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# Observations on the Solidification of Paraffin

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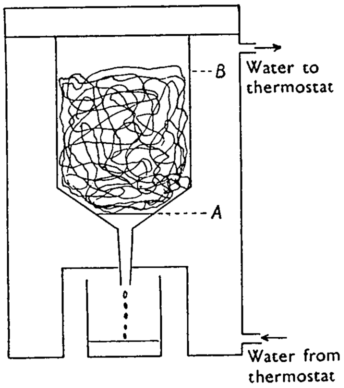
Solidification of macrocrystalline refined paraffin, M.P. 54·5 °C. was studied in a hot stage Kofler microscope provided with Foucault–Toepler 'Schlieren' illumination. A hot plate designed by one of the authors was also used. Other samples were observed, such as fractions of the original sample, obtained by sweating or by crystallization with urea; also several mixtures. Room temperature examination was completed under a usual polarizing microscope. Results and conclusions are in good agreement with those by Rhodes, Mason & Sutton (1927). Other details are presented related to the structure of paraffin; the discussion gives strong evidence for the belief that paraffin solidifies from melt in a smectic phase.

The often remarkable features of the solid phase of waxes, fats and related substances have been investigated from time to time, as a resource for identification, detection of frauds, or better understanding of transition phenomena and structural properties; see papers by Padget *et al.* (1926), Rhodes *et al.* (1927), Watson (1931), Mehlenbacher (1936), Taub & Zweig (1939), Hessler (1953) and many others. As a preliminary step for studying the solid phase of vegetable waxes, we decided to observe the solidification of paraffin, the composition of which is simpler than that of the vegetable waxes, but somewhat related, as some paraffins are natural components of waxes, such as carnauba and licuri (ouricuri). The observations completed up to now are described in this paper, including the evidence of the smectic phase formed when molten paraffin wax is cooled. G. Friedel (1922) suggested such a possibility in waxes when he wrote: 'Homoeotropy is not a phenomenon restricted to smectic substances. It is also found in nematic ones, and in certain soft materials that seem to be crystalline, as beeswax and ozokerite. These, indeed, show a structure so fine and confuse that it is difficult to say if they are smectic or, as it is more probable, crystallized'. Also Rhodes, Mason & Sutton (1927) foresaw the connection between paraffin and 'liquid crystals' when they wrote: 'The transition from plates to needles is certainly more than a simple alteration of habitus or a change in the relative development of the various crystallographic faces, such as is exhibited by many substances. It is probably more or less closely related to the behaviour of "plastic" or "liquid" crystals'.

## Material and methods

The investigation was carried out with a Kofler (hot stage) microscope. Some devices were adapted in order to obtain the 'Schlieren' effect (Zocher & Machado, not publ.), resulting in better visibility of details, the refractive index of which was little different from that of the surrounding medium, and also showing immediately where was the higher index. The samples were placed between slide and cover glass, and observed during melting and solidification at a magnification ×100. Heating and cooling were suitably controled. In certain cases uncovered samples were observed in order to follow the formation of surface wrinkles, using a hot stage designed by Machado (1957) and made at the Instituto de Óleos. In many cases examination was completely carried out at room temperature, in a polarizing microscope. The initial sample was a commercial macrocrystalline refined paraffin, melting at 54·5 °C. Narrower portions were isolated by sweating, or by the urea process as described by Hessler & Meinhardt (1953), which separates normal from branched paraffins. Urea forms hexagonal crystals with paraffin (Schlenck's *adducts*) in which very fine tubes containing the paraffin are parallel to the optic axis. When these adducts are examined between slide and cover-glass in the polarizing microscope, and water is allowed to penetrate, urea is rapidly dissolved, liberating fibrillar masses of paraffin which show positive birefringence, the highest refractive index corresponding to light vibrating in a plane parallel to the length of the fibrils. This behavior is the opposite to that usually shown in elongated forms found in paraffins, fats and waxes, and results from the obligatory position of paraffin molecules in the adducts' tubules, with their length parallel to the length of the tubules. However, if alcohol–water (equal parts of each, approximately) is allowed to penetrate, instead of pure water, the fibrils show *negative* birefringence, probably because, retaining a relative mobility, as a result of slight solubility in alcohol, they are able to arrange themselves in accordance with their normal tendency when they are liberated from the adduct.

