

LXII.—*Photomicrographic Methods applied to Two-component Salt Mixtures.*

By WALTER MATTHEW MADGIN.

DISCUSSING the deduction of the type of a two-component system, Freeth (*J. Physical Chem.*, 1925, **29**, 497) states that the methods of thermal analysis are not conclusive in many cases. Such methods

would be expected to be most inconclusive in systems where the melting point of each component is lowered by addition of the second component and where the solids are wholly or partially miscible: in both of these systems cooling curves may be misleading, e.g., when the rate of cooling is too rapid and gives rise to cored structure, and the systems may be mistaken for simple eutectic systems. The very successful application of photomicrographic methods to the study of metallic alloys suggests that similar methods might be of value in the cases discussed above, and, in fact, Schemtschuschny (*Z. anorg. Chem.*, 1908, 57, 267) has thereby obtained useful data as to the miscibility or otherwise of potassium chloride with potassium chromate, potassium dichromate, or silver chloride.

From the results of thermal analysis, Guthrie (*Phil. Mag.*, 1884, 17, 462) concluded that the salt pair potassium nitrate-lead nitrate formed a simple eutectic system, but he did not prove the non-existence of limited solid miscibility. Accordingly a photomicrographic study of this system has been undertaken, and the results afford confirmation of Guthrie's. In addition, they point to the conclusion, which would be difficult to deduce from thermal data, that the components of the system show little or no solid miscibility.

Pure lead nitrate is not fusible without decomposition, but with potassium nitrate it forms fusible mixtures of low melting point which are stable provided they do not contain more than 70% of lead nitrate (Guthrie, *loc. cit.*). The melting point of this limiting mixture is given as 335°, which is therefore the highest working temperature permissible and is practically the melting point of pure potassium nitrate (330°; Briscoe and Madgin, J., 1923, 123, 1608). This restricted working temperature is an important consideration when synthetic mixtures are being prepared as described below.

EXPERIMENTAL.

The materials used were supplied as of pure quality and were recrystallised until analysis showed at least 99.9% purity.

Mixtures of potassium nitrate and lead nitrate in various proportions and cast in a suitable form for polishing were prepared in ordinary glass test-tubes ($\frac{5}{8}$ " diameter) by weighing an amount of lead nitrate in a tube and adding a weighed amount of potassium nitrate, which was always on top of the lead salt. The test-tube was placed in an electric heater similar to that described by Briscoe and Madgin (*loc. cit.*) but sufficiently large to cover most of the tube. By this procedure no decomposition of lead nitrate ever occurred,

since the temperature never exceeded 335° , and no lead nitrate could ever be left undissolved, being always below the potassium nitrate.

When complete fusion had occurred, the heater was slowly cooled by altering the external resistance, and the rate of cooling was adjusted so as to secure the growth of large crystals. The composition of the various mixtures used is shown below as % of potassium nitrate by weight, No. 4 being the eutectic mixture :

Mixture No.	1	2	3	4	5
KNO ₃ , %	89.6	77.8	65.5	48.6	35.9

Mixtures at or near the eutectic composition (Nos. 3, 4, and 5) required very slow cooling, *viz.*, 10° per hour, in order to yield moderately large crystals. Nos. 1 and 2 were cooled much more rapidly, being completely solidified in one hour (a fall of 130°); otherwise the primary crystals of potassium nitrate were much too large and the enclosed eutectic solid was difficult to detect.

The eutectic composition given above differs slightly from that given by Guthrie (*loc. cit.*) and was therefore redetermined as a preliminary to the present work. Further details of this determination will be published elsewhere.

The solidified mixtures obtained as described above were of such an amount as to fill the test-tubes to a depth of 1 inch. After removal from the test-tubes, the castings were sawn into pieces about $\frac{1}{8}$ " in length and the fresh-cut surfaces were polished.

Polishing of Specimens.—The surfaces were filed smooth, rubbed on emery cloth, and then on three grades of emery paper of increasing fineness. This gave a moderate polish but left scratches readily visible under the microscope; further polishing was therefore done on Selvyt cloth on a rotating wheel.

The result of these various treatments was a highly polished but flowed surface, with little or no structure visible, and as ordinary etching reagents could not be employed to remove this surface, 96% alcohol was tried (compare Schemtschuschny, *loc. cit.*). Polished specimens were placed in warm 96% alcohol for about 1 minute, then removed and repolished on the Selvyt cloth. Two or three repetitions of this treatment gave a highly polished surface which showed the structure of the specimen very clearly when examined under the microscope with vertical illumination. It was concluded that the small amount of water in the alcohol had been sufficient to remove the flowed surface and etch lightly the surface beneath.

