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# Various regular and irregular precipitate structures in gelatin gels

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VARIOUS REGULAR AND IRREGULAR PRECIPITATE  
STRUCTURES IN GELATIN GELS

by

Martin Stanley Ferguson

A thesis presented to the Department of Chemistry of  
Union College in partial fulfillment of the requirements  
for the degree of Bachelor of Science with a Major in  
Chemistry.

By Martin S. Ferguson

Approved by JWP Oster

May 26, 1956.

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INDEX

Subject	Page
Introduction.....	1
Historical.....	2
Apparatus.....	6
Experimental.....	9
Legend - Plate I.....	14
Plate I.....	15
Discussion.....	16
Summary.....	19
Bibliography.....	21

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GIFT OF AUTHOR

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## INTRODUCTION

In the field of Colloid Chemistry, precipitate structures in gels have been studied for quite sometime. The formation of a rhythmic band configuration known as Liesegang rings, when an insoluble salt is formed by the gradual diffusion of one ion into a gel containing the other ion has become a common phenomenon.

At the outset of this research project, the primary intent was to continue the work of R. DeSieno into a somewhat different regular structure obtained by ionic diffusion in the presence of mercury vapor. This phenomenon to be studied involves the formation and nature of radial lines produced when silver ions slowly diffuse under closely controlled conditions into chromated gelatin in the presence of mercury vapor.

In the process of varying such things as time, concentration of reactants and mercury area, striking results are obtained. Together with the occurrence of various radial structures, a number of unpredicted variations can be produced. The effect of these variables on precipitate structure will be discussed in this thesis.

## HISTORICAL

Gelatin has long been used in Colloid Chemistry to allow diffusion without convection. Its introduction as a filter for colloidal particles is made possible by the physical structure of the gel. Hence, bonding is such that ions can diffuse through, but the larger particles are held by the structure.

Many studies have been made utilizing gelatin in both physical and colloid chemistry. The most striking of these older phenomena is that of Liesegang Rings. These were discovered by R. Liesegang (10, 18, 20) in 1896 when he placed a drop of silver nitrate on a glass plate coated with a moist gelatin solution containing chromate~~x~~ ions. His experiments and subsequent ones have produced concentric circles of precipitates, which, as far as can be ascertained from a search of the literature, are of the macroscopic dimensions. Considerable work has been done on the nature and formation of Liesegang rings. Works of Hedges and Henley (13), Bary (1), and others (6, 7, 8, 27) have added much data to these formations in test tubes, but there are many contradictory opinions in the field. An extremely comprehensive survey of the subject up to 1926 is Hedges and Myers book "The Problem<sup>f</sup> of Physicochemical Periodicity", where an extensive bibliography may be found. In using a test tube to produce the structure, it is noted that a series of bands or discs corresponding to a thin strip cut transversely from the tube are formed.



Of the many theories advanced on the formation of Liesegang rings, the supersaturation theory of Wilhelm Ostwald, proposed in 1898, still enjoys much favor (10, 22). When silver and chromate ions diffuse towards each other, Ostwald states, a supersaturated solution of silver chromate forms and precipitation is delayed. When the precipitate has finally formed, there is a marked deficiency of chromate ions in the gel. Hence, the silver ion must travel a notable distance before a degree of supersaturation can again be reached. The distance would explain the appearance of clear spaces in the gel.

Other important theories have been advanced by Bradford (2) and Wolfgang Ostwald (23, 24) and have been modified by many including Katschek (6, 7, 8); Sen, Dhar and Chatterji (27); Hedges and Henely (13), and Holmes (17). Bradford's theory involves the adsorbent effect of the colloidal precipitate on the electrolyte in the immediate vicinity. Wo. Ostwald attributed the formation of rings to a reversal of the normal reaction  $2\text{AgNO}_3 + \text{K}_2\text{CrO}_4 \rightarrow \text{Ag}_2\text{CrO}_4 + 2\text{KNO}_3$  at regular intervals. This soluble reaction product gives rise to Ostwald's diffusion wave theory. All of the preceding theories have been severely criticized, and none have been accepted as explaining all facets of the phenomenon.

