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The structure and optical characters of iridescent glass

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1. Introduction

In the museums of Europe will be found exhibited specimens of ancient glassware excavated from archaeological sites and distinguished by a very beautiful iridescence. Nearly a century ago, Sir David Brewster (1840, 1859, 1860, 1864) examined and described specimens of such glass. According to him, the iridescence of glass which has suffered decomposition is due to its lamellar structure; in other words, the material is an ensemble of thin films optically distinct from each other. In consequence of this structure, it exhibits a large reflecting power, presenting vivid colours both by reflection and by transmission, these being complementary. Brewster noticed that only rarely do the laminae possess specularly reflecting surfaces; in many cases their surfaces are rough due to the presence of a large number of small cavities which may lie separate or run into each other; in other cases again, according to him, the films are covered with concentric stratified structures presenting between crossed nicols the phenomenon of a black cross.

Brewster's explanation of the iridescence of ancient glass appears to have been accepted without question by all subsequent observers. Considerable interest naturally attaches to the question why the glass acquires with time a laminar structure which in its normal state it does not possess. It is a matter of common knowledge that glass under prolonged exposure to wind and weather or to the action of suitable chemical reagents often acquires a superficial iridescence, and attempts have not been lacking to accelerate this process of attack and thus to reproduce experimentally some of the structures observed and described by Brewster in ancient glass. Some remarks on earlier attempts in this connection will be found in an interesting note by M Marcel Guillot (1934) who has shown that when a saturated solution of sodium bicarbonate is kept in contact with a surface of alkaline glass for some weeks or months, marked iridescence results; he suggests that such iridescence is due to the formation of stratified films by a chemical process analogous to the Leisegang phenomenon.

It should be remarked that Brewster's views regarding the structure and optical characters of iridescent glass are not altogether free from obscurity. The refractive index of the decomposed material presumably differs little from that of the original glass. Assuming this to be the case, it is not easy to understand how the coloured reflections arise. If in order to explain the optical effects, we postulate the existence of thin films of air separating the decomposed layers of glass from each other, it is not understood why the films are actually adherent to each other and to the glass, and why they exhibit in many cases a remarkable uniformity of colour and brightness over considerable areas. If, on the other hand, we assume that the cementing material is some solid substance, it would be necessary that its refractive index should be considerably higher or lower than that of glass, in order that sensible reflections should result; moreover, such an assumption would be difficult to reconcile with the astonishing rapidity of penetration of a liquid such as water or alcohol into the decomposed glass, and the equal facility with which it can evaporate and leave the iridescence unaffected.

For the reasons remarked above, it appeared to us worth while to re-examine the subject with a view to clarifying the position. The investigation was taken up in spite of the fact that we had at first no archaeological material available; the impulse to study the subject arose from the observation that specimens of decomposed glass of no great age picked up from the ground often showed beautiful effects when examined under the Leitz ultra-opak microscope. In this instrument, the illuminating beam has the form of a hollow cone which is reflected downwards and converges on the surface of the object. If the axis of the cone is normal to the surface, we have "dark field" illumination, the surface becoming visible by reason of the light scattered or diffracted by it. On the other hand, by suitably tilting the plate of glass, it is possible to arrange that the light "regularly reflected" by its surface enters the microscope, in which case, we have the ordinary or "bright field" observing conditions. These arrangements are specially suitable for the study of the structures produced in glass by its decomposition. The photomicrographs illustrating the paper (figures 1 to 30) were taken with the Leitz ultra-opak microscope and exhibit various types of structure observed in the course of this study. It should be mentioned that examination by transmitted light in the ordinary form of microscope is also useful in many cases, particularly if high powers are to be employed or when it is desired to work with polarised light.

2. Structures in iridescent glass

As was remarked by Brewster, the structures observed in decomposed glass are of rather varied type. In the present investigation, several distinct forms have been observed which give characteristic optical effects. These may be listed as follows: (a) cavities; (b) films without boundaries; (c) films with sharply defined boundaries; (d) films scattering light; (e) films with cavities, and (f) dark areas.

Cavities: Small cavities with a circular outline are very common in decomposed glass. When seen by diffracted light, these appear as luminous circles surrounding a dark area. The manner in which such cavities are formed in decomposed glass is made beautifully clear by a study of some plates of dark-blue glass which were picked up at the site of an extinct glass factory at Ennur near Madras. The plates exhibit by reflected light a large number of white circular spots of varying size on a dark ground; the spots in some areas are so close together as to form a continuous white film covering the blue glass. The individual white spots on careful examination are seen to consist of a number of concentric rings, the central region where the material is thickest being white, and the margins which are thinner showing traces of colour in the rings. The white material, though strongly adherent to the plate, can be removed by applying sufficient force; when it comes off, it leaves behind a hollow cavity exhibiting a number of concentric circular rings within its area, *these being in many cases vividly coloured*. The depth of the cavity formed by the removal of the white material is indicated by the difference in microscopic focus between top and centre which becomes evident after such removal. The circular rings are the step-like walls of the cavity which correspond to the diminishing diameter of the successive laminae in the decomposed material, the number of such laminae being greatest at the centre and least at the margins of the cavity. These laminae in the material removed appear to run more or less parallel to the surface of the glass plate.

Figures 1 and 2 in plate I and figures 3 and 4 in plate II illustrate the foregoing remarks, the white patches with indistinct rings being the material produced by the decomposition of the glass, and the concentric rings with dark centres being the cavities formed by its removal. Figures 3 and 4 are photographs of multiple cavities, the latter being on an enlarged scale; it will be noticed how the rings surrounding neighbouring cavities join up sharply at their points of intersection. Figures 5 and 6 in plate III show cavities with comparatively few rings. Figure 7 in plate IV exhibits numerous cavities, while figure 8 in the same plate shows a large number of such cavities forming a continuous area.

