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Polychlorinated biphenyl contamination of paints containing polycyclic- and Naphthol AS-type pigments

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Abstract This study reports the concentrations and congener partners of polychlorinated biphenyls (PCBs) in commercially available paints. Polycyclic-type pigments containing dioxazine violet (pigment violet (PV) 23, PV37) and diketopyrrolopyrrole (PR254, PR255) were found to contain PCB-56, PCB-77, PCB-40, PCB-5, and PCB-12, and PCB-6, PCB-13, and PCB-15, respectively, as major congeners. Dioxazine violet is contaminated with by-products during synthesis from *o*-dichlorobenzene, which is used as a solvent during synthesis, and diketopyrrolopyrrole is contaminated with by-products during synthesis from *p*-chlorobenzonitrile. The concentration of PCBs in paint containing PV23 or PV37 was 0.050–29 mg/kg, and toxic equivalency (TEQ) values ranged 1.1–160 pg-TEQ/g. The concentration of PCBs in paint containing PR254 or PR255 was 0.0019–2.4 mg/kg. Naphthol AS is an azo-type pigment, and PCB-52 was detected in paint containing pigment red (PR) 9 with 2,5-dichloroaniline as its source. PCB-146, PCB-149, and PCB-153 were identified from paint containing PR112 produced from 2,4,5-trichloroaniline, as major congeners. These congeners have chlorine positions similar to aniline, indicating that these congeners are by-products obtained during the synthesis of pigments. The concentrations of PCBs in paints containing PR9 and PR112 were 0.0042–0.43 and 0.0044–3.8 mg/kg, respectively. The corresponding TEQ for PR112 was 0.0039–8.6 pg-TEQ/g.

Keywords Polychlorinated biphenyls · Congeners · Pigments · Dioxazine violet · Diketopyrrolopyrrole · Naphthol AS · By-product

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Introduction

Polychlorinated biphenyls (PCBs) are categorized as persistent organic pollutants (POPs). Their production and transportation have been restricted by government regulations in many countries and monitored closely by the Stockholm Convention. By virtue of their physicochemical stability, PCBs were originally manufactured as PCB technical mixtures, e.g., Aroclor. At present, they are not produced industrially. However, it has been recently acknowledged that PCBs are produced unintentionally during the manufacture of pigments and chemical products (Anezaki and Nakano 2013; Anezaki and Nakano 2014; Hu and Hornbuckle 2010; Shang et al. 2014; Takasuga et al. 2012). There are 209 theoretically possible congeners in a PCB mixture based on the chlorine substitution in a biphenyl backbone. Interestingly, the congener patterns of PCBs produced unintentionally in the pigments differ significantly from those of PCB technical mixtures. For example, it was found out that PCB congeners −11, −52, and −209 are produced as by-products during the manufacture of some azo-type and phthalocyanine-type pigments. Interestingly, PCB-11 was not found in PCB technical mixtures (Frame et al. 1996; Schulz et al. 1989) but in environmental media, such as atmosphere, water, and sediments, around the world (Basu et al. 2009; Du et al. 2008; Hu et al. 2008; King et al. 2002; Li et al. 2012; Litten et al. 2002; Rodenburg et al. 2010; Romano et al. 2013; Rowe et al. 2007). It is of great concern that low molecular weight PCBs are easily hydroxylated in the human body and are metabolized to more toxic substances. Several studies reported that various hydroxylated PCBs including low molecular weight PCBs showed agonistic and/or antagonistic activities against a variety of receptors, such as estrogen receptors (ERs)α/β, androgen receptor (AR), thyroid hormone receptor (TR), and aryl hydrocarbon receptor (AhR) (Arulmozhiraja et al. 2005; Kamata et al. 2009; Takeuchi et al. 2011).

In a previous study, the present authors have reported that PCB-11 and PCB-52 as well as PCB-35, PCB-77, PCB-101, and PCB-153 are produced as by-products in the pigments in oil paints from azo-type pigments manufactured from 3,3′-dichlorobenzidine (3,3′-DCB) and 2,2′,5,5′-tetrachlorobenzidine (2,2′,5,5′-TCB), including pigment yellow (PY) 13 and PY81. It was also observed that highly chlorinated PCBs (mainly PCB-209) are produced from pentachlorobenzene and hexachlorobenzene during the manufacture of phthalocyanine-type pigments such as pigment green 7 (Anezaki and Nakano 2014). Thus, it is likely that PCBs are formed when the pigment constituents include a biphenyl backbone, such as 3,3′-DCB and 2,2′,5,5′-TCB, or when chlorobenzene, which is used as a solvent during synthesis, undergoes a radical reaction. It was previously reported that PCBs are also included in some polycyclic-type pigments such as dioxazine violet and diketopyrrolopyrrole. Although there are few studies on these compounds, it is likely that other pigments may also contain PCBs derived from raw materials or chlorobenzene; hence, the need for further detailed research.

The Stockholm Convention restricts the transportation of materials containing more than 50 mg/kg PCB (Stockholm Convention 2001). In Japan, the shipment of such materials is controlled. In addition to shipment controls, the USA and Canada specify an annual average PCB concentration of 25 mg/kg or less in product lots (ETAD 2011). In the USA, pigments with PCB concentrations greater than 2 mg/kg must be reported to the Environmental Protection Agency (ETAD 2011). Within the European Union, in addition to the regulation of PCBs, it is mandatory to keep the concentration of polychlorinated terphenyl to less than 50 mg/kg (ETAD 2011). In these examples, national regulations on the PCB contents of pigments are stricter than the Stockholm Convention. It was also found that some pigments contain dioxin-like PCBs (DL-PCBs) and have toxicity similar to that of dioxins (Anezaki and Nakano 2014; Shang et al. 2014). Therefore, it is essential to establish precise concentration levels and congener information for various pigments. In this study, we report the PCB concentrations and congener patterns of paints containing pigments for which there is little or no prior research and discuss the possible mechanisms of their production. In addition, we report a summary of the types and congener composition of PCBs in pigments that have been studied earlier.

