X-Ray Studies on Paraffin Wax and Vaseline

By

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(Received August 12, 1930)

Abstract

The influence of temperature and mechanical operations were studied by taking the photographs of the X-ray diffraction patterns. *Influence of temperature*: The photographs taken at temperatures lower than the melting point have many spectral lines characteristic of the crystalline powder photographs. These lines generally decrease in intensity as the temperature rises and vanish at last when the substances are in the melting state, while amorphous bands appear in other positions. One intense line, however, remains until the melting state is reached and then suddenly vanishes. This transformation occurs in a different manner for each substance. *Effects of mechanical operations*: The effects of compression and rolling at the room temperature were studied with paraffin wax and the following results were obtained: (1) The wax comes to have a fibrous structure, the axis of which is perpendicular to the surface of compression and rolling. (2) The crystal planes which produce the most intense reflection are also nearly perpendicular to the same surface.

The paraffin waxes that consist of mixtures of the higher members of the hydrocarbons crystallise imperfectly and have not a definite melting point. The X-ray diffraction patterns taken with these substances at the room temperature have already been investigated by some authors[1]. The present experiment has been performed to study the influence of temperature and some mechanical operations upon two paraffin waxes having different melting points, and vaseline.

Influence of Temperature

The experimental apparatus and the working conditions were the same as in the previous experiment[2]. The two paraffin waxes were of Merck's manufacture; one had the melting point at 42°—44°C and

1. W. Friedrich, Phys. Zeit., **14**, 317 (1913)
   G. L. Clark, Applied X-Rays, p. 156.
   S. H. Piper, D. Brown and S. Dyment, Jour. Chem. Soc. (London), **127**, 2194 (1925)
2. These authors, These Memoirs, **18**, 337 (1930).

the other 68°—72°C. A in the first column of the following table represents the former wax and B the latter. The melting point of the vaseline, which was Kahlbaum's, was about 45°C. These samples were mounted in thin glass tubes 1 mm. in diameter. The distance between the sample and the photographic plate was 4.06 cms. Many spectral lines were observed in the photographs taken at various low temperatures, while bands were seen in those taken at the higher temperatures. All the spacings corresponding to these lines and bands were calculated by Bragg's equation and are tabulated in Table 1. The photographs are reproduced in Figs. 1 to 13 in

Table 1

Name	Temp.	State.	d (A.U.) for lines					d (A.U.) for bands	
			d_1	d_2	d_3	d_4	d_5	d_1'	d_2'
Paraffin wax, A	10°C	perfect solid	4.17	3.76	2.96	2.53	2.24		
	40°	very soft	4.17	3.75					
	44°	melting state	4.16					4.67	
	64°	perfect liquid						4.97	11.85
Paraffin wax, B	13°	perfect solid	4.17	3.77	2.96	2.52	2.26		
	41°	"	4.17	3.76	2.98	2.56	2.25		
	55°	"	4.16						
	64°	soft						4.70	
	70°	melting state						4.73	
	83°	perfect liquid						4.94	12.22
Vaseline	−8°		4.14	3.68					
	20°		4.14	3.68				5.28	
	51°							5.24	10.70

Plate 1. The photographs for the two paraffin waxes taken at the temperatures lower than the melting point show several sharp lines like those obtained by the aggregation of crystalline powders. The crystal structure, however, can not be determined on account of their distribution having no simple relation. Five lines were commonly observed in similar positions for both the paraffin waxes, and besides

these lines, one innermost line, which seems to correspond to the K_β line, is obtained. Their spacings agreed with the results obtained by Müller and Saville[1] for the hydrocarbons higher than $C_{21}H_{44}$. From this point of view, our samples are probably mixtures of the hydrocarbons higher than $C_{21}H_{44}$. The disappearance of the line corresponding to the very large spacing found by the above authors is probably due to the halation of the direct rays in the present experiment.

Generally, the intensity of the spectral lines decreases gradually as the temperature rises, and vanishes at last when the substances are in the melting state, while the amorphous bands now appear in other positions. This transformation occurs in a different manner in the two waxes.