Sweating was accomplished in the device shown in Text Fig. 1 which is essentially a metal funnel surrounded by a water jacket. Water circulated continuously, passing through a precision thermostat bath. For filling the funnel, water was first poured



Text Fig. 1. Device for the sweating of paraffin.

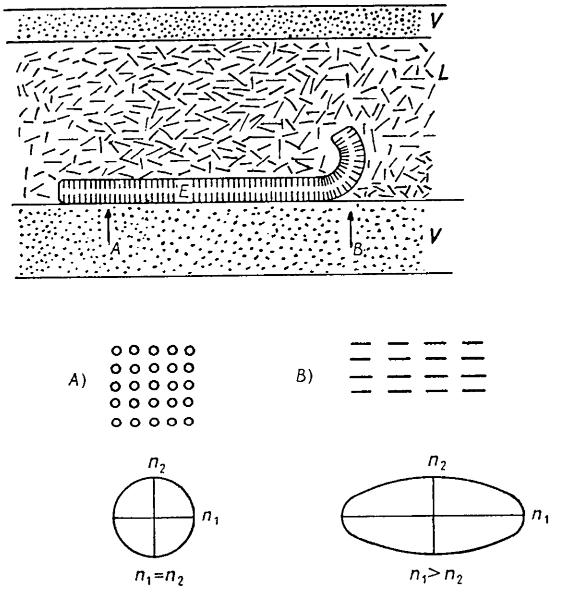
up to level *A*, then the remaining space was filled with steel wool and the molten paraffin was poured up to level *B*. Steel wool provides better heat conduction and facilitates the flowing of the sweated part. The following fractions were obtained from the initial sample:

| *T* °C. | *g* | % |
|---|---|---|
| 50 | 11·45 | 9·0 |
| 51 | 5·15 | 4·0 |
| 52 | 8·50 | 6·7 |
| 53 | 9·30 | 7·3 |
| 54 | 16·50 | 13·0 |
| 55 | 9·40 | 7·4 |
| 56 | 18·15 | 14·3 |
| 57 | 12·30 | 9·7 |
| 58 | 8·35 | 6·5 |
| 59 | 6·95 | 5·5 |
| 60 | 8·90 | 7·0 |
| Residue | 12·10 | 9·5 |

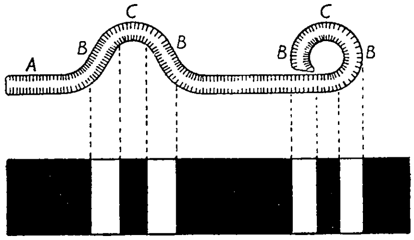
60% of the material melts above the melting point of the whole sample, in accordance with the fact that the melting point of a heterogeneous substance is the lowest temperature at which the lower fractions dissolve completely the higher ones.

## Results and conclusions

Under the polarizing microscope, between crossed polarizers, solid paraffin in a thin layer is seen as a network of birefringent needles or bands, limiting dark, apparently isotropic, spaces (Fig. 1, Plate 4). With natural light, one sees that such spaces are filled with solid paraffin. With convergent light, crossed polarizers, they behave as positive uniaxial structures with the optic axis parallel to the axis of the microscope. Sometimes the thickness increases by curved line steps, a structure known to appear in smectic phases and called 'gouttes à gradins' by Grandjean (Fig. 4, Plate 4). The same is observed on the surface of air bubbles in some slides (Fig. 17, Plate 5). The so-called needles often form a network with polygonal contours (Figs. 1, Plate 4 and 22, Plate 6). but they do not look like true needle shaped crystals. Indeed these false needles can be markedly curved, or can be divided lengthwise by a dark median band (Fig. 1, Plate 4), as is to be expected in the folds or rolls of an uniaxial plate (Text Figs. 2 and 3). The sign of the birefringence of the false needles is negative, the electric vector of the light vibrating perpendicularly to the length of the needle which is the direction of the higher refractive index. It follows that the long-chain paraffin molecules are arranged transversely in the false needles. This fact is opposed to the implication contained in Hessler's statement (1953) that in the solidification of waxes needles would be determined by the shape of the molecules.



