Physiology. — *Some remarkable properties of a double refracting liquid.* By G. VAN ITERSON JR.

(Communicated at the meeting of June 30, 1934).

Professor CARL NEUBERG, Director of the „Kaiser Wilhelm Institut für Biochemie" in Berlin, lecturing in Delft on June 8th 1934, stated among other things that he had been able to prepare mono phosphoric-glyceric acid and several of its salts. He mentioned also that at a similar lecture in Prague on May 17th 1934 he had been told by Prof. H. ZOCHER that it was the latter's impression that liquid crystalline salts might be present among these salts.

I should like to make the following communications about the results of an investigation on the properties of the acid cadmium salt of phosphoric-glyceric acid, which salt I received from Prof. NEUBERG. Naturally, my investigations had to be limited, partly because the total quantity of liquid at my disposal amounted only to about 20 cm^3.

According to NEUBERG this cadmium salt has the following composition: $CH_2O.PO_3Cd$—CHOH—COOH. It has been prepared from the acid sodium salt of the phosphoric-glyceric acid by adding 6 cm^3 of water and 1.5 cm^3 of a 20 % cadmium-acetate solution to 3 cm^3 of a 10 % solution of the acid sodium salt. I wish to draw attention to the fact that the gelatinous liquid obtained in this way, contains not only the above named acid cadmium salt and its ions, but also sodium acetate, sodium- and acetate ions. This investigation therefore does not deal with one single chemical or a solution of one.

To determine whether any liquid crystals are present in this solution, it will be self-evident that I have placed a drop of this liquid under the polarizing microscope between crossed nicol prisms and have turned the stage. In this way there is a big chance that interference colours will be observed in several positions of the stage. There was nothing to be observed, however. Next I employed a gypsum plate "Red First Order", because the observation of faint double refraction becomes easier by this means. (Unless further indication is given, the use of the gypsum plate in this investigation is always in such a manner that the arrow on the plate — viz. the direction of the 1st bisectrix — divides the right angles of the 1st and 3rd quadrant into halves. The 1st and 3rd quadrants are the right-top and left-bottom ones). An extremely faint double refraction could be discerned in this manner; with difficulty, regions of a faint blue colour could be seen, as well as slightly yellow ones. The result was not encouraging, however. Nevertheless, I saw a little more clearing up close to the sides of the cover

glass, which made me decide to investigate the liquid enclosed in a capillary.

On viewing this object after it had been lying on the table for a few minutes (it will be made clear later on that this is not without influence), between crossed nicols and after the insertion of a gypsum plate, red first order, I observed a peculiar phenomenon. I have tried to reproduce this phenomenon on Plate I, these drawings being somewhat sketchy, however. The two black bordering lines do not represent the wall thicknesses of the capillary only; they represent also the very indistinct neighbouring layers. The coloured parts represent therefore only those regions situated toward the centre of the capillary.

With the capillary in a horizontal position, there appeared transverse — viz. vertical — bands, alternately coloured yellow, red, and blue. The yellow and blue bands were approximately of equal width, the red bands were narrow. As an example, I mention here a capillary of an internal diameter of 1.3 mm, yellow and blue bands of 75 μ, and red bands of 15 μ.

Rotating the capillary to the left made the image change: at an angle of about 22.°5 there were twice as many transverse red bands as at first, while the yellow and blue bands had become less purely coloured. At an angle of 45° the yellow bands had disappeared, there being only narrow blue bands and wide red ones visible. An angle of 67.°5 produced an image approximately the same as that at 22.°5. In a vertical position of the capillary the original image was almost restored, the bands having exchanged places, so to say.

The diversity of images was not exhausted herewith; at an angle of 135° narrow yellow and wide red bands were present, while at 112.°5 and at 157.°5 again different images were visible.

