

RHYTHMIC CRYSTALLIZATION OF SODIUM SULFATE  
IN THIN AGAR-AGAR FILMS.

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The so-called Liesegang phenomenon, the rhythmic formation of bands or rings, has been studied by a number of investigators.<sup>1</sup> The usual method is to make up a dilute solution of a salt in a gel and allow another salt to diffuse into the gel with the formation of an insoluble precipitate. Very spectacular results can be obtained in this manner; silver chromate in gelatine, lead chromate in agar-agar and many other combinations give good results. The phenomenon has been considered similar to band formation in agates and other minerals,<sup>2</sup> in starch granules,<sup>3</sup> in gallstones,<sup>3</sup> and in butterflies' wings.<sup>3</sup> The rhythmic banding seems to be of some importance in biology and geology and needs further study. Results obtained with a simpler system should be easier to interpret. The accidental observance of bands formed in sodium sulfate crystallizing from a one per cent agar-agar film led to this study.

**Experimental.** A solution of sodium sulfate in one per cent agar was poured into a test tube wetting the walls. At the end of 24 hours a rhythmic formation of nearly 30 rings of solidified salt was observed in the upper part of the tube. From the lowest ring three or four dendritic growths extended downward. Other similar tubes were made up and the ring formation could be followed under the microscope with ease. The time required for each band varied from 20 seconds to several minutes; in general the time was shorter in the upper part of the tube. The velocity of ring formation varied also with the diameter of the tube.

To determine the best concentration of sodium sulfate to use, several tubes of different concentration were made up. To minimize complications due to interaction of the salt and gel, the amount of the latter should be kept as small as is consistent with a satisfactory gel formation. A tube containing no salt gave a smooth transparent gel with little opalescence. Similar results were obtained with a solution of 0.005 M sodium sulfate. Below 0.1 M little banding effect was observed. At 0.5 M no definite banding was seen but some of the agar was coagulated, while at a 1.0 M concentration the coagulation was very marked. An intermediate concentration, 0.25 M gave best results.

For these experiments the agar-agar was dialyzed with many changes of distilled water for five days, and the sodium sulfate was recrystallized. The solutions were made up to a strength 0.25 M in a

<sup>1</sup> Hatschek, Second Report on Colloid Chemistry 21 (1919). Liesegang, "Kolloid-chemie 1914-1922," Leipzig, 1922.

<sup>2</sup> Liesegang, "Lehrbuch der Mineralogie," Berlin, 1920, pp. 434-445.

<sup>3</sup> Beechhold, "Colloids in Biology and Medicine." Van Nostrand, 1919.

one per cent agar-agar at about  $60^{\circ}\text{C}$ . The temperature of the solution before the cooling process was found to have little effect on the results. The solution was poured on a clean glass plate in such a way as to give a nearly uniform deposit. The pH of these solutions was usually within the limits 6.5 and 7.0.

The main factors affecting the ring formation are the temperature, the humidity, the rate of drying, and the light. Some of these may be not without influence on others, thus the humidity and temperature together with air currents are the chief factors in determining the rate of drying.

**The Temperature Effect.** The most important condition governing the results seems to be the temperature at which the plate is allowed to stand. Sodium sulfate has a transition point at  $32.40^{\circ}$ , an anhydrous form being stable above this temperature and the decahydrate tending to crystallize out of solution below this point. There is also a metastable heptahydrate and the possibilities of the existence of other forms must be considered in explaining the several characteristic forms obtainable.

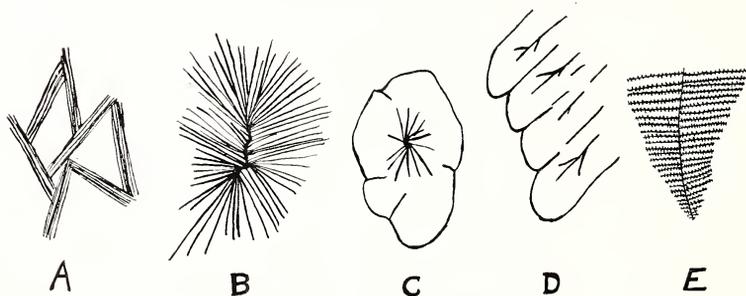
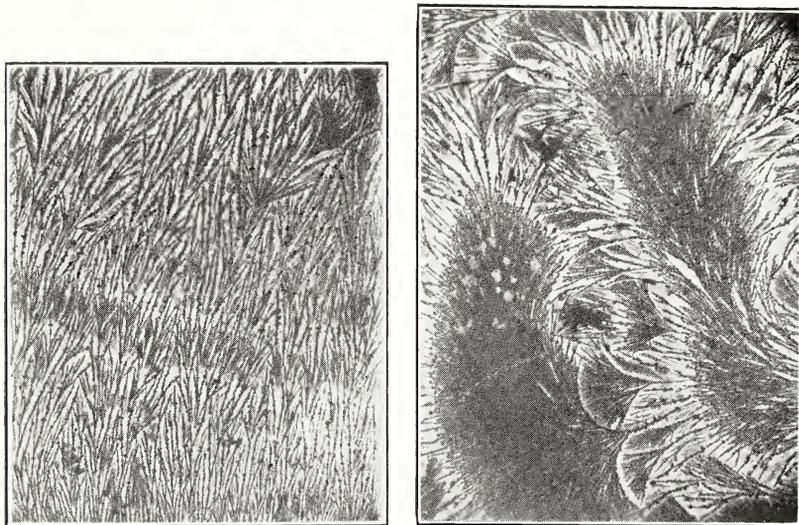