Examination of the cavities and of the material removed therefrom by transmitted light under a high power microscope confirms the structure and the manner of formation described above. The high powers of the microscope reveal a large number of fine edges running round the walls of the cavities, and it is seen that these walls are laid out in step-like terraces. Seen by transmitted light between crossed nicols, the walls of a cavity appear as an array of concentric dark and bright circles traversed by a black cross. These effects arise from the fact that a laminar diffracting edge which is not parallel or perpendicular to the electric vector in the light incident on it gives rise to elliptic polarisation (Raman and Rao, 1927). Brewster described certain structures in decomposed glass which he considered as similar to the concentric spherical laminations of a pearl or an onion and which he found to exhibit a black cross in polarised light between crossed nicols; this phenomenon he ascribed to the results of oblique transmission of light through a pile of plates. This, however, is a different phenomenon; on the other hand, Brewster's descriptions of some of the structures exhibiting a black cross between crossed nicols agree so closely with those illustrated in figures 1 to 4 of the present paper that we are obliged to assume that he was really observing the same phenomena as that described above.

Films without boundaries: The general appearance of iridescent glass and in particular, the intensity and hue of the colours exhibited by it and the distribution of the same on the surface depend greatly on the particular sample under study and the treatment it has undergone. We must in this connection distinguish between the effects noticed in the earlier stages of decomposition and in the later stages where the decomposition is far advanced; the difference has also to be remembered between the cases in which the surface is untouched and those in which the underlying iridescent films have been exposed by removal of the upper layers containing the decomposed material. The type of iridescence referred to under the present sub-heading appears to belong to the earlier stages of decomposition; its distinguishing feature is that there are no sharp boundaries dividing the differently coloured regions. This type of film is illustrated in figure 9 in plate V, figure 11 in plate VI and figure 16 in plate VIII. It will be seen that, except for a few detached patches, the variations of intensity over the surface of the plate are more or less gradual.

Films with sharply defined boundaries: In sharp contrast with the foregoing type of iridescence, we have the discontinuous distributions of colour in map-like patterns illustrated in figure 10 in plate V and figures 13 and 14 in plate VII. This is a common type of structure and is to be found sometimes even in the earlier stages of decomposition. Its characteristic features are a strict uniformity of colour and brightness over each "area" in the "map" and a sharply defined boundary limiting each such area. Further, the brightness and colour of the different areas is very varied, ranging from the darkest tones to the brightest and from the most saturated hues to the palest. There can be no doubt that this type of iridescence is due to a laminated structure bounded by sharp edges; the uniformity of colour and brightness over each "area" in the "map" indicates that the laminae are of uniform thickness and solidly adherent, and not loose formations separated by air films. Indeed, any tendency to separation of the laminae by air films is revealed by a variation of colour over each "area" and in some cases even by a succession of colours of the Newton's rings type appearing within it. For instance, we notice that figure 12 in plate VI clearly reveals the presence of a film of air of variable thickness between the laminae. Figure 15 in plate VIII is specially interesting as it shows the extreme sharpness of the boundaries of colour, which in the photograph are recorded as laminar edges on a dark field by reason of the light diffracted by them. Figure 13 in plate VII is also of interest, as it exhibits detached areas of iridescence showing the luminosity at the edges due to diffraction, as also the reflection and scattering of light by the film itself against a background of undecomposed glass.

Films scattering light: The fact that in figure 15, the edges of the iridescent area are seen as luminous lines diffracting light while the film itself is invisible, shows that it is possible to obtain films *which reflect without appreciably scattering light*. In general, however, the surface of decomposed glass scatters light rather strongly; the intensity of such scattering varies greatly and depends both on the nature and extent of the decomposition of the surface and the treatment it has undergone. With certain exceptions, the films which scatter most light usually reflect the least light and display the feeblest iridescence; *per contra*, the films which reflect the most light and display the most vivid iridescence generally scatter the least amount of light. As a consequence of this, it will be noticed that when the surface is held at the proper angle to reflect the light, the iridescent areas are the brightest and the scattering areas are the darkest; when the plate is turned away from the correct angle, the iridescent areas are dark and the scattering areas are bright. It is also noticed that the parts of the films which are seen to scatter most light by this rough test are those in which the decomposed material which is usually white remains still adherent to the glass; when this is removed, the iridescent reflections become more prominent. It may be presumed that the scattering of light by the films is due to the optical heterogeneity of the material formed by the decomposition of the glass. It is however not easy to distinguish such scattering microscopically from that due to cavities present in the film which are too small or too close together to be resolved completely.

The scattering of light by unresolved or imperfectly resolved structures in decomposed glass is evident in many of the figures reproduced with the paper, as for instance, the right half of figure 8 in plate IV, the central bright area in figure 9 in plate V, figure 12 in plate VI, figure 13 in plate VII and the bright areas in figures 17 and 18 in plate IX.

Films with cavities: Examined with the Leitz ultra-opak microscope under "dark field" conditions, decomposed areas in glass usually exhibit illumination, the intensity of this varying enormously with the conditions. In many cases, the luminosity is due for the greater part to the presence of hollow cavities of lesser or greater size, which are either discrete or which run into each other to form patterns or networks of the most varied forms. Under the conical illumination of the microscope, the cavities appear as small luminous circles, vividly coloured, and in most cases, a great many circles lying in a well-defined "area" have the same colour and thus remind one of flowers laid out in a bed. Illustrations of such patterns appear in figures 19 and 20 in plate X (the latter being a part of the field appearing in figure 19 magnified threefold), figures 21 and 22 in plate XI, figures 23 and 24 in plate XII and figure 26 in plate XIII. In many cases numerous small cavities appear superposed on single large ones, giving rise to beautiful patterns in colour. By suitable illumination, the cavities may be caused to appear reversed and stand out in relief in the field of the microscope. Illustrations of the effects then observed are reproduced in figure 25 in plate XIII and in figures 27 and 28 in plate XIV.

