UDC 615.778.475-011 : 541.486[546.621]

139. Kyoji Hayano and Sataro Imado : Studies on Aluminum Complex Compound of PAS (Supplement). X-Ray Analysis of Calcium Alumino-*p*-aminosalicylate.

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As reported in a previous paper of this series,[1] the crystals of calcium alumino-*p*-aminosalicylate[*2] (Al-PAS-Ca) lose the seven moles of crystal water, present outside the complex ion, when dried at 105°. Experiments using thermal balance indicated that the complex molecule lost its seven moles of crystal water at around 130° and further elevation of temperature hardly caused any decomposition, showing a state of equilibrium. The manner of decomposition when the temperature was raised to 200° was examined with a thermal balance.

In this case, the usual chemical analyses seemed to be unsuitable and, examinations were made through X-ray diffraction. X-Ray diffraction patterns are shown in Fig. 1, in which (I) is that of Al-PAS-Ca crystal, (II) is that of (I) when the temperature was raised to 200° in a thermal balance, and (III) is that of *m*-aminophenol.

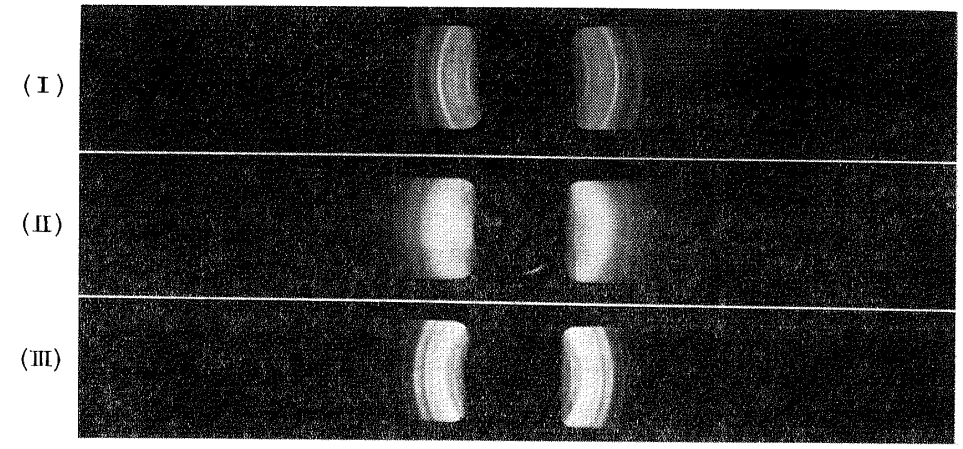

Fig. 1. X-Ray Powder Diagram

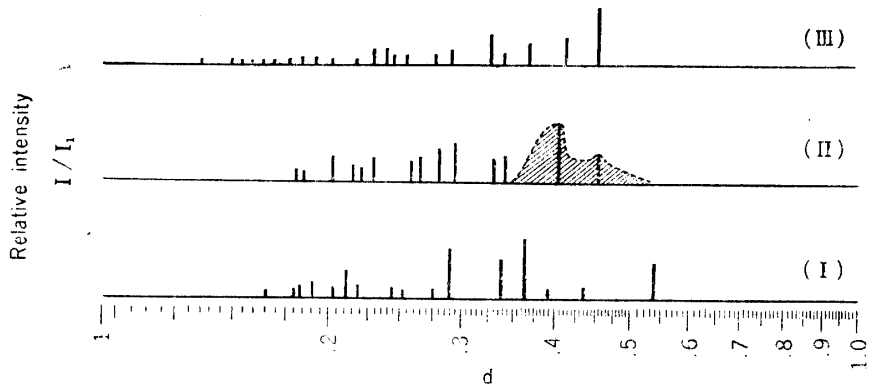

Fig. 2. Observed Relative Intensities and Spacings from Fig. 1

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*2 See Part I of this series (p. 756) for chemical term of this compound.
1) Part II : This Bulletin, **7**, 761(1959).

