PCB CONGENER PROFILE OF UNINTENTIONAL FORMATION FROM PIGMENT MANUFACTURING PROCESS

Nakano T[1]*, Anezaki K[2]

[1] Graduate School of Engineering, Osaka University, 2-1, Yamadaoka, Suita 565-0871, Japan; [2] Hokkaido Research Organization, Environmental and Geological Research Department, Institute of Environmental Sciences, N19W12, Kita-ku, Sapporo 060-0819, Japan

Introduction

A report from Japan Dyestuff and Industrial Chemicals Association (JDICA) revealed that some organic pigments contained a trace amount of polychlorinated biphenyl (PCB) unintentionally formed in the manufacturing process. In response to the report, the Ministry of Economy, Trade and Industry (METI) decided performing the survey immediately the current situation. As an urgent measure for the time being, METI instructed manufacturer to stop manufacture, import and shipment, if organic pigments contained PCBs more than international guideline. (Pigment : Generic term for water-insoluble or oil-insoluble powder used for coloring. Organic pigments are those comprising organic compounds.)

Regarding PCB in organic pigments, Uyeta et al[1] have pointed out that phthalocyanine related pigment may contain in PCB in 1976. Although PCB was not detected in the starting materials themselves for pigment manufacture, such as urea, phthalic anhydride, copper chloride, ammonium molybdate and trichlorobenzene, PCB was detected in the pigments of a manufacturing process using trichlorobenzene as a reaction solvent. PCB in the pigment increased with the increase in amount of copper-phthalocyanine-blue manufacture. Authors also reported that PCB is not detected when a hydrocarbon solvent like isopropyl xylene was used as a reaction solvent. Regarding precursor and PCB formation mechanism during the phthalocyanine pigment production, pigments manufactured using trichlorobenzene contains PCBs, PCB-209 contains in the phthalocyanine green formed from perchlorinated process of phthalocyanine-blue[1]. Authors pointed out that manufacturer should take appropriate measures to reduce PCBs in the product of pigment manufacture using the appropriate manufacturing techniques of the phthalocyanine pigment to establish the regulatory guidelines, reducing PCB level.

We have reported [2, 3] PCBs level and profile as unintentional formation product of the organic pigments such as a commercial azo pigment, phthalocyanine pigment. We have presented about the PCB congener-specific profile in pigments, and the reaction mechanism expected from pigment manufacturing process.

Materials and methods

Polycyclic pigment was studied commercially available pigment in Japan and overseas , the dioxazine violet (PV23). The congener assignment was confirmed using GC-TQMS (450-GC/320-MS, Bruker) with HT8-PCB capillary column (Kanto , 60m × 0.25mm). Regarding to dioxazine violet pigment such as PV23, this pigment is synthesized by ring-closing reaction of 3-amino-N-ethylcarbazole and chloranil in o-dichlorobenzene solvent.Thermal PCB product of o-dichlorobenzene with/without Chloranil, 3-amino-N-ethyl-carbazole, radical initiator have been determined congener specifically. The dominant congeners were PCB-5(2,3-), PCB-12(3,4-), PCB-40(2,2’,3,3’-), PCB-56(2,3,3’,4-), PCB-77(3,3’,4,4’). The formation process of these congeners were estimated via 2 types of o-dichlorobenzene radicals.We investigated experimentally unintentional formation from o-dichlorobenzene to confirm their formation process[4]. Using various Polychlorobenzenes(PCBz) as reaction solvent were tested under the similar conditions with PV-23 manufacturing process.

Regarding radical reaction, V-70L : rac-2,2'-Azobis[(2R*)-2,4-dimethyl-4-methoxypentanenitrile] was used as radical initiator.

