On the Fibrous Structure of Paraffin

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Abstract

Studies of the fibrous structure of paraffin which has been drawn into the shape of a wire, and of its relation to temperature are herein reported.

Long chain molecules of paraffin arrange themselves perpendicularly[1] to the surface of the thin films which were prepared by melting and pouring paraffin on a flat surface, or by vaporising the solvent from its solution on a flat surface, or on the thin film of paraffin made on a curved surface of mercury. On the other hand compressed or rolled paraffin sheets have a fibrous structure, the axis of which is perpendicular to the surface of compression and rolling[2], with chain molecules lying parallel to the fibre axis. The following results were obtained when paraffin was drawn into wire form.

Paraffin was maintained at a temperature a few degrees below its melting point, and was drawn by hand into the form of a wire in the soft state. These paraffin wires were illuminated by an X-ray beam normally to the wire axes; one of the diffraction photographs obtained is reproduced in Fig. 1, Plate I. When the photograph was taken by projecting the X-ray beam parallel to the wire axis, the diffraction pattern was of complete rings, showing that the fibre axis coincides with the axis of the wire. Fig. 2, Plate I was obtained when paraffin in the soft state described above was pushed through a die of 1 mm diameter. This photograph is almost the same as that of Fig. 1, Plate I. Paraffin used in the present experiment was of Merck's manufacture and has a melting point of 42°–44°C. Fig. 3, Plate I was obtained when paraffin, softened by soaking in ether, was pushed through a die into wire form. A similar fibre photograph was obtained when benzene was used in place of ether. The fibre photographs thus obtained were almost entirely the same as reproduced in Figs. 1 and 2 in Plate I. As can be seen on the photographs, the reflection due to the atomic

1. e. g. G. L. Clark: Applied X-rays.
2. S. Tanaka and A. Tsuji: These Memoirs, **13**, 369 (1930).

planes of the long spacings appears on the equator, the long chain molecules of paraffin do not lie parallel to the wire axis but lie in the plane perpendicular to it, and the direction of the fibre axis is approximately normal to the atomic plane which produces the most intense reflection. Fig. 4, Plate I was also obtained when paraffin softened by soaking in ether was made into wire form by the use of a die. This photograph is different from Fig. 3, Plate I. In this case the paraffin was in a very viscous state, and though the long chain molecules of paraffin lie nearly in the plane perpendicular to the wire axis, the normal to the plane which produces the most intense reflection inclines to the fibre axis at an angle of about 30°. The chief spacings were calculated by Bragg's equation and are tabulated in Table I. As is seen in the table the long spacing seems to vary more or less depending upon the methods of preparing the specimens.

Table I

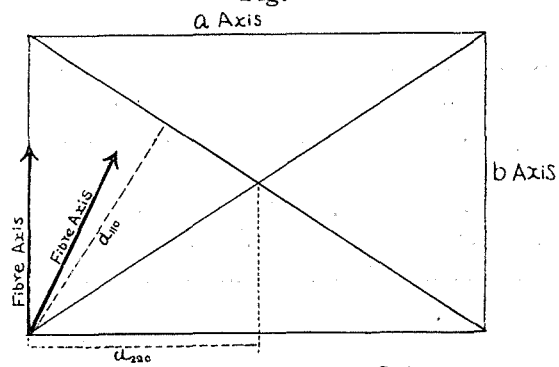
Method of preparing the specimen		Main spacing d_1	Side spacing d_2	d_3	d_4	d_5	d_6	d_7	d_8
Elongated by hand while being softened by heat		31.9	4.17	3.77	5.47	2.57	2.29	2.18	
Pushed out through a die in the softened state	after heat	27.1	4.14	3.75					
	after soaking in ether (1st form)	28.6	4.16	3.77					9.53
	after soaking in ether (2nd form)	31.6	4.17	3.77					
Index		(001)	(110)	(200)					

According to Müller[1] and Hengstenberg[2] the crystals of paraffin, $C_{29}H_{60}$ and $C_{35}H_{72}$, are orthorhombic. Plane (110) gives the strongest reflection and plane (200) next to the strongest. The spacings of these planes are 4.14 Å, 3.72 Å respectively (by Hengstenberg). These values accord with the d_2 (the strongest) and d_3 (the next strongest) in Table I. Paraffin which consists of a mixture of the higher members of the hydrocarbons with different number of carbon atoms, is supposed to build a mixed crystal whose structure is analogous to the above single pure compounds. The main reflections on the photographs then seem to be explained by taking approximately the [110] and the [010] axes

1 A. Müller: Proc. Roy. Soc. **120** A, 437 (1928).
2 J. Hengstenberg: Zeit. Krist. **67**, 583 (1928).

respectively in the above two cases. The arrows in Fig. 1 show such directions of the fibre axes.

