POLYCHLORINATED BIPHENYL CONTAMINATION IN POLYCYCLIC-TYPE PIGMENTS AND SILICONE-BASED GLUES

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Introduction

Polychlorinated biphenyls (PCBs) were mass-produced and used throughout the world until the 1970s, owing to their excellent physical and chemical stability. However, they were subsequently classed as persistent organic pollutants (POPs) because of their toxicity, diffusivity, and persistence in the environment, and their international transfer was restricted by the Stockholm Convention. It is stipulated that, by 2028, all PCBs should be correctly disposed of, leading to countries now actively working towards this target. The main origin of PCBs is industrial production of so-called technical PCBs such as Aroclor, Chlophen, and Kanechlor. However, it was recently found that PCB congeners that are not categorized as technical, such as 3,3′-dichlorobiphenyl (PCB-11), are present as impurities in some organic pigments and chemical products. These were often detected as the main congeners, and different congener patterns were exhibited compared to technical PCBs[1-5]. As a result, such pigments are attracting increasing attention as a source of PCBs that has so far been overlooked.

In a previous paper, we reported on the concentrations and congener patterns of the PCBs present in azo-type and phthalocyanine-type organic pigments, and speculated on the process by which these byproducts were formed[6]. It has also been found that certain concentrations of PCBs are contained in some polycyclic-type pigments and chemical products (silicone-based glue). Accordingly, this study reports on the concentrations and congener patterns of PCBs within such substances.

Materials and methods

The oil pigments dioxazine violet (pigment violet (PV) 23) and diketopyrrolopyrrole (pigment red (PR) 254, 255) were analyzed, in addition to a silicone-based glue and the organotin used in the production of the glue. Each sample was accurately weighed on the order of mg, and placed in a separating funnel with a small amount of conc. H_2SO_4. Hexane (100–150 mL) was then added and the mixture was shaken vigorously. This process was repeated until the hexane lost all color. This layer was subsequently washed with purified water, and dehydrated with Na_2SO_4. A surrogate was added to the liquid extract and it was concentrated by rotary evaporation. It was then added to a multilayer silica-gel column and eluted with 200 mL of hexane. The eluent was added to a Supelclean sulfoxide SPE tube, and the impurities were removed using 9 mL of hexane. A Discovery Ag-ION SPE tube was then attached to the bottom of the SPE tube, and the sample was eluted with 50 mL of 5% dichloromethane in hexane. The eluent was concentrated and recovery standard substances were added to make a 50 μL nonane solution. Quantification of the PCBs, pentachlorobenzene (PeCBz), and hexachlorobenzene (HxCBz) was performed by high resolution gas chromatography (HP6890, Agilent Technologies, USA)–high resolution mass spectrometry (JMS700D, JEOL, Japan), and they were analyzed with an HT8-PCB capillary column (60 m, 0.25 mm i.d., Kanto Kagaku, Japan). The limits of detection were 0.00005–0.0006 mg/kg for PCBs, and 0.0006–0.001 mg/kg for PeCBz and HxCBz.

Results and discussion

1. Dioxazine violet (PV23)

As shown in Table 1, seven different oil pigments produced by seven manufacturers were analyzed to assess the presence of PV23. For all PCBs, the concentration was in the range 0.045–6.5 mg/kg, with that of four pigments exceeding 0.5 mg/kg, the level at which a substance is classed as PCB-containing in Japan. However, no pigments exceeded 50 mg/kg, which is the level specified by the Stockholm Convention, above which transportation is restricted. For both PeCBz and HxCBz, the concentrations were below 0.0026 mg/kg. For all samples, the dichlorinated substances (PCB- 5 and PCB-12) and the tetrachlorinated substances (PCB-40, PCB-56, and PCB-77) were detected as the main congeners. For some samples, dichlorinated PCB-7, PCB-9, and

PCB-10 were identified, while others were observed to contain the monochlorinated PCB-1 and trichlorinated PCB-16. On the whole, di- and tetrachlorinated substances accounted for over 95% of PCBs, but with concentrations varying among samples. Of the three tetrachlorinated congeners, PCB-77 is a dioxin-like PCB, and was found to have a toxicity equivalence quantity (TEQ) range 1.1–110 pg-TEQ/g. PV23 is synthesized by the warming and ring-closing reaction of 3-amino-9-ethylcarbazole and 2,3,5,6-tetrachlorobenzoquinone in *o*-dichlorobenzene[7]. As each of the di- and tetrachlorinated congeners found in these particular samples had two adjacent chlorine atoms on one of the aryl groups of the biphenyl backbone, there is a strong suggestion that these byproducts were formed as a result of the radical reaction of *o*-dichlorobenzene to form biphenyls (Fig.1).