Dark areas: On examination of the photographs reproduced in figures 1 to 28, plates I to XIV, it will be seen that in numerous cases extensive "dark areas" are to be observed. These may, in some cases, merely represent areas of undecomposed glass which do not scatter light and therefore fail to appear on the photographic plate under "dark field" conditions. Such cases may be readily identified by tilting the specimen so that the reflected light enters the microscope, as the dark areas then turn bright. On making this simple test, it is found that decomposed glass does exhibit in many cases extensive areas which are dark both under "bright field" and under "dark field" observing conditions, in other words, do not either reflect, or scatter light appreciably. This result is theoretically intelligible, for reflection can be abolished without involving scattering of light, if the change of refractive index at the surface takes place in a continuous manner instead of being discontinuous, in other words, if it is spread over a depth which is not small compared with the wavelength of light. The superficial decomposition of glass may lead to such a result if it extends over a sufficient depth, and if the gradient of refractive index produced thereby is continuous instead of being oscillatory. The latter condition would give rise to an iridescent reflection, while the former would abolish reflection altogether.

3. Effect of immersion in liquids

If a piece of iridescent glass is breathed upon when cold, moisture condenses on it and the colour of the film apparently vanishes immediately; it however reappears when the plate is warmed up. Brewster noticed the apparent suppression of colour produced by placing a drop of water or alcohol on the film, as also its restoration when the fluid has evaporated. He noticed further that oil or balsam penetrates the film slowly and unequally, producing a succession of tints on the plate during its advance. A careful study of these and other effects produced by contact with liquids is evidently of importance in order to elucidate the problem of the structure of these films and their optical characters.

It should be remarked in the first place that the observations made in the rather crude way mentioned above are deceptive. *In reality, the iridescence of decomposed glass does not disappear on immersion in a liquid; on the other hand, the colours actually become more vivid, though their intensity is considerably diminished.* This is readily shown, for instance, by dipping the plate in a cell containing water and observing it within the liquid by reflected light. The iridescence can then be readily seen through the sides of the cell, and may conveniently be examined with the aid of a hand-lens. Its general appearance is made more striking on submergence by reason of the diminished reflection of light from the front of the film and the back of the plate, as well as by the reduction in the amount of scattered light. This improvement is particularly marked for oblique incidences. *When the plate is in air, the colours of decomposed glass disappear when the light falls sufficiently obliquely; but with the plate submerged in water, the colours may be observed right up to grazing incidence.* It is thus clear that the range of study is considerably extended by the use of the technique of immersion of the film in a liquid cell.

A special feature of the Leitz ultra-opak microscope is that its stage is of ample size and can accommodate a container for liquid in which the objective as well as the material under study can be immersed. The instrument can therefore be very conveniently used for studying the iridescence of submerged films. The disturbance due to the reflection of light from the free surface of the liquid is avoided completely, and the iridescence can be seen under either "bright field" or "dark field" conditions as desired; the effects following immersion can also be watched from instant to instant. Using this procedure and examining a variety of examples, the results already stated are readily verified. In seeking to explain the effects observed, we have to remember that the liquid has a twofold influence; firstly, the reflection at the external surface of the film is greatly diminished; secondly, the liquid enters the cavities of the film—those visible in the microscope as well as the invisible cavities forming part of its structure; as a result of this penetration, the optical properties of the film are altered in a manner depending upon the quantity of liquid which penetrates, its distribution within the thickness of the film and the refractive indices of the film and of the liquid.

A little consideration indicates that the effects referred to above would be most pronounced when the refractive index of the liquid approximates most closely to the refractive index of the film. When this is the case, the surface reflection would be negligible and the variations of index within the film would be greatly reduced; we should accordingly expect the iridescence to become enfeebled in intensity. *Per contra*, we should expect the iridescence to be less enfeebled when the refractive index of the liquid deviates considerably from that of the film. These anticipations from theory are found to be fulfilled in observation. A variety of liquids can be used e.g., water, glycerine, carbon tetrachloride, benzene, carbon disulphide and monobrom-naphthalene and suitable admixtures thereof, so that the immersion liquid can have any desired refractive index from 1·33 to 1·66. In every case, *it is found that immersion produces a marked change of colour. The diminution of its intensity is most striking when the immersion liquid has a refractive index about the same as that of the glass used and is less marked when the refractive index of the liquid is either greater or less.* Judging from the observations, it would appear possible to determine the index for minimum iridescence fairly accurately. The fact that the colours do not vanish for any index is significant but is not surprising when we recollect that the penetration of liquid can scarcely be expected to produce a complete uniformity of refractive index within the film.

4. Effect of absorption of liquids

When the plate is completely immersed in a liquid, the latter can penetrate the film to the maximum extent provided sufficient time is allowed. It is however of interest to be able to study the effect of absorption of liquid on the iridescence of the film when the latter is not actually submerged. Further, it is desirable also to be able to study the cases in which the absorption is incomplete and takes place to an extent which can be controlled, and when it is variable with time. For this purpose, again, the Leitz ultra-opak microscope is very suitable. A convenient technique is to place a drop of the chosen liquid on the film while it is under observation in the field of the microscope. The properties of the liquid which should be capable of influencing the results under these conditions are its refractive index, its speed of spreading over the surface and of penetration into the film, as well as its rate of evaporation. Benzene, for instance, penetrates quickly and also evaporates quickly. Water also enters the films quickly but is slower to evaporate, while monobrom-naphthalene is slow in both respects. An interesting variation of the technique is to use a mixture of liquids, e.g., benzene and monobrom-naphthalene which can penetrate quickly but which on evaporation leaves the less volatile component behind in the film, thus altering its optical characters.

