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Coarsely crystalline veinlets within the main veinlets may be explained by the filling of shrinkage cracks under lower temperature conditions, which are further evidenced by the kaolinitic borders along these later veinlets. It seems probable that these phenomena were formed by conditions ranging from pyrometasomatism to hydrothermal alteration. Similar conclusions with regard to contact silicates were reached by Agar in his studies of contact metamorphism in the western Adirondacks.⁵

⁵ Agar, W. M., Proc. Am. Phil. Soc., vol. **62**, pp. 95–174, 1923, Contact Metamorphism in the Western Adirondacks.

THE PREPARATION OF THALLOUS FORMATE

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INTRODUCTION*

Thallous formate is extremely useful in petrographic laboratories because its aqueous solutions are liquids of densities which rise to 3.5 on saturation, properties which make such solutions important both for the separation of minerals of varying density and the determination of densities of individual minerals. The saturated solution is fairly stable, and may be diluted within certain limits; concentration to a density greater than 3.5 may be obtained by saturating at a higher temperature and using the solution at that temperature.¹

These desirable qualities are offset by the high market price of the compound, and this paper was written at the suggestion of Dr. Sampson to see whether the compound could be prepared in an ordinary laboratory by a comparatively economical process.

The principle of the method finally decided upon is to dissolve metallic thallium in sulphuric acid, and add barium formate, which precipitates barium sulphate and leaves thallous formate. In Miss Vassar's paper² on Clerici solution, two methods of preparing thallous carbonate are described, and thallous formate can

* For general information on thallium, see A. V. Petar, Thallium, U. S. Bur. Mines, Information Circular 6453, 1931.

¹ Such hot solutions cannot be used with magnetite and similar minerals, as it was found that the thallous formate was decomposed. H. Vassar found the same thing true with respect to sulphides. (Am. Min., vol. 10, p. 123, 1925).

² Op. cit., p. 124.

be formed easily from the carbonate by adding formic acid; but it is believed that the following method is simpler.³

PROCEDURE

The raw material consisted of sticks of metallic thallium about half an inch in diameter. They were dissolved in sulphuric acid,⁴ the reaction being largely:

(1) $2Tl+H_2SO_4 \rightarrow Tl_2SO_4+H_2$, and

(2) $2Tl+2H_2SO_4 \rightarrow Tl_2SO_4+2H_2O+SO_2$.

Due to the dilution of the acid used, the first equation represents the preponderating reaction, and it was found that the use of the recommended metal-acid ratio was sufficient to dissolve the metal completely.⁵ The reaction was carried on at 100 C. by leaving the mixture on a hot water bath, and was complete within twenty-four hours.

The thallous sulphate so formed is not very soluble, so it is best to keep the solution at 100°C., at which temperature 185 grams can be dissolved in a litre of solution. It may be necessary to add more water to prevent the separation of crystals.

The next step requires barium formate, and this can be easily prepared by boiling an aqueous suspension of barium carbonate with a slight excess of concentrated formic acid.⁶ This will often leave a residue of siliceous impurities, which should be separated by filtering.

The third step calls for careful attention to detail, if time is to be saved subsequently The boiling dilute solution of barium formate is added slowly to the boiling solution of thallous sulphate with constant stirring After adding enough to produce almost complete reaction, the precipitate is allowed to settle. and small quantities of hot barium formate solution are added to the pale yellow supernatant liquid until such an addition fails to give a fresh precipitate of barium sulphate.

³ Another method of forming thallous formate is described in "Methods of Preparing and Cleaning some common heavy liquids used in ore testing" by R. G. O'Meura and J. B. Clemmer (U. S. Bur. Mines, Rept. Investigations 2897, 1928), but it also is rather long.

⁴ For every 100 grams of Tl use 20 cc. of concentrated H₂SO₄, diluted 1:6.

⁵ A small amount of black, insoluble residue remaining probably represents certain impurities in the raw material, but it is not necessary to filter it off.

⁶ For 100 grams of Tl use 73 grams of BaCO₃.

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The main reaction is:

(3) $Tl_2SO_4 + Ba(HCOO)_2 \rightarrow 2HCOOTl + BaSO_4$,

but since the thallous sulphate solution contained a slight excess of free sulphuric acid, the following reaction will take place simultaneously:

(4) $H_2SO_4 + Ba(HCOO)_2 \rightarrow 2HCOOH + BaSO_4$.

The mixture is now boiled for about an hour and allowed to stand for a day or two. This will favor the growth of crystalline barium sulphate, and make separation of the residue much easier.

The solution, which contains thallous formate and formic acid, is decanted through a Buchner funnel which should be equipped with hardened filter paper. The barium sulphate is shaken with water slightly acidulated with formic acid, and these washings are also passed through the filter. Finally the barium sulphate is brought onto the filter, and washed thoroughly with the dilute formic acid.

The combined filtrates and washings are now heated on a water bath, and evaporated to dryness; evaporation may be accelerated with the help of a gentle stream of warm air directed at the surface of the liquid. More water is then added, and the process is repeated until the odor of formic acid has disappeared. Due to the common ion effect, free formic acid precipitates thallous formate before the maximum density can be attained, so it must be eliminated before making up the final solution. The crystals of thallous formate can then be dissolved in a small quantity of warm water and brought to the required density by evaporation or dilution.

Reconcentration of Dilute Solutions

In using thallous formate solutions for mineral separation dilute solutions of washings accumulate. It will probably be found that a fine yellow precipitate forms in these washings; this is due to the fact that when saturated solutions of thallous formate are diluted beyond a certain limit, hydrolysis results in the formation of insoluble complex salts. Since reconcentration can only reverse the process after prolonged treatment, it was found best to proceed according to the following method. The solution with its suspended residue is placed on a water bath, and enough formic acid is added to dissolve the precipitate. It is then evaporated to dryness and held on the water bath until the odor of formic acid has disappeared, after which the amount of water necessary to form a solution of high density is added to the crystals of thallous formate.

This method was used successfully in reworking several batches of discarded solutions which had been contaminated with the hydrolyzed salt.

MATERIALS

The price of thallium metal has fluctuated greatly. That used for this investigation was obtained from Eimer and Amend, New York, at a cost of \$17.00 for 500 grams, in November, 1931. The cost of the other materials is slight; and since 100 grams of the metal will yield almost exactly the theoretical 122 grams of thallium formate, the price per 100 grams of the formate is about \$3.00 at the above price of thallium.⁷

⁷ To obtain 100 grams of thallous formate (HCOOTI), we require:

Amount	Price
82 grams	\$2.80
16 cc.	.02
60 grams	.12
28 cc.	.05
	\$2.99
	82 grams 16 cc. 60 grams

THE BEARDSLEY METEORITE

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To the long list of Kansas meteorites this will add another, bringing the total number up to 22 falls for that state.

On October 15, 1929, the residents in the vicinity of Beardsley and surrounding villages to a distance of 40 miles or so were startled by a dazzling light followed by the usual thunderous sounds about 11:30 P.M. Those who were abroad at that hour saw a fire-ball pass from E.S.E. to W.N.W. and disappear at a considerable altitude. Unfortunately no scientist visited the locality until almost two years later so that the data are not as definite as they might have been.

In the village of Beardsley Mrs. Ray Gaines leaned out of the open window on the north side of the house and heard distinctly the fall of two stones, one of which seemed to fall in the yard. A whizzing noise was heard preceding each impact. A search was made by the Gaines' during the next few days and two stones were found, one of 4 oz. about 20 meters east of the house was evidently one of those heard to strike. The other was found some 40 rods to the east and a little south of the house. This one weighed