Table 1 Concentrations of PCB congeners, PeCBz, and HxCBz in oil paints manufactured from dioxazine violet pigments (unit: mg/kg)

		Code	007	S-1108	H138	733	436	413	604
PCBs		Manuf.	C	D	E	G	H	I	J
Congener IUPAC #	Chlorine positions	C.I. name	PV23	PV23	PV23	PV23	PV23	PV23	PV23
#1	2-MoCB		0.0043	0.028	0.016	0.00096			
#2	3-MoCB			0.00058					
#5	2,3-DiCB		0.22	1.7	0.74	0.20	0.0089	0.019	0.029
#7	2,4-DiCB		0.0093		0.0033				
#9	2,5-DiCB		0.021		0.0074				
#10	2,6-DiCB		0.0083						
#12	3,4-DiCB		0.17	1.2	0.44	0.17	0.013	0.018	0.037
#16	2,2′,3-TrCB		0.0047	0.12	0.0053	0.010		0.00015	Tr
#20/33	2,3,3′-TrCB 2′,3,4-TrCB		0.0085	0.18	0.0099	0.020		Tr	Tr
#35	3,3′,4-TrCB		0.00068						0.00054
#40	2,2′,3,3′-TeCB		0.049	0.37	0.031	0.070	0.0015	0.011	0.0062
#56	2,3,3′,4′-TeCB		0.24	1.8	0.14	0.37	0.011	0.057	0.041
#77	3,3′,4,4′-TeCB		0.15	1.1	0.062	0.2	0.011	0.031	0.028
Σ PCBs			0.88	6.5	1.5	1.0	0.045	0.14	0.14
WHO-TEQ(pg-TEQ/g)			15	110	6.2	20	1.1	3.1	2.8
Chlorobenzene									
PeCBz				0.0011			0.0011		0.0013
HxCBz			0.00059	0.00047		0.00078	0.0012	0.00047	0.0026

Cluster congeners that co-elute on HT8-PCB column is expressed by "/".
WHO-TEQ is calculated for dioxin-like PCB congener(#77) using WHO-TEF.
Blank spaces indicate that none of that component was detected.

2. Diketopyrrolopyrrole (PR254, PR255)

Eight different oil pigments produced by six manufacturers were analyzed for the presence of PR254 and PR255 (Table 2). The concentrations of all of the PCBs were in the range 0.0095–2.3 mg/kg, with one pigment exhibiting a concentration exceeding 0.5 mg/kg. It was found that the PCB concentrations of the oil pigments that contained PR255, which does not have a chlorine substituent, were lower than that of the pigments containing PR254 alone. The concentrations of PeCBz and HxCBz were both below 0.013 mg/kg. In the majority of cases, dichlorinated congeners were detected as the main components, accounting for over 87% of the total PCB concentration, with PCB-8, PCB-13, and PCB-15 identified in particularly high proportions. Sample 042 from manufacturer G displayed different results, with monochlorinated PCB-3 accounting for 99% of the total PCB concentration. For all six of the dichlorinated congeners, each aryl group of the biphenyl backbone had a single chlorine substituent; there was no occurrence of two chlorine atoms being present on the same ring. PR254 is synthesized by heating and curing *p*-chlorobenzonitrile and a succinate ester(e.g., diethyl succinate)[7-8]; therefore, the congener pattern indicates that the radical reaction of *p*-chlorobenzonitrile was involved in the mechanism by which these PCB byproducts formed (Fig. 2).