In making the observations mentioned, it is convenient to work with a film which initially shows a uniform colour so that the variations of the same with the quantity of liquid absorbed can be more readily recognised. Films with a uniform colour over a considerable area may be obtained by chemically iridising glass. (A reagent bottle which had developed a strikingly uniform internal iridescence was broken up and furnished suitable material for these investigations.) Figure 29 in plate XV is a photomicrograph of such a plate with a drop of monobrom-naphthalene placed on it. The sharply bounded black central area (with a bright overlying ring due to reflected light) is the portion of the film actually covered by the liquid. The moderately dark circle surrounding the drop is the area of the film internally saturated with liquid, while beyond the same is seen a succession of dark and bright rings which indicate a variation in the quantity and distribution of the liquid absorbed by the film. In the actual experiments, these rings exhibit varied colours which are even more striking than the colour of the part of the film free from liquid.

When a comparatively non-volatile liquid such as monobrom-naphthalene is used, the pattern surrounding the drop when fully developed remains practically static and can therefore be photographed easily. The case is entirely different when a quickly spreading and volatile liquid such as benzene is used. The colour patterns due to its absorption and subsequent evaporation change with extraordinary rapidity, so much so that they can only be observed visually. The essential point is that the colour of the film is greatly altered by the presence within it of even small quantities of fluid and is fully restored only when the same has completely evaporated or has been otherwise removed. Using the technique of a non-volatile substance dissolved in a volatile fluid, it should be possible to introduce definite quantities of a substance of known refractive index into a measured area of the film and to correlate the same with the changes of colour produced thereby.

5. Effect of mechanical pressure

The penetration of liquid into the iridescent film which is shown by the change in colour resulting therefrom indicates that the material of the film, at least in some cases, has an "open structure" which permits of entry of fluid. Such partial emptiness may be ascribed to the loose packing of the material in a manner which may be either continuous or periodic. If this view be correct, it should be possible by mechanical compression to increase the density of the film and at the same make it more uniform. The experiment is readily tried, and in the particular case of the chemically iridised glass used in obtaining figure 29, it is strikingly successful. Figure 30, plate XV, shows a uniform film which had been subjected to the rolling pressure of the rounded end of an ivory rod. It will be noticed that the whole of the compressed area appears dark in the picture, the greenish-blue iridescence having turned dark-red as the result of pressure. The margin of the compressed area shows a bright belt, indicating that the first effect of the pressure is actually to increase the intensity of the iridescence. Spectroscopic examination showed that the bands in the spectrum of the reflected light brighten and then shift as the result by the application of pressure: with greatly increased pressure, their intensity falls off to a small value.

It must be remarked, however, that the effect of mechanical pressure on the iridescence is by no means equally striking in respect of all films. It must be presumed that in those cases where the pressure produces a relatively small effect, the structure is more compact and the film should then have a smaller capacity for absorbing liquid. This is a matter however to be tested by more detailed investigation.

6. Polarisation phenomena

A careful study of the state of polarisation of the light reflected at various angles of incidence should evidently be capable of furnishing useful information regarding the optical properties of the film responsible for the iridescence. Preliminary observations indicate that the coloured reflections exhibit the maximum polarisation at an angle of incidence which does not differ much from the Brewsterian angle for the undecomposed glass. At this angle and for incidences somewhat more oblique, a distinct change in the colour of the film to the complementary tint is noticed, at least in some cases, when the observing nicol is turned to the position which transmits the minimum of reflected light. Such an effect is to be expected if the film has a refractive index less than that of the undecomposed glass. On the other hand, when the film is submerged in a liquid, the effect mentioned above is not noticeable, and the polarisation of the reflected light is found to be sensibly complete at or about the Brewsterian angle of incidence for the liquid-glass boundary. This is to be expected if the colours are then due to relatively small fluctuations of refractive index within a stratified film having nearly the same refractive index as glass. Precise measurements would however be necessary to distinguish between the different possibilities regarding the manner in which the refractive index fluctuates within the film and to determine its average value in relation to that of the glass.

7. Summary

A study of numerous specimens and of 30 photomicrographs of the same shows that the structures in decomposed glass may be divided into six categories exhibiting distinct optical phenomena: (1) Cavities with terraced walls; (2) films exhibiting iridescence of varying colour without defined boundaries; (3) films exhibiting map-like patterns of colour with sharply defined laminar boundaries; (4) films containing unresolved or imperfectly resolved structures scattering light; (5) films containing hollow cavities, and (6) dark areas which neither reflect nor scatter light. Contrary to Brewster's observation, the colours of decomposed glass actually become more striking when the material is covered by liquid; the intensity diminishes but does not disappear even when the index of the surrounding fluid is identical with that of the film. The films are capable of absorbing liquid in variable amount, their colours being altered thereby. The openness of internal structure indicated by this fact is confirmed by observations on the effect of mechanical pressure on the iridescence, and on the polarisation of the reflected light at various incidences both in air and when submerged in liquids.