Fig. 1



Cross Section of Unit Cell

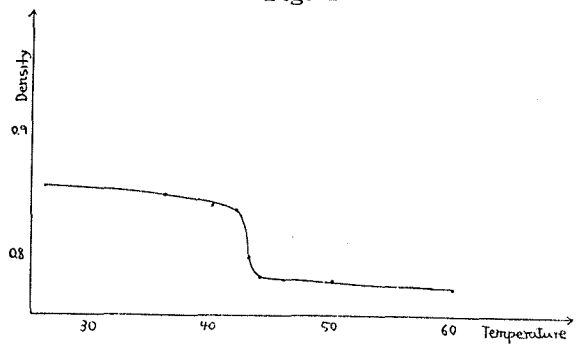
Next the effect of temperature upon the fibre structure of paraffin was studied. The specimen shown in Fig. 4, Plate I was heated at 40°C for an hour. After it was cooled to the room temperature the X-ray photograph was again taken, and no difference was found before and after the heat treatment. The same experiments were repeated by heating the specimens at 42°, 44°, and 46°C. The photographs reproduced in Fig. 5, Plate I were obtained by heating at 46°C, which is a little higher than the melting point of the paraffin used. It is clear from these photographs that the main aspect of the fibre structure is not altered by such heat treatment, though a slight tendency of the interference maxima to become diffused is perceived. This point is very interesting, and seems to point out clearly the existence of long chain molecules in paraffin.

Next the net densities of paraffin near the melting point were measured. The method used is essentially the vacuum method[1] devised by U. Yoshida and B. Takei, but somewhat

Table II

Temperature	Net density
26°C	0.856
36	0.850
40	0.841
42	0.838
43	0.799
44	0.781
46	0.780
50	0.779
60	0.773

Fig. 2



1. U. Yoshida and B. Takei: These Memoirs, **15**, 1 (1932).

adapted to the needs of this case; and a picknometer was used in the liquid state. The results observed are given in Table II and Fig. 2. As seen from Fig. 2 the density of the paraffin used decreases rapidly between 42°C and 44°C, and remains nearly the same above 44°C. This indicates that the paraffin was certainly in a liquid state at 46°C, and that the fibre structure of paraffin was still retained in the liquid state at a temperature a little above its melting point.

In conclusion, the writer wishes to express his sincere thanks to Professor U. Yoshida for his kind guidance, and also to Dr. K. Tanaka for the facilities afforded him during the present experiment.

Plate I

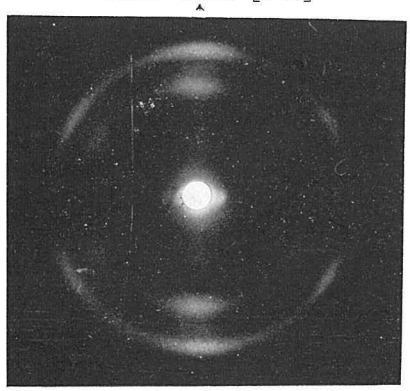


Fig. 1 (Anticathode Fe, Distance 3.95 cm)

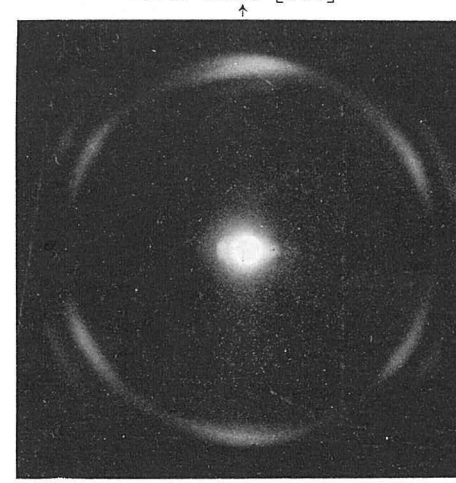


Fig. 2 (Anticathode Cr, Distance 3.95 cm)

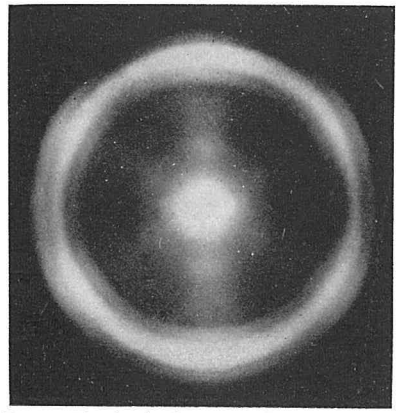


Fig. 3 (Anticathode Fe, Distance 3.95 cm)

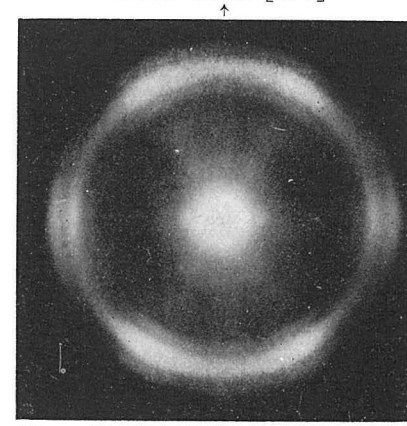
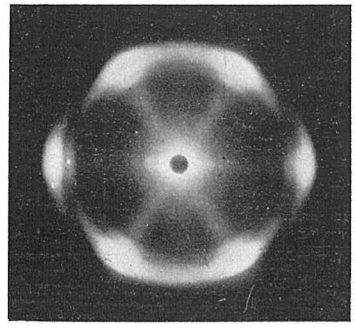
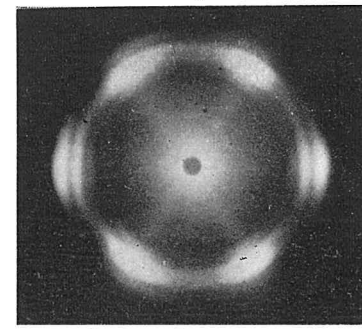


Fig. 4 (Anticathode Fe, Distance 3.95 cm)



(a) Before heat treatment



(b) After heat treatment

Fig. 5 (Anticathode Fe, Distance 2.95 cm)