Materials and methods

Reagents and chemicals

Commercially available oil and acrylic paints were purchased within and outside Japan. We analyzed eight kinds of paint, produced by seven companies, that contain polycyclic pigments including dioxazine violet (pigment violet (PV23), PV35), and nine kinds of paints, produced by seven companies, that contain diketopyrrolopyrrole (pigment red (PR)254, PR255). For paints containing the azo pigment Naphthol AS (PR9, PR112), 13 kinds of paints produced by four companies were analyzed. Standards of PCBs were purchased from Cambridge Isotope Laboratories Inc. (MA, USA) and Wellington Laboratories Inc. (Ontario, Canada). NK-MBP-MXC (Wellington) was used for the surrogate, and the syringe spike was prepared by the authors by combining the ^{13}C-labeled PCB standard products (CIL and Wellington), while diluting them when necessary. Organic solvent and silica gel designed for dioxin analysis, and concentrated H_2SO_4 (super special grade) were obtained from Wako Pure Chemical Industries, Ltd. (Japan). Supelclean sulfoxide SPE tubes (Numata et al. 2008) and Discovery Ag-ION SPE tubes were obtained from Supelco (USA).

Sample analysis

The paint pretreatment method, GC-MS analysis method, surrogate, and syringe spike adopted for this study are the same as those used previously (Anezaki and Nakano 2014). Several milligrams of each paint type was sampled, dispersed in hexane, and treated with sulfuric acid until it was decolorized. The hexane layer was washed with water, dehydrated, and divided, and the surrogate was added. Then, it was treated with a multilayer silica gel column, the Supelclean sulfoxide SPE tube, and the Discovery Ag-ION SPE tube. The eluate was concentrated, and the syringe spikes were added to make a 50 μL nonane solution.

Congener-specific analysis of PCBs was carried out in all paint samples. Quantification of PCBs was performed by HRGC (HP6890 Agilent Technologies, USA) in combination with HRMS (JMS700D, JEOL, Japan). The samples were analyzed with an HT8-PCB capillary column (Matsumura et al. 2002) (60 m, 0.25 mm i.d., Kanto Kagaku, Japan) with the following temperature program: 120 °C for 1 min, 20 °C/min to 180 °C, 2 °C/min to 260 °C, 5 °C/min to 300 °C, and held at 300 °C for 8 min. This method resulted in the separation of the 209 congeners into 193 peaks. The HRMS was operated in selected ion monitoring mode for each congener group. The monitored ions were referenced against the values reported in the literature (Takasuga et al. 1995). For the concentrations of PCB congeners, it was assumed that the

HRGC–HRMS relative sensitivity for PCB congeners with the same chlorine number would be the same; the concentrations were then calculated for each congener. The assignments for each congener in the chromatogram were checked against values in the literature (Matsumura et al. 2002) and by analysis of fly ash samples.

Quality control and quality assurance

The limits of quantification (LOQ) varied depending on congener and sample size. The LOQ values for pigment samples were found to be 0.0001–0.0006 mg/kg for each PCB congener. The concentrations for the peaks were determined by isotope dilution quantification using surrogates. The surrogate recovery rates (calculated using syringe spike) of PCBs were within the range 50–120 %, and those of monochlorinated biphenyl were within the range 40–80 %. Laboratory blanks were also checked regularly. The lab blank values were found to be extremely low (<0.001 mg/kg), and therefore, the sample values were not blank-corrected.

Results and discussion

Concentration levels and congener profiles

Tables 1, 2, 3, and 4 show the C.I. names and PCB congener concentrations in paints containing dioxazine violet, diketopyrrolopyrrole, and Naphthol AS. Blank values and congeners omitted from the tables are indicated by ND (not detectable). Toxic equivalency (TEQ) is shown for pigments with DL-PCBs detected.

For dioxazine violet, PCBs were identified from paints containing either PV23 or PV37, the PCB concentration ranged from 0.050 to 29 mg/kg, and no paints exceeded a PCB concentration of 50 mg/kg, the upper limit prescribed by the convention on POPs. The PCB congener profiles revealed that PCB-56 was the dominant congener overall, followed by PCB-5, PCB-12, PCB-40, and PCB-77, respectively, and these five congeners accounted for more than 92 % of the total PCB concentration recorded. From Codes 138 (PV23) and 106 (PV37) produced by Company C, we detected the same congeners as those identified from the pigments of other firms and found that the dichlorinated substances of PCB-5 and PCB-12 were dominant, accounting for 79 and 76 % of the total PCB concentration, respectively. Including PCB-40, PCB-56, and PCB-77, they accounted for 96 % of the total PCB concentration. All of the paint samples contained PCB-77, which is classified as a DL-PCB, with a TEQ of 1.1–160 pg-TEQ/g.

As for diketopyrrolopyrrole, PCBs were detected from paints containing PR254 or PR255 and the PCB concentration ranged from 0.0019 to 2.4 mg/kg; all were less than 50 mg/kg. For Code 042 produced by Company D, PCB-3 was dominant and other major congeners were dichlorinated PCB congeners, including PCB-15, PCB-13, and PCB-6. Some other dichlorinated substances, such as PCB-4, PCB-8, and PCB-11, and mono- and trichlorinated congeners were identified, but in all cases dichlorinated congeners comprised more than 85 % of the total PCB concentration. DL-PCBs were not detected.