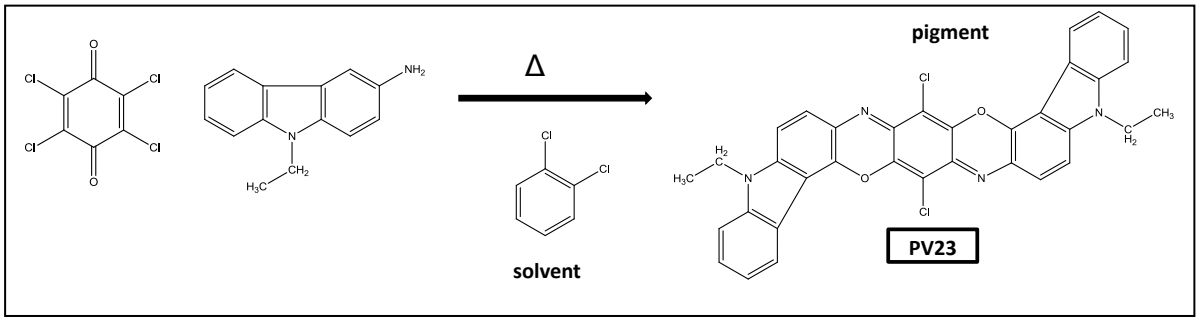

Fig.1 Formation reaction of pigment violet (PV23)