Text Fig. 2. Formation of a smectic plate (*E*) in melted (*L*) paraffin, between slide and cover-glass (*V*). At (*A*) where the long chain molecules are arranged perpendicularly to the glass-paraffin interface, the plate displays isotropic behavior because it is uniaxial positive with the optical axis parallel to the axis of the microscope. At (*B*), where the margin rolls up, birefringence appears because the molecules (and the optical axis) are inclined or perpendicular to the axis of the microscope.



Text Fig. 3. Folds or rolls of smectic plates cause birefringence in double bands, as is frequently observed.

With the analyzer removed it can be seen that the socalled needles disappear completely when their length is parallel to the vibration of the electric vector of the light (Figs. 2, 3, Plate 4). This shows that the

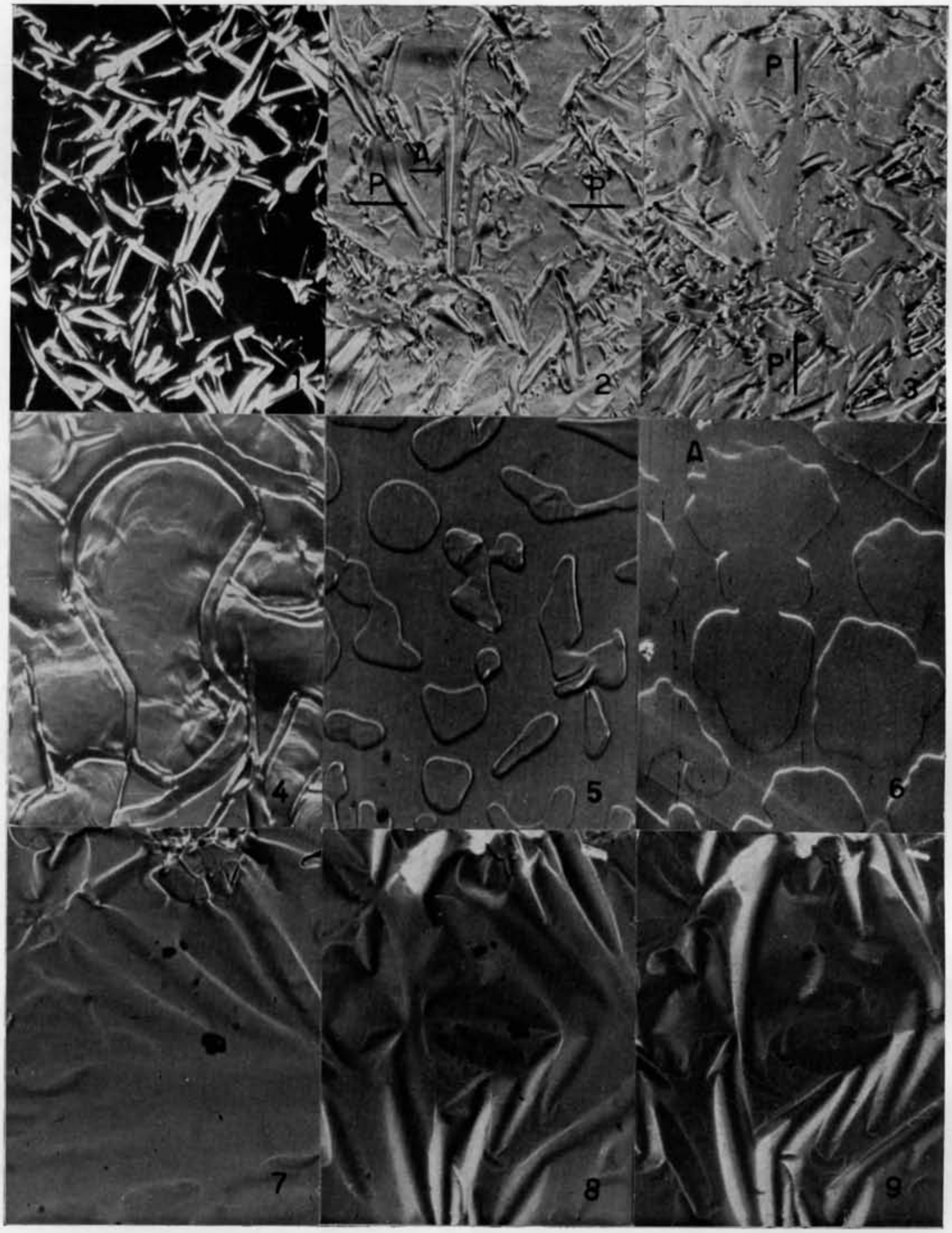


Fig. 1. Common aspect of paraffin solidified in a thin layer between slide and cover-glass. Notice that the bright bands are frequently double. Crossed polarizers. 150×. Figs. 2 and 3. Paraffin solidified between slide and cover-glass, examined at room temperature under a microscope with 'Schlieren' illumination and one polarizer. The same field is seen in two positions *PP'* of the polarizer. A fold (*A*) disappears completely when the light vibrates following its length. 130×. Fig. 4. Area showing curved line steps known to appear in smectic phases, as in the 'gouttes à gradins' of Grandjean. 'Schlieren' illumination. 130×. Fig. 5. Round smectic plates beginning to form when melted paraffin is cooled. 'Schlieren' illumination, 200×. Fig. 6. Round plates grow and coalesce. In certain places the contour is undulated because the plate wets the slide (*A*). 'Schlieren' illumination, 200×. Figs. 7, 8 and 9. Successive steps in the cooling of paraffin in a hot stage of very uniform temperature (9). Wrinkles appear and grow, showing birefringence in the inclined surfaces. Polarizers not completely crossed. 150×.

refractive index parallel to the needle length is the same as that of the adjoining intervals, thus strengthening the idea that the 'needles' are not isolated objects but foldings or rollings of the plates that also cover the adjoining space. Isotropic behavior results when the molecules are parallel to the microscope axis, and birefringence appears in those places where they are inclined or perpendicular to it (Text Figs. 2 and 3). Paraffin-glass or paraffin-air interfaces have a bearing on the arrangement of the molecules perpendicular to the surface in question. Solidifying paraffin seems to be easily oriented by external influences. An example is presented in Fig. 27, Plate 6, where the intergrowth of beta-naphthol crystals and paraffin platelets is to be seen. The latter show parallel extinction.