The Wax named A :—This wax becomes very soft at 40°C and the lines in the photograph corresponding to d_3, d_4 and d_5 vanish. The line for d_2 disappears nextly at the melting state while the line for d_1 still remains accompanied by the appearance of a diffuse band just inside of it. This diffuse band becomes an ordinary amorphous one when the wax melts completely and becomes liquid. This is summarized in Table 1, and the photographs taken at each stage are reproduced in Plate 1. The increase in the spacings d_1' and d_2' corresponding to the bands is probably due to the ordinary influence of the temperature[2] upon the X-ray diffraction in liquids.

The Wax named B :—The melting point of this wax is much higher than that of A, and consequently the five lines are all found in the photograph taken at 41°C. In the photograph taken at 55°C, however, only one line corresponding to the spacing d_1 remains in spite of the wax being still perfectly solid. It becomes soft at 64°C and the photograph has the amorphous band like the diffraction in liquids. From this it seems that the structure of wax B seems to change into the liquid state before it melts. After this point it gives the diffraction band like ordinary liquids, as is shown in Table 1.

A diffuse band accompanied by a faint inner maximum was given by both waxes A and B in the perfectly liquid state, and the smaller spacing seems to agree with the diameter of the cross section of long molecules observed by G. W. Stewart[3] and the present authors.[4]

1. A. Müller and W. G. Saville, Jour. Chem. Soc. (London), **127**, 599 (1925)
2. These authors, loc. cit.
3. G. W. Stewart, Phys. Rev., **31**, 174 (1928)
4. These authors, These Memoirs, **13**, 17 (1930)

Vaseline:—The photograph taken at ordinary temperature shows two sharp lines and a faint diffuse amorphous band, which resembles that obtained with the wax when in the softening state. If the sample is cooled to $-8°C$, the amorphous band disappears and the two lines become intense. If it is heated to 51°C, it becomes liquid and there remains only a diffuse band. From the above facts, it is clear that the structure of vaseline at the room temperature is like that of wax in its softening state, and it becomes crystalline or amorphous on being cooled or heated from this temperature.

Effects of Mechanical Operations

The influence of compression and rolling at room temperature (25°—30°C) was investigated with respect to the paraffin wax B. A camera having circular slits of diameter 0.5 mm. was employed and the distance between the sample and the photographic plate was 3.5 cms. The rectangular plate of paraffin wax, 2—2.5 mm. in thickness, was held between pieces of paper and compressed or rolled. When the photograph was taken with the paraffin wax before any mechanical treatment, there could be observed many concentric rings, as is shown in Fig. 14, Plate II. The distribution of the intensity of the rings was altered by the treatment of the sample, this being mostly observed in the intense three inner rings. (The innermost one seems to be the K_β line).

Effects of compression:—The thickness of the sample was first reduced by the compression about 23%, 60% and 90% i.e. from 2.40 mm. to 1.85 mm. 0.97 mm. and 0.25 mm. The photographs were taken at each stage by projecting the X-ray beam normally to the compressed surface, and then they showed no marked change excepting that all the lines become somewhat sharper. This shows the irregularity of the arrangement of the micro-crystals with respect to the direction of the compression.

Next the X-ray beam was projected normally to the direction of the compression, and a very intense part of the rings appeared in the position perpendicular both to the direction of the X-ray and the compression, as is seen in Figs. 15 and 16, Plate II. Fig. 15 and Fig. 16 were obtained with the samples compressed 27% and 78% respectively. The samples compressed more strongly gave photographs not different from Fig. 16. In this case small strips were cut off from the compressed wax, and if they were too thin for the X-rays, several strips were put together. The authors ascertained by taking the photographs with a sample in two directions that the influence of this piling was negligible. The ones obtained by projecting the X-rays parallel to the direction of the compression were always similar to Fig. 14 and the others to Fig. 15 or Fig. 16. The effect could be observed only in the inner comparatively intense rings and not in the outer faint ones. The reflection corresponding to the intense part must be made by the crystal planes parallel to the direction of the compression.

Finally the photographs were taken by projecting the X-rays at an inclination of 50 and 30 degrees to the direction of the compression. The intense parts of the rings moved towards this direction according to the degree of the inclination. Figs. 17 and 18, Plate II are reproductions of the photographs taken when the inclination was 50 and 30 degrees respectively.

