

Preparation of Fluoboric Acid from Fluosilicic Acid and Boric Acid, and a Comparison of the Protective Value of Electrodeposited Lead from Fluosilicate and From Fluoborate Baths

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Abstract

Lead fluoborate electroplating baths give smoother and more impervious deposits than do lead fluosilicate baths. Unfortunately, fluoboric acid costs about 40 cents per pound compared to about 11 cents for fluosilicic. The high cost results from the present method of manufacture using boric acid and expensive hydrofluoric acid. The fluoborate baths are only used where the value of a superior quality of the deposit more than counterbalances the extra cost.

Boric acid will react with fluosilicic acid forming fluoboric acid and gelatinous silicic acid which is very difficult to filter. The loss of acid in the residue after filtration is the great objection to this method.

Method of Analysis

Knowing the quantity of fluosilicic acid in an experiment, the conversion to fluoboric acid was calculated by difference from the weight of sodium fluosilicate that was precipitated in 50 per cent alcohol.

Materials Used

A 27.4 per cent water solution of fluosilicic acid was available from a tank car of commercial acid as used by a lead refinery. This acid was made by the Davison Chemical Company, Baltimore from the silicon tetrafluoride evolved by the reaction of sulfuric acid on phosphate rock in the manufacture of superphosphate fertilizer. The boric acid was the ordinary crystalline material supplied for laboratory use.

Experiments

The use of a solution of boric acid on the fluosilicic acid always gave such a bulky gelatinous mass of silicic acid that satisfactory filtration could not be accomplished. No greater recovery of the total acids in the filtrate than 55 per cent could be obtained by gravity filtration.

It is a well known fact that a solid reagent in a solution of the other material that is to be precipitated gives a more granular and

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therefore a more easily filtered precipitate. Therefore, all of the following experiments were with solid boric acid. In each case, the residue was allowed to drain by gravity. Then the residue was washed with one fourth as much water as the original volume of fluosilicic acid. Variations in temperature, time of reaction, stirring, etc., were all tried.

An equivalent quantity of solid crystalline boric acid was allowed to stand quietly on the fluosilicic acid for varying periods of time. About 48 hours was needed for equilibrium at which time all but 16 per cent of the fluosilicic acid had been converted and 75 to 80 per cent of the total acids were recovered in the filtrate. These results show that the rate of reaction on mere standing at room temperature is too slow and the recovery is not satisfactory. Of course, the recovery is dependent on the physical condition of the silicic acid residue which determines the efficiency of gravity filtration. The use of ten per cent excess of boric acid under these same conditions did not materially change either the time required or the per cent of conversion.

Apparently the solid pieces of boric acid must become coated with a rather impervious layer of silicic acid whereby the rate of reaction is reduced. If this is true, stirring of the reaction mass should speed up the reaction. With an equivalent quantity of solid boric acid and mechanical stirring at room temperature, an equilibrium was reached in two to three hours with the unconverted fluosilicic about 17 per cent and the total recovered acids about 88 per cent. With 10 per cent excess of solid boric acid, in stirred mixtures at room temperature, the equilibrium time, yield and recovery were not essentially changed. Even 100 per cent excess of boric acid raised the yield to only 10 per cent of unreacted fluosilicic acid in two hours but the total recovery was not changed. These results show that complete reaction is not a matter of quantity of boric acid used.

Equivalent weights of the boric acid and fluosilicic were used in the rest of the experiments. The unreacted fluosilicic acid was 40 per cent after 27 hours at 37°. The results were little better than 65°, although the speed of reaction was greater. Unreacted fluosilicic acid was 20 per cent and recovery was 81 per cent in 1.5 hours.

At 95°C, the equilibrium was reached in one hour with stirring, and the per cent of unchanged fluosilicic acid was 10 per cent, and the total recovery was about 80 per cent. This seems to be about the best results that could be obtained. However, the extra trouble of operating at 95°C more than counter-balances the time saved in reaching the equilibrium.

The use of boric acid, powdered to 40 mesh gave greater speed of reaction and as little as 10 per cent of unchanged fluosilicic acid, but the total recovery of acids was down to 70-75 per cent due to more bulky silicic acid.

A more dense form of the solid boric acid was prepared by previously heating the boric acid until it melted. Lumps of this dense form gave a rate of reaction that was very slow even at 95°C with stirring. After three hours the recovery reached 84 per cent but the unreacted

fluosilicic acid was 30 per cent. This indicates that long continued reaction time might be satisfactory as recovery is improved by the change to dense boric oxide.

The fused boric acid, ground to 40 mesh, was also slow in reacting, and the conclusion is that previous fusing of the boric acid is not desirable.

Protective Value of Lead Electrodeposited from Fluosilicate and Fluoborate Baths.

The relative protective values of electrodeposited lead from the fluosilicate and the fluoborate baths showed the fluoborate much superior. Each bath contained five per cent of lead and seven per cent of free acid. All the acid ions in one were fluosilicate, and in the other fluoborate of the purity made by the method described here. The addition agent was 0.05 gm. glue and 0.1 gm. of goulac² per 100 ml. The lead deposits, 0.001 inch thick on iron, were tested with feroxal reagent for porosity. The deposit from fluosilicate showed 17 spots while only 6 spots showed on the fluoborate deposit in the same time

Summary

It is recommended that an equivalent weight of crystals of boric acid be stirred with the fluosilicic acid at 95°C. A 90 per cent change to fluoboric acid and an 80 per cent recovery of total acids is reached in one hour. At room temperature, about the same equilibrium is reached in three hours. Lead plated from a bath made with fluoboric acid showed only about a third as many pinholes as did a deposit from a fluosilicate bath.

²This is the residue from sulfite paper manufacture.