Table I. X-Ray Diffraction Data from Fig. 1

(I)			(II)			(III)		
d	I/I_1	θ	d	I/I_1	θ	d	I/I_1	θ
5.41	0.60	8.20	4.56	0.40	9.74	4.56	1.00	9.74
4.34	0.20	10.22	4.14	1.00	10.74	4.15	0.44	10.70
3.91	0.13	11.38	3.44	0.40	12.92	3.72	0.38	11.96
3.64	1.00	12.22	3.32	0.33	13.44	3.44	0.19	12.90
3.37	0.67	13.21	2.96	0.67	15.08	3.30	0.50	13.50
2.89	0.83	15.48	2.83	0.53	15.80	2.93	0.25	15.24
2.74	0.13	16.34	2.67	0.40	16.76	2.78	0.16	16.06
2.49	0.10	18.00	2.59	0.33	17.26	2.57	0.13	17.50
2.43	0.13	18.52	2.39	0.40	18.80	2.47	0.15	18.24
2.18	0.20	20.60	2.22	0.20	24.42	2.41	0.25	18.66
2.10	0.43	21.54	2.16	0.27	20.98	2.32	0.23	19.46
2.02	0.13	22.48	2.03	0.40	22.24	2.18	0.08	20.70
1.90	0.23	23.96	1.86	0.13	24.50	2.03	0.09	22.26
1.83	0.13	25.00	1.83	0.20	25.00	1.94	0.11	23.48
1.75	0.10	25.75				1.86	0.10	24.50
1.65	0.10	28.00				1.78	0.04	25.70
						1.70	0.06	27.00
						1.65	0.03	27.80
						1.59	0.04	28.90
						1.55	0.05	29.70
						1.50	0.04	30.90
						1.36	0.03	34.50

d: Spacing I/I_1: Relative intensity θ: Diffraction angle

From the position of diffraction lines, the Bragg angle, θ, and lattice spacings, d, were calculated. Relative intensity, I/I_1, of the diffraction line was determined by using a standard intensity scale. These results are shown in Fig. 2 and in Table I.

The angle of diffraction, θ, in diffraction curve measured by Norelco X-Ray Diffractometer is also given in Table I for comparative reference. The value of lattice spacings, d, was obtained from the nomograph prepared from θ–d reference table.[2)]

The maximum of diffraction of (I) and (III) in Fig. 1 is clear but that of (II) is a diffused diffraction line widely distributed over the range of d=3.63~5.20 Å.

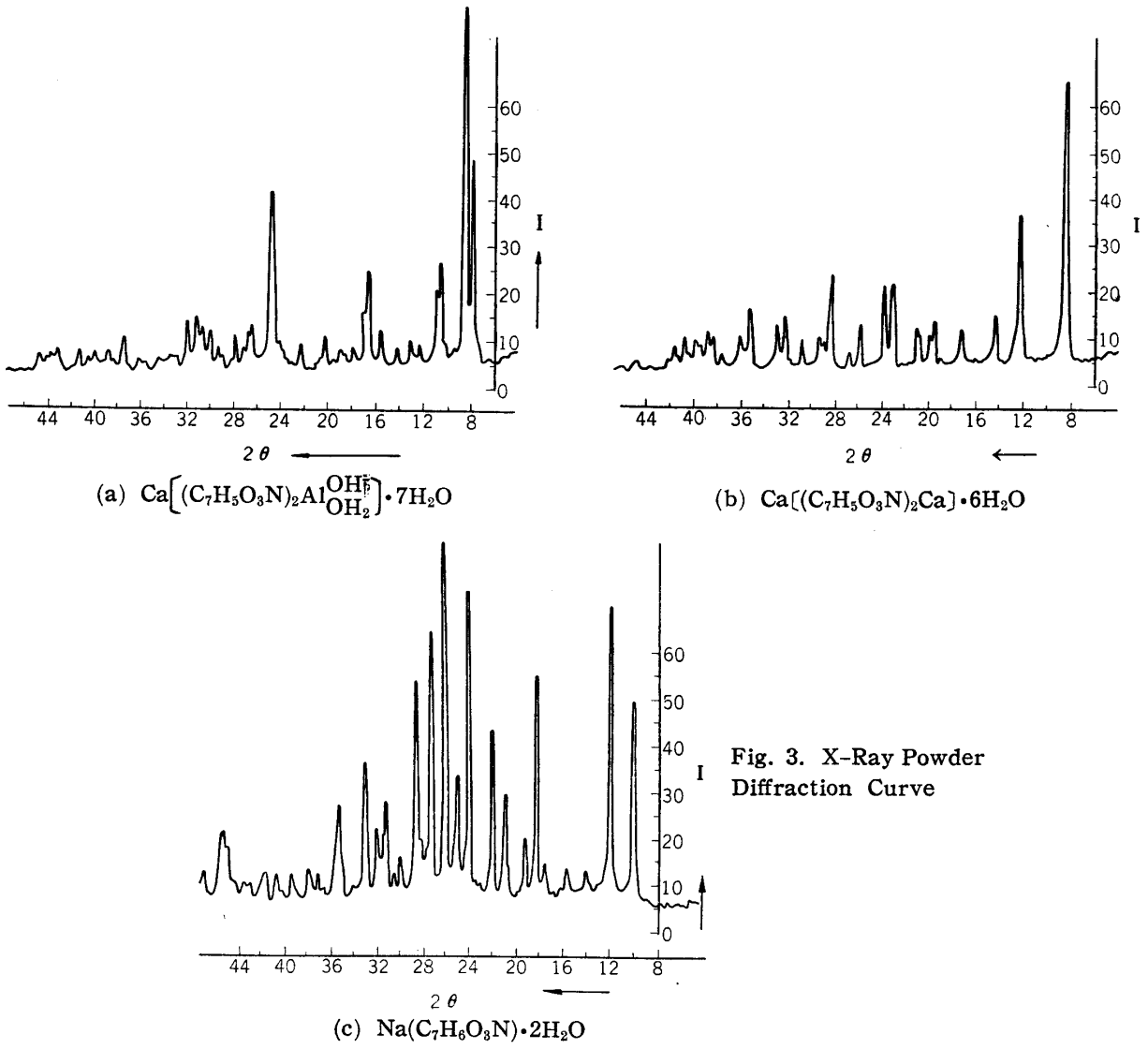
It is still difficult, at this stage, to make any decisive conclusion about the reason for this diffused diffraction lines but since it does not correspond to any of the diffraction patterns of Al–PAS–Ca crystals, aluminum oxide, or calcium carbonate, it may be a halo caused by resinous substance formed by polymerization of *m*-aminophenol produced.