In the HT8-PCB column, the relative retention time (RRT) was similar for PCB-5 and PCB-8, and for PCB-12 and PCB-13. Thus, it was difficult to separate them; however, PCB-5 and PCB-12 were detected in dioxazine violet, and PCB-8 and PCB-13 were identified in diketopyrrolopyrrole as baseline separated single peaks. They were identified based on RRTs shown in the literature (Matsumura et al. 2002) and by comparing PCB-8 and PCB-12 as reference standards.

For Naphthol AS, PCBs were detected in paints containing PR9, with PCB concentration ranging from 0.0042 to 0.43 mg/kg. For all paints, PCB-52 was the predominant PCB, and it accounted for more than 78 % of the total PCB concentration. PCB-101, PCB-18, PCB-26, PCB-31, and others were also detected. In paints containing PR112, PCB concentrations ranged from 0.0044 to 3.8 mg/kg. For all paints, PCB-146 was the dominant congener, and other major congeners were PCB-149, PCB-153, PCB-118, PCB-101, and PCB-109. In particular, Code 517 produced by Company F contained a broad range from mono- to octachlorinated congeners. For all of the paints, the detected hexachlorinated substances were PCB-146, PCB-149, and PCB-153 only, but these three congeners accounted for 48–95 % of the total PCB concentration. Paints with PR112 contained DL-PCBs, such as PCB-77 and PCB-118, and hence, the TEQ was 0.0039 to 8.6 pg-TEQ/g. No paints containing PR9 or PR112 had a PCB concentration of more than 50 mg/kg. In the HT8-PCB capillary column, it is impossible to separate PCB-149 from PCB-139, but it was assumed that PCB-149 was detected solely for PR112. The details will be described later.

It was found that some paints containing Naphthol AS include pigment white (PW) 6. PW6 is a pigment composed mainly of titanium dioxide, which is classified as rutin type, anatase type, and brookite type. Of these, the rutin type is mostly used as a pigment because it is stable (Buxbaum and Pfaff 2005). Rowe et al. (2007) and Praipipat et al. (2013) detected high levels of chlorinated PCBs (e.g., PCB-209) in the lower Delaware River, which is the site of a titanium dioxide purification plant, and mentioned that PCBs are produced unintentionally during the extraction of titanium. We analyzed nine kinds of paints composed of mainly PW6 produced by nine companies, the rutin type and anatase type titanium dioxides sold by Wako Pure Chemical Industries, Ltd. (Japan) and Kanto Chemical Co., Inc. (Japan), to check

Table 1 Concentrations of PCB congeners in polycyclic-type (dioxazine violet) paint pigments (unit, mg/kg)

	Code Company Country C.I. name	007 A Japan PV23	S-1108 B Japan PV23	138 C Japan PV23	106 C Japan PV37	733 D UK PV23	436 E Italy PV23	413 F UK PV23	604 G France PV23
PCBs congener IUPAC #	Chlorine positions								
#1	2-MoCB	0.0059	0.031	0.021	0.53	0.0037			
#2	3-MoCB		0.0012	0.0004	0.011	0.0006			
#3	4-MoCB			0.0006	0.011	0.0004			
#5	2,3-DiCB	0.22	1.7	0.75	13	0.20	0.012	0.022	0.031
#7	2,4-DiCB	0.0093		0.0033	0.038				
#9	2,5-DiCB	0.021		0.0074	0.091				
#10	2,6-DiCB	0.0083			0.028				
#12	3,4-DiCB	0.17	1.2	0.44	9.1	0.17	0.013	0.018	0.037
#16	2,2′,3-TrCB	0.0064	0.12	0.0049	0.10	0.010		0.0024	0.0005
#20/33	2,3,3′-TrCB 2′,3,4-TrCB	0.012	0.18	0.0078	0.22	0.018		0.0037	0.0011
#35	3,3′,4-TrCB	0.0007	0.0050						0.0005
#40	2,2′,3,3′-TeCB	0.049	0.37	0.033	0.77	0.071	0.0022	0.012	0.0068
#56	2,3,3′,4′-TeCB	0.24	1.8	0.15	3.5	0.37	0.012	0.058	0.042
#77	3,3′,4,4′-TeCB	0.15	1.1	0.062	1.6	0.20	0.011	0.031	0.028
ΣPCBs		0.89	6.5	1.5	29	1.1	0.050	0.15	0.14
WHO-TEQ(pg-TEQ/g)		15	110	6.2	160	20	1.1	3.1	2.8

Cluster congeners that co-elute on HT8-PCB column are expressed as "/". WHO-TEQ is calculated for dioxin-like PCB congener (#77) using WHO2005-TEF

whether they contained PCBs. PCBs were not present or barely detected in all the paints and the titanium dioxide concentration was ≤0.001 mg/kg. From this result, it was concluded that the production of PCBs from titanium dioxide

Table 2 Concentrations of PCB congeners in polycyclic-type (diketopyrrolopyrrole) paint pigments (unit, mg/kg)

	Code Company Country C.I. name	170 A Japan PR254	012 C Japan PR254	042 D UK PR254	603 D UK PR255	263 E Italy PR254	503 F UK PR108 PR254	369 G France PR254 PR255	371 H Netherlands PR254	377 H Netherlands PR254 PR255
PCBs congener IUPAC #	Chlorine positions									
#1	2-MoCB	0.0061	0.0098							
#2	3-MoCB	0.011	0.019							
#3	4-MoCB	0.027	0.062	0.12		0.0040				0.0005
#4	2,2′-DiCB	0.010	0.040						0.0004	0.0003
#6	2,3′-DiCB	0.092	0.69	0.0005	0.0020	0.0092	Tr	0.0027	0.0074	0.0025
#8	2,4′-DiCB	0.013	0.070						0.0013	0.0020
#11	3,3′-DiCB	0.0032	0.027	0.0018					0.0006	0.0026
#13	3,4′-DiCB	0.075	0.69		0.0079	0.11	0.0006	0.0074	0.018	0.0044
#15	4,4′-DiCB	0.088	0.74	0.0043	0.0086	0.17	0.0014	0.0096	0.027	0.0039
#18	2,2′,5-TrCB		0.0071							
#26	2,3′,5-TrCB		0.0022							
#31	2,4′,5-TrCB		0.0025			0.018				
Σ PCBs		0.33	2.4	0.12	0.018	0.31	0.0019	0.020	0.054	0.016