Let us follow, now, with Foucault–Toepler ('Schlieren') illumination the cooling of molten paraffin in a thin layer, between slide and cover-glass, in the hot stage of a Kofler microscope. When only the liquid phase exists, the field is, of course, homogeneous. As cooling slowly proceeds, round plates appear lying flat on the slide (Fig. 5, Plate 4). Because their refractive index is only slightly higher than that of the molten paraffin, they are scarcely visible with common illumination, but are clearly brought out by the method referred to above. They are uniaxial positive, displaying isotropic behavior because their optical axes are parallel to the axis of the microscope. The mobility of these plates (movements by growing and by flowing) as well as their coalescence (Fig. 6, Plate 4) demonstrate that they are a smectic phase, and their optical behavior shows that the paraffin molecules are arranged as illustrated in Text Fig. 2. The mobility referred to is the one characteristic of smectic phases, which behave as a liquid in the directions contained in the plane perpendicular to the optic axis, and as a solid in the direction of this axis. The borders of these plates tend to roll up (Figs. 15, 19, 21, Plate 5 and 6) and also folds may appear (Figs. 7, 8, 9, 10, 11, 12, Plate 4 and 5) showing the expected birefringence. Between crossed polarizers these formations may simulate needles (Figs. 1, 20, 22, Plate 4 and 6). The micrographs composing Figs. 7, 8, 9, Plate 4, illustrate the progressive accentuation of surface wrinkles, as observed in an uncovered preparation of paraffin cooled slowly in the hot stage designed by Machado (1957), which provides uniformity of internal temperature better than Kofler's. Figs. 13, 14, 15, (Plate 5), show the growth of a pseudo-isotropic smectic plate. In the last picture two borders are already rolled up. Immediately above, another plate is seen as a narrow band, because it is in a transverse position, its optical axis being perpendicular to the microscope axis. The tip of this plate has rolled up around an axis perpendicular to the plane of the figure. Other very thin needle-like plates, curved or twisted, may be seen, some of them beginning to grow from the molten paraffin.