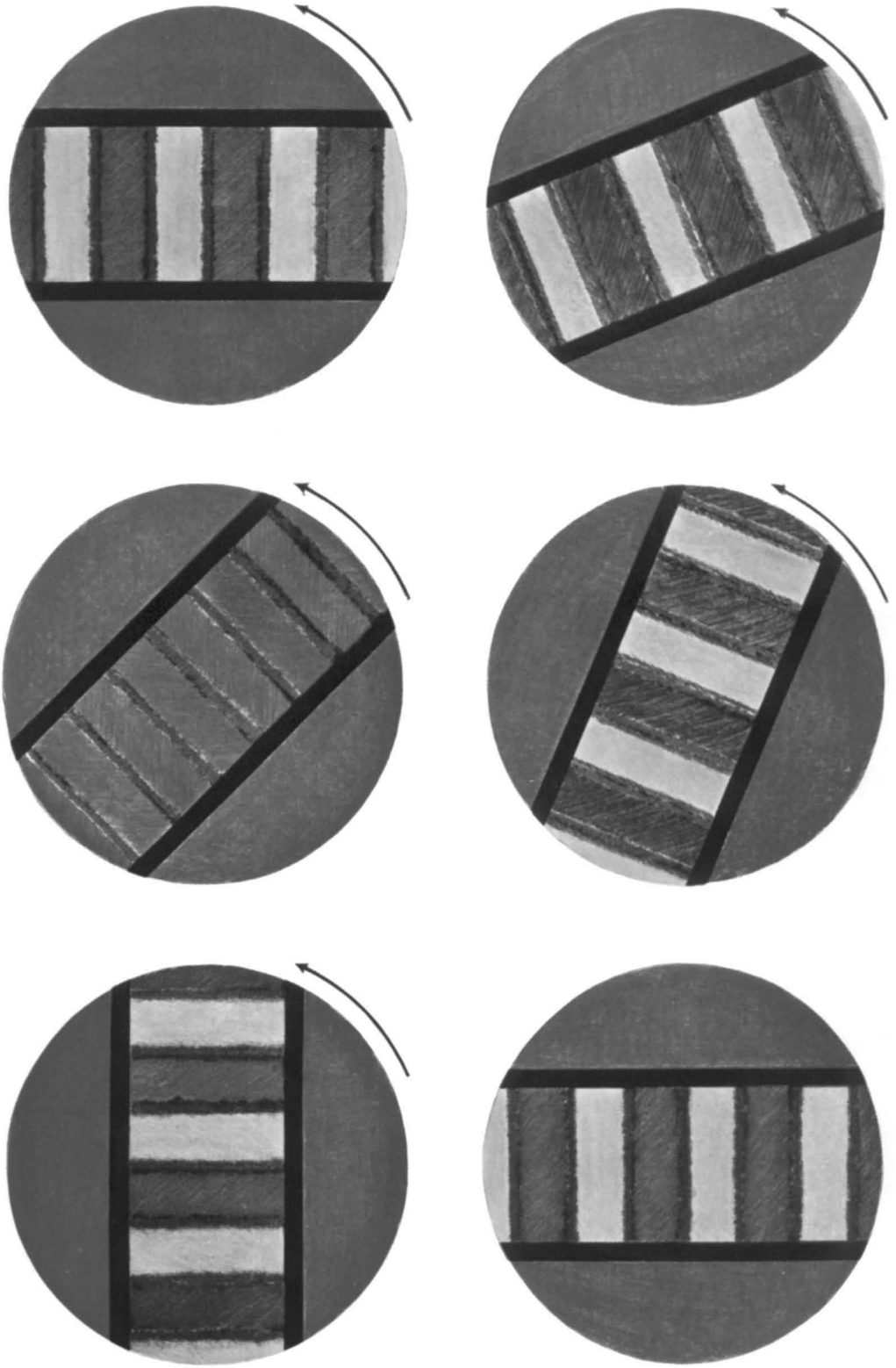
At 180°, however, the original image reappeared.

Not less surprising, although less colourful, were those things to be observed when the gypsum plate red first order was not inserted. In this case there were present small dark transverse regions between light bands On rotating, the number of dark bands doubled at first. At 45° the original number had come back again, but the dark bands were wide, and the light ones narrow. By further rotation, twice the number of dark bands appeared again, while in the vertical position the original status had reappeared.