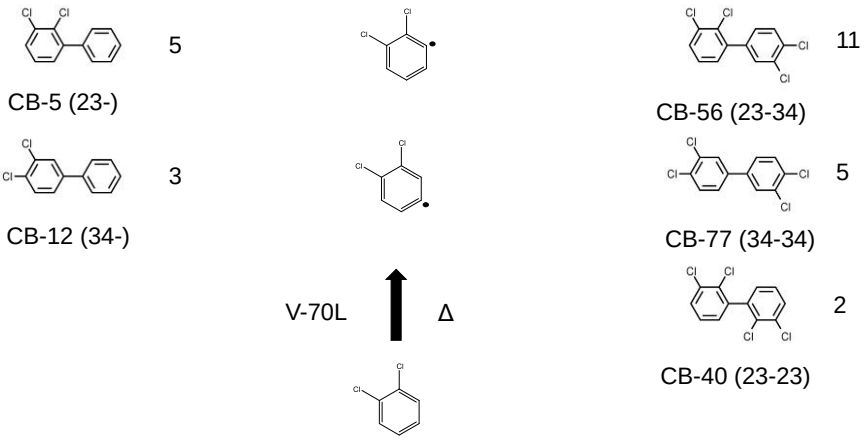

Fig.2 Radical coupling from *o*-dichlorobenzene

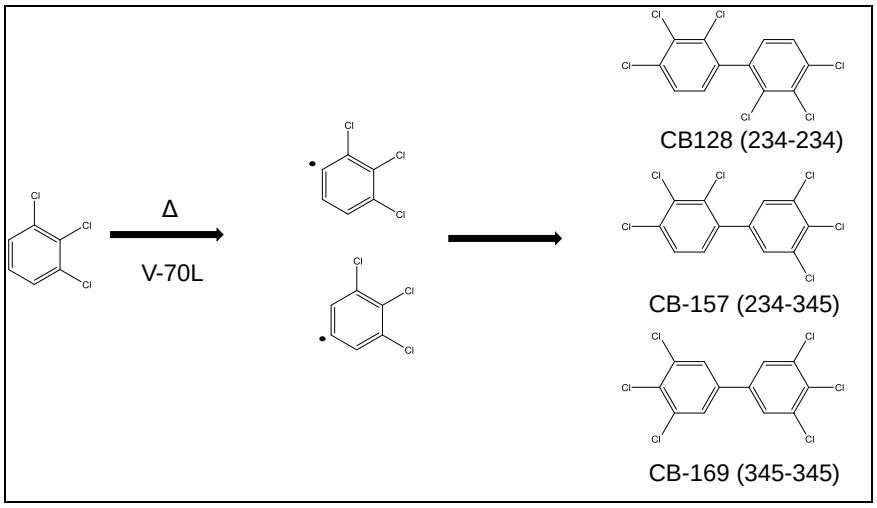

Fig.3 Radical coupling from 1,2,3-trichlorobenzene

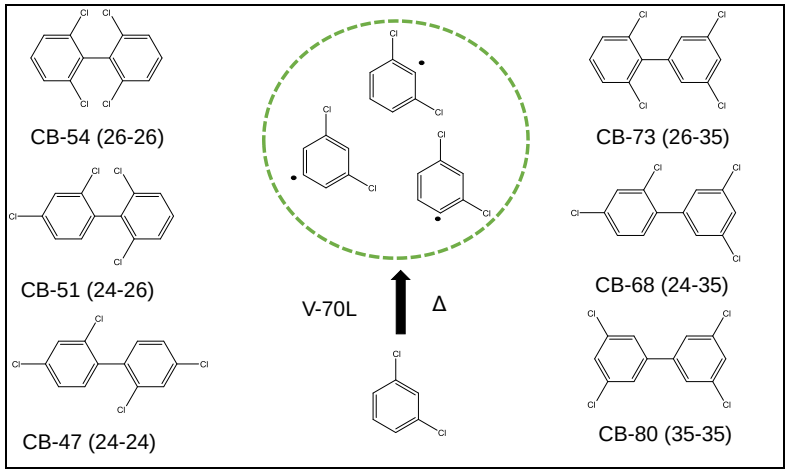

Fig.4 Radical coupling from *m*-dichlorobenzene

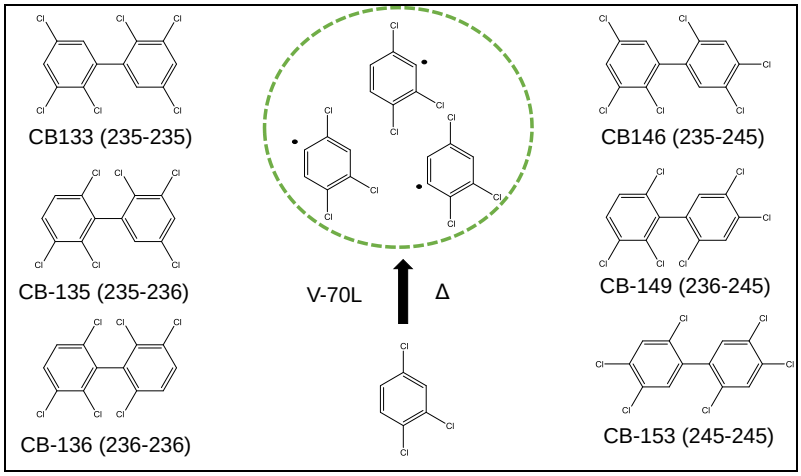

Fig.5 Radical coupling from 1,2,4-trichlorobenzene

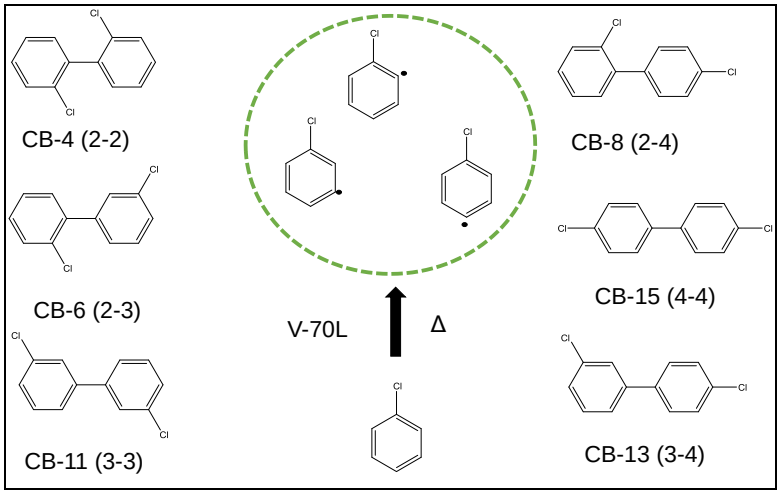

Fig.6 Radical coupling from chlorobenzene

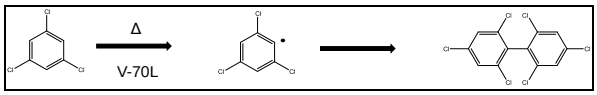

Fig.7 Radical coupling from 1,3,5-trichlorobenzene

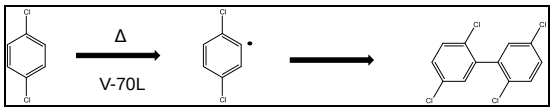

Fig.8 Radical coupling from *p*-dichlorobenzene

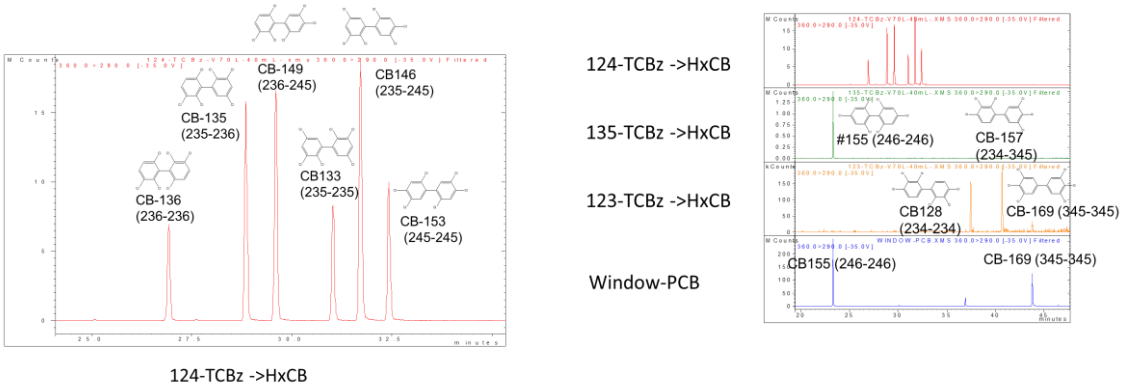

Fig.9 GC/MS-SIM chromatohram of PCB isomers formed from various trichlorobenzenes

Results and discussion

Fig.1 shows Formation reaction of pigment violet (PV23). Radical reaction products formed from each chorobenzenes are very simple and the isomer ratio is relatively constant. PCB isomers are formed in response to the number of