CLXXVIII.—*Experiments on the Formation of Mother-of-Pearl.*

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IT is known that mother-of-pearl, like the substance of the pearl, consists of calcium carbonate associated with water and an organic substance (conchiolin). The following is a typical analysis of mother-of-pearl (G. and H. Harley, *Proc. Roy. Soc.*, 1888, **43**, 461): Calcium carbonate, 66·0; organic matter, 2·5; water, 31·0%; total 99·5%.

As early as 1814, Brewster (*Phil. Trans.*, 1814, **104**, 397) explained the iridescent colours of mother-of-pearl as being due to two factors—a grating effect on the surface, and an interference effect caused by a thin film of calcium carbonate. The grating effect on mother-of-pearl can be easily transferred to a film of gelatin dried on its surface, and the distance between the lines can be measured. In a recent paper, Lord Rayleigh (*Proc. Roy. Soc.*, 1923, *A*, **102**, 674) has shown that the second effect is not due to a single film, but is caused by alternate layers of calcium carbonate and conchiolin, forming a series of equally spaced thin parallel plates. He ascribes the surface effect to the edges of the closely packed alternate layers of inorganic and organic matter. This alternating structure is suggestive of the periodic precipitations which occur in the well-known Liesegang phenomenon, and as a matter of fact both Liesegang (*Kolloid Z.*, 1913, **12**, 181) and Clément and Rivière (*Compt. rend.*, 1922, **174**, 1353) have tried to produce structures similar to mother-of-pearl by the periodic precipitation of calcium phosphate in gelatin. Thus Liesegang allowed sodium phosphate to diffuse from an aqueous solution into a gelatin jelly containing calcium nitrate. The periodic structures obtained in this way exhibit some iridescence, but after a time they lose their lustre and become dull and " chalky." In order to avoid effects due to foreign electrolytes, it was decided to study the precipitation of calcium carbonate from an aqueous solution of calcium bicarbonate containing a gelatinising organic colloid.

EXPERIMENTAL.

The solution of calcium bicarbonate was prepared by passing carbon dioxide into a saturated solution of lime water. In this way a stock solution could be prepared at room temperature containing 0·0134 g.-mol. of calcium carbonate per litre.

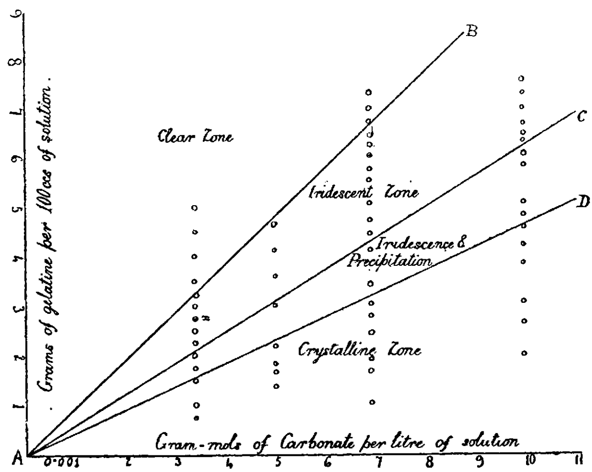
With organic colloids such as gum arabic, gum tragacanth, and fish glue, no iridescent structures could be obtained by the method employed in these experiments. The best results were obtained with commercial leaf gelatin (containing 10% of moisture and 1·924% of ash). Iridescent deposits could not be obtained with a sample of highly purified and almost ash-free gelatin prepared in this laboratory. Liesegang (*Z. physikal. Chem.*, 1914, **88**, 1) has found that the best rings of silver chromate are produced when the gelatin contains small quantities of " gelatose " (a hydrolytic product of gelatin) as well as acid. All samples of commercial gelatin contain " gelatose " and therefore are most suitable for the production of Liesegang periodic layers.

The method of procedure was as follows. Varying amounts of gelatin were weighed into a series of test-tubes, to which measured volumes of water were added. The tubes were then stoppered and the gelatin was allowed to swell, after which it was dissolved by immersing the tubes in hot water. When the solutions had cooled to about 40°, measured volumes of the calcium bicarbonate solution were run in, the contents of each tube thoroughly mixed, and drops from each placed on clean glass plates. The thin layers of gelatin–bicarbonate solution thus produced were allowed to evaporate slowly at room temperature. More rapid evaporation either at higher temperatures (*e.g.*, 50°) or in desiccators containing drying agents (or alkalis to absorb carbon dioxide) failed to give iridescent deposits of calcium carbonate. Another factor of importance in the production of iridescence is the initial thickness of the layer of solution on the glass plate. The best results are obtained when this thickness lies between 1 and 3 mm.

An examination of the dried layers showed that for a given initial concentration of calcium carbonate the result depended on the concentration of gelatin. With any given initial calcium carbonate concentration and increasing gelatin concentrations, four types of product, corresponding to four fairly well demarcated regions, were in general obtained :

Region 1.—If the gelatin concentration lies below a certain value, there is produced an irregular crystalline deposit, with a thicker aggregation of calcium carbonate crystals at the centre, but no iridescence.

FIG. 1.