Tr: below LOQ

Table 3 Concentrations of PCB congeners in azo-type (Naphthol AS derived from 2,5-dichloroaniline) paint pigments (unit, mg/kg)

	Code Company Country C.I. name	027 C Japan PR9	010 C Japan PR9	26 I Japan PR9 PW6	409 I Japan PR9	20 I Japan PR9	532 I Japan PR9
PCBs congener IUPAC #	Chlorine positions						
#4	2,2′-DiCB			0.0007		0.0030	0.0004
#6	2,3′-DiCB			0.0011		0.0046	0.0003
#8	2,4′-DiCB	0.0004		0.0055		0.024	0.0001
#9	2,5-DiCB			0.0005		0.0012	0.0008
#13	3,4′-DiCB			0.0008		0.0075	
#15	4,4′-DiCB			0.0006		0.0023	
#17	2,2′,4-TrCB			0.0010		0.0041	
#18	2,2′,5-TrCB	0.0003	0.0015	0.0016		0.0077	0.0029
#20/33	2,3,3′-TrCB 2′,3,4-TrCB	Tr	Tr			0.0004	Tr
#25	2,3′,4-TrCB			0.0006		0.0027	
#26	2,3′,5-TrCB		0.0022	0.0023		0.0082	0.0027
#28	2,4,4′-TrCB	Tr	Tr	0.0002		0.0022	Tr
#30	2,4,6-TrCB			0.0001			
#31	2,4′,5-TrCB	0.0004	0.0043	0.0025		0.0089	0.0054
#49	2,2′,4,5′-TeCB			0.0002			
#52	2,2′,5,5′-TeCB	0.0082	0.14	0.094	0.0042	0.32	0.13
#70	2,3′,4′,5-TeCB		0.0003				
#84	2,2′,3,3′,6-PeCB					Tr	Tr
#86	2,2′,3,4,5-PeCB		0.0003				
#92	2,2′,3,5,5′-PeCB		0.0002	0.0002		Tr	0.0003
#93/95/98	2,2′,3,5,6-PeCB 2,2′,3,5′,6-PeCB 2,2′,3′,4,6-PeCB	Tr		0.0006		0.0021	0.0004
#101	2,2′,4,5,5′-PeCB	Tr	0.0009	0.0074		0.027	0.0013
#110	2,3,3′4′,6-PeCB	Tr				Tr	Tr
#153	2,2′,4,4′,5,5′-HxCB			0.0002			
ΣPCBs		0.0093	0.15	0.12	0.0042	0.43	0.15

Tr: below LOQ. Cluster of congeners that co-elute in HT8-PCB column are expressed by "/"

could be ignored for the Naphthol AS paints containing PW6 analyzed in this study.

By-product of PCBs

Dioxazine violet

Dioxazine violet is synthesized by heating and ring-closing 3-amino-9-ethylcarbazole and 2,3,5,6-tetrachlorobenzoquinone for PV23, or 2,5-diethoxy-4-benzoylaminoaniline and 2,5-diacetylamino-3,6-dichloro-1,4-benzoquinone for PV37 in the presence of *o*-dichlorobenzene (Faulkner and Schwartz 2009). Most of the detected PCBs were di- and tetrachlorinated forms, and all of the tetrachlorinated PCBs (PCB-40, PCB-56, and PCB-77) had a structure in which two chlorine atoms occupy ortho-meta or meta-para positions of the biphenyl backbone. In addition, even the dichlorinated congeners that were produced such as PCB-5 and PCB-12 had adjoining chlorine atoms in ortho-meta or meta-para positions. The radical reaction of *o*-dichlorobenzene, which is used as a solvent during synthesis, might have resulted in the unintentional formation of biphenyl congeners (Fig. 1). The concentration order of PCB-56>PCB-77>PCB-40 observed in our analysis suggests steric hindrance in the formation of tetrachlorinated congeners.

Table 4 Concentrations of PCB congeners in azo-type (Naphthol AS derived from 2,4,5-trichloroaniline) paint pigments (unit, mg/kg)