Fig. 1. At high temperatures a brush-heap structure of crystallized anhydrous sodium sulfate is formed. As the temperature falls rosettes are formed, B, which gradually grow into the lichen-like growths of C and D. At room temperatures there frequently crystallizes out the fern-shaped growth E.

Eight plates were poured at  $60^{\circ}$ . Two were left in the oven at this temperature, two were allowed to cool at  $23^{\circ}$ , two were placed on ice, while two were kept at  $35^{\circ}$  before further cooling. The pair in the oven was covered with a continuous brush-heap structure without any periodicity of arrangement, (fig. 1A). The plates standing at room temperature showed the same effects as most of the plates studied and as described below. The bands formed on the plates on ice were more numerous and closer together with a few crystals of larger size. At  $35^{\circ}$  the characteristic brush-heap structure formed around the edges (fig. 1A and B) merged into lichen-like growths (fig. 1C and D). These latter might be modified by dendritic growths. On cooling to room temperature, characteristic fern-like growths formed in rhythmic bands,

(fig. 1E). If, then, a plate is seeded with a little decahydrate, an immediate and considerable growth of a new form starts in, all around inside the fern-like growth, but separated from it by a space 1 to 4 mm. across. Figure 4C shows such a transition. This new form comes down rhythmically but consists of needles (fig. 2). As the needles approach the limits of the area of supersaturation, the rate of growth decreases and the ends grow till the monoclinic shape of the decahydrate is plainly visible. As the gel dries out, certain places along the needles thicken into bead-like crystals. On longer standing the decahydrate effloresces and the fern-shaped form appears to do so, also. The very



Figs. 2 and 3 are microphotographs of the needle-shaped decahydrate. Fig. 2 shows the rhythmic banding nicely with the development of certain parts into bead-like crystals. Fig. 3 shows the formation of peacock feathers, probably aided by lack of uniformity in the gel.

rapid growth on seeding with decahydrate indicates this form to be less soluble than the fern-shaped. The latter might be the anhydrous salt, the heptahydrate or an unknown hydrate. If it were the anhydrous form, it could not effloresce without preliminary transition to the stable decahydrate. The rectangular growths of the fern-shaped form suggest the rhombic growth of the anhydrous salt. Attempts to find what form it was by seeding supersaturated solutions of sodium sulfate at room temperatures resulted in failure; the fern-shaped material always dissolved.

**Humidity.** The shape assumed by the sodium sulfate was determined largely by humidity conditions. Plates made up under identical

conditions were placed in atmospheres containing moisture at 4.2 mm. and at 16.3 mm. and saturated, the relative humidities being 20, 80, and 100 per cent, respectively. At the lowest humidity clearly defined rosettes were formed similar to those produced above the transition point. The vapor pressure being below that of the decahydrate, the anhydrous form crystallizes out directly. The plates at 80 per cent humidity behaved like those exposed to the room atmosphere. When the air was saturated with moisture the film has no chance to dry out and no crystals were formed. On further exposure to air of lower moisture content, the characteristic growths were observed.

**Rate of Drying.** The rate of crystal growth is also affected by the rate of drying. If the drying is very slow the diffusion becomes the predominant factor and the growth of a few dendrites rather well separated is the result. On the other hand too rapid a drying gives a continuous growth of crystals. This holds true for both the fern-shape and the decahydrate. The results obtained at different heights in the tube are to be connected directly with the rate of drying. In general, the slower the drying the wider the bands.