Microscopic examination showed the existence of two distinct crystalline substances, one white and the other dark grey. Since the specimens were white, this difference is attributed to alteration



FIG. 1 ($\times 50$).
89.6% KNO_3 .

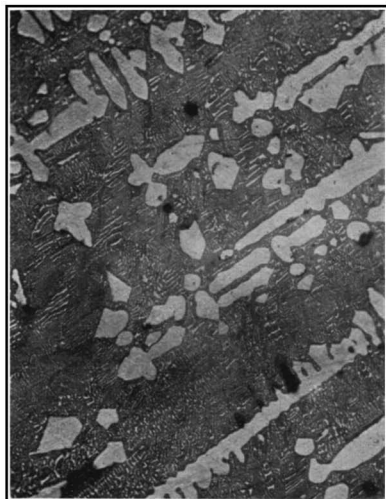


FIG. 2 ($\times 50$).
36% KNO_3 .

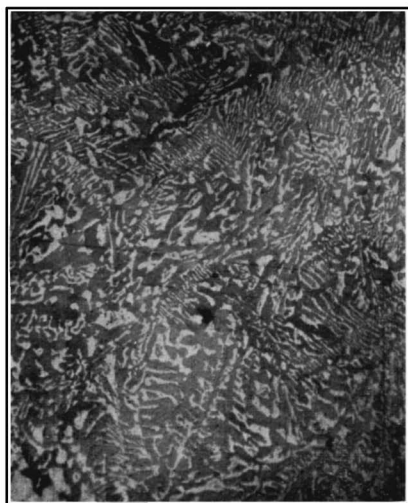


FIG. 3 ($\times 100$).
48.6% KNO_3 .

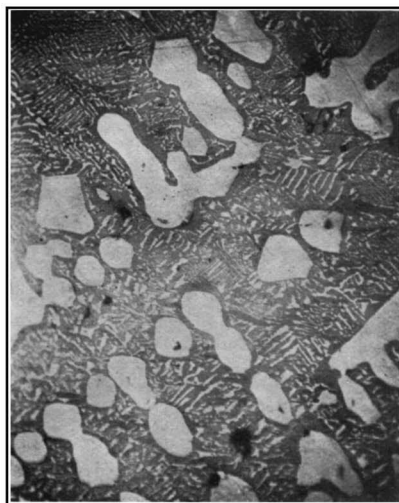


FIG. 4 ($\times 100$).
36% KNO_3 .

[To face p. 460.]



FIG. 5 ($\times 100$).
77.8% KNO_3 .



FIG. 6 ($\times 100$).
48.6% KNO_3 .

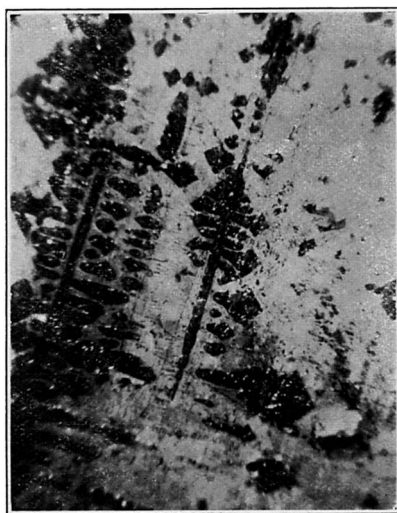


FIG. 7 ($\times 50$).
36% KNO_3 .

in reflecting power, which, according to Schemtschuschny (*loc. cit.*), is caused by the extensive dissolution of one component in the alcohol leaving hollows on the surface. These hollows appear dark grey under the microscope. The structural arrangement of the crystals in the specimens under microscopic examination was characteristic of a eutectic system, namely, large crystals of the component which is in excess, surrounded by areas containing an intimate mixture of smaller crystals of each pure component. These mixtures showed the familiar banded structure of eutectic mixtures.

Photomicrographs of the polished surfaces were prepared, vertical illumination being used, and the results are shown in Figs. 1, 2, 3, and 4, the relevant compositions being given.

Figs. 1 and 2 show large primary crystals of the individual nitrates surrounded by areas of eutectic mixture. Fig. 4 is similar to Fig. 2 but is of greater magnification. Fig. 3 represents a eutectic mixture (lead nitrate appearing white and potassium nitrate dark grey) wherein the banded structure characteristic of eutectic mixtures is clearly shown.