Values given in Table I indicated the presence of a diffraction line of *m*-aminophenol, formed by decomposition of Al–PAS–Ca crystal, in the diffraction patterns of (II). Other diffraction lines are probably that of Al–PAS–Ca anhydrate in the main.

Fig. 3 shows the diffraction patterns recorded by the Norelco Diffractometer for X-ray analysis of Al–PAS–Ca crystal (a) and also of basic PAS–Ca (b) and PAS–Na (c), recorded at the same time, for reference. The patterns recorded by the Norelco Diffractometer were used as data to measure the relative intensities of diffraction exactly. Also they may be used as fundamental materials in order to identify these substances in future.

All X-ray diffraction patterns were taken with copper Kα radiation (wave length: λ=1.5418 Å), filtered through a nickel foil, and exposed at 30 KVP, 10 mA, for 30 minutes. The radius of the camera was 28.65 mm. and the powdered sample was sealed in a Terex glass capillary of ca. 0.4 mm. in internal diameter and ca. 0.6 mm. in external

2) K. Kubo, S. Kato: Kogyo Kagaku Zasshi, **56**, 391(1953).



(a) $Ca\left[(C_7H_5O_3N)_2Al\begin{matrix}OH\\OH_2\end{matrix}\right]\cdot 7H_2O$

(b) $Ca[(C_7H_5O_3N)_2Ca]\cdot 6H_2O$

(c) $Na(C_7H_6O_3N)\cdot 2H_2O$

Fig. 3. X-Ray Powder Diffraction Curve

diameter.

The curves obtained with the Norelco Diffractometer were recorded at 30 KVP, 15 mA, with Cu-Kα of 1.5418 Å, time constant of 4 seconds, goniometer velocity of 2°/min., and recording speed of ⅔ in./min. In Fig. 3, θ is the angle of diffraction and I is the quantity of X-ray.

Summary

X-Ray diffraction of calcium alumino-*p*-aminosalicylate was taken by powder photography, and the angle of diffraction and lattice spacings were calculated from the position of its diffraction patterns, together with relative intensity of diffraction lines.

The sample of calcium alumino-*p*-aminosalicylate heated to 200° in thermal balance was found to contain *m*-aminophenol.

Diffraction was also recorded by the Norelco Diffractometer, and the angle of diffraction and relative intensity obtained from it were compared with those found by the powder method.

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