Cooling rate, uniformity of temperature, sample composition, impurities or intentional mixtures bear influence upon the rolling up and folding of the plates. On one and the same slide, areas can be found with few rolled up edges, even after several successive meltings and solidifications, whereas other areas show frequent rolling up (Fig. 19, Plate 6). The birefringence of the rolled-up edges is in accordance with Text Fig. 2. The higher index is perpendicular to the axis of rolling. Figs. 17 and 18 (Plate 5) show plates that grew with their optical axis perpendicular to the microscope axis, and formed relatively wide birefringent bands, easily curved around axes perpendicular to the figure. In Fig. 18 (Plate 5) one of these plates can be seen with both ends semicircular.

It is a fair assumption that in the beginning of their formation, the plates are formed by molecules of the higher melting component. When these become scarce, the apposition of the molecules of a lower component takes place and the plate starts to roll up, probably owing to a variation in the interfacial tension.

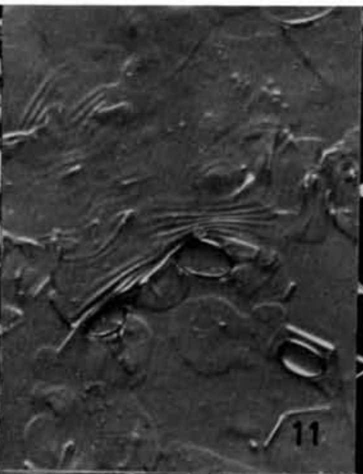
Figs. 23, 24 (Plate 6) show the same field with 'Schlieren' illumination and between crossed polarizers, respectively. The dark spaces with isotropic behavior (Fig. 24, Plate 6) are seen to be filled with solid paraffin (Fig. 23, Plate 6) and correspond to plates with the optical axis parallel to the microscope axis. The birefringent bands (Fig. 24, Plate 6) are plates with the optical axis perpendicular to the microscope axis, and they show remarkable curves, one of which is a closed ring. Fig. 25, (Plate 6) illustrates how heating paraffin with sulfuric acid brought about the formation of many closed rings.

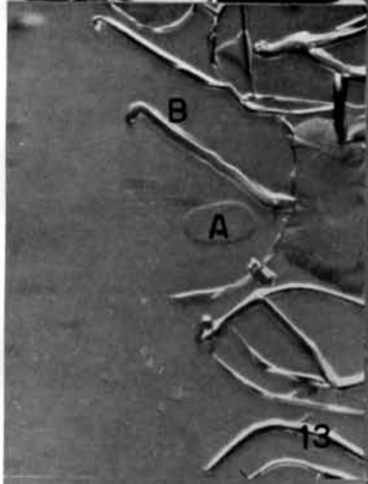
The rolling or incurving as described corresponds to the *divergency* of smectic phases (Zocher & Jacobowitz, 1933).

