# Polychlorinated Biphenyls in the Phthalocyanine Pigments

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In recent years there has been considerable public concern about the presence of polychlorinated biphenyls (PCBs) residues in the environment. Many studies have indicated that these residues resulted from the use of commercial formulations of PCBs in various industrial application(JENSEN et al. 1969, KOEMAN et al. 1969, NISBET et al. 1972, RISEBROUGH et al. 1968, ZITKO et al. 1971). However, little attention has been given to the possible presence of PCBs in some organic chemicals.

There have been some cases where gas chromatographic profiles, similar to the profile from commercial PCB formulations containing 54% chlorine, were determined in extracts of blue color printed on food packaging materials and blue color printing inks. Consequently, we undertook the analysis for PCB in the phthalocyanine pigments which are used as a source of the blue color.

## Materials and Methods

Phthalocyanine pigments were mainly sampled in the Tokyo and Osaka areas in Japan, from June to December, 1972 and from July to September, 1975.

Analyses for PCB in the pigments were carried out by hexane extraction, Florisil column clean up and electron capture gas chromatography. Approximately 100 mg sample was weighed into a 125 ml Erlenmeyer flask, and refluxed with 50 ml hexane on the steam bath for 30 min. The refluxed solution was filtered through glass fiber paper, the filtrate placed on a 10 g, 19 mm i.d. Florisil column and eluted with 200 ml hexane. The eluate was concentrated to 5 ml and analysed by electron capture gas chromatography.

The quantitation of PCB residues was done by measuring the total peak height of the electron capture response for the residue against that of Kanechlor 500, a commercial PCB formulation containing 54% chlorine manufactured in Japan. Recoveries using this procedure ranged from 87.6% to 95.9%(average of 92.0%) with samples fortified with Kanechlor 500 at 100 ppm.

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Gas chromatography was with a Shimadzu GC 4BM equipped with a $^{63}$Ni electron capture detector, 2% DC-200 on Gas-Chrom Q in 1.5 m long x 3 mm i.d. glass column operated at a column temp. of 180°C. A determination of each gas chromatographic peak was carried out by a Shimadzu-LKB 9000 gas chromatograph-mass spectrometer operating at an ionizing energy of 70 eV, and an accelerating voltage of 3.5 kV.

To reconfirm the presence and the levels of PCB found in pigments quantitative perchlorination was carried out as follows(MIDZUTANI et al. 1972, ARMOUR 1973). An amount of sample to give one to 10 µg of PCB residue was placed in a 20 cm long x 10 mm i.d. glass test tube, and the solvent completely removed under reduced pressure. The residue was treated with 0.5 ml antimony pentachloride in a sealed glass test tube heated at 230°C for 2 hrs in an oil bath to form the fully chlorinated decachlorobiphenyl. Afterwards the cooled reactant was extracted with 50 ml benzene. The benzene solution was washed succesively with 30 ml 20% hydrochloric acid, 25 ml 20% tartaric acid, and two, 20 ml portions of water, dehydrated with anhydrous sodium sulfate, and concentrated to 5 ml.

Decachlorobiphenyl formed by perchlorination of a mixture of chlorobiphenyls was easily detectable as a single peak by electron capture gas chromatography using a 2% DC-200 column at 220°C. Residue values were determined based on the electron capture response to the decachlorobiphenyl derivative compared to standard decachlorobiphenyl; results were expressed in terms of PCB containing five chlorines. PCB levels obtained by the two methods of quantitation, total peak height and decachlorobiphenyl derivative, were in close agreement.

## Results and Discussion

PCB extracted from phthalocyanine pigments of different manufactureres gave gas chromatographic profiles similar to a commercial PCB containing 54% chlorine;gas chromatograms are shown Figure 1. PCB from phthalocyanine green was found to be decachlorobiphenyl. Each peak in the electron capture gas chromatograms of extracts of phthalocyanine blue was evaluated by gas chromatography-mass spectrometry. The number of chlorines in chlorobiphenyls causing the peaks was found to be similar to that in the commercial PCB, Kanechlor 500. Decachlorobiphenyl in phthalocyanine green was identified in the same manner.

