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Original article

New simple procedure to produce white lead for special use in the plastic arts and in restoration

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ABSTRACT

Paints based on the pigment white lead have traditionally been used in art. Currently, however, this pigment is difficult to find, either in powder or in paint, with sufficient purity and without undesired additives. Furthermore, the traditional methods of producing it are not feasible to use in the studio or laboratory. Therefore, the present work proposes a new method of producing the pigment on a small scale, to be used in the fields of the plastic arts, in restoration of works of art, and in research. The method consists of precipitating white lead from aqueous solutions of lead nitrate and sodium carbonate. The procedure is simple, quick, and without unpleasant materials or handling, and the resulting pigment is of great purity and similar to traditional white lead.

1. Introduction

Until the 19th century, white lead was the most widely used white pigment, but at present it is extremely difficult to find. The main reason is the prohibition of its use in domestic paints since the 1970s, although not in art paints. The volume used of this type of paint for artists, restorers, researchers, and other professionals is so small that the pigment industries do not find its production profitable. Europe, the United States, and other countries no longer manufacture the pigment. However, supplies continue to be available from China and India, where the product is sold under the name of white lead, composed exclusively of lead carbonate, $PbCO_3$, which chemically differs from traditional white lead and in which the main component was basic lead carbonate $(PbCO_3)_2{\cdot}Pb(OH)_2$ [1]. It should be pointed out that the white lead that contains basic lead carbonate has greater coverage than that containing exclusively lead carbonate. Also, the above-mentioned suppliers sell it mixed with other white pigments, such as zinc oxide. In addition, it can be found to be mixed with oil, but with often unknown additives.

To have traditional white lead available for its good coverage, the artist or restorer could synthesize it on a small scale in the laboratory or in the studio [2]. Historically, numerous methods were used for industrial production [3].

1.1. German method or the chamber method

This consists of placing in a chamber, thin plaques of lead of angular shape suspended on a wooden framework. The carbon dioxide from a coke oven is injected into the lower part of the chamber together with the vapours of acetic acid produced by the evaporation of mild vinegar in a copper cauldron. If the temperature is about 60 °C, the process is verified in 6 or 8 weeks, after which the lead is spent and the white lead accumulated on the bottom is collected manually.

1.2. Dutch method

In this method, the floor of the chamber is covered with manure. On top cylindrical jars of varnished clay are placed after being filled with vinegar to one-fourth of their volume. Over this series of jars, fine sheets of lead are placed to form a spiral. An effort is made for the acetic acid vapours from the vinegar (but not the vinegar itself) to make contact with the lead. Over this, boards are placed and covered the manure, and then a new series of clay jars containing vinegar are covered with lead sheets. This process is repeated to form several layers (Fig. 1). The acetic acid vapour transforms the lead into basic acetate and the carbon dioxide generated by the fermentation of the manure transforms the product into basic lead

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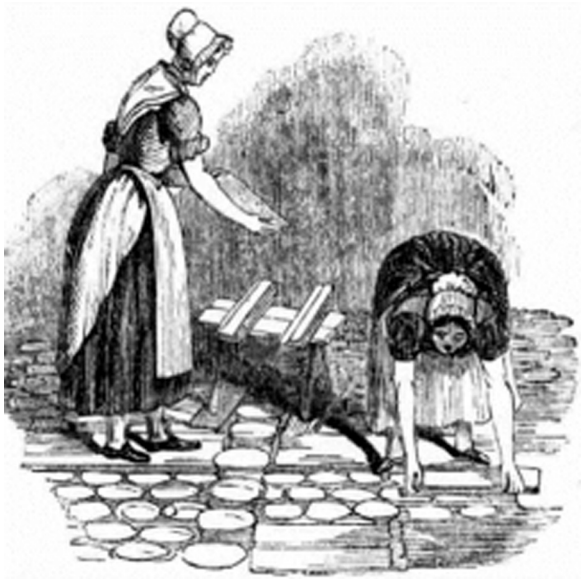

Fig. 1. Women preparing the successive layers of manure, clay jars of vinegar, sheets of lead, and boards, following the Dutch method of producing white lead [13].

carbonate. In warm-climate countries such as Spain, the process lasts some 12–14 days whereas in cool-weather countries such as Holland, the process may require up to 6 or 7 weeks. The product, as in the German method, is washed with warm water to eliminate lead acetate residues and then is ground wet, dried, and sold.

One problem with this method is the formation of black lead sulphate, which can ruin the white lead produced. This is due to the hydrogen sulphide vapours given off by the manure. An improvement over the method made in Spain in the mid-19th century replaced manure by tree bark, which also ferments with the emission of carbon dioxide, but without giving off hydrogen sulphide. The white lead produced in this way is thus of superior quality and whiteness [4].