formed radical species. Chlorobenzene forms 6 PCB isomers (CB-4, CB-6, CB-8, CB-11, CB-13, CB-15). *o*-dichlorobenzene forms 3 PCB isomers (CB-56, CB-77, CB-40). *m*-dichlorobenzenes forms 6 PCB isomers (CB-54, CB-51, CB-73, CB-47, CB-68, CB-80). *p*-dichlorobenzene forms only one PCB isomer (CB-52). 1,2,3-trichlorobenzene forms 3 PCB isomers (CB-128, CB-157, CB-169). 1,2,4-trichlorobenzene forms 6 PCB isomers (CB-136, CB-135, CB-149, CB-133, CB-146, CB-153). 1,3,5-trichlorobenzene forms only one PCB isomer (CB-155) (Fig. 2-Fig.8). Fig.9 shows GC/MS-SIM chromatograms of PCB isomers formed from various trichlorobenzenes

References:

1. Uyeta, M., Taue, S. and Chikazawa, K. (1976); *Bulletin of Environm. Contam. & Toxicol.*, 16: 417-421
2. Anezaki, K. and Nakano, T. (2013); *Environ Sci Pollut Res*, DOI 10.1007/s11356-013-1977-2
3. Anezaki K, Kannan N, Nakano T. (2014); *Environ Sci Pollut Res Int.* 2014 May 10.
4. Nakano T, Anezaki Y, Takahashi G, Tawara K. (2013); *Journal of Environ. Chem.*23,107-114 (Jap)