I must add immediately that the above described phenomena were not always observed: in several instances the images were much more complicated. The reason for this will be given below, but here let it be stated that this diversity made the phenomena still more enigmatic to me in the beginning. It follows that the remarkable behaviour of this liquid led me to further investigation. I shall presently return to the experiments with capillaries, but shall first discuss a few other observations.

Firstly, it appeared to me that when a big drop of liquid was placed on a slide without cover glass, the surface of the liquid showed distinct

PLATE I.



Formation of bands in the wall-layer of a capillary, (diam. approx. 0.1 mm.) through which a solution of the acid cadmium salt of phospho-glyceric acid has been sucked. Observations in different positions between crossed nicols, (vibrational directions, vertical and horizontal); gypsum plate red first order inserted with the arrow at 45°.

double refraction between crossed nicols. The colours to be observed disappeared practically completely when the cover glass was put on.

When a glass rod was moved back and forth through a drop without cover slide, the liquid became distinctly double refracting; it showed thus a surprisingly strong example of double refraction of fluids in motion. This double refraction was of very long duration, moreover. Rubbed under an angle of 45°, the liquid became blue on insertion of a gypsum plate, and remained so for many minutes, though spots appeared after some time.

This observation led me to perform an experiment which is known to give a peculiar result with several liquid crystals: I placed a little lens in a drop of the liquid. On oscillating this lens one observes, between crossed nicols, sectors which have become double refracting; one never observes the appearance of coloured rings, as crystalline matter sometimes shows. If the lens is rotated by hand a few times in the liquid, there appear four light quadrants (blurred in outline) and a distinct dark cross, the arms of which are horizontal and vertical. When the gypsum plate is inserted, the image is even more beautiful: the first and third quadrants become yellow, the second and fourth, blue, and between them the cross is red.

I was then led to an experiment that is comparable to the well-known one of J. C. MAXWELL, and which was afterwards studied especially by KUNDT and his students, and since then has been worked on by a great number of researchers, i.e. double refraction which appears in a liquid placed between rotating cylinders.

This is very easily done in this case: one places a metal ring of about 5 mm height in the hollow of a flat microscopic cubicle, formed by glueing a slide with a circular hole onto an ordinary slide. If one places a drop of the liquid inside and outside the ring, forming a layer of about 0.5 mm or less, and then turns the metal ring around a few times with the fingers, one observes double refraction both inside and outside the ring. When a gypsum plate red first order is inserted, quadrants are formed which are blue and yellow in pairs. Herein the arms of the cross are vertical and horizontal, and the colours inside and outside the ring are the same in the corresponding quadrants.

I must draw attention to the fact that if one performs the original experiment of MAXWELL-KUNDT in a similar manner, as for instance with castor oil, for which naturally a pair of cylinders of a few centimeters in height is necessary in place of the metal ring, one sees quite another image. The arms of the cross will appear at an angle of 45°, and the colours inside and outside the ring will be in opposition. This I shall return to presently.

Another remarkable property of the liquid is the following: If one heats the almost completely clear solution of the acid cadmium salt, it becomes cloudy at a temperature of about 60°; with further heating it turns completely white; an amorphous precipitate is being formed. This dissolves

on cooling, and a completely clear liquid is formed. This liquid does not show anything in the above described experiment. The phenomena take place again, however, when the liquid is cooled again to a temperature of less than 45°C.

If one continues the cooling in a capillary under the microscope with crossed nicols and a gypsum plate, one observes in the beginning an opaque, amorphous, very fine precipitate. Gradually on cooling, this becomes transparent. It is then, viewed with crossed nicols and a gypsum plate, yellowish, but there is no double refraction visible; the precipitate has a depolarizing effect. On further cooling the liquid becomes completely clear, and does not show double refraction anywhere.