Staining Action of Hydrogen Sulphide.—It was suggested to the author by Dr. J. A. Smythe that hydrogen sulphide might react with lead nitrate and leave potassium nitrate unaffected, thus distinguishing sharply between the structural constituents and possibly affording a method of detecting the existence of solid solutions if such occur.

Accordingly a current of dried hydrogen sulphide was passed over the polished specimens prepared as previously described. Little reaction occurred at the ordinary temperature, but a pronounced reaction was manifest at 70°, the specimens becoming deeply stained with a black lustrous deposit of lead sulphide. After these stained specimens had been polished on the dry Selvyt cloth, the structure was revealed very well under the microscope, the lead sulphide showing a bright lustre and reflecting light brilliantly in a manner resembling naturally occurring galena. Figs. 5, 6, and 7 are photomicrographs of these stained specimens, prepared by using oblique illumination; since the lead sulphide now appears black and the potassium nitrate white, there is a reversal of colours from those in Figs. 1—4.

Examination by Transmitted Light.—Small quantities of the various mixtures were fused on microscope-slide glasses and allowed to crystallise slowly under a cover slip. When examined under a petrological microscope, in transmitted light, the specimens showed evidence of two different crystalline materials, but the eutectic structure, previously shown by photomicrographs, was not visible. Doubtless this absence of structure is due to the conditions of

cooling between two plane glass surfaces, where complex capillary forces would exist, and this does not provide a convenient method for examining structure.

Results.—The photomicrographs show that potassium nitrate and lead nitrate mixtures containing between 89.6% and 36% of the former afford no evidence of solid miscibility and form a eutectic system; banded eutectic structure is easily recognisable in all cases, and staining with hydrogen sulphide enables the two components to be differentiated readily. However, the possibility of partial solid miscibility is not excluded in mixtures of compositions outside the above range. Mixtures containing less than 36% of potassium nitrate would have melting points above 335° and therefore could not be examined. On the other hand, microscopic examination of specimens containing 93, 96, and 98% of potassium nitrate showed the presence of the usual eutectic structure in all cases and, after the specimens had been stained with hydrogen sulphide, the presence of banded eutectic areas between large primary crystals was much more easily recognisable. The photomicrographs of these specimens are not included, as they did not show any fundamental differences from the specimens illustrated.

The stained specimens (Figs. 5, 6, and 7) provide valuable evidence of the absence of solid miscibility. If solid lead nitrate was in any way miscible with potassium nitrate, lead sulphide staining should penetrate throughout the white crystals of potassium nitrate. The absence of such penetration (*e.g.*, Fig. 5) is evidence that the two components are immiscible in the solid state.

Figs. 2, 4, and 7 show that lead nitrate, the constituent in excess, tends to form dendrites much more than potassium nitrate appears to do. It is seen in Fig. 4 that the primary crystals of lead nitrate are surrounded by dark-coloured bands which do not appear to contain any of the lead salt. According to Huntington and Desch (*Trans. Faraday Soc.*, 1908, 4, 51) this phenomenon is due to segregation, large crystals growing at the expense of small crystals when both are in contact with a saturated solution, and it may be in some way related to the tendency of lead nitrate to exhibit dendritic growth. Similar phenomena were not observed in mixtures containing excess of potassium nitrate. It was thought that the formation of these bands surrounding primary crystals might be the outcome of supercooling, since Guthrie (*loc. cit.*) has shown that the eutectic mixture and also those mixtures containing excess of lead nitrate exhibit pronounced supercooling, whereas mixtures containing excess of potassium nitrate do not manifest such supercooling. However, Lamplough and Scott (*Proc. Roy. Soc.*, 1914, 90, A, 600) have confirmed the conclusions of Huntington and Desch

and have shown that these bands surrounding primary crystals may be formed without supercooling and may be absent when supercooling occurs.

Summary.

(1) A method of preparing etched and polished surfaces of mixtures of lead and potassium nitrates is described, and such surfaces are illustrated by photomicrographs.

(2) Hydrogen sulphide reacts with the lead nitrate in these mixtures, and in the photomicrographs the resulting lead sulphide enables the structure to be seen very clearly.

(3) It is concluded that solid potassium nitrate and lead nitrate are completely immiscible when the former exceeds 35% by weight in any mixture. Mixtures containing more than 65% of lead nitrate cannot be investigated.

(4) The results are in agreement with Guthrie's thermal analysis of the same system.

UNIVERSITY OF DURHAM (ARMSTRONG COLLEGE),

NEWCASTLE-UPON-TYNE.

[Received, December 30th, 1929.]