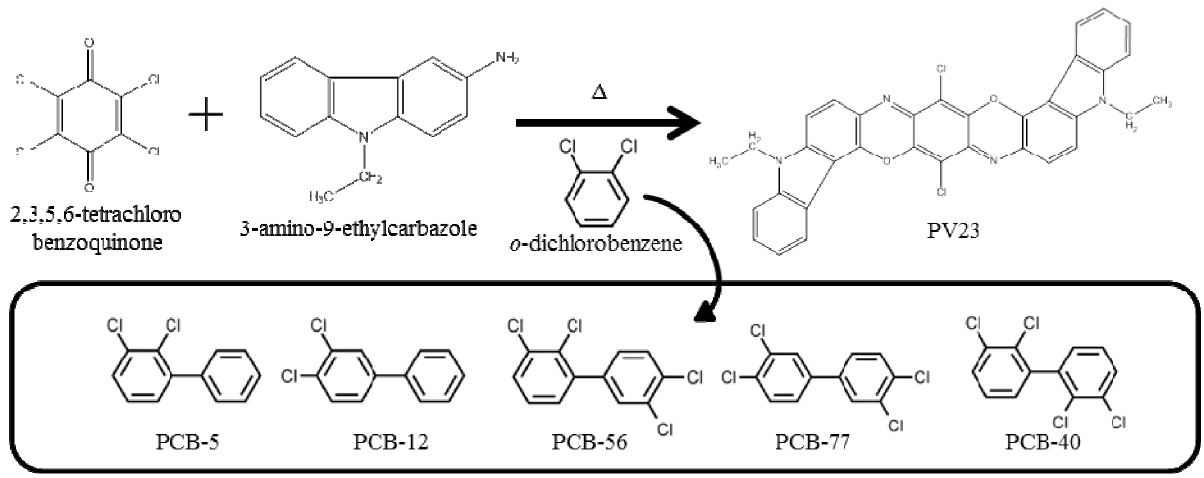

Fig. 1 PCB byproducts formed during the manufacture of dioxazine violet pigments.

Table 2 Concentrations of PCB congeners, PeCBz, and HxCBz in oil paints made from diketopyrrolopyrrole pigments (unit: mg/kg)

PCBs		Code	170	PG012	371	377	042	603	263	369
		Manuf.	C	E	F	F	G	G	H	J
Congener IUPAC #	Chlorine positions	C.I. name	PR254	PR254	PR254	PR254 PR255	PR254	PR255	PR254	PR254 PR255
#1	2-MoCB		0.0050							
#2	3-MoCB		0.010	0.016						
#3	4-MoCB		0.026	0.053			0.12		0.0023	
#4	2,2′-DiCB		0.0096	0.036						
#6	2,3′-DiCB		0.013	0.067	0.00063					
#8	2,4′-DiCB		0.091	0.68	0.0045	0.00078		0.00069	0.0067	0.00034
#11	3,3′-DiCB		0.0030	0.025						
#13	3,4′-DiCB		0.075	0.69	0.018	0.0041	0.0015	0.0079	0.11	0.0074
#15	4,4′-DiCB		0.088	0.74	0.026	0.0046	0.0040	0.0084	0.16	0.0094
#31	2,4′,5-TrCB								0.019	
Σ PCBs			0.32	2.3	0.049	0.0095	0.12	0.017	0.31	0.017
Chlorobenzene										
PeCBz			0.00053	0.0022		Tr	0.013		0.00043	0.00076
HxCBz			0.00061	0.0035	0.0010	0.00021	0.00091	0.00051	0.0014	0.00079

Blank spaces indicate that none of that component was detected.

3. Silicone-based glue and organotin

In previous studies involving the analysis of PCBs in air samples, we detected congener patterns that were significantly different from those of technical PCBs. It was speculated that the High Volume Air Sampler (HV) that was used to collect the samples may be contaminated. Accordingly, we studied the presence of PCBs in the materials used to construct the HV. The glue used in the quartz fiber filter holder was found to contain PCBs, with the level in one glue batch exceeding 50 mg/kg. PCB-2 and PCB-3 were observed to be the dominant monochlorinated substances, and the dichlorinated compounds were found to be those with a single chlorine substituent on each aryl ring, which is a similar congener pattern to that detected for the HV (Table 3). The main component of this glue is silicone, and as it is known that organotin is used for the moisture-curing of this polymer, the PCBs in organotin were also analyzed (Table 3). The congener pattern of the glue was similar to chlorotriphenyltin, but the concentrations were completely different, demonstrating that the PCB impurities were unlikely to come from this particular component. We now plan to analyze the PCBs in the silicone component of the glue in order to elucidate the source of the PCB contamination.