**The Effect of Light.** Similar plates were placed under identical temperature and humidity conditions in the dark, in diffuse daylight and in direct sunlight. In diffuse light and in the dark the growth was similar to that usually observed but in the direct sunlight the formation of numerous narrow bands was promoted. Part of this result may be ascribed to a greater drying rate but part is probably due to a "trigger" action of the light on relieving supersaturation. This was observed with several plates where some control of the band width could be exercised by intermittent illumination. Light should have more or less effect on all rhythmic bandings.<sup>4</sup>

**The Mechanism of Rhythmic Banding.** Previous authors working with bands formed as a result of chemical interaction have considered supersaturation,<sup>5</sup> diffusion,<sup>6</sup> absorption of electrolyte by gel,<sup>7</sup> (protective action of the gel), or coagulation of the gel by the electrolyte,<sup>8</sup> in explaining the results obtained. There is little doubt that all of these take part in the phenomenon to an extent varying with the conditions. In our more concentrated solutions a marked coagulation of the gel occurred, while in most dilute solutions absorption prevented crystal for-

<sup>4</sup> Hatschek, Proc. Roy. Soc. 99A, 496 (1922). Davis, J. Am. Chem. Soc. 45, 2261-3 (1923). Tryhorn & Brockton, Trans. Faraday Soc. (1923). Dhar & Chatterji, J. Phys. Chem. 28, 41-50 (1924).

<sup>5</sup> Wilhelm Ostwald, "Allg. Chemie," 2d Ed. II. 778, 780.

<sup>6</sup> H. N. Holmes, J. Am. Chem. Soc. 40, 1187 (1918). R. Fricke, Z. physik. Chem. 107, 41 (1924). S. C. Bradford, Science 54, 463 (1922). C. H. Schlessner, Kolloid. Z. 31, 347 (1922); 34, 338 (1924).

<sup>7</sup> Cit. 1, Sen and Dabe, Kolloid Z. 34, 270 (1924). Chatterji and Dhar, *ibid.*, 31, 15 (1922).

<sup>8</sup> Cit. 1.

mation. At intermediate concentrations, neither is in sufficient excess to become predominant. The peacock-feather-like growth illustrated in figure 3 indicates a lack of uniformity in the gel resulting in differences in the rate of absorption and in the rate of crystallization.

The periodic growth can be readily followed under the microscope. As the gel cools and especially as moisture evaporates from the surface supersaturation occurs and the crystals starting at the edges shoot inward over the supersaturated area, slowing up as the saturation line is approached. Some of the salt diffuses to the ends of the needles which then thicken and widen about as fast as they lengthen for a little while. In the meantime the agar continues to lose moisture, becoming supersaturated. When a sufficiently unstable condition is reached crystals shoot out from the blunt ends with considerable velocity to form another band and the process is periodically repeated.

The recent analysis of the Liesegang phenomenon made by R. Fricke,<sup>9</sup> combines diffusion effects with some supersaturation. In the experiments just described supersaturation is a factor more obviously important than with the usual rhythmic banding, but his method of analysis is applicable.

**Other Salts.** Fourth molar solutions of sodium, cupric and ferric chloride, potassium sulfate and permanganate were made in one per cent agar-agar. The permanganate was reduced by the agar and ferric chloride was too deliquescent to give good results. Sodium and cupric chlorides gave fern-like growths which started usually from many nuclei with initial cross-like structures (fig. 4A). Often a more rapid growth

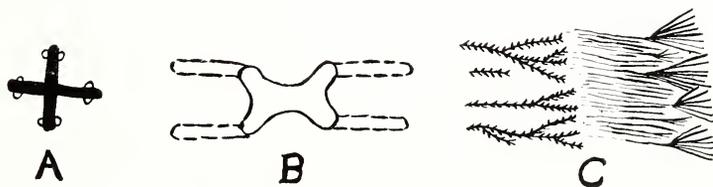


Fig. 4. (A) A typical growth of sodium chloride nuclei. (B) A typical growth of potassium sulfate crystals. (C) Crystals of the fern-shaped form on the left followed by a narrow band and needle-shaped decahydrate, the latter being formed as a result of seeding.

resulted in a fan-shaped bundle of needles being formed with later changing over into a row of cubes. Some evidences of periodic growth were obtained but the distinct banding of sodium sulfate was absent. DuNoüy has recently described a banded crystallization of sodium chloride under the influence of a trace of saponin.<sup>10</sup> Copper sulfate gave beautiful bands but the fineness of the crystals obscured much of the blue color. Potassium sulfate formed growths rather unlike sodium sul-

<sup>9</sup> R. Fricke. *Cit.* 6.

<sup>10</sup> P. L. DuNoüy. *Science* 60, 337 (1924).

fate except in a few times when the latter was anhydrous. In potassium sulfate the crystals tended to start from isolated nuclei with little tendency towards banding. The interesting typical growth of the nuclei is given in figure 4B. The rhombic character of the crystal results in the formation of four horns something like a pair of ice tongs.

#### SUMMARY.

In the rhythmic crystallization of sodium sulfate, (and a few other salts), from one per cent agar-agar films supersaturation plays a part more obviously important than is found in the usual Liesegang phenomenon.

The effects of variable conditions of concentration, temperature, humidity, rate of drying and light are described and explained.

Sodium sulfate crystallizing from agar films at room temperature often forms a metastable fern-shaped growth which later appears to effloresce.