# POLYCHLORINATED NAPHTHALENES CONTAMINATIONS IN SOME COMMERCIAL PRODUCTS IN JAPAN

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## Introduction

In January 16, 2002, it appeared that more than 18 metric tons of polychlorinated naphthalenes (PCNs) had been imported by Japanese domestic company (Showa DDE Co.) from U.K. from 1998 to 2000 without abidance by rule of regulation and manufacture of chemical substances in Japan. This rule was established in 1973 after the adversity accident of "Kanemi disease" by polychlorinated biphenyls (PCBs) and PCNs were listed in the group of the most hazardous chemicals (class I) in 1979. The PCNs imported illegally was used to make "Neoprene FB" as synthetic rubber product by polymerization of chloroprene from 1999 to 2001. Total amount of Neoprene FB which manufactured was reported as 259 metric tons and more than 207 metric tons were exported to foreign countries. Rest of them and manufactured "rubber compounds" were used in weather-resistant products, adhesives, shoe soles, paints and many kind of products in Japan. Only less than 800kg of Neoprene FB was recalled by end of February and more than 29 metric tons was supposed to still exist in commercial products. It's known that Neoprene FB and the rubber compounds have been used by 42 domestic companies to make wide variety of commercial products in Japan by April 30, 2002.

One more unexpected trouble reported February 2002. About 54 metric tons of rubber compound for adhesive which was made with Neoprene FB (contains PCNs) had been imported by Sumitomo 3M Co. from Canada after December, 1995. This rubber compound was used to manufacture three series of aerosol adhesive bombs. Total amount of product was reported more than 210,000 bombs and it was announced to be recalled at end of February under direction of Ministry of Economy, Trade and Industry (METI). Amount of PCNs in adhesive material which imported was declared about 40kg by Sumitomo 3M.

These were ignorant illegal mistakes by private companies under insufficient control of hazardous chemicals in Japan.

This study was oriented to conduct follow-up work of these incidents from both domestic and international point of view. The most important point, there is no information of isomer-specific data of PCNs in any material and product related Neoprene FB. It's essential to conduct isomer-specific risk assessment of PCNs as dioxin-like compounds, because PCNs constitute 75 isomers and some of these has been estimated its toxicity equivalency factors (TEFs) as a dioxin-like compound [2].

## Materials and Methods

Aerosol adhesive bombs and its control (same kind of adhesive bomb from different manufacturer from Sumitomo 3M) were purchased from market in March, 2002. Neoprene FB and related rubber compounds were provided under the request to cooperate this national follow-up project. Samples were dissolved into methylene chloride and toluene before quantification. Exact amount of solution was passed through the acidic silica multi-layer glass column. Eluate by 200mL of hexane was concentrated

and applied to double-column HPLC (graphitic carbon and pyrenil silica HPLC) clean up which enable to high resolution separation of each isomer of PCNs.

HRGC-HRMS (JMS-700D, JEOL Co.) was used to obtain isomer-specific data of PCNs. Pair of single ion

