

*Dyeing of Polyvinyl-*n*-butylboronate with  
Congo Red*

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In the course of studies on organoboron compounds, a number of polyvinyl-*n*-butylboronates having various esterification grades were obtained. These products could be made into films from solutions in some organic solvents. The films of the boronates were dyed with congo red unexpectedly deeper than those of polyvinylalcohol itself<sup>1)</sup> inspite of the less hydrophilic property.

The samples used for dyeing experiments were prepared as follows: boronate films were made from carbon tetrachloride solutions on a mercury dish and dried in the air at room temperature. The films of PVA were made from aqueous solutions in the same way, and thermally treated at 180°C for ten minutes in order to make them insoluble in water. For comparison a part of the boronate films was thermally treated in the same way. The other part remained untreated. The films were nearly 0.1 mm. thick and were cut in pieces with the size of 1 cm.×2 cm. For dyeing purpose all films were immersed into a 0.5% solution of congo red at 25°C. The equilibrium of sorption was reached in most cases within two or three days, and from the curve of the sorption rate the quantity of the dye sorbed in equilibrium can be estimated.

The results are shown in Table I in which  $D$  represents the apparent diffusion coefficient and  $E_g$  the esterification grade which can be estimated by the following equation from the boron content ( $B$ ) of the boronates,  $E_g = 133.74 \times B \% / (16.41 - B \%)$

TABLE I. SORPTION OF CONGO RED BY BORONATES

	$E_g$ %	$D \times 10^{-2}$ (25°C)	Dye sorbed I	(g./g. dry film) $\times 10^{-2}$ II*
B-1	75.4	2.12	10.386	10.294
B-2	80.6	2.83	13.860	11.709
B-3	85.6	4.03	19.809	16.364
PVA	0	—	4.90	4.70

\*II=films heat-treated.

The results show that the quantity of the dye sorbed on the films increases with the increasing  $E_g$ , and the relation between the thermal treatment and non-treatment is not

remarkable. It is also noteworthy that the apparent diffusion coefficient grows with  $E_g$ .

These results suggest that because of esterification of PVA with boronic acid, that is, due to the introduction of the boron atom into PVA, the dyeing occurred through co-ordination between the boron and the nitrogen atom<sup>2)</sup> which is contained in the molecule of congo red, but not through hydrogen bond, and that the introduction of boron made the dense crystalline structure of PVA to a loose one, and the amorphous part was increased, as seen in the case of polyvinylborate studied by Sakurada.<sup>3)</sup>

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2) The IR spectra of dyed films have shown absorption bands at 1550 and 3200  $\text{cm}^{-1}$ , which can be assigned respectively to the azo and the amino group of congo red, but the former is shifted slightly to a higher frequency and the latter to a definitely lower one. Hence the authors think the co-ordination possibly takes place between the boron atom and the amino group of congo red.

3) I. Sakurada et al., *Kobunshikagaku*, 15, 491 (1958).

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1) K. Fujino and F. Fujimoto, *J. Soc. Textile and Cellulose Ind.* (in Japanese), 15, 138 (1959).