Lowering the temperature still further, one gradually observes the appearance of colours, which may become extremely bright after some time. There is, however, no question of coloured *bands*. If the capillary is lying under an angle of 45° or of 135° one observes a blue or a yellow colour advancing slowly in the capillary, and becoming brighter: usually this colouration starts from both menisci, but not always. In the horizontal position the phenomenon is much more remarkable; one usually observes in the right half a synchronous advancing of a blue upper half and a yellow lower half. They are separated by a red — viz. neutral — region. In the left half, one observes the opposite. These two figures meet each other, but stay separated by a red transverse band. Especially if a short drop has been placed in the capillary, there appears a remarkable image, which reminds one of a coat of arm with four fields (écartelé).

I wish to indicate here directly that it is also possible to obtain this same optical phenomenon with gelatin. When one lets gelatin congeal in a glass tube — not a capillary in this case — there occurs no double refraction unless one increases or decreases the pressure of the air in the tube from one side (this can be done with rubber nipples). In this case a colouration will be seen similar to that described above, and one may displace the coloured part at will by changing the air pressure.

If one applies this last mentioned treatment to the cadmium salt solution which has first been made isotropic and then cooled, one sees something similar, and one may even observe a resiliency which brings to mind quite definitely the experiment with gelatin. There is no doubt that the cooled liquid has turned into a gel. However, extreme care is necessary herewith, because if one presses or sucks a little too strongly the entire mass begins to move, a flow is started, and the regularity of the colour distribution is partly destroyed.

Again there occur coloured transverse bands, yellow and red ones or blue and red ones alternating. If for instance a slight pressure is exerted towards the right, then these layers are curved to the right; in the upper half of the capillary they are yellow, in the lower half, blue. If the pressure is exerted towards the other side, everything is reversed, and in

between these two there is a position of the layers where the situation exists as previously described.

Herewith I have returned to the starting point, and must now describe how the originally observed phenomenon begins. I observed that it did not occur by treating the liquid carefully. It became apparent to me that quite drastic destruction of the equilibrium is favourable. The coloured bands are best made visible as follows: after one has sucked a little of the liquid into the capillary, one removes the capillary from the liquid. Next one sucks and blows the drop in the capillary a few times back and forth. Once is really enough, but the quicker the motion the more beautiful the results. A certain speed is best obtained after a few repetitions. If one places the capillary under the microscope at an angle of 45°, using crossed nicols and a gypsum plate, one observes that the layer at the wall which is retained where the drop has passed, has a beautiful blue colour. In the drop itself there is little to be observed in this position. When the capillary is placed horizontally under the microscope, one does not see anything special in the layer at the wall in the beginning. But soon there occurs in this layer the first indication of the formation of bands. In the beginning they are only slightly coloured, but bradually the colours become clearer and after a few minutes they are intense. Here I should like to indicate that the bands usually do not form complete rounds, but if they do, the colour is nicest at the lower side of the capillary. At the same time one sees the beginning of a very slow displacement of the bands. They become most clear when the layer of liquid thickens because of the action of surface tension, in which case the bands sometimes displace very rapidly. If both thickened parts of the layer at the wall come so close together as to unite into one drop bordered by two concave menisci, no bands are visible, but a "coat of arms" can be seen, with two yellow and two blue fields, which are now, however, the inverted images of the coat of arms described before. Close observation shows that these fields are not regularly made up; they are striped, and there are sometimes red or blue spots in a yellow field, and red and yellow ones in a blue field.

At times the larger drops, after being sucked and blown back and forth, show beautiful regular bands, but often they are irregular — they are seldom as beautiful as they are in the layer at the wall, although this may be the case occasionally. I have tried to ascertain whether the layers lie deep in the liquid. It is certain that they do not form transverse partitions; if one rotates the capillary, the image changes. Mostly there appear to be broken layers. Quite often they are only slightly thicker than the layer at the wall; this may be interpreted from the interference colours which are slightly higher sometimes than those in the layer at the wall.

