On the Silver Chromate Banding in Silicic Acid Gel.

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It was stated that silver chromate readily forms periodic banding in gelatine, but not in agar-agar or in silicic acid. But by suitably modifying the conditions, Bradford[1] could obtain the bands of silver chromate in agar-agar. On the other hand, Dhar and Chatteriji[2] concluded that the banding was formed by periodic coagulation of peptised sol. The silicic acid has not the peptising power on silver chromate, so that silver chromate does not form bands in silicic acid gel. This case is frequently pointed out as an example of the specific influence of the gel as a medium for the reaction. On the contrary to Dhar and Chatteriji's presentation, Hatschek[3] has succeeded in obtaining the bands of silver chromate in silicic acid gel. He had prepared the gel by an unusual method, based on the fact that the silicic acid is gelatinised on mixing a sodium silicate solution with a somewhat large quantity of potassium dichromate solution. After setting the gel he superposed a concentrated solution of silver nitrate on it. He could thus obtain the banding of silver chromate in silicic acid gel.

When we persuit the experiments of rhythmic precipitates in silicic acid gel, usually the gel is prepared as follows. One volume of sodium silicate solution is mixed with an equal volume of solution of some acid, pouring the water glass into the acid and mixing quickly and thoroughly, and then the inner electrolyte is added into it to adequate concentration. After setting the gel, diffusing electrolyte is superposed on it. The present author tried to make the silver chromate bands in the silicic acid gel which was made by this usual procedure. It was recognised with many experiments on the formation of rhythmic banding in silicic acid gel, that the concentration of the acid which is used to make a gel, that is to say, the hydrogen ion concentration of the gel, has a profound influence on whether the bands are formed or not. The fact that the formation of the rhythmic bands of silver chromate had been hitherto unobtainable seemed to be owing to the hydrogen ion concentration of the silicic acid

(1) Bradford, "Alexander's Colloid Chemistry, Theoretical and Applied," Vol. I, 790, New York (1926).

(2) Dhar and Chatteriji, *Kolloid-Z.*, **37** (1925), 89.

(3) Hatschek, *ibid.*, **38** (1926), 151.

gel. In the present study, the silicic acid gels were made by mixing equal volumes of sodium silicate solution (density 1.06) and nitric acid solutions having different concentration. The obtained results in these gels are summarised in the following table.

Table 1. $AgNO_3$ 5% ; 6.0 c.c. of Na_2SiO_3 (1.06) solution + 6.0 c.c. of HNO_3 + 0.4 c.c. of 5% $K_2Cr_2O_7$.

Concentration of HNO_3 (N)	Nature of the rhythmic banding
0.67	Typical rhythmic precitates consisting of relatively coarse crystals of red black plates were obtained. The intervals between bands were large.
0.63	Typical rhythmic precipitates as shown in Fig. 1. (the left of the three) were obtained. Crystals were small needles.
0.58	At the top of the gel Liesegang bands accompanied by dendrites were recognised. In the middle, only dendrites were seen, and at the bottom again rhythmic bands appeared but they were those formed by diurnal cause.
0.55	The result was analogous to the case of 0.58 N. But the number of formed Liesegang bands was less.
0.50	No Liesegang band was formed. Dendrites and diurnal bands were seen.

With more concentrated nitric acid than 0.70 N, the silicic acid is not gelatinised. From the foregoing table we can recognise that in the gel of relatively high hydrogen ion concentration the silver chromate banding is formed. In the gel of low hydrogen ion concentration, the decomposition of sodium silicate is not complete, and the rest of sodium silicate reacts with silver nitrate, and so silver silicate is also formed. The silver chromate forms with this silver silicate either complicated bands accompanied by dendrites or only dendrites. The colour of the precipitates forming well-defined bands is red-black but the colour of dendritic bands or dendrites is reddish brown. As frequently stated in older literatures, the banding could not obtained in silicic acid gel, because of the comparatively narrow range of the acidity that is favourable to the band formation of silver chromate.

According to Hatschek's method, somewhat large quantity of potassium dichromate is needed, for it must gelatinise the silicic acid gel. As the result of the existence of a large quantity of potassium dichromate, the obtained bands are close to each other and the empty spaces between the bands blurred and hardly discriminated. By the method which is now presented, we can regulate the concentration of potassium dichromate at will. The formed bands are more distinct being marked by gaps and empty spaces.

The influence of the kinds of acids which are used to make the gel, was also investigated. Of course, hydrochloric acid is inadequate for this purpose, because it unites with silver nitrate and precipitates an almost completely insoluble silver chloride. So, nitric, sulphuric and acetic acids were used.