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Figure 1 (× 150)

Figure 2 (× 150)

Plate I

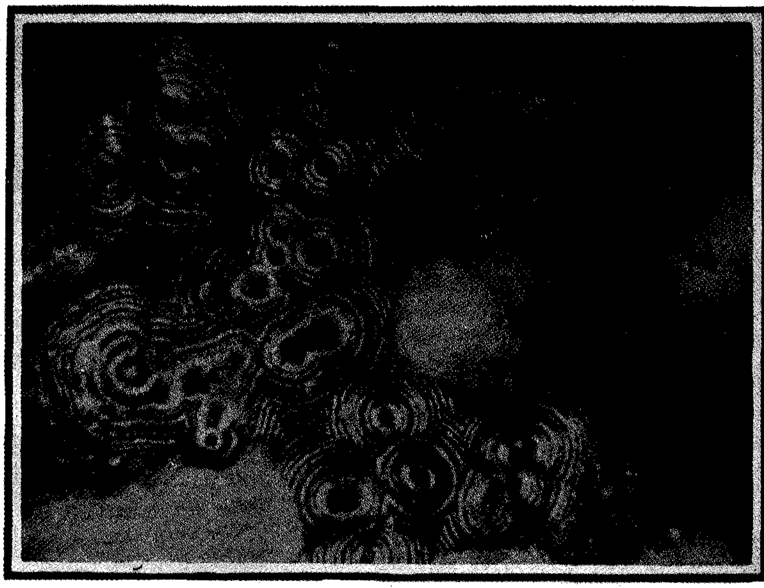

Figure 3 (× 180)

Figure 4 (× 350)

Plate II

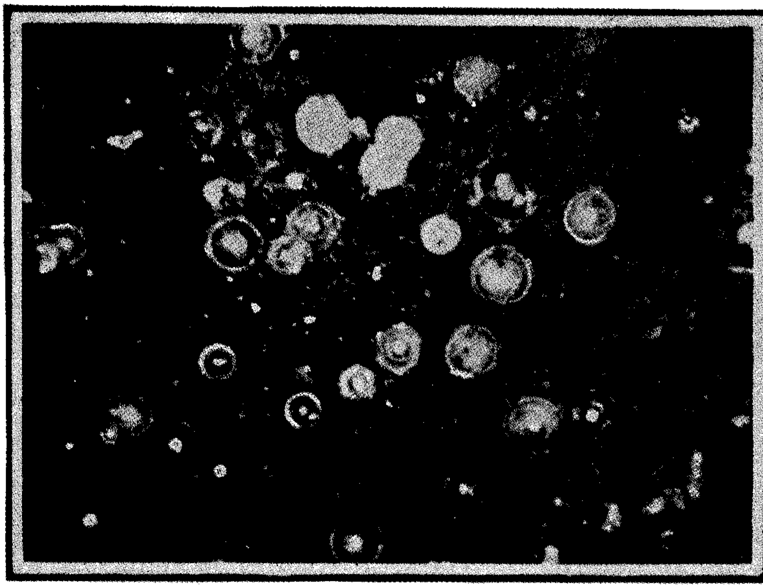

Figure 5 (× 120)

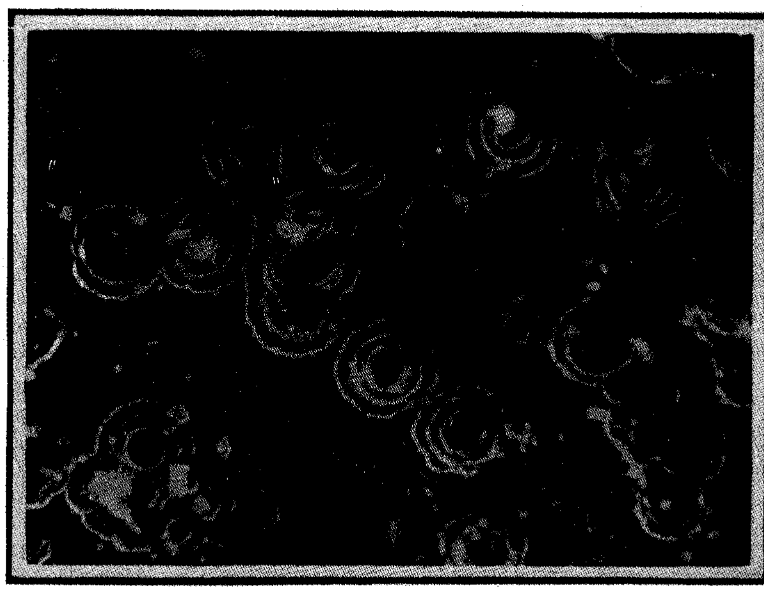

Figure 6 (× 180)

Plate III

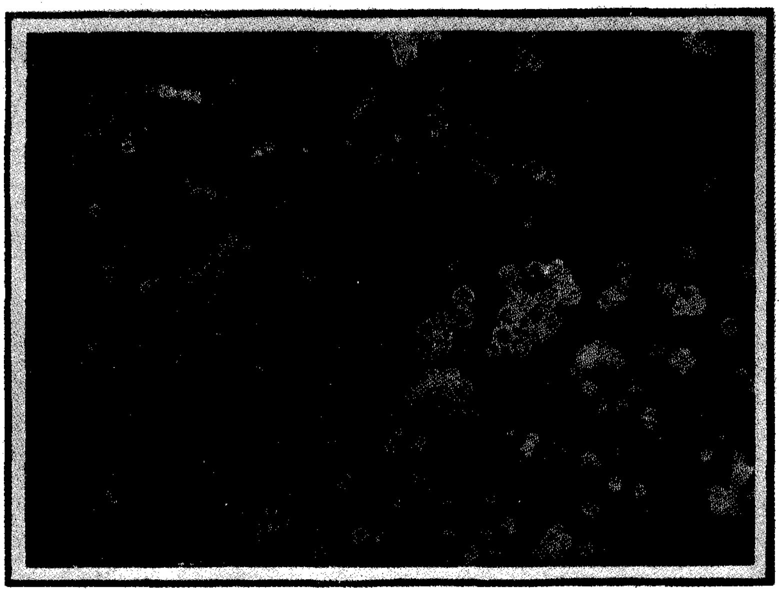

Figure 7 (× 300)