The formation of radial lines mentioned in the introduction was first observed in 1943. Literature on the phenomenon is

surprisingly lacking, and it is surmized that little has been done on the subject.

H. Friedeberg (5) presented a paper in 1954 concerning methods of obtaining the radial structure, but gave no further references nor explanations of their cause.

R. DeSieno (4) in 1955 attempted to expand and continue the work, but came to no positive conclusions as to their structure. As a result of the work however, DeSieno theorized that a precipitate is formed throughout the thickness of the gel. Then, as the silver is continually reduced at the gel surface, the precipitate disappears as indicated by the reaction  $\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^{++} + \text{CrO}_4^{--}$  running to the right. This explanation makes no attempt to explain why the lines run in the observed direction or what causes the separations between the lines. Further observations of DeSieno that may prove meaningful include: 1) mercury seems to be indispensable to formation and is found in the surface mirror of the gel, 2) the concentration of chromate must be very low (0.01-.1% by weight, or several hundred times less than the silver nitrate), 3) formation of the lines was found only in gelatin gel.

Other structures in gels include many miscellaneous irregular growths. Numerous experiments may be carried out for novelty's sake. Among these are some produced in silicic acid gels (16). Typical examples are the formation of lead iodide



crystals in an attractive fern-like structure, the metallic "Lead Tree", and the very distinct amorphous copper chromate banding in these gels.



### APPARATUS

The apparatus used in the major part of this experimentation is a modification of the final developments made by DeSieno. This includes a six-inch desiccator with a pool of water in the bottom, and another pool of mercury in a petri dish supported above the water. This arrangement allows the atmosphere within the desiccator to be quickly saturated with both mercury and water vapor. The chromated gelatin in liquid form is applied to a microscope slide and is allowed to set. Then, towards the center of the gel, a fine capillary tube containing relatively concentrated silver nitrate is supported in contact with the surface by a small piece of ordinary modeling clay. The slide unit is then placed in the desiccator and is sealed in the mercury atmosphere for at least forty-eight hours.

The capillaries mentioned above are made in the following manner. Seven millimeter soft tubing is drawn out to a capillary in a wing tip flame. Small sections of about four or five centimeters are then drawn into finer tips at their ends. These tubes were of sufficiently small diameter to allow gradual diffusion into the gelatin gel.

Standard solutions of potassium chromate and silver nitrate are prepared at the outset. The original chromate solution is

made 0.100M and must be diluted down to the range of 0.01-.1% by weight ( $5 \times 10^{-4}$  to  $5 \times 10^{-3}$ M). A 0.50M silver nitrate solution is sufficiently strong so that silver ions easily diffuse into the gelatin.

An early attempt was made to construct an air-tight cell from a ground petri-dish and a glass plate. Mercury and water are placed in the cell similar to the desiccator arrangement, and the arm of the capillary must be bent to be contained within the apparatus. The cell is designed so that the reaction may be followed under a microscope with a long focal length. A binocular type microscope made by the Bausch and Lomb Optical Company is sufficient for this operation. This cell did not live up to expectations, but the author is convinced that further research would make this method practical. Problems encountered in its operation will be discussed in the "experimental" section of this paper.

The photographs included in this thesis were taken with a standard camera for photomicrography (3). The slide was lighted with a microscope illuminator obliquely from above. An exposure time of one minute was used for the negative in all cases. Kodak Panatomic-X sheet film was used, and it was developed with Kodak Universal M-Q developer. Prints were made on Kodak semi-mat paper.

All measurements given in this paper were made with an



eyepiece micrometer used with a sixteen millimeter objective and a ten x eye-piece with the tube at full draw. A stage micrometer manufactured by the American Optical Company was used to calibrate the eye-piece scale. This method gives a quick comparison of ring distances on various slides.

The use of this equipment and the results obtained with it will be explained in greater detail in following sections.

### EXPERIMENTAL RESULTS

Experimentation to obtain ideal conditions under which radial bands are formed met with considerable difficulty. In varying concentration of reactants, some very odd effects and structures were obtained until it was realized that dilution errors were causing them. Further experiments using petri-dishes as explained in the apparatus section met with failures worth noting.