Concerning the thickness of the layer at the wall in which the phenomenon takes place so beautifully, I have found the thickness of this layer by weighing the liquid retained by the wall and by measuring the diameter of the capillary. This thickness amounted to about 0.05 mm = 50 μ. If one

takes into consideration that the interference colour between crossed nicols (without gypsum plate) is usually grey first order, then this leads, roughly to a value of the product

$$d(n_1—n_2) \text{ of about } 0.1\ \mu.$$

This means a value of

$$n_1—n_2 = 0.002.$$

As a comparison let it be stated that the difference between both indices of refraction of the effective index ellipse for a gypsum plate amounts to 0.009.

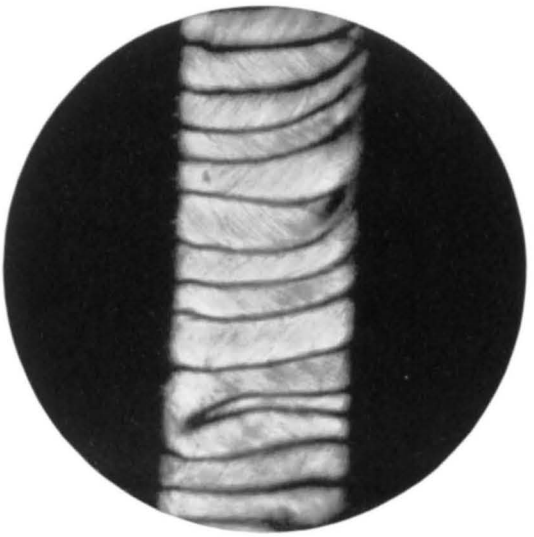
If a wall layer in which the bands are forming regularly, i.e. usually on a place where the layer shows little or no thickening, is left quietly to itself, then a striation becomes visible after five to ten minutes, which eventually becomes very pronounced. We refer here to figure 1 and 2 on Plate II. Viewing these striae superficially, it seems as if only the yellow and blue bands are striated, the yellow ones from the left top to the right bottom, and the blue ones from right top to left bottom. Observing more closely, however, one sees that the striae curve at the edge of the band, where the colour changes into red. Especially without the red first order plate does the real nature become clear, and it is better still if *in this stage of the experiment* one makes his observations with slanting illumination, without the use of nicols. (In earlier stages of the experiment one sees scarcely any structure in the wall layer without the use of nicols). It appears thus that the striations are parts of a system of parallel sinusoids, which may be present very regularly over fairly big distances in the capillary; one must necessarily conclude that these sinusoids are lying closely packed against the inner wall of the capillary. In reality, therefore, these curves are not lying on a flat plane, and may thus not be called sinusoids; the amplitude is relatively small, however, as compared with the diameter of the capillary.

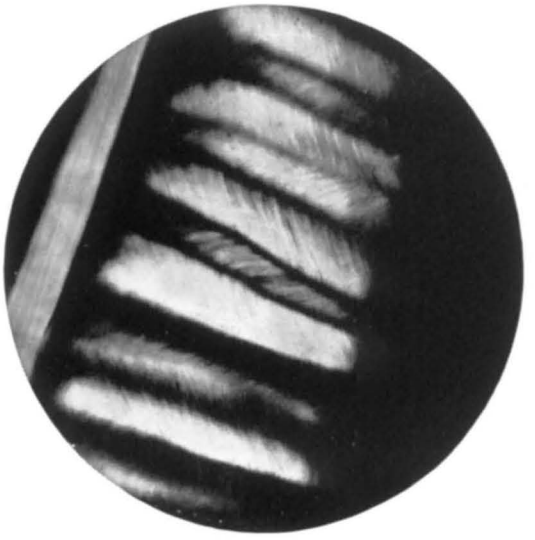
Once this observation was made it could be determined that the sinusoids possess very small amplitudes, shortly after the wall layer has been formed by the motion back and forth, but that these amplitudes increase after the liquid has been left to itself.

The striking phenomenon of the band formation can herewith be explained. Assuming that double refracting long stretched particles are aligned by the flow, which particles behave as double refracting crystalline needles with the largest axis of the index ellipsoid in the direction of the needle and supposing that these particles arrange themselves along parallel sinusoids when the flow has stopped, then all colour appearances such as described for the liquid in the capillary, become readily explainable. One has only to put a sinusoid (cut from paper) to the plate I, to understand it. Moreover, it is now apparent that the appearances are not always the same, since they depend on the amplitude and the wave length of the

PLATE II.