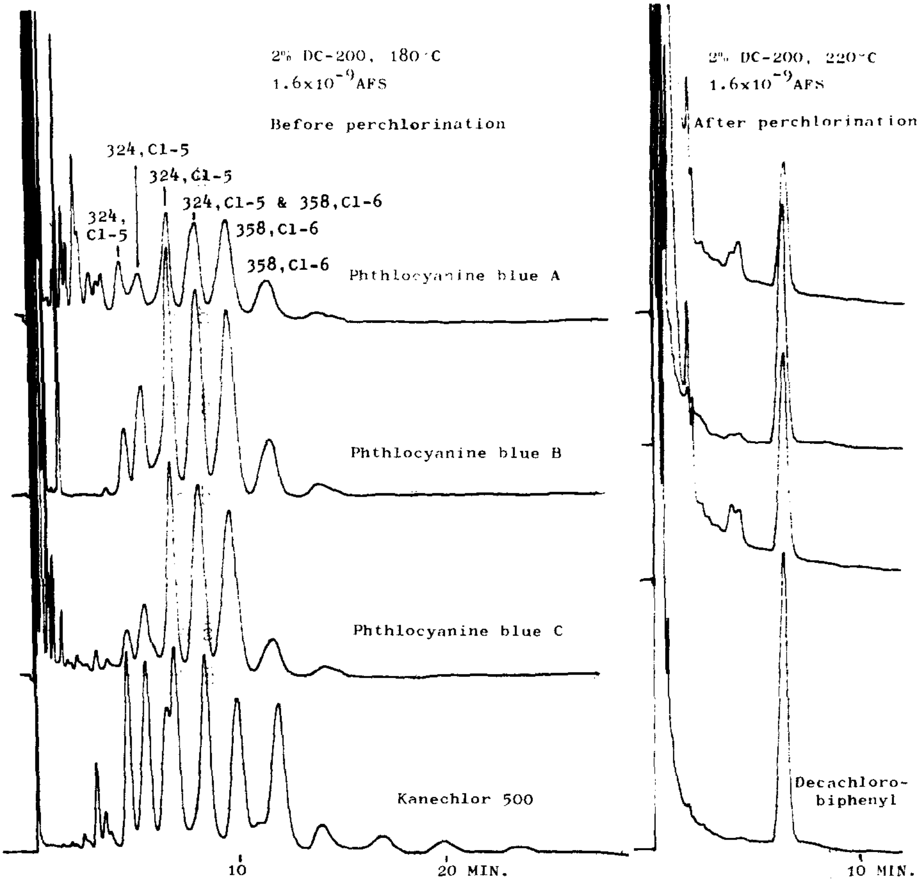

Figure 1. Polychlorinated biphenyls in phthalocyanine blue pigments. The molecular ion m/e and the number of chlorines of major peaks were determined by GC-Mass spectrometry.

PCB levels determined in phthalocyanine pigments were below approximately 200 ppm as shown in TABLE 1. No PCB was detected in some samples.

Commercially, two basic processes are used for the preparation of phthalocyanine pigments:(1) from phthalonitrile and copper or a copper salt, and (2) from phthalic anhydride, urea, and copper or a copper salt. The phthalonitrile process was favored in Germany, at least prior to 1945. The urea process seems to be favored in England, the United States(MOSER et al. 1963) and in Japan.

TABLE 1.

Mean levels of polychlorinated biphenyls in phthalocyanine blue and phthalocyanine green

| Pigment | Makers | No. of samples, 1972 | PCB, ppm av. range | No. of samples, 1975 | PCB, ppm av. range |
|---|---|---|---|---|---|
| Blue | A | 3 | 90( 50-166) | 3 | 166(132-220) |
| | B | 4 | 88( 66-117) | 7 | ND |
| | C | 2 | 138(124-151) | 4 | 153(142-174) |
| | D | - | - | 6 | 42(0.3-110) |
| | E | - | - | 3 | 0.3(0.2-0.3) |
| | F* | 2 | 4( 3- 4) | - | - |
| | G* | 2 | 186( 72-300) | - | - |
| | H* | 2 | 243(186-300) | - | - |
| | I* | 2 | ND | - | - |
| | J* | - | - | 1 | 21 |
| Green | K | 2 | 64( 60- 68)** | 1 | 1** |
| | L* | - | - | 1 | 42** |
| | M* | - | - | 2 | 63( 16-110)** |

*imported samples, other are domestic.
**decachlorobiphenyl values.

PCB was usually found in products produced by the urea process involving trichlorobenzene as the reaction medium. It is assumed that some pigments found to contain no PCB were manufactured without a solvent as the reaction medium or with a solvent other than an organochlorine solvent such as trichlorobenzene; for example, nitrobenzene(MOSER et al. 1963) and polyalkyl benzenes(MATSUURA 1974).

No PCB was detected in urea, phthalic anhydride, copper chloride, ammonium molybdate and trichlorobenzene that are usually used in the preparation of pigments. Precautions were taken to avoid contamination of samples by PCBs in our laboratory. Interaction between individual materials and trichlorobenzene was not investigated. However, PCB was found in pigments synthesized by the urea process with trichlorobenzene as the reaction medium. PCB in the reactant progressively increased with increased production of phthalocyanine blue. If the pigment was synthesized using hydrocarbon solvents, such as isopropyl xylene, as the reaction medium no PCB was detected in the pigment(MATSUURA 1974). The precursor and mechanism of formation of PCB in the solvent (trichlorobenzene) process of phthalocyanine pigment production is under investigation.

This study indicates that pigments prepared using trichlorobenzene contain PCB. Therefore, it may be assumed that the presence of PCB in phthalocyanine blue was caused by a manufacturing process using trichlorobenzene as the reaction medium. On the other hand, it may be assumed that decachlorobiphenyl in phthalocyanine green was formed by perchlorination from PCB in phthalocyanine blue.

PCBs are a widespread environmental contaminant. Regulatory guidelines have been established and actions taken in Japan. Today technology exists for the manufacture of phthalocyanine pigments free from PCB. Therefore, it is expected that manufactureres of these pigments should consider appropriate measures to ensure that their products do not contain this persistent contaminant.

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