Figure 8 (× 180)

Plate IV

Figure 9 (×65)

Figure 10 (×65)

Plate V

Figure 11 (×100)

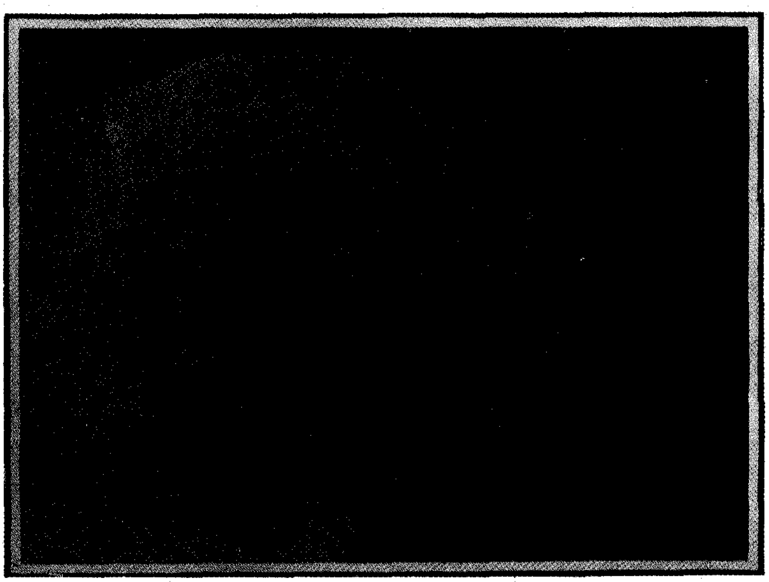

Figure 12 (×180)

Plate VI

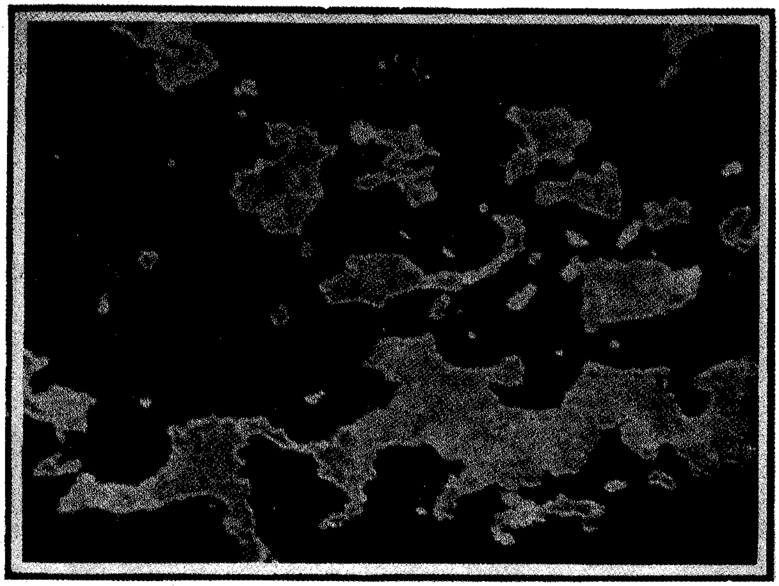

Figure 13 (× 180)

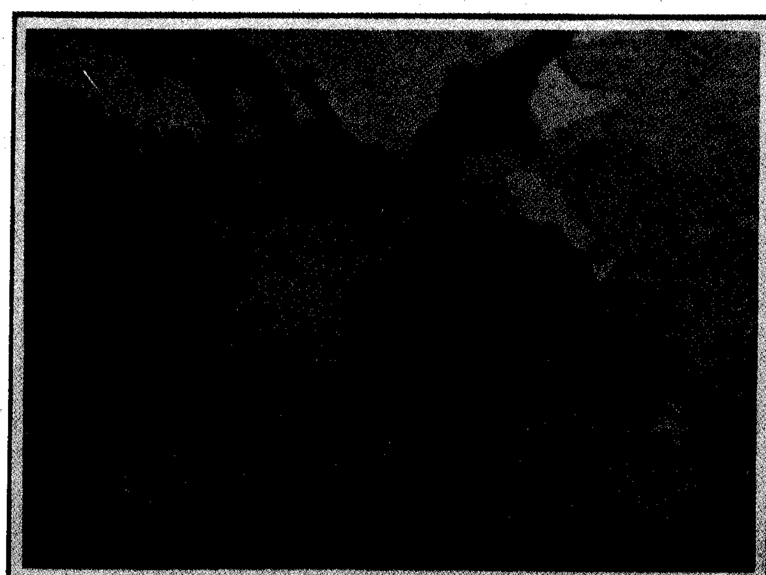

Figure 14 (× 100)

Plate VII

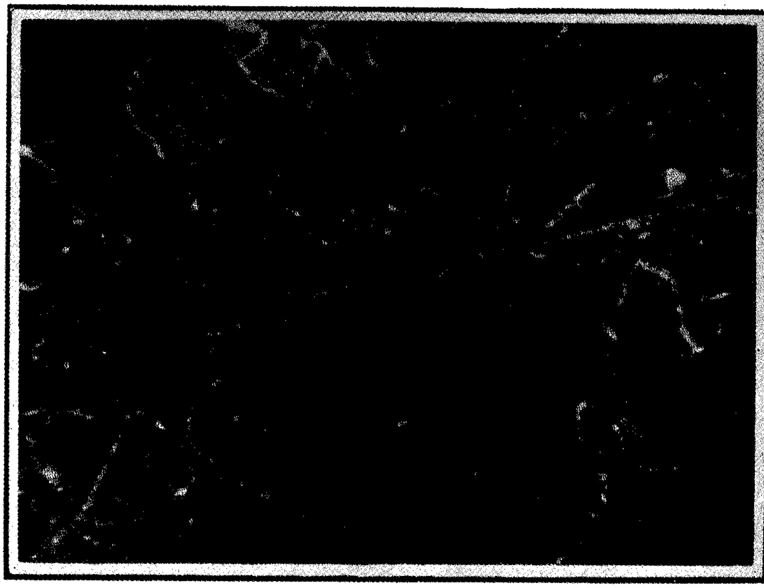

Figure 15 (× 90)