In order to observe the reaction as it proceeds, some method of containing the system in a compact unit must be developed. Variations using the petri dishes were not fully explored and data obtained were scant. Chief difficulties encountered were failure of the silver ions to diffuse completely, and formation of a fog inside the system when it was viewed under a powerful direct light. It seems possible that the silver nitrate concentration must be much higher when it diffuses from a bent capillary tube. It was observed that flow from the capillary was almost negligible and that the reduced silver surface on the gel covers a diameter of only about one centimeter. No characteristic structures were obtained by this method except that a very heavy silver deposit was centrally located. Under a high magnification the silver seemed to possess a definite crystalline form.



A method to eliminate the fog in this small system was not developed. The use of a water cell as a heat filter in front of the illuminator may serve to solve this problem.

To observe the phenomenon as obtained by Friedeberg and DeSieno, further experimentation was carried out using straight capillaries and enclosing the reaction in an air-tight atmosphere of saturated mercury vapor within a desiccator.

As stated at the outset of this section, many unique forms were obtained by varying concentrations. First attempts produced little more than a solid shiny silver mirror on the surface of the gel. With a ratio of silver to chromate ion of five to one, very inconsistent results were obtained. Most notable of the structures found were those of microscopic Liesegang rings. These rings were the most reproducible of the structures found. They began about a millimeter from the point of application of silver nitrate and continued out concentricly for a few millimeters. The rings were evidently of reduced silver, and were bright in appearance. Measurements of various samples ascertained that these rings were about 0.005-0.01 millimeters apart.

Using the same relative concentrations (0.5M  $\text{AgNO}_3$  and 0.1M  $\text{K}_2\text{CrO}_4$ ), structures similar to radial bands were observed. Many of these were noted to be superimposed upon the microscopic Liesegang rings. These bands conformed in every way to these



found in DeSieno's work except that they faded out towards the outside of the gel. Instead of exhibiting a complete break, the lines became thinner until they disappeared. This difference has led the author to believe that the structure was not comparable to DeSieno's. The lines were, However, very narrowly spaced, and measurements of their average distance apart was found to be 0.02-.04 millimeters.

Using the same concentrations as above, it was noted many times that with a very narrow capillary the silver did not entirely cover the surface. A test was devised utilizing these concentrations. Several small tubes and several tubes three times the diameter of the small ones were drawn out. These were placed on gels in the usual manner and the heights of silver nitrate solution was noted. Upon diffusion of the solutions for several days, the small tubes had released only four millimeters of silver nitrate, while the larger tubes were empty. In each case the diameter of the silver deposit was the same: about six millimeters. When the slides were turned over, the unreduced precipitate could be seen. Using the large bore tubes gave a layer of red, then white precipitate. In the samples using a small diameter tube only a white precipitate was present. The significance of these observations will be treated later in the discussion.

The appearance of the precipitate raised some question



as to its nature. Several qualitative tests were run to narrow down the possibilities of its composition. Application of a few drops of ammonium hydroxide dissolved the red precipitate immediately, and the white precipitate was soon dissolved also. This would indicate a silver salt or salts which, judging from the color, would probably be the chromate and chloride. When a few drops of nitric acid were added to the mass, the gel and silver surface dissolved and the red and white precipitates formed a suspension. There was no sign that the precipitate would dissolve in nitric acid. Addition of a few drops of dilute hydrochloric acid caused the gel to dissolve very slowly, leaving the precipitates.

Some interesting structures, rings, and lines are formed in control experiments. The control consisted of a system as before, but omitting the chromate ions and mercury vapor. These tests showed unmistakable but diffuse and widely spaced Liesegang rings. The rings are darkened and macroscopic; appearing a millimeter or more apart. Another structure evident in the control may be described as modified radial bands. The bands are regular, but are curved around in one direction. Appearance of such a phenomenon is unexplained. Also present are various irreproducible random lines.

Apparent in the regular preparations are various sizes of silver crystals. These range in size from large ones on the

surface to very minute flecks both on the surface and within the gel. In many of the more concentrated reactions radial lines are noticed that are neither regular nor characteristic. These radiate from the center at random angles.