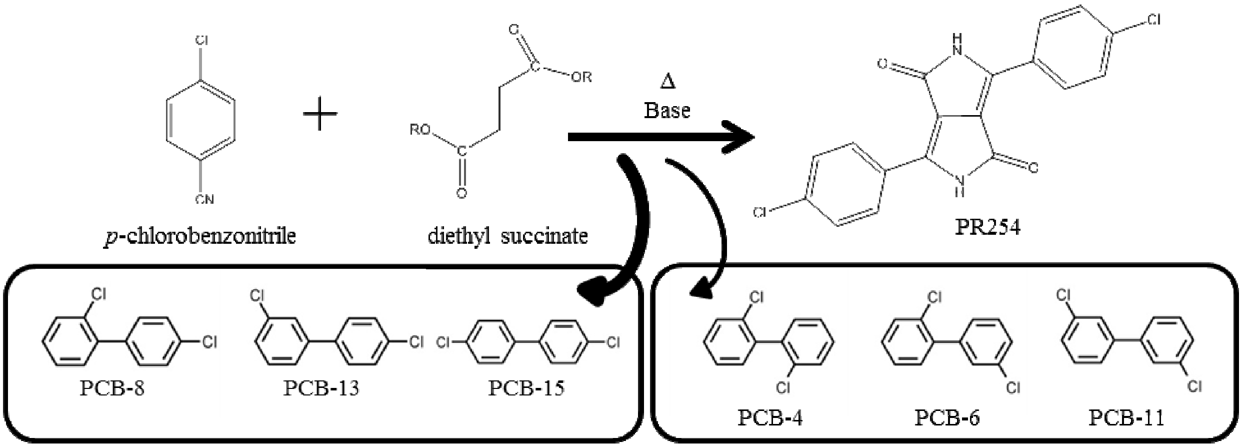

Fig. 2 PCB byproducts formed during the manufacture of diketopyrrolopyrrole pigments.

Table 3 Concentrations of PCB congeners in silicone-based glue and organotin (unit: mg/kg)

PCBs		Sample	glue Lot.2011	glue Lot.2012	Trichlorophenyltin	Dichlorodiphenyltin	Chlorotriphenyltin	Trichlorobutyltin	Dichlorodibutyltin	Chlorotributyltin
Congener IUPAC #	Chlorine positions	Manuf.	A	A	B	B	B	B	B	B
#1	2-MoCB		2.4	9.8	0.14		0.39			
#2	3-MoCB		21	16	0.011		0.24			
#3	4-MoCB		17	12	0.015		0.27			
#4	2,2′-DiCB		0.41	0.11			0.00026			
#5	2,3-DiCB				0.0013					
#6	2,3′-DiCB		4.7	1.0			0.00088			
#7	2,4-DiCB		0.015		0.0044		0.00028			
#8	2,4′-DiCB		2.4	0.28			0.0029			
#9	2,5-DiCB		0.024		0.00048		0.00048			
#10	2,6-DiCB				0.00061					
#11	3,3′-DiCB		5.4	0.59			0.00049			
#12	3,4-DiCB				0.0016					
#13	3,4′-DiCB		5.5	0.68			0.00085			
#14	3,5-DiCB				0.00015					
#15	4,4′-DiCB		2.1	0.12			0.0045			
Σ PCBs			61	40	0.18		0.91			

Blank spaces indicate that none of that component was detected.

Acknowledgements
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References

1. Hu D, Hornbuckle K C. (2010); *Environ Sci Technol.* 44: 2822–2827
2. Rodenburg L A, Guo J, Du S, Cavallo G J. (2010); *Environ Sci Technol.* 44: 2816–2821
3. Hu D, Martinez A, Hornbuckle K C. (2008); *Environ Sci Technol.* 42: 7873–7877
4. Li YM, Geng DW, Hu YB, Wang P, Zhang QH, Jiang GB. (2012); *Chin Sci Bull.* 57: 1499–1503
5. Takasuga T, Nakano T, Shibata Y.(2012); *Organohalogen Compd.* 74: 1437–1440
6. Anezaki K, Takahashi G, Tawara K, Nakano T. (2012); *Organohalogen Compd.* 74: 1433–1436
7. Faulkner EB, Schwartz RJ. (2009); High performance pigments, 2nd edn. Wiley, New York.
8. Shamekhi SS, Nourmohammadian F. (2012); *Prog. Color Colorants Coat.* 5: 1–6