Figure 16 (× 65)

Plate VIII

Figure 17 (×90)

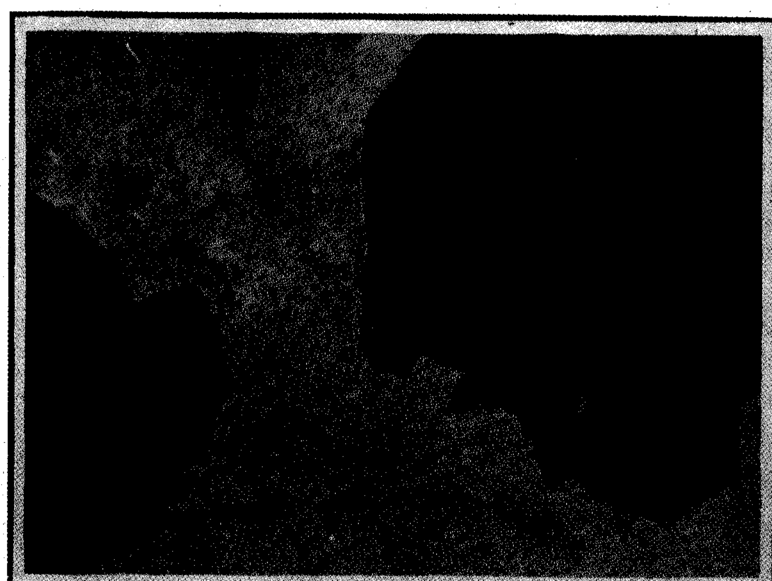

Figure 18 (×90)

Plate IX

Figure 19 (× 65)

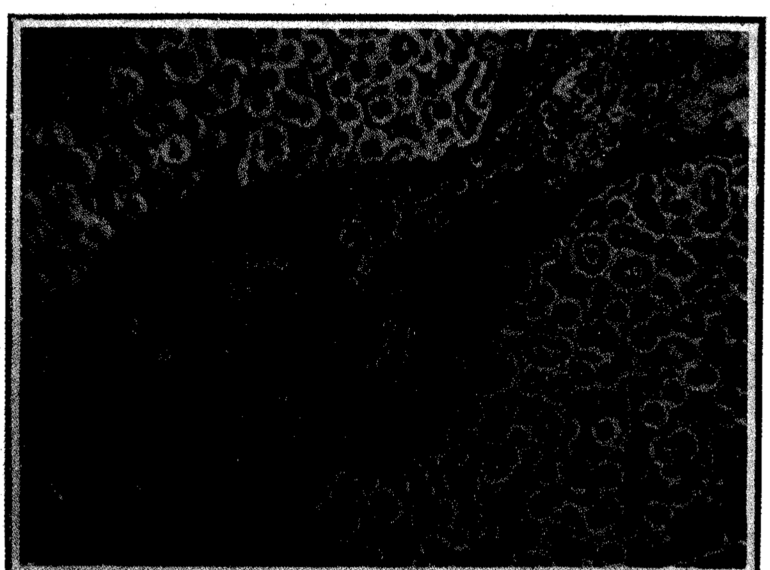

Figure 20 (× 180)

Plate X

Figure 21 (× 120)

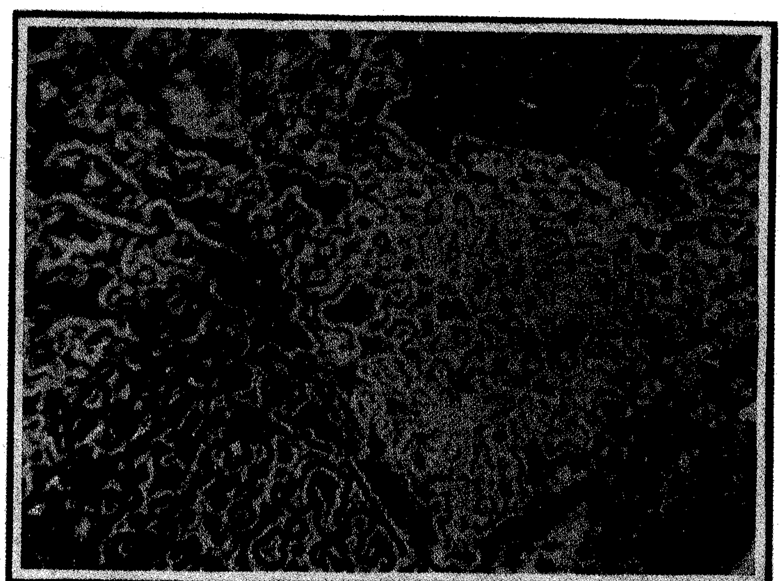

Figure 22 (× 250)