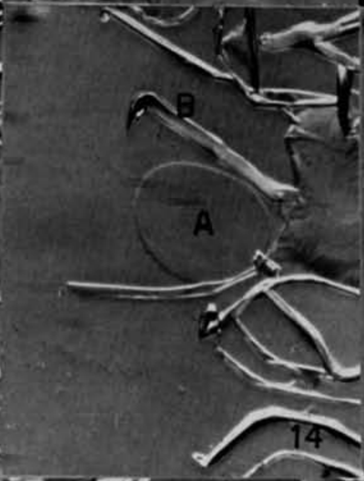
After cooling to room temperature, these aspects remain apparently unchanged under the microscope, suggesting that paraffin solidified from melt is a smectic phase. It should be borne in mind, however, that the possibility of submicroscopic crystallization in pseudo-morphosis exists, and this could only be established by the electron microscope, or X-ray diffraction.

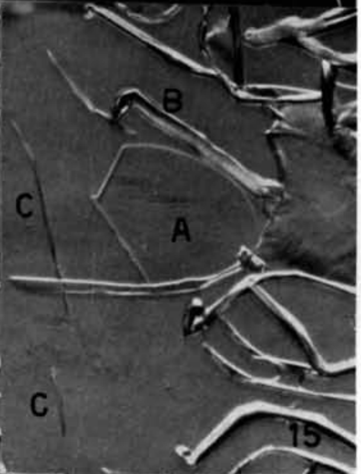
As has already been pointed out, in cooling molten paraffin, needle-like forms may appear before, or together with, the plates. They present, however, the same optical properties as the plates, and not those that would correspond to true crystalline needles. In some instances the false needles are plates that roll up very early, as may be inferred from Fig. 26, Plate 6, where some of those 'needles' are not completely rolled up. The rolling up seems, also, to be related to the available energy of deformation. Repeated partial melting and slow cooling, lessen the rolling tendency. In other instances, the needle-like forms seem to be very thin twisted plates, with the optical axis in various positions (Fig. 16, Plate 5).

In order to study the variations of aspect in the solid phase of paraffin, several mixtures or treatments









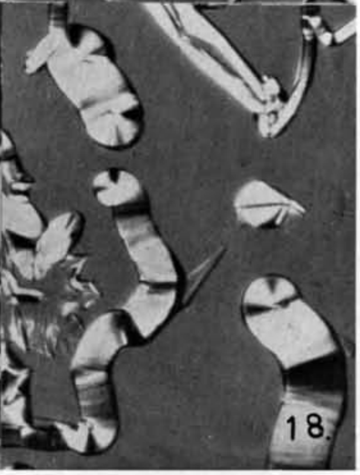
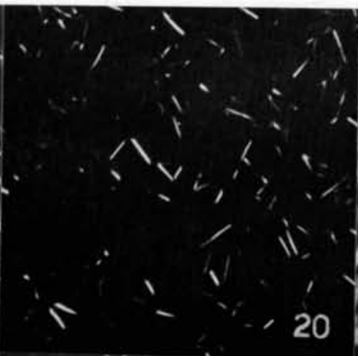
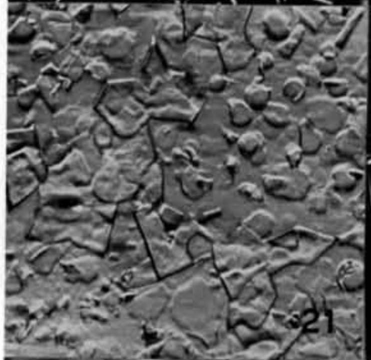
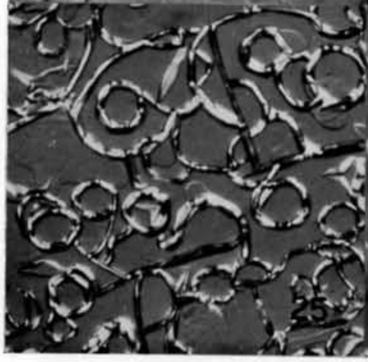
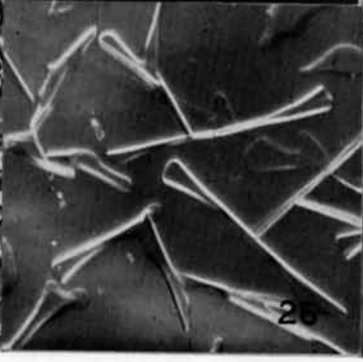