	Code	016	517	571	33	533	396	316
	Company	C	F	F	I	I	J	J
	Country	Japan	UK	UK	Japan	Japan	Netherlands	Netherlands
	C.I. name	PR112 PW6	PR112	PR112	PR112 PR207 PW6	PR112	PR112	PW6 PR112 PY42
PCBs congener IUPAC #	Chlorine positions							
#1	2-MoCB		0.0001					
#2	3-MoCB		0.0001					
#3	4-MoCB		0.0002					
#5	2,3-DiCB		0.0003					
#6	2,3′-DiCB		0.0001					
#9	2,5-DiCB		0.0003					
#11	3,3′-DiCB		0.0004					0.0002
#12	3,4-DiCB		0.0053	0.0008				
#17	2,2′,4-TrCB		0.0002					
#18	2,2′,5-TrCB		0.0002					
#20/33	2,3,3′-TrCB 2′,3,4-TrCB		0.0035					
#22	2,3,4′-TrCB		0.0001					
#23	2,3,5-TrCB		0.0030					
#24	2,3,6-TrCB		0.0019					
#25	2,3′,4-TrCB		0.0001					
#26	2,3′,5-TrCB		0.0002					
#28	2,4,4′-TrCB		0.0003					
#29	2,4,5-TrCB		0.029	0.0035			0.0015	
#31	2,4′,5-TrCB		0.0004					
#35	3,3′,4-TrCB		0.0017					
#37	3,4,4′-TrCB		0.0015					
#45	2,2′,3,6-TeCB		0.0062					
#48	2,2′,4,5-TeCB	0.0033	0.15	0.0048		0.0009	0.023	0.0021
#52	2,2′,5,5′-TeCB		0.0030	0.0029				
#56	2,3,3′,4′-TeCB	0.0005	0.016					
#59	2,3,3′,6-TeCB		0.0080					
#63	2,3,4′,5-TeCB						0.0008	
#64	2,3,4′,6-TeCB		0.0064					
#67	2,3′,4,5-TeCB	0.0051	0.17	0.0052		0.0014	0.026	0.0025
#70	2,3′,4′,5-TeCB		0.0069			Tr		Tr
#74	2,4,4′,5-TeCB	0.0039	0.13	0.0037		0.0009	0.018	0.0019
#77	3,3′,4,4′-TeCB	0.0010	0.017	0.0005		0.0003		
#83	2,2′,3,3′,5-PeCB		0.0012					
#84	2,2′,3,3′,6-PeCB		0.0015					
#90	2,2′,3,4′,5-PeCB	0.0001	0.0019					
#91	2,2′,3,4′,6-PeCB	0.0001	0.0016					
#92	2,2′,3,5,5′-PeCB	0.0002	0.0013					
#95	2,2′,3,5′,6-PeCB	0.0001	0.0027	0.0001				0.0001
#97	2,2′,3′,4,5-PeCB	0.0013	0.042	0.0016		0.0006	0.0007	
#99	2,2′,4,4′,5-PeCB	0.0003	0.0035	0.0002			0.0002	
#101	2,2′,4,5,5′-PeCB	0.0045	0.097	0.0090	0.0001	0.0010	0.012	0.0011
#102	2,2′,4,5,6′-PeCB	0.0001	0.0013	0.0001				
#109	2,3,3′,4′,5-PeCB	0.0024	0.098	0.0018		0.0006	0.0005	

Table 4 (continued)

	Code Company Country C.I. name	016 C Japan PR112 PW6	517 F UK PR112	571 F UK PR112	33 I Japan PR112 PR207 PW6	533 I Japan PR112	396 J Netherlands PR112	316 J Netherlands PW6 PR112 PY42
#110	2,3,3′4′,6-PeCB	0.0011	0.049	0.0014	Tr	0.0002	0.0005	Tr
#118	2,3′,4,4′,5-PeCB	0.0082	0.23	0.014	0.0001	0.0022	0.014	0.0012
#120	2,3′,4,5,5′-PeCB	0.0001	0.0017	0.0001				
#135	2,2′,3,3′,5,6′-HxCB	0.0001	0.056	0.0047				
#136	2,2′,3,3′,6,6′-HxCB	0.0001	0.022	0.0017				
#146	2,2′,3,4′,5,5′-HxCB	0.10	1.5	0.12	0.0021	0.018	0.078	0.0069
#149	2,2′,3,4′,5′,6-HxCB	0.044	0.64	0.070	0.0016	0.0095	0.040	0.0038
#153	2,2′,4,4′,5,5′-HxCB	0.039	0.40	0.046	0.0005	0.0098	0.030	0.0023
#172	2,2′,3,3′,4,5,5′-HpCB		0.0075					
#174	2,2′,3,3′,4,5,6′-HpCB		0.0017					
#176	2,2′,3,3′,4,6,6′-HpCB		0.0001					
#178	2,2′,3,3′,5,5′,6-HpCB		0.0002					
#179	2,2′,3,3′,5,6,6′-HpCB		0.0025					
#180	2,2′,3,4,4′,5,5′-HpCB	0.0001	0.024					
#183	2,2′,3,4,4′,5′,6-HpCB		0.0006					
#187	2,2′,3,4′,5,5′,6-HpCB	0.0044	0.053	0.0012	0.0001	0.0011	0.065	0.0038
#194	2,2′,3,3′,4,4′,5,5′-OcCB		0.0004					
#199	2,2′,3,3′,4,5,5′,6′-OcCB		0.0006					
#203	2,2′,3,4,4′,5,5′,6-OcCB		0.0011				0.0003	
ΣPCBs		0.22	3.8	0.30	0.0044	0.047	0.31	0.026
WHO-TEQ (pg-TEQ/g)		0.34	8.6	0.47	0.0039	0.095	0.42	0.036

Tr: below LOQ. Cluster of congeners that co-elute in HT8-PCB column are expressed by "/." WHO-TEQ is calculated for dioxin-like PCB congener (#77, #118) using WHO2005-TEF

Diketopyrrolopyrrole

PR254 and PR255 are synthesized by heating and curing *p*-chlorobenzonitrile (PR254) or benzonitrile (PR255) and succinate ester (e.g., diethyl succinate) (Faulkner and Schwartz 2009; Shamekhi and Nourmohammadian 2012). Among a variety of diketopyrrolopyrrole pigments, PR254 and PR255 contained PCBs. A paint composed of only

