RHYTHMIC PRECIPITATES. II. ON THE INFLUENCE OF LIGHT AND THE EFFECT OF AGING.

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It is a well-known fact that light affects the formation of rhythmic precipitates and the aging of jellies before superimposing the diffusing solution has the remarkable effect on the formation of periodic structure. Many papers[1] on these subjects were published, but the results obtained by different authors show the lack of agreement.

These different results are probably caused by the complicated effects of both light and aging. Therefore, experiments on the influence of light must be carried out completely in the same condition (for instance, temperature, concentrations of inner and outer electrolyte, aging of gel) except that of light. And for the same reason, experiments on the effect of aging of gel must be carried out in the same condition excepting that of age. Irradiation with light affects the ring formation and even the diffused light in the room has considerable influence, so it is recommended that the experiment should be undertaken in the dark room. The experiments undertaken by present writer have been carried out on these precautions. The system of gelatine-silver chromate has been studied principally.

Effect of Complete Darkness. It is interesting to study, whether the rhythmic precipitates can be formed or not, in complete darkness. Küster[2] states that no bands of silver chromate were formed while Davis[3] obtained good bands in the dark. Blair[4] reported that the bands formed in complete darkness show irregularity. The experiments carried out by the present author are as follows. Three samples of gelatine solutions were prepared, the first sample was made in complete darkness while the second and the third in an ordinary room. Let the first and the second set in the dark place and the third in the light. Three days later, silver nitrate solution was poured on these gels. After standing the former two in the dark and the latter in the light for a week, rhythmic precipitates of silver chromate were recognised in all three

(1) See Hedge, "Liesegang Rings," (1932), 17, 26.
(2) *Kolloid-Z.*, **13** (1913), 192.
(3) *J. Am. Chem. Soc.*, **44** (1922), 2698.

test-tubes and no irregularity was noticed. From this fact it has been asserted that the formation of bands is not affected by the darkness.

Influence of Visible Ray. According to Blair[4] the bands become irregular when the gel has been irradiated with visible light. But recently Cluzet and Kofmann[5] stated that the formation of rhythmic precipitates was unaffected by visible light. The present writer found that the radiation of visible ray has an important effect on the formation of bands though the bands do not become irregular even by the strong irradiation of direct sun light. The experiment was done as follows: allowed the gelatine gel containing potassium dichromate as an inner electrolyte to set in test-tubes and kept in a dark place. Then each of the test-tubes was exposed to direct sun light for different interval of time. To avoid the effect of heat ray, the day light was filtered through the layer of water. In this case, the number of the formed bands increases in proportion to the time of exposure. And when exceeded a certain time interval, the bands were formed too close to each other and the whole

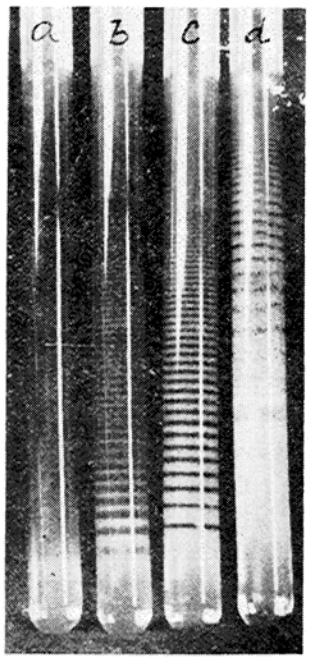

Fig. 1.

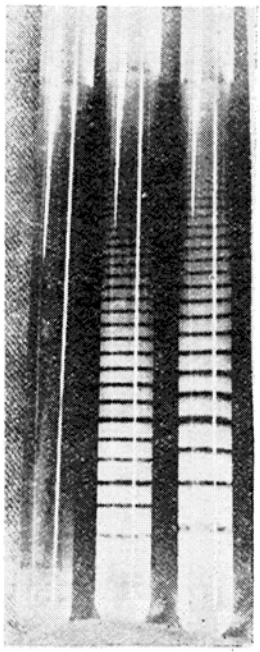

Fig. 2.

(4) *Phil. Mag.*, **49** (1925), 90.
(5) *Compt. rend. Soc. Biol.*, **104** (1931), 1001; *Brit. Chem. Abs.*, (1931), 694.

appeared as dark brown strip. Some of the results obtained are shown in Fig. 1. The samples in this photograph have been made from 2.5% gelatine sol containing 0.1% potassium dichromate, allowing to set in a dark. Sample (a) in the photograph was exposed ca. 3 hours, (b) 2 hours, (c) 1 hour and (d) kept in a dark throughout. Afterwards 15% silver nitrate solution was poured on the gels and the test-tubes were stood in a dark.

Analogous result was also obtained by the influence of diffused light which is shown by Fig. 2. Gelatine solution which was prepared as above described, was poured into three test-tubes and left to set. One was exposed about 5 hours to direct sunlight and the other kept in an ordinary room about 3 days long and the last kept in the dark throughout. Then 15% silver nitrate solution was poured on the gels, and kept all tubes in the dark. The left in the photograph is one exposed to direct sunlight, the middle to diffused light and the right is one which kept in a dark place.

From these results, we can conclude that visible light causes the number of bands to increase and the distance between bands to shorten. It seems that these changes which are caused by the exposure to light, are due to the transformation of gel structure and to the interaction of gelatine and potassium dichromate. After long exposure, gel becomes somewhat difficultly soluble and does no more reset. From this fact, it is probable that the gel changes somewhat in its structure or at least the micelle of gelatine suffers some changes.

