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PREPARATION OF FERROUS FORMATE

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This invention relates to a method of preparing ferrous formate. More particularly, it relates to a method of preparing the ferrous formate in an unoxidized form.

Although ferrous formate can readily be formed as a result of a comparatively simple double decomposition reaction between ferrous sulfate and sodium formate it has heretofore been relatively difficult to isolate this material in its unoxidized form since it is readily oxidized in the presence of water.

It is, therefore, an object of this invention to provide a method of preparing ferrous formate in a comparatively simple and inexpensive manner.

A further object of this invention is to provide a method which will permit good yields of the material so that it can be made in an economic manner.

It has been found that these objects and advantages can readily be attained if the double decomposition reaction between ferrous sulfate and sodium formate is carried out in the presence of an acid. It has been found that the addition of formic or hydrochloric acid to the reactants or a combination of them will prevent the oxidation of the product. Other strong acids, such as sulfuric may also be used, the only condition being that they do not form precipitate with the ferrous ion. The minimum concentration of acid which has been found necessary to completely prevent the oxidation is in the neighborhood of 5% by volume.

In accordance with the method of this invention the ferrous sulfate and sodium formate are brought together in the presence of the acid medium whereupon the ferrous formate precipitates in the form of a white precipitate while the sodium sulfate formed remains in solution. This reaction proceeds in accordance with the following equation:

$$FeSO_4 + 2\,NaCOOH \longrightarrow Fe(COOH)_2\downarrow + Na_2SO_4$$

If no acid is present during the precipitation of the ferrous formate it will have a dark brown color indicative of oxidation to the ferric state.

It has further been found that when the ferrous formate is precipitated in the presence of an acid the yield of recoverable formate is increased considerably thereby decreasing the cost of the product. Therefore, although the presence of 5% by volume of acid is sufficient to insure the isolation of an unoxidized product it has been found advantageous to increase the acid concentration up to 10% in view of the resulting increase of yield of product.

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After the ferrous formate has been precipitated it is filtered and dried under vacuum to prevent oxidation of the material which would take place if this portion of the process were to be carried out in air. Since ferrous formate has been found to be very susceptible to oxidation when wet, rapid drying of the precipitate is recommended. The temperature of drying must, however, be low enough to prevent oxidation and yet high enough to dry the precipitate in a reasonable time. The temperature range of 75° C.–95° C. has been found suitable for this purpose.

The ferrous formate can be obtained in various manners. One can for instance add solid ferrous sulfate to an acid solution of sodium formate or conversely or one may mix together two previously prepared solutions of the reactants. The resulting reaction occurs at room temperature and the solution can be stirred during precipitation. Still another method for obtaining the formate particularly when coarse crystals are desired, consists in dissolving sodium formate in an acid solution heated to 90–100° and dissolving ferrous sulfate in an acid solution at the same temperature. The two solutions can then be combined while they are hot and stirred during cooling. The coarse crystals obtained are less susceptible to oxidation.

The ferrous formate which is obtained in accordance with the method herein described is particularly well adapted for use in preparing manganese doped iron magnets as described in co-pending application Serial Number 273,552, filed February 26, 1952, of which this is a continuation-in-part.

The following are some examples of methods of preparation of ferrous formate:

Example I

45 kg. of sodium formate are dissolved in 13 l. of 10% (by volume) formic acid solution at 25–30° C. To this is added 10 kg. of solid ferrous sulfate, the solution being stirred during precipitation of ferrous formate. The precipitate is filtered and dried under vacuum at 70° C. 4.6 kg. of ferrous formate are recovered for a 75% yield.

Example II

5 kg. of sodium formate are dissolved in 20 l. of 5% (by volume) formic acid solution at 25–30° C. 10 kg. of solid ferrous sulfate are added to solution which is stirred during precipitation. Precipitate is filtered and dried under vacuum at

70° C. 85% yield (5.7 kg. of ferrous formate) is obtained.

Example III

5.4 kg. of sodium formate are dissolved in 20 l. of 10% formic acid and to this is added, with constant stirring of the solution, 11.1 kg. of ferrous sulfate. Temperature of the solution is 25–30° C. The precipitate is filtered and dried as indicated. An 87% yield is obtained (5.8 kg. of ferrous formate).

Example IV

15 kg. of ferrous sulfate are dissolved in 12 liters of 10% formic acid solution with stirring. 5.4 kg. of sodium formate are dissolved in 5 l. of 10% formic acid and then added to ferrous sulfate solution. The temperature of the solution is 25–30° C. and it is stirred during precipitation. The product is filtered and dried under the usual conditions. Obtain an 81% yield (5.4 kg. of ferrous formate).

Example V

10.0 kg. of sodium formate are dissolved in 22 l. of 5% hydrochloric acid-2% formic acid solution with stirring. To this is added 21 kg. of ferrous sulfate, temperature of solution is 25–30° C. The precipitate is filtered and dried under the usual conditions. A 74% yield is obtained (9.8 kg. of ferrous formate).

Example VI

5.0 kg. of sodium formate are dissolved in 15 l. of 5% hydrochloric acid and to this is added, with constant stirring, 11.2 kg. of solid ferrous sulfate. Temperature of solution is 25–30° C. The precipitate is filtered and dried under usual conditions. In one case a yield of 81% (5.4 kg. of ferrous formate) is obtained and in another 87% yield is obtained (5.8 kg. of ferrous formate).

Example VII

1 kg. of sodium formate is dissolved in 1 l. of hot 5% hydrochloric acid (temperature=90° C.) and 2.2 kg. of ferrous sulfate are dissolved in 2 l. of hot 5% hydrochloric acid (90° C.). These solutions are combined while hot and stirred during cooling. The precipitate is filtered and dried under the above-mentioned conditions. This material thus prepared is more coarsely crystalline than the others. The yield is 69% of theoretical (921 kg. ferrous formate).

What we claim is:

1. The method of preparing ferrous formate comprising reacting ferrous sulfate with sodium formate in the presence of an acid in which ferrous formate is insoluble.

2. The method of preparing ferrous formate comprising reacting ferrous sulfate with sodium formate in the presence of at least 5% by volume of an acid in which ferrous formate is insoluble.

3. The method of preparing ferrous formate comprising reacting ferrous sulfate with sodium formate in the presence of formic acid.

4. The method of preparing ferrous formate comprising reacting ferrous sulfate with sodium formate in the presence of more than 5% formic acid.

5. The method of preparing ferrous formate comprising reacting ferrous sulfate with sodium formate in the presence of hydrochloric acid.

6. The method of preparing ferrous formate comprising reacting ferrous sulfate with sodium formate in the presence of more than 5% hydrochloric acid.

7. The method of preparing ferrous formate comprising reacting ferrous sulfate with sodium formate in the presence of more than 5% sulfuric acid.

8. The method of preparing ferrous formate comprising reacting ferrous sulfate with sodium formate in the presence of an acid in which ferrous formate is insoluble, filtering out the ferrous formate precipitate resulting from the reaction, and drying the ferrous formate precipitate under vacuum.

9. The method of preparing ferrous formate comprising reacting ferrous sulfate with sodium formate in the presence of at least 5% by volume of an acid in which ferrous formate is insoluble, filtering out the ferrous formate precipitate resulting from the reaction, and rapidly drying the ferrous formate precipitate under vacuum at a temperature in the range of 75° C. to 95° C.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,082,087	White	June 1, 1937

OTHER REFERENCES

Chem. Abstracts, vol. 26, page 964 [3].