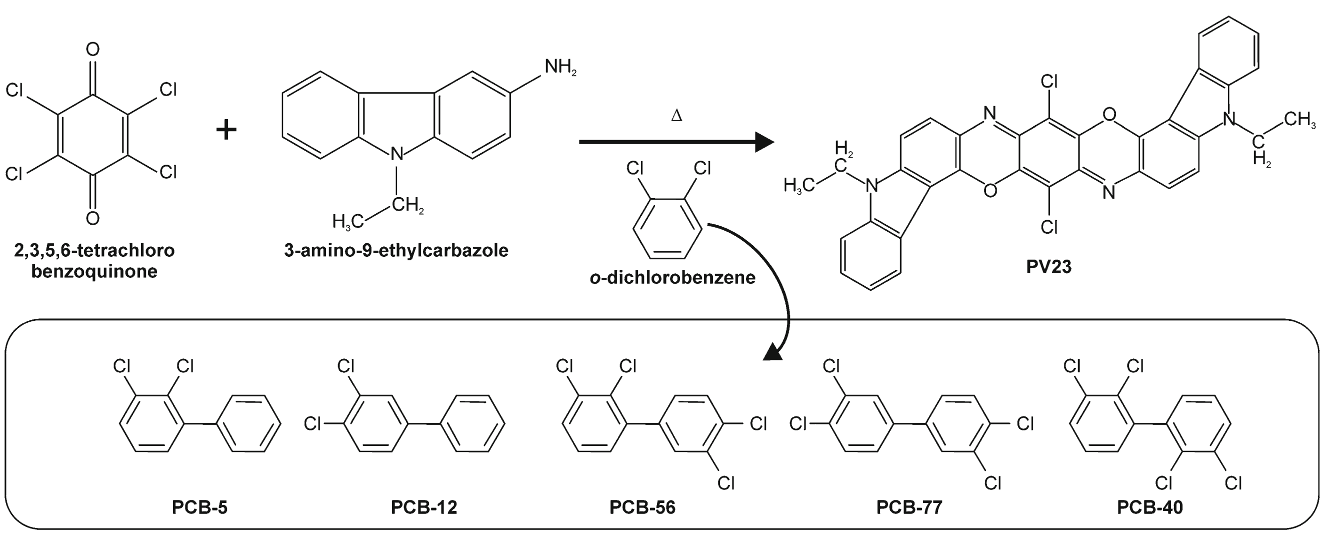

Fig. 1 PCB by-products in the manufacture of polycyclic-type (dioxazine violet) pigments

PR254, which is produced from *p*-chlorobenzonitrile, had higher concentration of PCBs than other paints containing different pigments. Most of the detected congeners were dichlorinated substances, including PCB-6, PCB-13, and PCB-15. All of them had a structure in which one chlorine atom was substituted at each of the two aryls of the biphenyl backbone, and none of the congeners had a structure in which two chlorine atoms were substituted at one aryl. These results of the congener pattern analysis indicate a strong influence of the biphenyl formation mechanism as a result of the radical reaction of *p*-chlorobenzonitrile (Fig. 2). It is unknown why a paint (Code 603 produced by Company D) composed only of PR255 produced from benzonitrile included the same congeners as PR254.

Naphthol AS

Naphthol AS is a product name for 3-hydroxy-2-naphthoic acid anilide used as the grounder for naphthol dyes, and there exist several dozens of them (Herbst et al. 2004). Among them, PR9 and PR112 contained PCBs. They are synthesized by coupling diazotized 2,5-dichloroaniline (2,5-DCA) and 2,4,5-trichloroaniline (2,4,5-TCA) with 3-hydroxy-2-naphthoanilide and 3-hydroxy-2-naphtho-*o*-toluidide, respectively. PCB-52 detected from PR9 has a structure in which two chlorine atoms are at the second and fifth positions of two aryls of the biphenyl backbone. In addition, PCB-18, PCB-31, and PCB-101, which were detected at certain ratios, have a structure in which chlorine atoms are placed at the second and fifth positions of one aryl. This indicates the effects of 2,5-DCA. Namely, it was considered that diazonium salt obtained from 2,5-DCA forms an aryl radical and is coupled with other aromatic substances, producing biphenyl derivatives (Fig. 3). The hexachlorinated substances PCB-146, PCB-149, and PCB-153, which are the major congeners of PR112, have three chlorine atoms at the second, fourth, and fifth positions in the biphenyl backbone. In addition, most of the detected congeners, including PCB-118, PCB-109, PCB-101, PCB-110, PCB-67, PCB-48, and PCB-74, have chlorine atoms at the second, fourth, and fifth positions (or the second, third, and fifth positions) of one aryl. It was considered that biphenyl derivatives were produced from 2,4,5-TCA such as PR9 (Fig. 4). With the HT8-PCB capillary column, it was impossible to separate PCB-48, PCB-95, PCB-97, PCB-109, PCB-149, and PCB-187 from PCB-47, PCB-93/98, PCB-117, PCB-107, PCB-139, and PCB-182, respectively; however, considering the effects of 2,4,5-TCA, it can be inferred that the former congeners were detected as single peaks for PR112. Accordingly, Table 4 shows them as single substances.

This study did not analyze paints containing PR2. PR2 is rarely used for paints because its weather resistance and light fastness are inferior to those of newer pigments. However, it is synthesized from 2,5-DCA, and so there is a high possibility that PCBs, such as PCB-52, are unintentionally produced in PR2 like PR9.