Region 2.—If the gelatin concentration is somewhat higher, iridescent specks appear, generally in the centre, together with a visible deposit of calcium carbonate crystals all over the area. In this case the calcium carbonate usually formed a series of coarse irregular rings.

Region 3.—With a still higher gelatin concentration there is no visible deposit of calcium carbonate, and the whole area, now quite translucent, shows a beautiful mother-of-pearl-like iridescent colour, varying with the angle of observation.

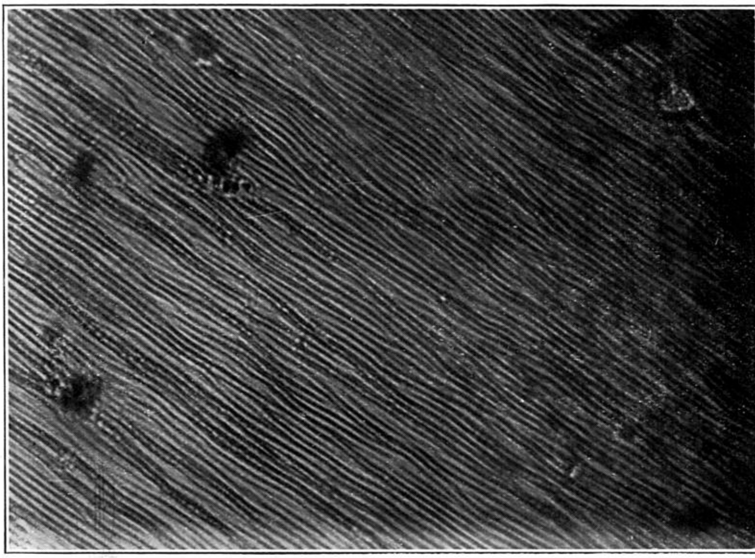
Region 4.—Finally, if the gelatin concentration exceeds a certain value, the layer remains clear and translucent, but exhibits no colour.

The general nature of the results obtained is well shown in the accompanying figure. The lines AB, AC, AD, together with the axes, divide the diagram into the four regions or zones already described, although it must be understood that the positions of these lines are not fixed with any great degree of precision.

Microscopic examination of the thin iridescent plates of gelatin–calcium carbonate corresponding to the zone AB—AC shows that the slowly decomposing calcium bicarbonate has deposited the calcium carbonate in a series of more or less regular and parallel layers or sheets resembling those of a Liesegang structure. Various photomicrographs were taken and the spacing of the layers was determined by means of a Hilger travelling microscope. There were present 4000—6000 layers per cm. The accompanying photograph shows the type of structure obtained.

Discussion of Results.

These experiments show that it is possible to prepare a clear, translucent, thin plate or sheet of dried gelatin containing a very fine spatially periodic precipitation of calcium carbonate and exhibiting the iridescent colour effects characteristic of mother-of-pearl. The colours shown by the preparations described in this paper are in all probability due to a grating effect caused by the closely-spaced layers of calcium carbonate, although it has not been found possible to determine by means of sections the exact orientation of these layers with respect to the surface of the thin plate of gelatin. Nevertheless, the photomicrographs show clearly enough that the layers of calcium carbonate do not lie parallel to the surface of the gelatin plane, but must be oriented at an angle to it which probably does not differ much from 90°. Each drop of solution produces a thin, more or less circular, lens-shaped disc on the glass plate. It is probable that the precipitation of calcium carbonate begins at the surface of the outer rim, and proceeds rhythmically in a series of closely-spaced concentric rings towards the central part of the surface of the evaporating disc of solution. As evaporation of water and carbon dioxide proceeds, this rhythmic precipitation is carried more or less vertically downwards, *i.e.*, at right angles to the main surface of the disc. The result of such a periodic precipitation would be to yield a grating surface capable of producing colours in reflected light, provided the spacing be fine enough. Although this is the most probable explanation of the colour effects described in this paper, the possibility of colour production by interference of light reflected from a series of parallel plates cannot be excluded. Taken in conjunction with the work of Brewster and of Lord Rayleigh, the synthetic chemical experiments described leave little doubt as to the origin of the colours exhibited by mother-of-pearl. The thin sheets of gelatin–calcium carbonate which have been obtained approach very closely in their nature and structure



Microphotograph of gelatin-calcium carbonate. ×560.
(Corresponding to x *in the figure.)*

[*To face p.* 1384.]

to natural mother-of-pearl, and may indeed be described as " elements " of mother-of-pearl, although, of course, the organic colloid used is different from the " conchiolin " of the natural material.

Summary.

1. The deposition of calcium carbonate from a thin layer of an aqueous solution of calcium bicarbonate in the presence of gelatin has been studied.

2. The nature of the deposit depends upon the initial concentration of calcium bicarbonate and the ratio of gelatin to calcium bicarbonate.

3. For any given initial concentration of calcium bicarbonate there is a range of gelatin concentrations which yield translucent layers showing the iridescent colours characteristic of mother-of-pearl.

4. The structure of mother-of-pearl has been discussed in the light of these experiments and the physical work of Brewster and of Lord Rayleigh.

In conclusion, the author wishes to express his thanks to Professor Donnan for suggesting this problem to him and for his kind interest and guidance in the work.

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