OBSERVATIONS BETWEEN CROSSED NICOLS.





Figures 1 and 2. Band formation in the wall layer of a capillary, after sucking through of a solution of the acid cadmium salt of phospho-glyceric acid. Especially fig. 2 shows the "striation" of the bands. 40 times enlarged.

Figure 3. Formation of bands after smearing out of a sol of benzo-purpurine 4B on a slide. 60 times enlarged (observ. between crossed nicols).

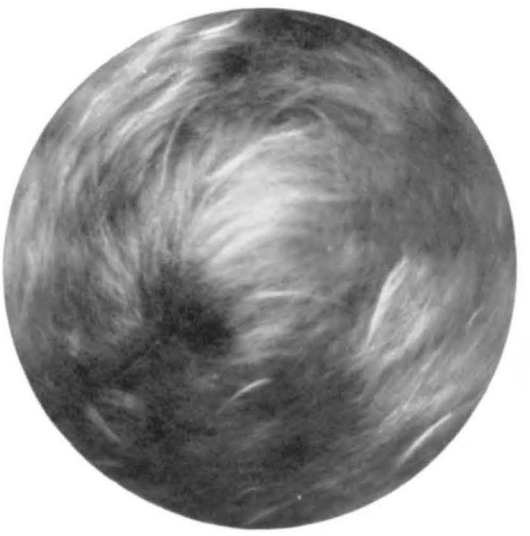


Figure 4. Fibres built up of fibrillae in a solution of the acid cadmium salt of phospho-glyceric acid. 60 times enlarged (dark field illumination).

sinusoids. Often these are in such a way that the sinusoid intersects with its x-axis under angles of about 45° and 135°, and in this case colours will be observed as illustrated by our plate. Sometimes, however, the amplitudes are such that these angles are approximately 60° and 120°. The image then changes; the coloration to be expected can always be foretold from the course of the sinusoids. Before I consider the theoretical side of the problem, let me describe a few more experiments.

Firstly, one can introduce a little glass rod into the capillary, the diameter of which differs only slightly from that of the capillary. Moving the rod quickly back and forth for a short time and then allowing the liquid to come to rest, one observes exactly the same phenomenon as described above for the wall layer. It follows that no free liquid surface is required to produce the appearance of the double refracting particles aligned along sinusoids.

With this experimental set-up one may repeat also the experiment of MAXWELL-KUNDT in a different way, namely by rotating the glass rod in the capillary quickly, with the fingers. If one does this with the capillary in the horizontal position under the microscope, then the liquid during the rotation has the colour of the rest of the field i.e. red first order; the particles align themselves along the lines of flow, which are vertically situated in this case. If one lets the liquid come to rest, one observes the appearance of bands, which in this case, however, are situated longitudinally in the capillary, wide yellow, narrow red, and wide blue bands alternating regularly. Parallel sinusoids are thus formed which progress along with their x-axis around the glass bar. Here it is more obvious still that the curves are not real sinusoids.

After the cause of the phenomenon in the capillary was ascertained, I tried to obtain similar bands by quickly rubbing the liquid with a small rod on a slide, and this succeeded also, the bands, however, being not so nicely shaped. The experiment had better results when a rather thick layer of liquid was let to flow along the slide, and then left to itself. These experiments proved to be of importance because they admitted dark field illumination, wherewith it appeared that the liquid showed initially a general TYNDALL effect only, but that with the formation of the sinusoids an image appeared which became gradually clearer, until finally beautiful sinusoids could be seen.

It is of interest, that the structure of the bands became macroscopically visible in these thick layers which had flowed along the slide, after the liquid had rested a long time and after some of the water had evaporated out of it. By rotating the slide one observed even a "moiré-design" which without doubt has something to do with the opposedly aligned situation in these successive bands.