One of the most serious difficulties with this method is reversal of diffusion. In certain cases when the chromate concentration in the gel was too great, chromate ions diffused up the tube and formed a silver chromate precipitate within the walls. This is best prevented by use of sufficiently low chromate concentration.

Reproducible production of radial bands has been verified by using the concentrations suggested by DeSieno. That is, the silver ion concentration must be several hundred times that of the chromate ion. Very good results were obtained with approximately 0.06% chromate. Liesegang rings were also formed in this preparation.

The significance and interpretation of these results will be discussed in the following section.



LEGEND \* PLATE I

(1) Upper Photograph

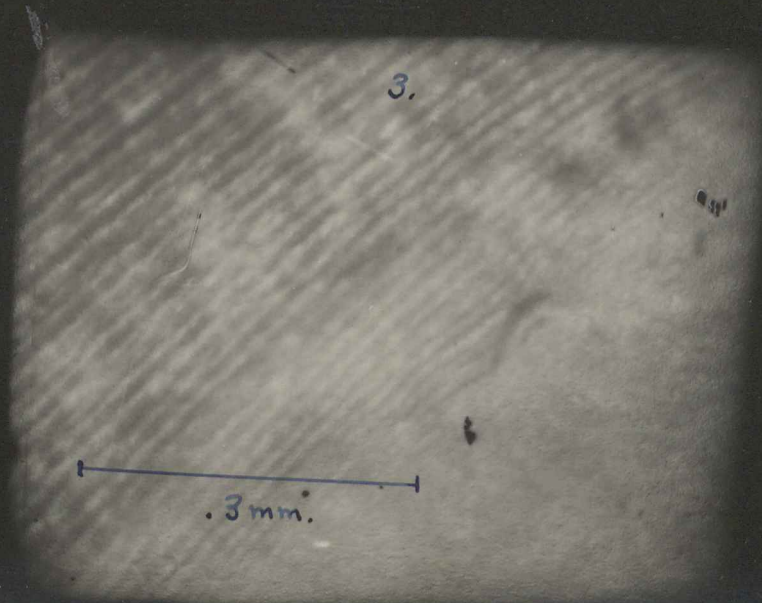
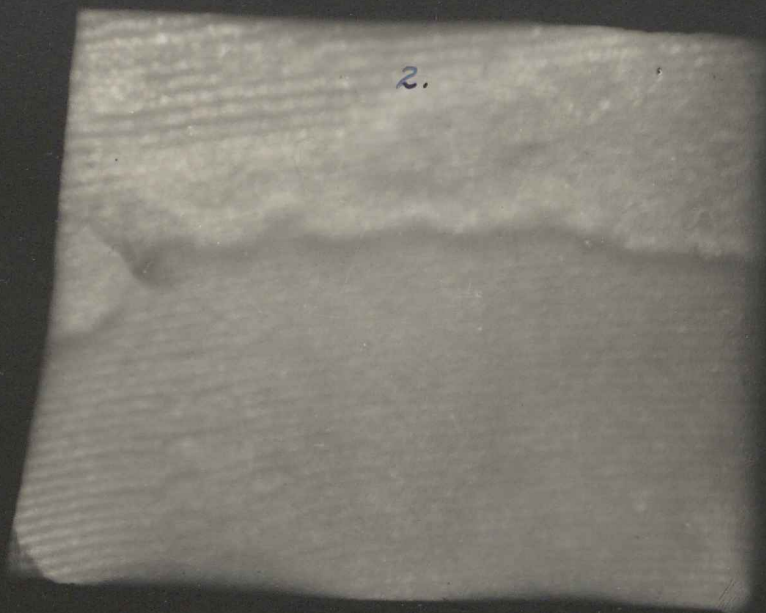
This photo shows the Liesegang rings formed when 0.50M  $\text{AgNO}_3$  diffused into weakly chromated gelatin in the presence of mercury vapor. All three photos were taken using the low(16 mm. objective) power magnification. Note wide rings and a radial structure beginning in upper right.

(2) Middle Photograph

Illustration of the effect of increasing the chromate concentration to 0.10M. A very fine regular structure. There is also present a random line running through the center.

(3) Lower Photograph

Another slide showing microscopic Liesegang rings. These start and proceed to the upper left of photo.