1.3. The American method of Carter

Melted lead given a sand texture by streams of vapour is used. This product is placed in revolving drums in which an aqueous solution of acetic acid and carbonic acid is injected.

1.4. Moderate method

This method is called moderate because it uses only carbonic acid without the need to use acetic acid or vinegar. It uses ordinary unrefined lead in the form of dust particles in a water suspension. While it is being stirred, it is bubbled with air for 24 to 36 h to form lead hydroxide. This hydroxide is separated from the untransformed lead and in suspension with water is injected with gases from the combustion of coal or wood rich in carbon dioxide, previously cooled, desulphured, and free of coal dust. The carbon gas then forms basic lead carbonate.

1.5. The French moisture method

Part of the litharge (lead oxide) is dissolved in a boiling solution of neutral lead acetate to produce the basic lead acetate. This is injected with carbon dioxide until the liquid begins to have a slight acidic reaction. The white lead separates as a precipitate.

1.6. Electrolyte methods

These methods are based on transforming the metal lead into the ion Pb^{2+} by an electric current. The Sperry method uses lead anodes (which dissolve in the process) and iron cathodes, separated by a diaphragm of linen cloth that divides the electrolyte bath into two parts. In the anode zone, the solution contains sodium acetate and the quantity of carbonate needed to precipitate the white lead. The carbonate that is spent in the area of the anode is renewed and thus migrates through the linen membrane towards the cathode area, where it is found in a high concentration [5]. This was the last profitable industrial method used in the 20th century until the ban on the use of white lead except for artistic applications. Today, it is not profitable to produce white lead industrially.

2. Aim

To manufacture white lead in the studio or laboratory using the above methods, the user will be met by some of the following technical disadvantages: slowness, foulness, and/or difficulty. Therefore, it becomes necessary to have a simple, quick, and non-repulsive method that provides pure white lead of quality and that can be easily used in the studio. The present work proposes such a method.

3. Procedure to produce white lead

3.1. Chemical basis of the synthesis

Basic lead carbonate is a complex salt formed by two moles of lead carbonate and one mole of lead hydroxide: $(PbCO_3)_2{\cdot}Pb(OH)_2$.

Lead carbonate can be synthesised individually by placing an aqueous solution of a Pb^{2+} salt in contact with an aqueous solution of carbonate, CO_3^{2-} according to the following equilibrium heavily shifted to the right:

$$Pb^{2+}(aq.) + CO_3^{2-}(aq.) \rightleftarrows PbCO_3 \downarrow \quad (1)$$

Similarly, lead hydroxide can be synthesised individually by placing a solution of Pb^{2+} salt in contact with an alkaline solution according to the following equilibrium, also shifted to the right:

$$Pb^{2+}(aq.) + 2OH^{-}(aq.) \rightleftarrows Pb(OH)_2 \downarrow \quad (2)$$

The solubility products of both substances are very small as they are highly insoluble (K_{sp} $PbCO_3 = 7.4 \times 10^{-14}$ y K_{sp} $Pb(OH)_2 = 1.43 \times 10^{-15}$) [6].

The b n the result of co-precipitating two moles of lead carbonate together with one mole of lead hydroxide.

This is equivalent to multiplying Eq. (1) by 2 and adding the result to Eq. (2):

$$\frac{\begin{array}{c} 2\left(Pb^{2+}(aq.) + CO_3^{2-}(aq.) \rightleftarrows PbCO_3 \downarrow\right) \\ Pb^{2+}(aq.) + 2OH^{-}(aq.) \rightleftarrows Pb(OH)_2 \downarrow \end{array}}{3Pb^{2+}(aq.) + 2CO_3^{2-}(aq.) + 2OH^{-}(aq.) \rightleftarrows (PbCO_3)_2 \cdot Pb(OH)_2 \downarrow} \quad (3)$$

In essence, the basic lead carbonate is formed when the 3 moles of the ion Pb^{2+} are precipitated with 2 moles of the ion CO_3^{2-} in the presence of two moles of hydroxyl ions, OH^-. A sufficiently high pH ensures the presence of the hydroxyl ions.

Only two water-soluble lead salts are capable of releasing Pb^{2+}: lead (II) acetate and lead (II) nitrate. Lead (II) acetate is the one that is described in the old techniques. On the other hand, lead (II) nitrate was never used historically as a source of lead (II) to manufacture white lead because it was not industrially available. This was due to the fact that lead (II) nitrate could be synthesised

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