The author conceives, from these facts, that at first the gelatine reacts with potassium dichromate on the exposure to light and moreover the micelle of gel changes to insoluble modification. This modification has a less protective action from crystallization of silver chromate than before. So the bands become closer and the number of them increases.

Blair studied the effect of visible light by the exposure to the radiation with ½ watt lamp instead of sunlight, from very short distance (6 in. range), and recognised that the bands become irregular. In writer's opinion, by the radiation from a short distance as in Blair's experiment, the energy of light delivered to the gel system does not distribute equally as in the case of parallel ray as sunlight. Hence the irregular bands were formed.

Influence of Ultra-violet Ray. According to Blair, ultra-violet ray from quartz mercury lamp makes the formation of bands impossible even in a few hours, while Cluzet and Kofmann found that the formation of

Liesegang rings was retarded by ultra-violet light. The retardation of formation of rings is also recognised by the author's experiment. And rings became finer and closer each other than in the non-illuminated case. Some of the results obtained are shown in the photograph (Fig. 3). The same sol (6.5% gelatine, 0.1% potassium dichromate) was poured into three test-tubes of fused silica, one exposed about ten hours; the second about five hours and the third was kept in the dark. The lamp used for this experiment was an Acme mercury quartz lamp which was made by Shimazu Seisakusho. Input of the current applied to the apparatus was 108 volts and 10.2 amperes. Distance to the test-tubes from the lamp was about 30 cm. In the photograph the left is one which was exposed about ten hours and the middle about five hours and the right unexposed one.

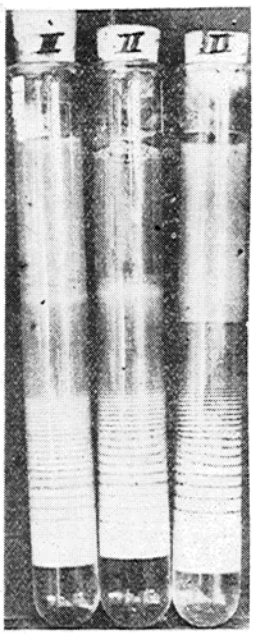

Fig. 3.

In the case of copper chromate bands in silica gel the effect of irradiation with ultra-violet light was not recognised.

Effect of Aging. It is interesting that the banding is affected with the age of jellies before superimposing the diffusing solution. Schleussner[6] recommended to keep a gelatine gel for twenty four hours before pouring the outer electrolyte. The most interesting observation which has ever been done, is that of Blair.[4] He has made measurements which show that the distance of the last band from the upper end of jelly increases regularly with the age of gel. This result was also reproduced by the present author.

The writer has found another interesting fact. When the experiment was carried as follows, the effect of aging on the formation of bands did not appear. The gelatine solution was prepared and poured into several test-tubes and allow to set. Later, after different time intervals, each of the test-tubes excepting one, was warmed and the gel melted and allowed to reset. In this manner, the gels of different age were prepared. Then silver nitrate solution was poured on them. In this case, the formed bands in the respective tubes appeared quite equal and identical to that of unmelted gel, i.e. the most aged gel.

(6) *Kolloid-Z.*, **31** (1922), 347.

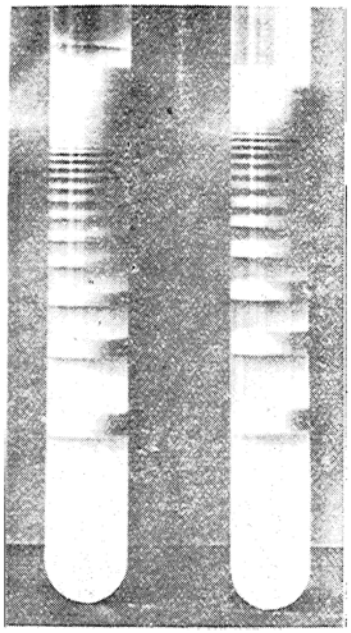

Fig. 4.

From these results the writer concludes that the aging effect of gel on the formation of Liesegang rings is not caused by the change of structure of gel as Blair considered, but by the change of modification of gelatine into the less protective one by an interaction of potassium dichromate and this change proceeds with the age. And it is considered also that the decrease of potassium dichromate after aging was not recognised as Blair observed, for this change of modification is probably caused by spending very small amount of potassium dichromate.

Effect of aging was also studied on the system of copper chromate in silicic acid gel within the range of three months. The remarkable results as in the case of silver chromate in gelatine was not seen. But in the aged gel the first band becomes generally thicker than that in the newly formed gel. And the second and other consecutive bands become inversely thicker in fresh gel than in older ones. According to Koenig,(7) a fresh silica gel gives the best bands, the effect becoming more and more irregular, the longer the gel is kept before diffusion begins. But in the author's experiment on copper chromate bands, the long aged silicic acid gel also gave good bands as shown in the photograph (Fig. 4). The gel in the left tube was one aged eighty days before diffusion started and the gel in the right test-tube one freshly prepared having the same composition. In both tubes very beautiful strata are recognised and show no irregularity.

In conclusion the writer expresses his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his kind advices on this paper.

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(7) *J. Phys. Chem.*, **24** (1920), 466.