**Table 1.** Isomer-specific data of PCNs in contaminated commercial products in Japan.

| PCN isomers | IUPAC | HW 1001 | imported PCNs | Neoprene FB | rubber coated sheet | aerosol adhesive bomb 333 (serial no.) | | control |
|---|---|---|---|---|---|---|---|---|
| | | | | | | 2A1LC1 | 25K0LB1 | |
| | | % | % | ug/g | ug/g | ug/mL | ug/mL | ug/mL |
| Σ DiCNs | | 3.3 | 1.4 | 494 | 8.5 | 4.2 | 14 | - |
| 123 | 13 | <0.63 | <0.23 | <40 | <3.0 | <2.2 | <3.2 | - |
| 124/(137)/146 | 14/24/(21) | 22 | 26 | 8,930 | 181 | 190 | 325 | - |
| 125 | 15 | 5.3 | 3.1 | 875 | 51 | 27 | 55 | - |
| 126 | 16 | 1.1 | 1.7 | 521 | 7.9 | 4.7 | 4 | - |
| 127 | 17 | 1.5 | 2.2 | 657 | 21 | 4.5 | 7.5 | - |
| 128 | 18 | 0.64 | 1 | 340 | 3 | <2.2 | 3.2 | - |
| 135 | 19 | 2.6 | 4.8 | 1,550 | 33 | 13 | 18 | - |
| 136 | 20 | <0.63 | <0.23 | <40 | <2.9 | <2.2 | <3.2 | - |
| 138/145 | 22/23 | 9.2 | 6.9 | 2,530 | 54 | 39 | 92 | - |
| 137 | 25 | <0.63 | 1.3 | 454 | <2.9 | 3.5 | 5.5 | - |
| (236) | (26) | <0.63 | <0.23 | <40 | <2.9 | <2.2 | <3.2 | - |
| Σ TriCNs | | 42 | 47 | 15,860 | 351 | 282 | 510 | - |
| 1234 | 27 | 0.61 | 1.2 | 425 | 9.6 | 8.7 | 7 | - |
| 1235/1256 | 28/36 | 1.4 | 3.5 | 1,160 | 14 | 23 | 16 | - |
| 1236 | 29 | 0.67 | 1.5 | 560 | 10 | 11 | 8.1 | - |
| 1237/1245 | 30/32 | 1.2 | 1.2 | 442 | 10 | 14 | 9.9 | - |
| (1238) | 31 | <0.2 | <0.2 | <60 | <3 | <5.9 | <2.3 | - |
| 1246/1247/1257 | 33/34/37 | 2.9 | 4.7 | 2,110 | 46 | 60 | 40 | - |
| 1248 | 35 | 7.7 | 8.4 | 3,540 | 70 | 84 | 78 | - |
| 1258 | 38 | 13 | 19 | 8,010 | 182 | 238 | 203 | - |
| (1268) | (40) | <0.08 | <0.2 | <60 | <3 | <5.9 | <2.3 | - |
| 1278 | 41 | 0.92 | 1.5 | 594 | 14 | 11 | 9.6 | - |
| 1357 | 42 | 0.46 | 1.6 | 623 | 11 | 13 | 7.7 | - |
| (1358/1368) | (43/45) | 7.5 | 9.7 | 4,230 | 109 | 144 | 103 | - |
| (1367) | (44) | <0.2 | <0.2 | <60 | <3 | <5.9 | <2.3 | - |
| 1458 | 46 | 6.2 | 5.7 | 2,680 | 75 | 98 | 115 | - |
| 1467 | 47 | 0.72 | 1.5 | 605 | 9.7 | 16 | 11 | - |
| 2367 | 48 | <0.2 | <0.2 | <60 | <3 | <5.9 | <2.3 | - |
| Σ TetraCNs | | 43 | 59 | 24,980 | 560 | 721 | 608 | - |
| 12345 | 49 | <0.08 | <0.04 | <10 | <2.2 | <0.61 | <0.42 | - |
| 12346 | 50 | 0.15 | 0.56 | 242 | 2.8 | 9.1 | 4.5 | - |
| 12356 | 51 | 0.13 | 0.28 | 136 | 2.5 | 6.6 | 2.2 | - |
| 12357/12467 | 52/60 | 0.36 | 1.1 | 459 | 8.8 | 21 | 6.3 | - |
| 12358 | 53 | 0.65 | 1.2 | 492 | 4.7 | 23 | 11 | - |
| 12367 | 54 | <0.08 | 0.57 | <10 | <2.2 | <0.61 | <0.42 | - |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| (12368) | 55 | <0.08 | <0.041 | <10 | <2.2 | <0.61 | <0.42 | - |
| 12378 | 56 | <0.08 | <0.041 | 43 | <2.2 | 2.2 | 0.73 | - |
| 12456 | 57 | 0.28 | 0.77 | 295 | 6 | 12 | 5.3 | - |
| 12457 | 58 | 0.084 | 0.14 | 85 | 2.5 | 4.5 | 1.1 | - |
| 12458 | 59 | 1.5 | 0.12 | 672 | 13 | 32 | 16 | - |
| 12468 | 61 | 0.9 | 1.5 | 795 | 19 | 32 | 12 | - |
| 12478 | 62 | 0.52 | 0.98 | 412 | 16 | 14 | 5.9 | - |
| Σ PentaCNs | | 4.6 | 7.2 | 3,630 | 75 | 156 | 64 | - |
| 123456 | 63 | - | <0.005 | 5.8 | - | 0.29 | 0.13 | - |
| 123457/123568 | 64/68 | - | 0.025 | 9.2 | - | 0.58 | 0.25 | - |
| 123458 | 65 | - | <0.005 | 2.4 | - | 0.22 | 0.086 | - |
| 123467/123567 | 66/67 | - | 0.015 | 1.9 | - | 0.2 | <0.08 | - |
| 123578 | 69 | - | 0.035 | 13 | - | 0.74 | 0.26 | - |
| (123678) | 70 | - | <0.005 | <3 | - | <0.15 | <0.08 | - |
| 124568/124578 | 71/72 | - | 0.006 | 14 | - | 1.2 | 0.26 | - |
| Σ HexaCNs | | - | 0.081 | 46 | - | 3.2 | 0.99 | - |
| 1234567 | 73 | - | - | - | - | - | - | - |
| 1234568 | 74 | - | - | - | - | - | - | - |
| Σ HeptaCNs | | - | - | - | - | - | - | - |
| OctaCN | 75 | - | - | - | - | - | - | - |
| total PCNs | | 93 | 115 | 45,010 | 995 | 1,166 | 1,200 | - |