Unintentional PCBs in pigments

Table 5 summarizes the pigments that contained PCBs. Results from previous reports are also included (Anezaki and Nakano 2014). All pigments have characteristic PCB congener profiles based on the raw materials and reaction solvents involved in the synthesis that differ drastically in PCB composition noticed in PCB technical mixtures. PCB-11 is a major congener present in yellow pigments, such as Pigment Yellow 14, but it is not present in PCB technical mixtures, as mentioned in the "Introduction." In Japan, the amount of pigments produced or imported in 2010 was approximately 29,000 t, of which approximately 3,900 t were estimated to be yellow pigments including PCBs. Yellow pigments containing PCBs are considered to account for 20 % of organic pigments produced worldwide. Because yellow pigments are abundantly used, pollution caused by PCBs is considered to be a serious and lingering

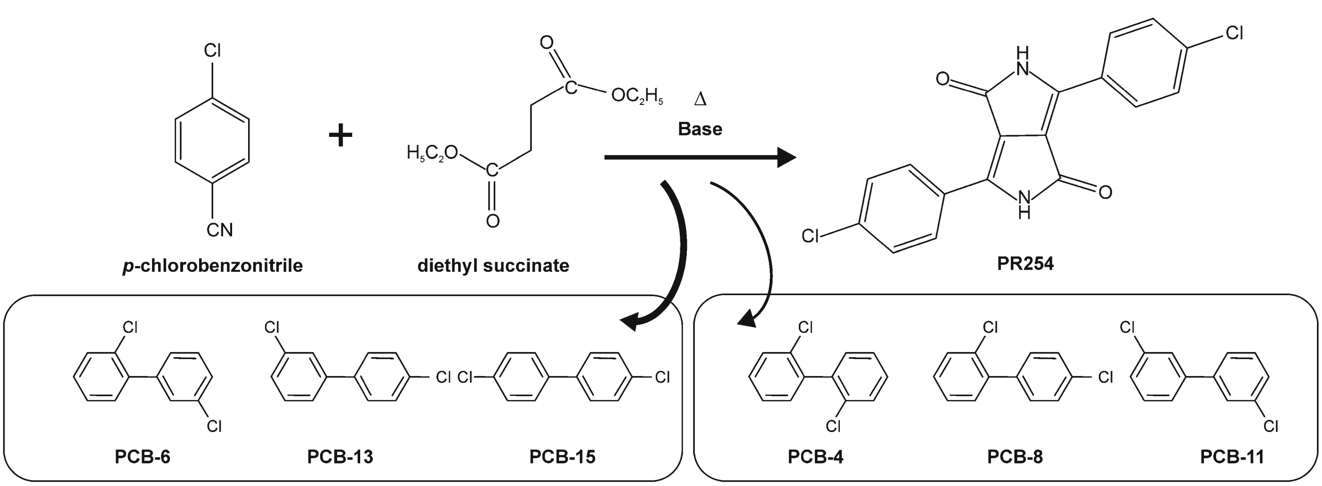

Fig. 2 PCB by-products in the manufacture of polycyclic-type (diketopyrrolopyrrole) pigments

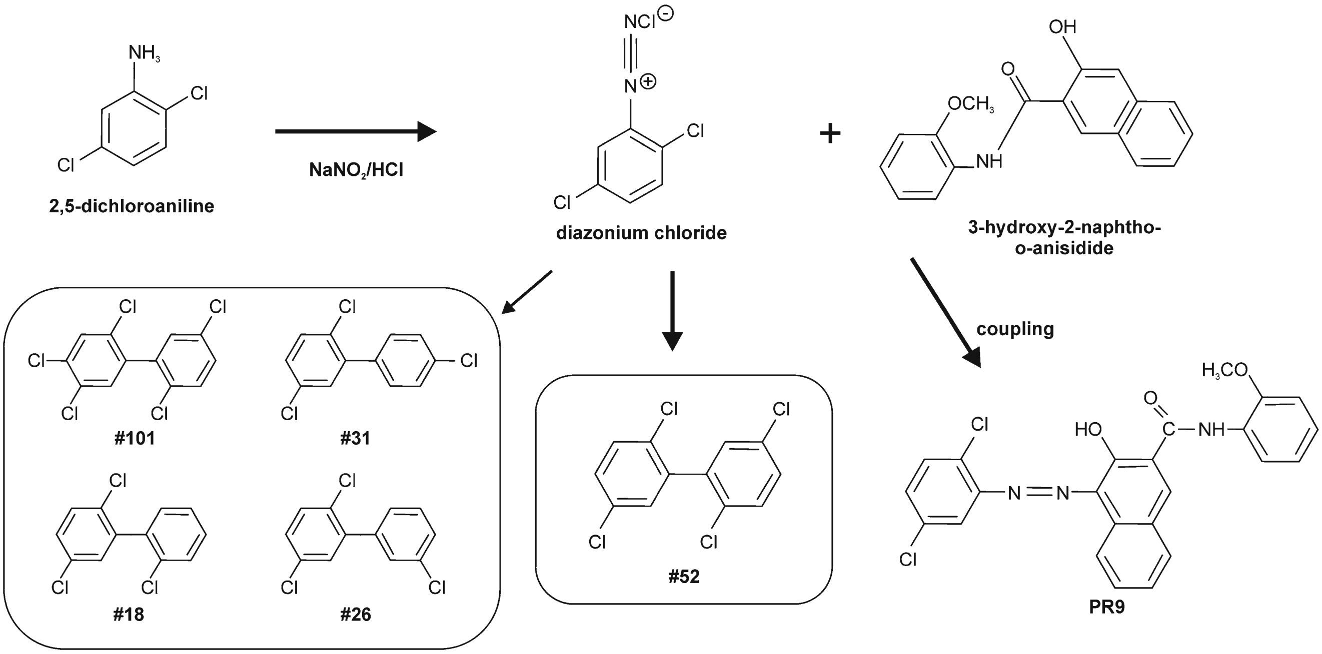

Fig. 3 PCB by-products in the manufacture of azo-type (Naphthol AS derived from 2,5-dichloroaniline) pigments

environmental hazard. Therefore, the levels of these pigments need continuous monitoring. PCB-209 in phthalocyanine, PCB-40, 56, and 77 in dioxazine violet, PCB-6 and 13 in diketopyrrolopyrrole, and PCB-146 in Naphthol AS are not the major congeners detected as PCB technical mixtures (Frame et al. 1996; Schulz et al. 1989). When the concentrations of these congeners are different from those of other congeners, such as indicator PCBs, there is a possibility that pigments are polluting the environment. In support of our observation, Rodenburg and Meng (2013) found that PCB-12 concentrations were different from those of the other PCB congeners in the air in Chicago. PCB-12 concentration was not in equilibrium according to Hendry's law, indicating a constant input derived from non-Aroclor sources (because commercial sources such as pigments have been vastly banned in the USA since the 1980s).