Plate XI

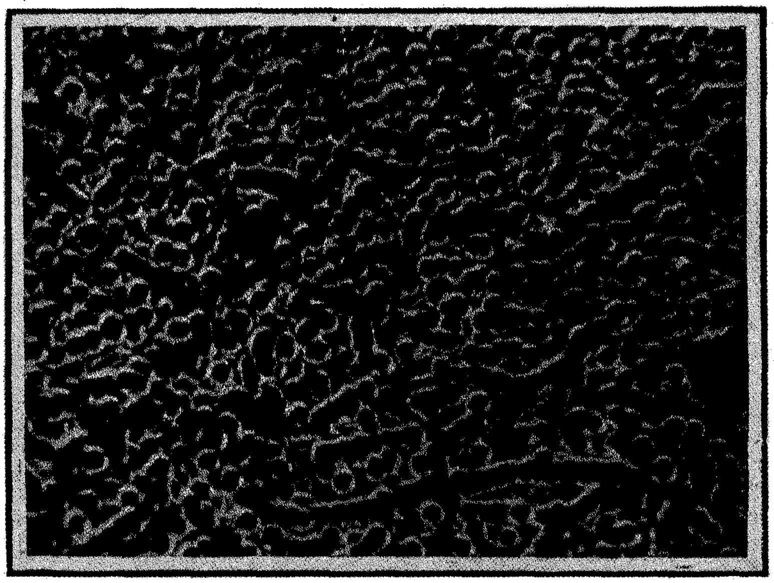

Figure 23 (×200)

Figure 24 (×180)

Plate XII

Figure 25 (× 120)

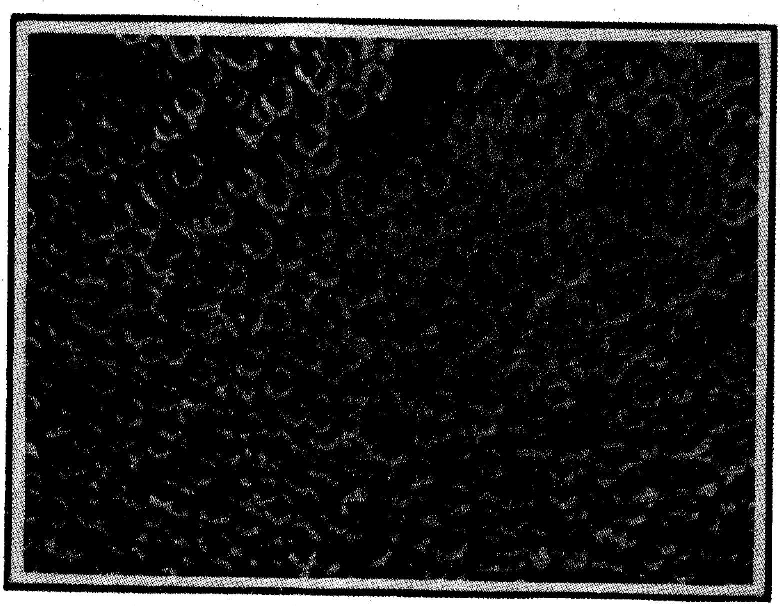

Figure 26 (× 300)

Plate XIII

Figure 27 (× 120)

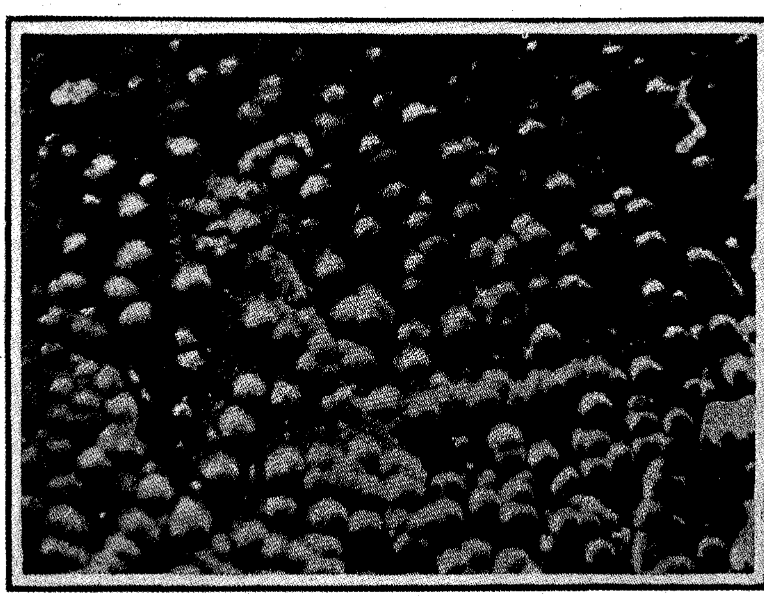

Figure 28 (× 120)

Plate XIV

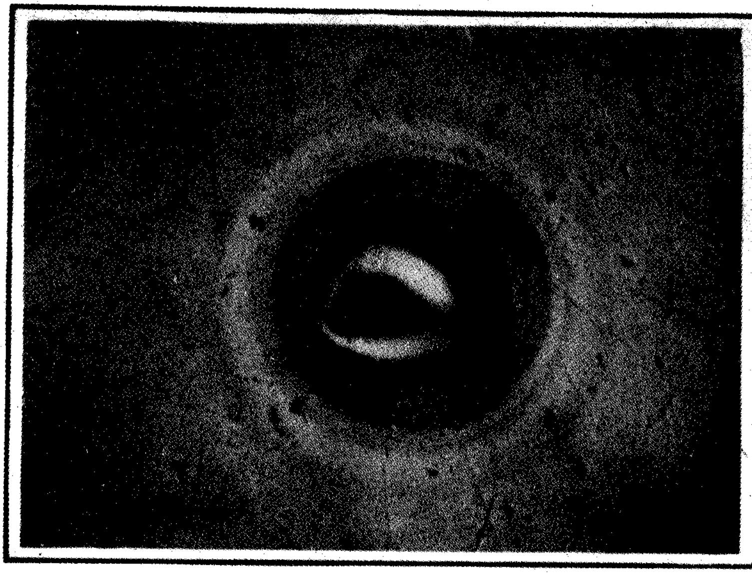

Figure 29 (× 100)

Figure 30 (× 100)

Plate XV