As I shall describe more elaborately in another publication, I have since observed that the inclination of double refracting particles to arrange themselves along parallel sinusoids is not absolutely restricted to the

solution of the acid cadmium salt of phospho-glyceric acid. I have been able to observe this property quite well in a capillary, using a sol of benzopurpurine 4B, which I prepared according to a method indicated by H. ZOCHER [1]). The bands are here much narrower, (in a capillary with an internal diameter of 1.15 mm the wave-length of the sinusoids was approximately 170 μ). With this solution I succeeded quite well in producing bands (alignment along parallel sinusoids) in a liquid layer, by smearing this layer between two slides and removing the top slide. On drying out layers thus prepared, these bands remain, and the very beautiful striation appears therein as described above for the experiment in the capillary. The parallel sinusoids can clearly be observed and followed in this manner, especially with the polarization microscope. It is even possible to fix a cover glass on such a dry prepared slide with Canada balsam, and to make a permanent microscopic record in this manner [2]). Figure 3 of Plate II has been prepared after such a „Dauerpraeparat".

This smear experiment succeeded also with an aged sol of vanadium pentoxide, but the sinusoids were not so nicely formed.

I put on record that the real nature of this phenomenon becomes much clearer with the study of the colourless solution of NEUBERG, than of the coloured sols.

With reference to the cause of the described phenomena, I should like to make a few remarks.

That the lines of the cross in the experiment of MAXWELL-KUNDT with the solution of the acid cadmium salt are horizontal and vertical may possibly be explained by assuming that we are dealing here with a liquid which possesses a very great elasticity (a small coefficient of elasticity). TH. SCHWEDOFF [3]) introduced this assumption as early as 1892, to explain why KUNDT found the cross of a collodium solution under angles which clearly deviated from 45° and 135°. Indeed, SCHWEDOFF and several other investigators found that various solutions (they are really lyophilic sols) possess a marked elasticity [4]).

It is indeed interesting that the solution of the acid cadmium salt possesses a very pronounced elasticity. The little lens rotated by hand in the above described experiment appeared for instance to be pulled back in the reverse direction after being released.

Still, it is my opinion that the deviating position of the cross is due here

---

1) Ueber freiwillige Strukturbildung in Solen, Zt. f. anorg. u. allgem. Chem. **147**, 1925, p. 92 en 93.

2) We remark here, by the way, that such a preparation acts as a grating, and that a refraction spectrum may be produced therewith analogue HERINGA's observations of a longitudinal cut of a tendon (these Transactions **35**, 1926, p. 763).

3) Sur une anomalie dans la réfraction double des liquides, J. d. phys. 3e ser., **1**, 49—52, 1892.

4) We refer here to H. FREUNDLICH's Kapillarchemie, 4, Aufl., 2. Bd., p. 312—317, 1932.

to another cause, and that with the said solution, as well as with the solution of wax and resin in toluene of R. REIGER [1]), the optical relaxation takes a much longer time than the mechanical relaxation. In the experiment with the little lens a double refraction does not change even after twenty-four hours, while it is not reasonable to assume that the mechanical recovery has not finished for the greater part by that time.

This reasoning leads us also, (as it did REIGER for his solution), to assume that the liquid is non-homogeneous. The formation of the striations in the liquid also point in that direction. The position of the cross will then be due to the alignment of long stretched double refracting particles in the direction of the lines of flow. We recall here how such an aligning influence has also been assumed by other observers [2]) for the explanation of deviating positions of the cross.

We state further that the position of the cross cannot be explained by assuming that our solution behaves like a rigid gel, in which, on its being distorted, stresses are produced. In that case the cross would take the position as in the case of ricinus oil (many homogeneous liquids behave this way [3]). As I have observed before, the homogeneous liquid, obtained by heating, congeals and becomes a gel, but this gel is extremely fragile. The phenomena which we described are exclusively to be observed when this gel is changed into a sol by shaking or stirring. May it be remarked also that the solution appears to be thixotropic; one or two days after having been stirred, it changes back into a gel.