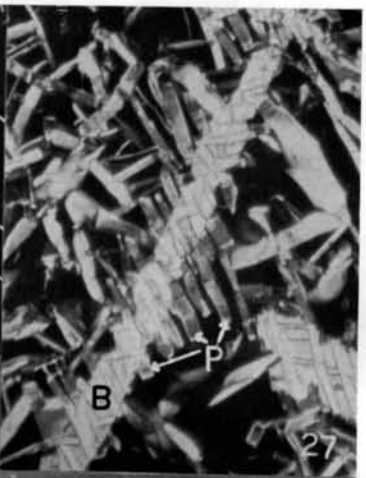
Fig. 10. Mixture of paraffin and guta-percha showing a great number of folds. Crossed polarizers. 130 ×. Figs. 11 and 12. Mixture of paraffin and rubber with 'Schlieren' illumination (Fig. 11) and between crossed polarizers (Fig. 12), showing the correspondence between folds and birefringence. 130 ×. Figs. 13, 14 and 15. Successive steps in a solidifying front of paraffin. A pseudo-isotropic smectic plate grows (*A*) and its margin rolls up in two places. Its optical axis is perpendicular to the plane of the figure, and the borders roll around axes parallel to the figure. Another plate is seen (*B*) which has the optical axis parallel to the plane of the figure, and its extremity rolls up around an axis perpendicular to the figure. Other plates, including some twisted acicular ones (*C*) begin to form in the mass of liquid paraffin. 'Schlieren' illumination. 130 ×. Fig. 16. A solidifying front in paraffin, with predomination of fine acicular twisted plates. 'Schlieren' illumination. 130 ×. Fig. 17. Well developed plate with the optical axis parallel to the slide (and to the plane of the figure), rolling up around axes perpendicular to the figure (and parallel to the microscope axis). At left, some air spaces showing curved steps. 'Schlieren' illumination; polarizers partially crossed. 300 ×. Fig. 18. Normal fraction of paraffin, separated with urea (10). Plates similar to those shown in Fig. 17 but better developed, with semicircular ends. 'Schlieren' illumination; polarizers partially crossed. 130 ×

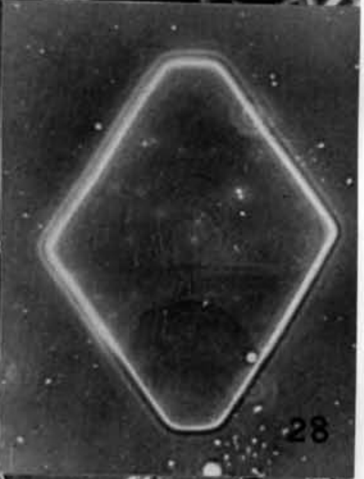












Figs. 19 and 20. Pseudo-isotropic plates with rolled-up margins, 'Schlieren' illumination; polarizers partially crossed (Fig. 19) and crossed (Fig. 20), showing how the birefringence of the rolled up borders simulate needles. 180×. Figs. 21 and 22. Mixture of paraffin and silicone (High Vacuum Dow Corning Grease) with 'Schlieren' illumination (Fig. 21) and between crossed polarizers (Fig. 22). 130×. Figs. 23 and 24. Saponified paraffin with 'Schlieren' illumination (Fig. 23) and between crossed polarizers (Fig. 24). Plates with the optical axis parallel to the plane of the figure show birefringence, and one is a closed ring. The intervals are filled with paraffin with the optical axis perpendicular to the figure, displaying isotropic behavior. 130×. Fig. 25. Closed rings abound in a preparation of paraffin heated with sulfuric acid. 'Schlieren' illumination; polarizers partially crossed. 130×. Fig. 26. 'False needles', that is, plates rolled up at an early stage. 'Schlieren' illumination. 200×. Fig. 27. The crystallization of beta-naphthol (*B*) orients the growth of paraffin platelets (*P*). 130×. Fig. 28. Paraffin crystal obtained from solution. Phase contrast American Optical Co., Bright-High 43/0·65 objective. Notice the spiral formed by monomolecular steps, with truncate acute angles. 350×. Fig. 29. Curious aspect shown by a higher fraction of normal paraffin. 'Schlieren' illumination and polarizers partially crossed. 100×.