### DISCUSSION

The use of a fine capillary has been shown to be the best method to provide silver ions. Widely varying results may be obtained by changing the size of the capillary or varying the concentration of reactants. Although the question of cause of radial banding is unanswered at this time, some very interesting occurrences may be noted.

The most significant and reproducible result is that obtained when both silver and chromate ions are concentrated. It was noted by DeSieno that after reduction by mercury vapor no precipitate could be seen in the gel interior. Contrary to this observation, a layer of red and white precipitate has been noted by this author.

The physical appearance of the precipitate suggests several possibilities concerning its presence. The appearance has always been the same; from the slide bottom, the order of occurrence is a small red circle, a larger white circle, a clear portion of gelatin, and finally the reduced silver at the gel surface. It is the order and distances that are significant. When the white substance was first seen, it was thought to be a chloride contamination. Testing of this layer with  $\text{NH}_4\text{OH}$ ,  $\text{HNO}_3$ , and  $\text{HCl}$  has indicated that this may be so. A test on the only possible contaminant, the gelatin, shows only a slight cloudiness that

might be attributed to silver chloride. It seems improbable that this very faint test could be the source of the intense white coloring in the gel.

A possibility that has no experimental background, but seems feasible is that the white substance may be an intermediate between the red silver chromate and the silver reduction product. The fact that this substance always occurs between the lower red precipitate and the clear gel lends support to this theory. Another possible variable in this connection is the thickness of the gelatin. It is noted that the precipitation phenomenon occurs profusely when there is a thick gel. This would indicate that either 1) the ions can not travel this distance to be reduced by the mercury, or 2) access of the mercury to the gel is restricted after a thin silver surface has been formed. Either explanation would account for the strange precipitation. These observations tend to back the theory that there is an intermediate formed and that the thickness of the gel may be significant to structural formation.

Some further comment must be made on the relative concentrations of silver and chromate ions. DeSieno found that radial bands were produced when the silver ion was one hundred or more times concentrated than the chromate ions. This relation was verified in these studies, but the cause was not determined. It is entirely possible that this great concentration difference



is necessary because of some physical aspects of the method of application. Further study into this variable would be highly desirable.

The appearance of macroscopic Liesegang rings in the control test was an innovation not expected. These controls were run in the absence of mercury vapor and chromate ion. Nevertheless, the gel took on a darkened appearance and rings were formed. A possible explanation of this phenomenon is that the slight chloride contamination in the gel mentioned before may have formed rings with the silver ion. Upon being exposed to light, these rings would darken and give the brownish appearance.

The microscopic liesegang rings pictured on page fifteen form a very regular structure. It was Ostwald's theory that distance between lines was inversely proportional to the concentration of reactants. This observation is borne out in the production of very close rings with concentrated solutions.

Further study into this phenomenon should include 1) study of the critical concentration range, 2) studies of reaction mechanism, 3) investigation of possibilities of other reducing agents, 4) characterization of the unexplained white precipitate within the gel, and 5) studies into other insoluble salts which may produce this phenomenon, and other related topics.

### SUMMARY

The diffusion of silver nitrate from a fine capillary into chromated gelatin in the presence of mercury vapor produces characteristic structures. These structures are related to the concentration of reactants. Silver ions in the capillary must be of sufficient concentration to allow diffusion into the gelatin. Chromate ions must be limited to a low concentration ( $5 \times 10^{-4}$  to  $5 \times 10^{-3}$ ) for successful production of radial lines. A ten percent gelatin solution is a suitable medium for the reaction. An induction period is necessary in order that the ions may diffuse and the structures may form.

Excellent microscopic Liesegang rings of reduced silver may be produced with concentrated reactants in the presence of mercury vapor. Mercury vapor is essential to the formation of radial lines, but not to Liesegang rings. The formation of a red and white precipitate deep within the gel surface may be an indication of the mechanism of reaction. Miscellaneous deposits of silver crystals and random structures are frequently observed.

The use of small petri dish cells described in this thesis may prove instrumental in observing the reaction.

The structures formed appear to be stable, and do not decompose after drying and exposure to the atmosphere. The form-



ation of rings in ordinary gelatin would indicate a contaminant which would produce an insoluble silver salt.

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