All the facts above mentioned will be naturally explained by the consideration that: (1) The paraffin wax, when it is compressed, comes to have a fibrous structure, the axis of which is perpendicular to the plane of compression. (2) The crystal planes which produce the most intense reflection are also nearly perpendicular to the plane of compression

Effects of rolling:—The rectangular plate of paraffin wax was carefully rolled down to reduce the thickness about 20%, 45% and 90%. When the photographs were taken by projecting the X-ray beam normally to the rolled surface, they did not show any marked change from those obtained with ordinary paraffin wax. If, however, the X-ray beam was projected parallel to the rolled surface, photographs similar to Fig. 15 and 16 were obtained. Fig. 19 is a reproduction of one of these. In this case the direction of rolling seemed to have no relation to the results, because two strips cut off parallel and perpendicular to the direction of rolling gave the same photographs. From these facts, it is clear that the structure of the rolled paraffin wax is also fibrous, the axis of which, and also the crystal planes producing the most intense reflection, are perpendicular to the surface of rolling.

In conclusion the writers' hearty thanks are due to Prof. M. Ishino for his interest in the research.

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The Osaka University of Engineering,
July 10, 1930.

Plate I

Paraffin Wax, A

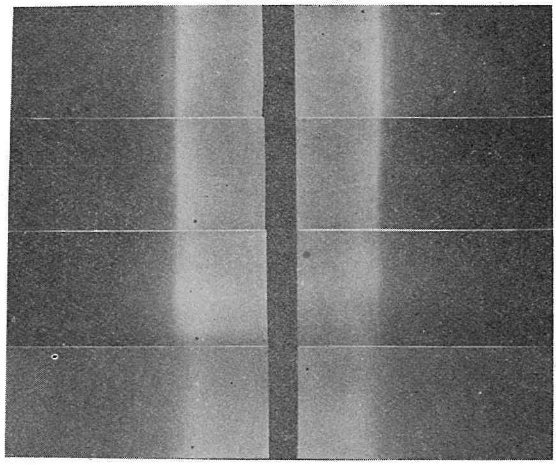

Fig. 1. 10°

Fig. 2. 40°

Fig. 3. 44°

Fig. 4. 64°

Paraffin Wax, B

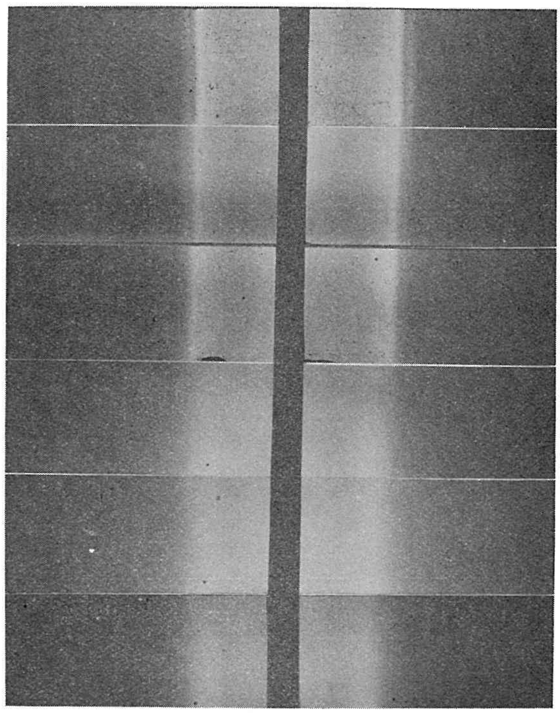

Fig. 5. 13°

Fig. 6. 41°

Fig. 7. 55°

Fig. 8. 64°

Fig. 9. 70°

Fig. 10. 83°

Vaseline

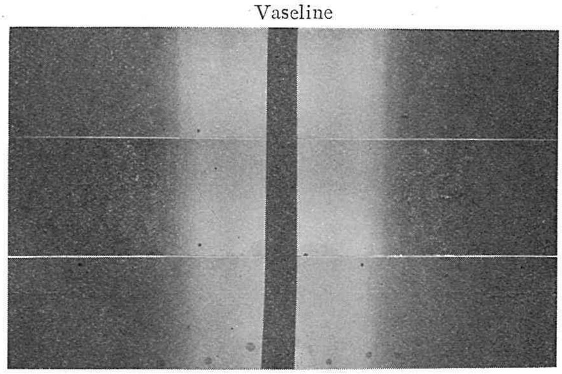

Fig. 11. −8°

Fig. 12. 20°

Fig. 13. 51°

Plate II

Fig. 14.