The idea that a non-homogeneity exists is also confirmed by the fact that if the solution is kept standing for quite a time, a white silky precipitate becomes visible which shows the phenomenon of „schlieren". There appear to have formed threads, which are double refracting, very pliable, and therefore often bent in many places. These threads are of various thicknesses; the maximum thickness I observed was 8 μ. On first sight they resemble pliable crystals, but appear to be made up out of a very great number of very thin fibrillae, of which the thickness could only be estimated (0.2 μ to 0.3 μ), and the length of which may be as long as the threads, viz. indefinitely long. A slight pressure on the threads make them fall apart into these fibrillae and an image is produced which reminds one of a cellulose fibre falling apart into its fibrillae [4]). I have given an illustration of this case in figure 4 on Plate II.

---

[1]) Ueb. optische u. mechanische Relaxationszeit, Ann. d. Phys. **336**, 93—97, 1910.

[2]) For instance H. ZOCHER, Ueber Sole mit nichtkugeligen Teilen, Zt. f. physik. Chem. **98**, 293—337, 1921 and specially H. FREUNDLICH, H. NEUKIRCHER u. H. ZOCHER, Ueb. die Elast. u. die Strömungsdoppelbrechung in Solen mit nichtkugeligen Teilchen I en II, Koll. Ztf. **38**, 43—54, 1926.

[3]) This may be shown also with a nice experiment of *B. Zopfii*, using the method according to H. JACOBSEN 1907.

[4]) See for instance my lecture "De wording van den plantaardigen celwand" Chem. Weekblad **24**, 166—187, 1927.

On the grounds of what I have described here and of further observations (among others, ultra-microscopic) which I hope to publish later on, I have come to the conclusion that the solution of the acid cadmium salt is a sol which has a tendency to spontaneous directed coagulation, the direction of which may be furthered by mechanical influence[1]). We leave open the question whether the observed fibrillae must be considered as extremely soft crystals (as for instance di-iodium-acetylen or nitron-oxalate) or that we are dealing with liquid crystalline matter, in one of the 18 meso-morphous states, which according to the theory of C. HERMANN[2]) must be supposed to exist between the non-ordered liquid and the real crystalline state.

When one sucks the solution through the capillary, or rubs it with a slide, these long, thin, sub-microscopic double refracting particles arrange themselves along each other. The subsequent contraction to sinusoids must supposedly be ascribed to the elasticity of the sol. I am not able to explain at this instant why completely regular parallel sinusoids are produced just here. It is not impossible that the typical sinusoidlike flow, which OSBORN REYNOLDS observed immediately after its surpassing the critical velocity in a liquid, plays a role here, especially since E. N. DA C. ANDRADE and J. W. LEWIS[3]) found that the critical velocity is less in a non-homogeneous liquid than in a homogeneous one. May be weakly undulating sinusoids formed by the flow are changed to more strongly undulating ones by the contraction of the liquid.

Finally, I should like to state here that it is my opinion that the here described tendency to form sinusoids during the coagulation of a sol shall prove to be of great significance for the explanation of structures in the plant and animal kingdoms. I hope to elucidate this in another publication, but will mention here as an example how figure 3 Plate II is practically completely identical with figure 143 of W. J. SCHMIDT's Die Bausteine des Tierkörpers, 1924, which figure represents a cross cut of a layer of connective tissue of the skin of a tortoise. The description added by SCHMIDT about the polarization colours makes the agreement still more striking.

It is my conviction that the phenomena which we have dealt with here will also throw light on, among others, the well-known interesting observations of G. C. HERINGA on the structure of the tendon (these Transactions 1926), on the much argued structure of animal hair (the sinusoids of sheep hair, for example), and on the coagulation of fibrin.

---

[1]) Vide H. FREUNDLICH, Ueber eine neue Art von Koagulation, Die Naturwiss. **14**, 1206—1208, 1926.

[2]) Die Symmetriegruppen der amorphen und mesomorphen Phasen, Zt. f. Krist. **79**, 186—222. 1931.

[3]) Ueb. das hydrodyn. Verh. von Ammoniumoleat-Lösungen, Koll. Zt. **38**, 260—261, 1926.