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AUTHOR(S):

Tanaka, Kenzo

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CITATION:

Tanaka, Kenzo. Examination of Thin Rubber Films by Electron Diffraction. *Memoirs of the College of Science, Kyoto Imperial University. Series A* 1938, 21(5): 169-172

ISSUE DATE:

1938-09-30

URL:

<http://hdl.handle.net/2433/257201>

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# Examination of Thin Rubber Films by Electron Diffraction

By Kenzo Tanaka

(Received Aug. 8, 1938)

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## Abstract

The molecular structure of thin rubber film deposited from its benzene solution on a polished metal surface by evaporating the solvent benzene was examined by the method of electron diffraction at various temperatures, and it was found that rubber molecules arranged themselves similarly to those of paraffin crystal.

It was reported in a preceding paper<sup>1</sup> that when a thin film of some organic long-chain molecules coating a polished metal surface is heated, the regular arrangement of the molecules of each substance becomes haphazard at a certain temperature which is characteristic of the substance and differs from its melting point. This temperature was called the transition-temperature of the molecular arrangement of the substance. In the present experiment the manner of the arrangement of the rubber molecules in a thin film deposited from its benzene solution on a polished metal surface was examined in the same manner as before.

To obtain rubber films of different thickness a small piece of polished copper which serves as the backing of the film was dipped for a moment in a benzene solution of rubber. The range of the rubber concentration of the solution was from 2 to 0.005 per cent. By subsequent evaporation of benzene, uniform coating of rubber was obtained, which was so thin as to show the interference fringe by the light in most cases.

The typical diffraction patterns obtained by an electron beam which impinged upon the rubber film in a direction almost parallel to its surface are such as shown in Fig. 1. But these are rare cases, and generally the rubber films deposited as above stated gave rise at first to diffuse halos of amorphous structure. However when these amorphous films were heated at about 70°C for a while and cooled to room temperature they gave rise to the same diffraction patterns illustrated in Fig. 1. The regular pattern showing the regular arrangement of the rubber molecules is well defined for very thin film and becomes more diffuse

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1. K. Tanaka: These Memoirs, 21, 85 (1938).

Fig. 1



with increasing thickness of the film, as in the case of the other substances.

The regular diffraction pattern as shown in Fig. 1 is explained as being due to a certain regular arrangement of long-chain molecules standing perpendicularly to the flat surface of the backing. The spacing calculated from the separations of the parallel layer lines which are nearly straight in the figure was 2.58 Å. This spacing is the same as the distance between alternate carbon

atoms in the zigzag structure of a long-chain molecule. The value of the inner potential estimated from the positions of the layer lines was less than one volt.

From the distances of the spots on the layer lines in the diffraction pattern as measured from the intersection of the plane of incidence

Table I

1	2	3	4	5	6
Paraffin		Rubber		Paraffin	Al-foil
Indices	Spacings Å	reflect.	transm.	transm.	transm.
100	7.45				
010	4.97	4.94			
110	4.13	4.07	4.07	4.12	4.15
200	3.72	3.69	3.69	3.77	3.72
210	2.98	2.98			2.94
020	2.48	2.50	2.47	2.47	2.47
120	2.37	2.37			
220	2.07	2.11		2.075	2.04
400	1.86	1.79			
410	1.74	1.66			
420	1.49	1.47			
040	1.24				
140	1.23	1.23			
240	1.18	1.11			

of the electron beam with the photographic plate, the lateral spacings of the regular arrangement of the long-chain molecules can be calculated. The spacings thus obtained are shown in the third column of Table I. In column 1 and 2 of the table the indices and the spacings of the planes parallel to *c*-axis of the crystal of paraffin found by Müller are given. The agreement between the values in column 2 and in column 3 shows that the lateral disposition of the molecules of rubber in the present case is the same as that of paraffin crystal. This arrangement of the molecules of rubber differs from that found in stretched rubber by means of X-rays.

The agreement between the structures of rubber and paraffin was also tested by transmission photographs. Rubber solution in benzene and paraffin solution in benzene were spread respectively as thin films on thin foils of aluminium which had been carefully cleaned. After the evaporation of the solvents the diffraction photographs were taken by sending the electron beam normally to the surface of the films. The results are shown respectively in columns 4 and 5 of Table I; and again the agreement is evident. Aluminium foils usually give rise to certain extra rings due to some fatty substances in the transmission photographs, such as shown in column 6 of Table I. These extra rings can be removed by carefully washing the foil; and in the examination of rubber and paraffin described above such cleaned foils were always used.

Next to see whether the regular diffraction pattern obtained with rubber may be due to some other fatty substances present in the rubber film as a contamination, diffraction photographs were taken with the backing only and with the backing which was dried after being covered thickly with benzene and volatile oil. The benzene and volatile oil were respectively the same as those used as the solvent of rubber and in cleaning the backing. But in these cases no such regular diffraction pattern as shown in Fig. 1 appeared even though the specimens were heated to about 90°C. Next, the surface of the rubber film which had given rise to the regular diffraction pattern as Fig. 1, was cleaned with volatile oil to remove any fatty substances which might be present on the surface of the rubber film as a contamination. But no appreciable change in the diffraction pattern was observed with such specimen before and after the cleaning.

By the results of these tests, the suspicion that the regular diffraction pattern observed with a thin film of rubber deposited on a

smooth surface of a metal might be caused by some fatty substances present in the film as a contamination, seems to be almost removed; and consequently the view that the rubber molecules arrange themselves in the same manner as paraffin in the present case seems to be almost certain.

When the thin rubber film in which the rubber molecules were arranged regularly as has been described, was heated in the vacuum of the electron diffraction apparatus, no appreciable change in the regular diffraction pattern was observed at a temperature below about 60°C, but with further rise of temperature the pattern became diffuse and finally vanished at about 66°C. Such transition-temperature at which the regular arrangement of the molecules becomes haphazard, was measured in the same way with ten specimens of different thickness. The transition-temperature thus measured ranged from 58°C to 66°C and no regular relation was found between the transition-temperature and the thickness of the film. This transition of the molecular arrangement of rubber from regular to irregular is reversible and when the heated specimen is cooled the molecules arrange themselves regularly as before nearly at the transition-temperature.

The writer wishes to express his sincere thanks to Prof. U. Yoshida for his invaluable suggestions.

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