Crystal Structure of Cyanoethyl Cellulose

In the X-ray study of cyanoethyl cellulose filaments[1], made from products of varying cyanoethyl content, it has been found possible to identify at least two forms of crystalline structure. Fig. 1 is an X-ray diagram of filaments made from alkali-soluble material, containing in this case 2·0 per cent nitrogen, corresponding to a substitution of less than one group per glucose residue in the cellulose. The X-ray diagram can be seen to be somewhat similar to that of hydrate cellulose; the normal repeat of pattern of 10·3 A. (approximately) of the cellobiose residue is retained along the fibre axis. It is most probable that the substitution of the cellulose occurs throughout the whole structure, and in these circumstances the obvious falling off in definition of the X-ray diagram is due to distortion of the crystalline lattice, caused by the replacement of certain of the (OH) groups by (OC_2H_4CN) groups. Fig. 2 is an X-ray diagram of acetone-soluble cyanoethyl cellulose filaments containing on an average 2·73 groups per glucose residue; complete cyanoethylation can be represented by the formula: $(C_6H_7O_2.(O.C_2H_4CN)_3)_n$. A preliminary study of this fibre diagram has shown that the crystal structure is built up in the following way.

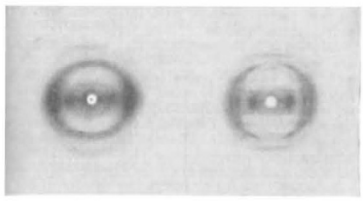

Fig. 1 Fig. 2

Fig. 1. X-RAY PHOTOGRAPH OF FIBRES OF ALKALI-SOLUBLE CYANOETHYL CELLULOSE WITH A NITROGEN CONTENT OF 2 PER CENT. COPPER *Ka* RADIATION. $D \approx 2{\cdot}1$ CM. (ON REPRODUCTION).

Fig. 2. X-RAY PHOTOGRAPH OF FIBRES OF CYANOETHYL CELLULOSE WITH AN AVERAGE SUBSTITUTION OF 2·73 CYANOETHYL GROUPS PER GLUCOSE RESIDUE. COPPER *Ka* RADIATION. $D \approx 2{\cdot}1$ CM. (ON REPRODUCTION).

(1) The period along the fibre axis is $15{\cdot}2_1$ A., which indicates that the repeat is made up of three glucose residues. Hence the cellobiose configuration of the normal structure is not retained.

(2) The structure of the ether presents some difficulties in interpretation, as it is not fully substituted; but the X-ray diagram can be indexed at least to a first approximation on a hexagonal lattice, with the intense reflexions on the basal layer line arising from the (100) plane, and with the (010) and (020) reflexions absent or very weak. A structure may be assigned as follows: $a = c = 9{\cdot}7_4$ A.; $b = 15{\cdot}2_1$ A. (fibre axis); $\beta = 120°$.

This would be consistent with one chain per unit cell, containing three consecutive tricyanoethyl glucose residues arranged on a three-fold spiral along the fibre axis. Further, the above structure has a theoretical density of 1·28 gm./c.c., which is in good agreement with the value of 1·27 gm./c.c. found in white spirit. It is, however, emphasized that this postulated structure is only provisional and may well be a sub-multiple of a larger cell. At present, however, this has been found to be the best possible approximation.

Infra-red studies of the material have shown that in the cyanoethers of low substitution it is possible that some amide groups may be present. It also appears that some of the ethers of equal nitrogen content are soluble in water, whereas others are only soluble in alkali; the cause of this difference is most probably to be found in a more uniform substitution throughout the cellulose structure by cyanoethyl groups in the case of the water-soluble specimens. A final interpretation of the X-ray diagram of tricyanoethyl cellulose must await the elucidation of the problems of the types of ether groups present, together with data from a fully cyanoethylated specimen.

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[1] Courtaulds, Ltd., and MacGregor, J. H., Brit. Pat. 588,751; and Brit. Pat. Applic. No. 34,508/1945.

X-Ray Diffraction Studies of a Nickel–Thoria–Kieselguhr Catalyst for Fischer–Tropsch Synthesis

A nickel–thoria–kieselguhr (100 : 18 : 100) catalyst prepared mainly according to Fischer and Meyer[1], and rendered completely alkali-free after reduction, by washing with water, was studied by the Debye–Shearer method.

A Debye–Shearer photograph of the kieselguhr used was taken before treatment. This photograph showed a number of sharp diffraction lines and a strong halo. It appears, therefore, that the kieselguhr consists of partly crystalline and partly vitreous or finely colloidal particles. The Bragg angles of reflexion and the spacings corresponding to the diffraction lines are given, along with their eye-estimated intensities, in Table 1.

TABLE 1

Bragg angles of reflexion for copper *Ka* corresponding to diffraction lines	Spacings corresponding to diffraction lines	Eye-estimated intensity
10° 39′	4·20	m.s. (diffuse halo)
13 22	3·37	m.w.
14 48	3·02	m.
15 52	2·81	v.v.w.
17 55	2·54	v.w.
19 42	2·30	w.
21 30	2·11	w.
23 45	1·92	w.
24 21	1·87	w.
28 39	1·62	v.w.
30 20	1·52	v.w.

The X-ray diffraction diagram of a powdered sample of the nickel–thoria–kieselguhr catalyst shows the presence of a few diffraction lines of nickel together with some diffraction lines of the kieselguhr. The weak lines of the kieselguhr having Bragg angles 17° 55′ and 30° 20′ only appeared in this photograph. This shows that in the process of depositing nickel on the kieselguhr the structure of the latter has undergone a change. The two lines of the kieselguhr which appear in this photograph have been identified to be the strong lines of ferric oxide present in the kieselguhr. The lines of silica observed in the photograph