Nitric acid is the most favourable, sulphuric acid comes next. Acetic acid forms silver acetate, that is somewhat difficultly soluble. And in the gel which is made by mixing sodium silicate solution and acetic acid, crystals of silver acetate grow in long needles. In the gel which is made from sodium silicate and sulphuric acid, silver sulphate crystals are also formed at the top of the gel, but this is not so remarkable as in the case of acetate. Fig. 1 shows the silver chromate banding in silicic acid gels. From left, the gels were made by mixing sodium silicate solution with nitric, sulphuric, and acetic acid respectively. Crystals formed in these gels are variously shaped. In many cases they are needles. At the bottom of a test-tube, the needle measures often more than 8 mm. long. But they are sometimes plates. These crystals were compared under a microscope, and observed that they consist of many small crystals. The needles were fern-like fronds under a microscope.

The plates are as shown in Fig. 2. The appearances of each crystals were rather different, but a single crystal separated from either a needle or a plate was the same. It crystallises in elongated hexagonal plates. Single crystals are taken in photograph and shown in Fig. 3.

As Hatschek[3] has already pointed out, Dhar and Chatteriji's coagulation theory[4] about the formation of rhythmic precipitates is not applicable. They support their theory with the non-formation of silver chromate bands in silicic acid.[2] But the last mentioned fact is clearly denied by the present experiments. Also the membrane theory is not correct, because the crystals in banding are separated from each other, no membrane formation being recognisable in the rhythmic precipitates, what may be observed in the photograph. The bands consist of well-

(4) Dahr and Chatteriji, *Kolloid-Z.*, **31** (1922), 15; **37** (1925), 2; **37** (1925), 89.

(5) Fischer and McLaughlin, *ibid.*, **30** (1922), 13; Traube and Takehara, *ibid.*, **35** (1924), 245.

developed crystals separated by relatively large spaces, allowing free passage to the diffusing electrolyte.

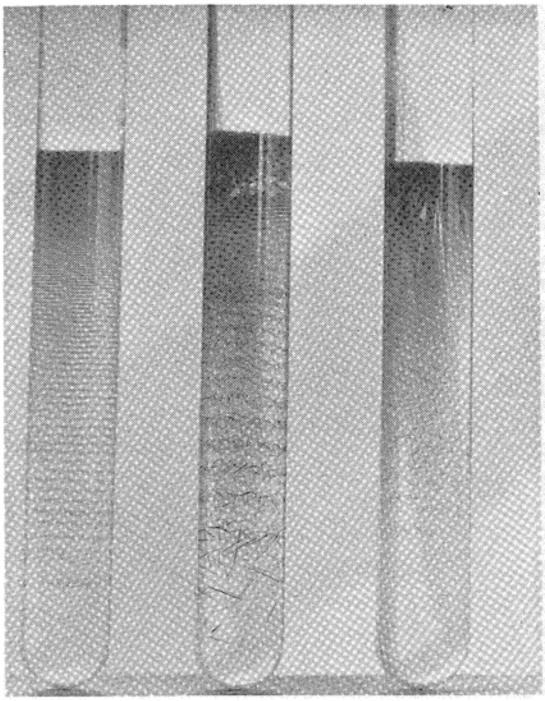
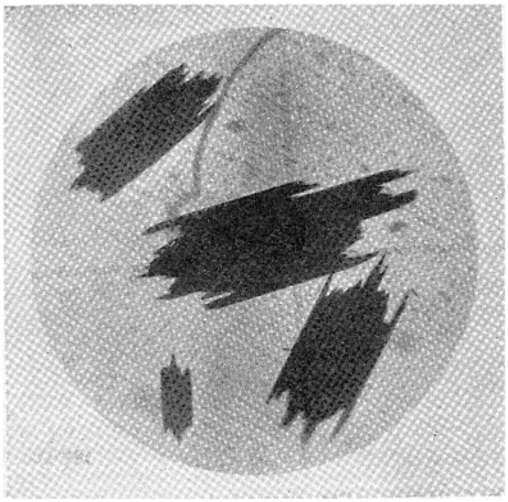
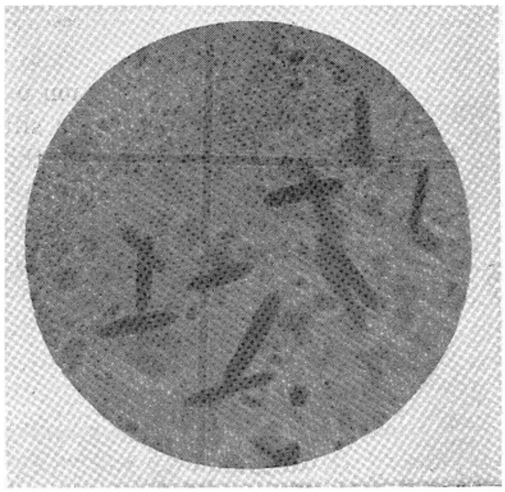


Fig. 1.



(×95)
Fig. 2.



(×310)
Fig. 3.

Summary.

(1) The formation of silver chromate bands in silicic acid gel which was made by a usual method, has been described.

(2) By this procedure, the concentration of chromate is regulated at will, and distinct banding is formed.

(3) The hydrogen ion concentration of the gel has a profound influence on the formation of rhythmic bands of silver chromate.

(4) Dhar and Chatteriji's theory and the membrane theory are not applicable.

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