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HALOGENOBENZOQUINOPHTHALONE AS A NEW PIGMENT TO REPLACE CADMIUM YELLOW. Part II.

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5,6,7,8-Tetrabromo-3'-hydroxybenzo[b]quinophthalone has been developed as a new pigment to replace cadmium yellow. This compound is very similar to cadmium yellow in color and has excellent pigment properties. The effects of bromo substituent of benzoquinophthalones on thermal behavior and on solubility are also discussed.

In our previous paper[1], we showed that 5,8-dibromo-3'-hydroxybenzo[b]quinophthalone [I] has good properties as a pigment to replace cadmium yellow (CdS). In the present paper, we wish to report on some properties of 5,6,7,8-tetrabromo-[II], 5,6,7,8,4'-pentabromo-[III], and 5,6,7,8,6',8'-hexabromo-3'-hydroxybenzo[b]quinophthalone [IV]. The thermal behavior by means of TGA, and the spectral and solubility data are summarized in Fig.1 and Table 1. The results obtained are as follows:

1) A little bathocromic shift was observed as increasing the number of bromo substituent. However, all of the four compounds were very similar to CdS in color.

2) The resistance to heat of [I] was greatly improved in [II]. However the additional bromo substituent on quinoline ring of [II] did not show any appreciable effect.

3) The great improvements of the resistance to solvents such as α-chloronaphthalene and DMF were made in tetrabromo derivative [II]. But in pentabromo [III] and hexabromo [IV] derivatives the resistance decreased drastically in spite of the increase of the number of the bromo substituent. Moreover it was apparent that the bromo substituent on naphthalene ring improved markedly the resistance to solvent while those on quinoline ring decreased drastically it.

Some pigment properties of [II] are summarized in Table 2. Each property is improved remarkably as follows in comparison with that of [I][1]:

1) The light fastness was improved by 0.5-1.5 degree on each substrate, especially on TiO_2 mixed substrates.

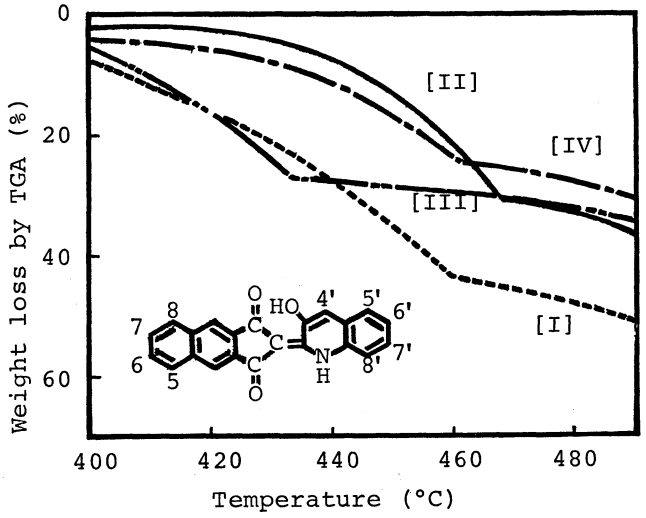

Fig.1 Thermal behavior of halogenobenzo[b]quinophthalone

- 5,8-dibromo-[I].
- 5,6,7,8-tetrabromo-[II].
- 5,6,7,8,4'-pentabromo-[III].
- 5,6,7,8,6',8'-hexabromo-[IV].

2) The fastness to heat and migration was also improved by 0.5-1.5 degree on the P.E., P.P. and P.V.C. substrates. These results were also suported by the observation of TGA.
3) The resistance to aqueous alkali, acid and hot water was perfect and no color change was observed.
4) The color values of [II] were 7-10 times as much as that of CdS.

Table 1. Some properties of polybromo-3'-hydroxybenzo[b]quinophthalones

Compd.	MW	Substituent	Mp[a] (°C)	λ_{max}[b] (nm)	ε ($\times10^{-4}$)	Weight loss by TGA(%) at (°C) 420	440	460	480	500	Solubility[c] ($\times10^2$g/l) DMF	Rs[d]	αCN[e]	Rs[d]
I	497	5,8-Br_2	410	450 475	4.4 6.6	15	28	44	49	54	1.0	3	13	4.5
II	655	5,6,7,8-Br_4	456	455 480	4.6 6.6	2	6	21	34	39	0.33	1	2.9	1
III	734	5,6,7,8,4'-Br_5	410	458 483	3.8 6.6	15	28	30	34	37	3.3	10	120	41
IV	813	5,6,7,8,6',8'-Br_6	430	460 490	4.7 7.0	5	11	23	27	32	6.7	20	50	17

a) Measured by means of DTA. b) Measured in α-chloronaphthalene in the concentration of $1/5\times10^4$mol/l. c) Solubility at room temperature.
d) Relative value of solubility. e) α-chloronaphthalene.

Table 2. Some properties of 5,6,7,8-tetrabromo-3'-hydroxybenzo[b]quinophthalone as a pigment*

Substrate	TiO_2 (%)	Fastness and/or Resistance to: Light (hrs) 100	200	400	Heat	Migration	Alkali	Acid	Hot water	Color value
Polystyrene (P.S.)	0	5	5	5	5	5	5	5	5	
	0.5	5	5⁻	4-5	5	5	5	5	5	8-9 (2G)
A. B. S.	0	5	5	5⁻	5	5	5	5	5	
	0.5	5	5⁻	4-5	5	5	5	5	5	8-9 (2G)
Polyethylene (P.E.)	0	5	5	5⁻	5	3-4	5	5	5	
	0.5	5	5⁻	4-5	5	3-4	5	5	5	7-8 (R)
Polypropylene (P.P.)	0	5	5	5⁻	5	5	5	5	5	
	0.5	5	4-5	4	5	5⁻	5	5	5	7-8 (3R)
Polyvinyl-chloride (P. V. C.)	0	5	5⁻	4-5	5	2-3	5	5	5	
	0.5	5	4-5	4	5	2-3	5	5	5	8-10 (G)

* Methods for the testing are as same as those of earlier article[1].

From these results and the earlier observations[1], it was concluded that 5,6,7,8-tetrabromo-3'-hydroxybenzo[b]quinophthalone [II] was the best organic pigment among the halogenobenzoquinophthalones.

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Reference

1) M.Matsuoka, T. Kitao and K. Konishi, Chem. Lett., 1974, 201.

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