Conclusion

None of the paints reported in this paper had a PCB concentration of >50 mg/kg, but there is a possibility that PCBs might

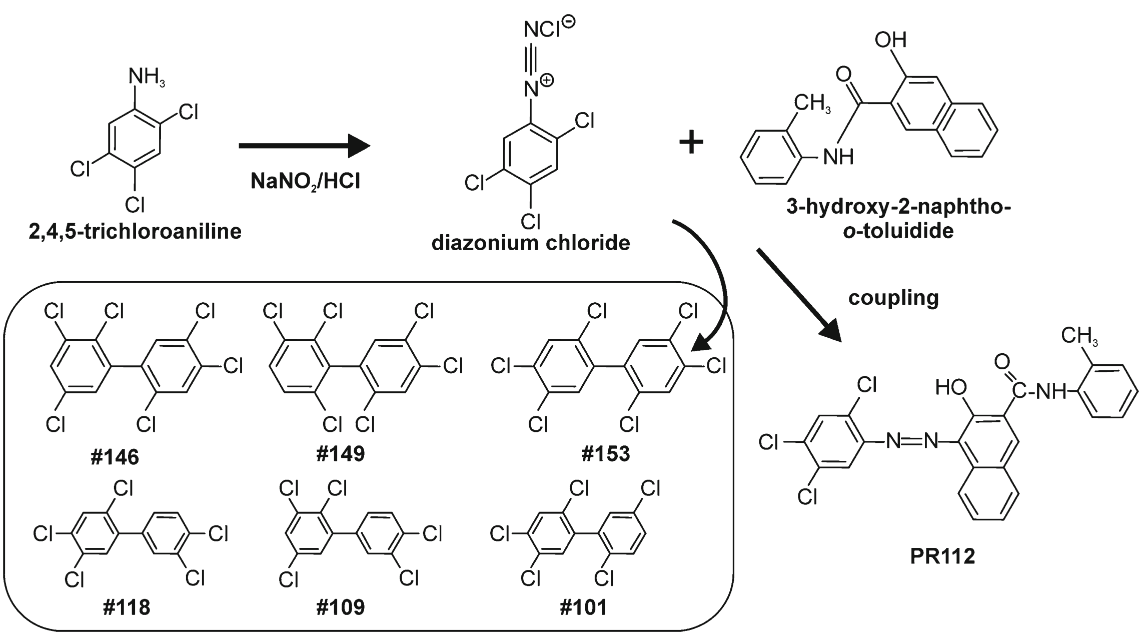

Fig. 4 PCB by-products in the manufacture of azo-type (Naphthol AS derived from 2,4,5-trichloroaniline) pigments

Table 5 List of unintentional PCB contamination of pigments

Chemical class	C.I. Name	Congener		Dioxin toxicity	Unintentional synthetic process	Note
		Dominant	Dependent			
Dis-azo pyrazolone	PY12, PY13, PY14, PY17, PY55, PY83, PY152, PO13, PO16	#11	#35, #77	Yes	Diazotization of 3,3'-dichlorobenzidine	There is a possibility that it is included in PY87, PY124, PO31, and PO34.
Dis-azo	PY81	#52	#101, #153	No	Diazotization of 2,2′,5,5′-tetrachlorobenzidine	
Phthalocyanine	PG7, PG36	#209	#206, #207, #208, etc.	No	Chlorination of chlorobenzene and its biphenyl derivatization	Pentachlorobenzene and hexachlorobenzene are also included.
Dioxazine	PV23, PV37	#5, #12, #40, #56, #77	#1, #16, #20/33, etc.	Yes	Biphenyl derivatization of *o*-dichlorobenzene	
Diketopyrrolopyrrole	PR254, PR255	#6, #13, #15	#4, #8, #11, etc.	No	Biphenyl derivatization of *p*-chlorobenzonitrile	
Naphthol AS	PR9	#52	#18, #31, #101, etc.	No	Biphenyl derivatization of 2,5-dichloroaniline	There is a possibility that it is also included in PR2.
Naphthol AS	PR112	#146, #149, #153	#67, #48, #74, #101, #109, #118, etc.	Yes	Biphenyl derivatization of 2,4,5-trichloroaniline	

PCB congeners are shown by IUPAC number

be included in pigments—the raw materials of paints—at extremely high concentrations. The pigment contents in paints vary, but organic pigments normally have stronger coloring power than inorganic ones. Therefore, the blend ratios of organic pigments are lower than those of inorganic pigments. For instance, the pigment contents in paints of a certain maker could be approximately 50 % by weight for the (inorganic) cadmium pigment-using color, approximately 10 % for the phthalocyanine pigment-using color, and approximately 4 % for the red organic pigment-using color. Because the PCBs in organic pigments are considerably diluted at the stage of manufacturing paints, the initial concentration of PCBs in pigments mostly exceeds 50 mg/kg.

The pigments shown in Table 5 are still manufactured and used worldwide. Though countries that have signed the Stockholm Convention dispose technical PCB wastes in accordance with the convention recommendation, there is an emerging possibility that PCBs are introduced unintentionally in the environment as a result of pigment production. This might have significant impacts on the environment. Hence, it is necessary to promote activities for reducing PCBs in commercially available pigments and to monitor pigment-derived PCB contamination in the environment. The use of congener specific analysis is indispensable in accurately assessing unintentionally produced PCBs.

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