were used. Mixtures were tried with substances that might be expected to increase the mobility of the smectic phase of paraffin by producing more regular forms, and decreasing the tendency to the formation of false needles, such as oleic acid, benzophenone, naphthalene, fat stains (sudan II, III and IV, Nile blue, nigrosin), some mesophases (*p*-azoxy-anisole, *p*-azoxy-phenetole, cholesteryl ester, *p*-azoxy-ethyl benzoate). No particularly interesting results were obtained. The stains were dissolved in the molten paraffin but did not remain in solution in the smectic phase, and so had no influence upon its mobility. This behavior differs from the one observed in soaps (Zocher & Jacobowitz, 1933), oleates for instance. Benzophenone considerably increases the mobility of nematic phases such as *p*-azoxy-anisole (Zocher & Jacobowitz, 1933), but did not noticeably affect the mobility of paraffin's smectic phase. It seemed probable also that the above mentioned mesophases would be soluble in the smectic phase of the paraffin, since their molecules exhibit a pronouncedly elongated shape, but no evidence was found of any resulting effect. Other mixtures were tried in view of their uses in industry, or for other reasons. It is known that the addition of beta-naphthol whitens the paraffin. In Fig. 27, Plate 6, it can be seen how beta-naphthol crystals orient the growing of paraffin plates. The well known 'booster' effect of carnauba wax when mixed with paraffin, often referred to simply as raising of the melting point, consists in the formation of a gel in which carnauba wax builds a reticular structure that surrounds and supports the remaining material like a sponge. A similar phenomenon occurs when lubricating oils containing paraffin are cooled (Gawlin *et al.*, 1953). In this case, however, the three-dimensional network is formed by the paraffin, and the oil is the occluded substance. The carnauba paraffin gel shows negative deformation birefringence, in agreement with the behavior of carnauba wax needles. When a lump of the gel is squeezed between slide and cover-glass, the wax needles tend to lie tangentially at the borders and, as they have negative birefringence, the higher index will be radial with respect to the compressed drop. The unsaponifiable part of carnauba wax behaves similarly. Silicone (High Vacuum Dow Corning Grease) is not miscible with molten paraffin, and so it facilitates the individualization of the pseudo-isotropic plates and the straight rolled borders (Figs. 21 and 22, Plate 6). Gutapercha (Fig. 10, Plate 5) and rubber (Figs. 11 and 12, Plate 5) increase the formation of folds, possibly owing to a decrease in mobility. In order to lessen the proportion of branched paraffins, oxidation was tried with hot sulfuric acid or sulfur. Fig. 25, Plate 6, shows a curious effect of heating with sulfuric acid. These different treatments and mixtures, even though they can bring out peculiar effects, demonstrate that the described behavior in paraffin solidification is general, with no essential variations.

True crystals of paraffin can be obtained from solution in several organic solvents. Dawson (1953) and Hamm (1954), using the electron microscope, studied crystals of *n*-paraffins of 36, 39 and 100 carbon atoms. From the shadow lengths exhibited by 23 crystals showing spiral growth, they concluded that, in this case, the steps are monomolecular and 45±10 Å thick, fairly close to the value obtained by X-ray diffraction —51·3 Å—corresponding to the length of one molecule. We prepared solutions of our original sample of 54·5 °C. M.P. paraffin (of course heterogeneous in composition) in xylol, carbon tetrachloride, petroleum fractions and, by letting the solvent evaporate between slide and cover-glass, obtained well developed crystals, plate-like, lozenge-shaped, bi-axial, orthorhombic, showing parallel extinction. Fig. 28, Plate 6 shows one of these crystals; phase-contrast made visible the steps, which spiral down with the same truncate acute angles as the crystal itself.

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