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A New Method for the Preparation of Thallous Hydroxide

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The salts of thallium and an organic acid are useful in determining the specific gravity of ores according to the method described by Sullivan.[1] One of the most satisfactory liquids for the purpose is a solution which has a specific gravity of 4.40 at 35°, containing ten parts of thallous formate, ten parts of thallous malonate and one part of water.[1] These salts and others are simply prepared from thallous hydroxide[2] and the organic acid or ester, the difficulty being the preparation of the thallous hydroxide.

R. Böttger[3] found that some thallous hydroxide is formed if thallium is kept under water which contains air in solution. Bahr[4] slowly produced the hydroxide by passing oxygen through cold water and thallous turnings. De Forcrand[5] prepared thallous ethoxide by passing air through alcohol containing thallium, according to the following reaction

$$2EtOH + Tl_2 + O \longrightarrow H_2O + 2EtOTl$$

The ethoxide added to water forms thallous hydroxide[6] and ethyl alcohol.

The method used by us until recently and by the majority of workers is that of Lamy,[7] who prepared thallous hydroxide by the action of barium hydroxide on thallous sulfate. This process requires the preparation of thallous sulfate and also includes a troublesome filtration. Kölliker[8] noted that the oxidation of thallium metal in air appeared to be much more extensive than is indicated in the literature.

In spite of the fact that several workers have noted that thallium can be oxidized quite readily in the presence of water, no one has prepared thallous hydroxide in this manner and therefore we have studied this method in our laboratory.

(1) J. D. Sullivan, Bureau of Mines, Technical Paper No. 381, "Heavy Liquids for Mineralogical Analysis."
(2) Menzies and Wilkins, *J. Chem. Soc.*, **125**, 1148–1152 (1924).
(3) Böttger, *Dinglers Journal*, **197**, 379 (1870).
(4) Bahr, *Z. anorg. Chem.*, **71**, 79 (1911).
(5) De Forcrand, *Compt. rend.*, **176**, 20 (1923).
(6) De Forcrand, *ibid.*, **176**, 873 (1923).
(7) Lamy, *Ann. chim. phys.*, [3] **67**, 392 (1863).
(8) Kölliker, *Chem.-Ztg.*, **43**, 231 (1919).

At first an attempt to speed up the air oxidation of thallium was made by passing air through boiling water containing mossy thallium. Due to the insolubility of air in water at this temperature, only a small amount of thallous hydroxide was formed. In order to bring the greatest possible surface of the metal in contact with air in the presence of enough water to complete the reaction $2Tl + H_2O + O \longrightarrow 2TlOH$ and dissolve the thallous hydroxide, mossy thallium was placed in a long tube through which air and steam were passed. By using a large amount of air, it was possible to produce a solution containing, on the average, 180 g. per liter of thallous hydroxide.

Experimental

Mossy thallium was prepared by pouring the molten metal from a height of 1.8–2.4 meters into a tub of cold water.

A heavy glass funnel 15 cm. in diameter was placed on a rigid support, and a disk of 10-mesh Nichrome gauze, 8 cm. in diameter, was placed horizontally in the funnel. A Pyrex glass tube, 9 cm. inside diameter and 1 meter in length, was set vertically in the funnel and 5800 g. of mossy thallium added, giving a column 60 cm. in height. The glass tube was provided at the top with a rubber stopper containing two 6-mm. inlet tubes. Air freed of carbon dioxide by bubbling it through sodium hydroxide solution was passed through one inlet at the rate of 2–3 liters per minute, and steam was passed through the other inlet at such a rate that the temperature of the moist air leaving the bottom of the funnel was 70–80°. The solution of thallous hydroxide was collected in a receiver placed below the funnel. Operation of the apparatus for twenty-four hours gave a yield of 26 liters of solution containing 180 g. per liter of thallous hydroxide equivalent to 4300 g. of metallic thallium. The height of the mossy thallium at the end of the run was 13 cm.

Summary

Thallous hydroxide has been conveniently prepared by passing steam and air through a tube containing thallium.

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