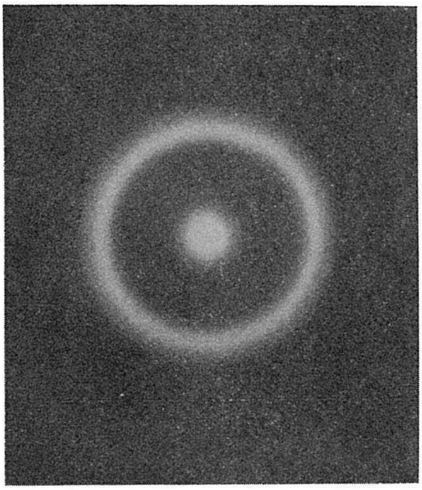

Fig. 15.

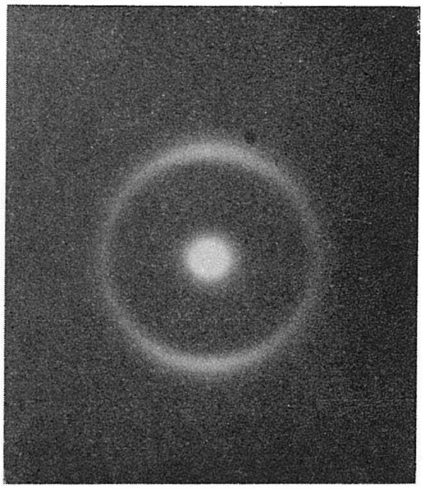

Fig. 16.

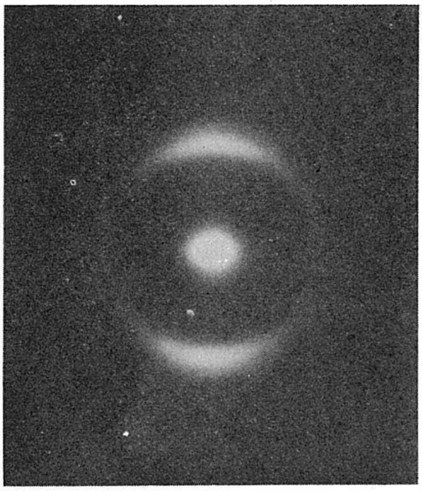

Fig. 17.

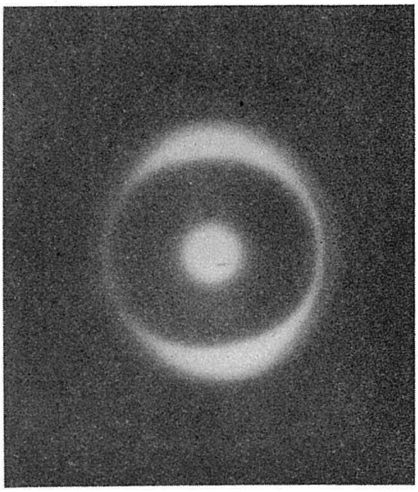

Fig. 18.

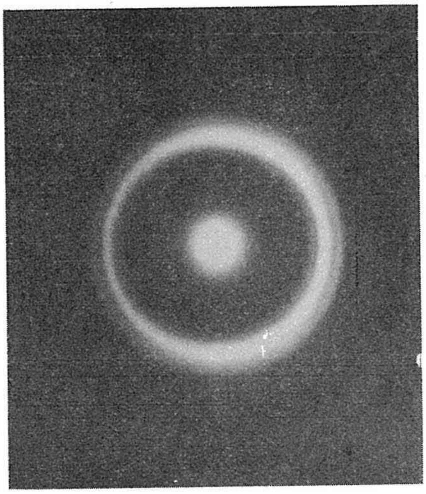

Fig. 19.