6. The herein-described method of producing amorphous lead hydrocarbonate from a solution of a basic lead acetate, which consists in mixing said solution while hot with water charged with carbon dioxide and passing through said mixture carbon dioxide in its gaseous form until the mixture begins to clear, substantially as and for the purposes set forth.

7. The herein-described method of producing lead acetates from ores containing lead carbonate, which consists in mixing together the ore, water, and acetic acid in substantially the proportions specified, and then heating this mixture to ebullition and maintaining the heat until the lead of the carbonate in the charge is converted and taken up in solution.

8. The herein-described method of making white lead from ores containing lead carbonate, which consists in heating the ore to ebullition with a solution of neutral lead acetate from a previous charge until the lead in the ore is converted into a basic acetate, which is taken up in solution and the carbon dioxide from the ore is driven off and stored, and then mixing the solution of basic acetate with carbonated water and passing through it the free carbon dioxide driven off from the ore, as set forth.

In witness whereof we have hereunto signed our names in the presence of two subscribing witnesses.

ELWYN WALLER.
CHAS. A. SNIFFIN.

Witnesses:

HENRY CONNETT,
HERBERT BLOSSOM.