monitoring with DB-1701 capillary column (J&W. 30m, 0.25mm i.d., 0.25um of film) was carried out to measure exact m/z of each PCN congeners as follows; T3CNs : 229.9457, 231.9427, T4CNs : 263.9067, 265.9038, P5CNs : 299.8648, 301.8618, H6CNs : 333.8258, 335.8229, H7CNs : 367.7868, 369.7839, O8CN : 401.7479, 403.7449. $^{13}$C-labled PCDD and coplanar PCBs were added into sample solution before clean up.as internal and recovery standard. Detailed analytical procedure was reported elsewhere [1].

**Result and Discussions**

Isomer-specific data of PCNs in contaminated commercial products in Japan were presented in table 1. Isomer composition of Halowax (HW1101) and imported PCNs were similar to each other and also comparable to Neoprene FB related rubber compounds. Amount of PCNs in Neoprene FB was 4.5 % and it's close to the value (about 4 %) which declared by manufacturer. Different two lots of aerosol adhesive bomb 333 shows similar isomer composition of PCNs to Neoprene FB. It's clear that control bomb (made with chloroprene) from different company contains no PCN.

**Table 2.** Toxicity equivalent quantities (TEQs) of PCN isomers in contaminated commercial products in Japan.

| PCN isomers | IUPAC | HW 1001 | imported PCNs | Neoprene FB | rubber coated sheet | aerosol adhesive bomb 333 (serial no.) | | control |
|---|---|---|---|---|---|---|---|---|
| | | | | | | 2A1LC1 | 25K0LB1 | |
| | | % | % | ug/g | ug/g | ug/mL | ug/mL | ug/mL |
| 12367 | 54 | 1.7E-04 | - | 967 | - | - | - | - |
| 12378 | 56 | 4.6E-05 | - | - | 2 | - | 0.099 | 0.034 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 12456 | 57 | 3.5E-06 | 10 | 27 | 1 | 0.021 | 0.042 | 0.019 |
| 123456 | 63 | 2.0E-03 | - | - | 12 | - | 0.57 | 0.27 |
| 123457 | 64 | 2.0E-05 | - | 2 | - | - | 0.006 | 0.003 |
| 123467/123567 | 66/67 | 1.3E-03 | - | 201 | 2 | - | 0.26 | - |
| 123568 | 68 | 1.5E-04 | - | 18 | 1 | - | 0.044 | 0.019 |
| 123578 | 69 | 2.0E-03 | - | 710 | 25 | - | 1.5 | 0.51 |
| (123678) | 70 | 9.9E-03 | - | - | - | - | - | - |
| 1234567 | 73 | 6.9E-04 | - | - | - | - | - | - |
| total TEQs | | | 10 | 1,925 | 43 | 0.021 | 2.5 | 0.86 |

Rubber coated sheet which ready to use for rubber band for office automation instruments contained much lower than Neoprene FB, but still significant PCNs, at several hundred ppm. Average concentration of PCNs in two lots of aerosol adhesive bomb is 1,180 ug/mL. It might be reasonable to estimate that nealy 500mg of PCNs exist in each bomb (contains 430mL of adhesive solution). On account of 210,000 bombs produced, total amount of PCN in adhesive bomb products could be estimate about 100kg. Although declared amount of PCNs in adhesive material used was about 40kg, difference between the two is acceptable as a variation of manufactures.

Table 2 shows that TEQs of PCN isomers based on dioxin-like toxicity. In contrast to similar concentration of total PCNs between two lot of adhesive bomb, there was significant difference of TEQs. Same kind of variation of TEQs were also found in the imported PCN and Neoprene FB related compounds. It's possible to explain that most of dioxin-like PCN isomers are constituted of penta, hexa and hepta chlorinated one and these are relatively difficult to detect in these samples without combination of double-column HPLC separation and HRGC-HRMS measurement.

As the result, it's worth to mention that significant amount of PCNs is supposed to still exist in wide variety of commercial products and no information is available about human exposure. It's necessary to conduct an isomer-specific risk-assessment of PCNs contaminated commercial products not only in Japan, but also to consider exported Neoprene FB and related products.

**References**

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