ANALYSIS OF TOXIC GAS PRODUCED BY HEATING TAR EPOXY RESIN PAINT TO ASSESS WORK ATMOSPHERE

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Two male workers were acutely intoxicated with gas produced by heating tar epoxy resin paint, and developed peripheral neuropathy. To assess the work atmosphere, we analyzed the degradation products by GC-MS. The major toxic products emitted by heating tar epoxy resin were hydrogen cyanide, phenol, and benzene, as well as naphthalene. From 1 m² of the surface of steel plates painted with tar epoxy resin, 2.4 g of hydrogen cyanide, 9.6 g of benzene, and 1.2 g of naphthalene were produced by heating at 1000°C. At 700°C, the amounts of phenol and p-isopropylphenol produced were 3.7 g and 0.57 g, respectively. Based on these results and the area of steel surface burned, the concentration of hydrogen cyanide, benzene, and phenol in the atmosphere of work environment was estimated to be 16, 64 and 24 mg/m³, respectively. Some of the symptoms of the workers including peripheral neuropathy might be related to the sole or cooperative action of the foregoing toxic chemicals mentioned above.

Key words: tar epoxy resin; combustion products; hydrogen cyanide; phenols; benzene; p-isopropylphenol; p-isopropenylphenol

INTRODUCTION

Since iron and steel rust in contact with moisture and oxygen, many products made with metals such as bridge structures of highway, oil and water tanks, outside plating of steel ships, and underground pipelines are coated with rust-proof paint, tar epoxy resin paint. It contains mainly epoxy resin, coal tar, bitumen, pigments, curing agents and solvents. In recent decades, it has been well documented that welding or flame-cutting produces inorganic fume and particles.1) In the metal working, heating technique of coated steel plates gives rise to organic contaminants in addition to inorganic fume and/or particles,5) although welders are usually instructed to remove the primer from the welding zone, and the sites to be heated in welding or flame-cutting are restricted to relatively small area. However, in straightening, repairing, or flame-cutting, the paint is not removed.

Epoxy resin are products of reaction between bisphenol A and epichlorohydrin. The resin is sensitizing and may cause contact dermatitis and allergic lung symptoms.3) Thermal degradation products of epoxy resin have been found to cause photoallergy, for which bisphenol A or related compounds have been suggested as the causative agents.4) With regard to disorders in the peripheral nervous system, however, there are few reports on the effects of thermal degradation products originating from epoxy resins or tar epoxy resins. We experienced two patients with acute peripheral neuropathy, who were exposed to thermal degradation products of paints on steel plates. In this study we analyzed the combustion products of the resin to evaluate atmospheric contamination in their work environments.

PATIENTS

Some parts of an old broken bridge structure were repaired in a workshop. Two male workers (aged 58-case 1 and 36-case 2) were engaged in repairing warped steel plates of the bridge structure (Fig. 1), which were built more than 10 years ago and were coated with tar epoxy resin paint to prevent steel corrosion. To straighten the
warped steel plates, they heated the inner surface (about 0.34 m²) of the box-like steel structure of about 50 m³ (2 × 2.5 × 10 m) using a burner employing LPG and oxygen. The temperature of steel was between 600 and 1,000°C. For two days (total 4 h), without any protective equipment and ventilation, they were exposed to the toxic gas which developed from the combustion of tar epoxy resin coatings. Both workers had previously been in good health. On the evening of the first day of exposure, both workers had headache and nausea. On the morning of the second day, after starting their work, one of them (case 1) developed intense numbness (paresthesia) in the right and left lower extremities and the other worker (case 2) had similar numbness in the right lower extremity. They had to leave their place of work. Next day they were admitted to a neighboring hospital because of these symptoms. One month later the symptoms improved slightly, and both patients were transferred to our hospital for further medical examination and treatment. On admission, neurological examination revealed that case 1 had hypesthesia, hypalgesia and dysesthesia in the left anterior tibia and very weak deep reflexes in the slower extremities. Case 2 had hypesthesia and hypalgesia in the entire right lower extremity. Furthermore, in case 1 the nerve conduction velocity was slowed in the right median and left posterior tibial nerve; the V60 to V90 velocities of the distribution of conduction velocities (DCV) for the median nerve were slow. Fifteen month later, both patients were completely asymptomatic, and no abnormal findings could be observed in the clinical laboratory tests. These findings suggest that exposure to unknown toxic gas had caused an acute and reversible disorder of the peripheral nervous system.

MATERIALS AND METHODS

Samples. The coated steel plates which had not been burned in the repair work were used for the preparation of samples. Coating materials on the surface of steel plates were scratched off with a hard steel knife, and then ground to form powder. Two grams of the coating sample were obtained from 133 cm² of the surface of steel plates. Another paint sample used was experimentally prepared by curing 2-component tar epoxy resin that was currently used to prevent steel corrosion in the same workshop. The content of the tar epoxy is as shown in Table 1 by the manufacture (Nihon Paint Co. Ltd.). After drying for two weeks, the tar epoxy resin cured was also ground to make powder sample for combustion experiments.

For the analysis of thermal degradation products of paint materials, we used two types of tube furnace. One of them was pyrex glass tube heated by Bunsen burner using natural gas (method I). In the tube furnace, 200 mg of the paint material were oxidatively pyrolysed in an air stream of 500 ml per min. The sample degradation began at about 15 seconds (350°C) after ignition and degradation was completely attained
at 40 s (about 500°C). The temperature in the furnace was monitored by a thermometer (Model 163, Chino Works Ltd., Tokyo, Japan). The smoke and gas emitted were trapped in a glass tube at -80°C, and then recovered into 4 ml of CS<sub>2</sub>. The solution was analyzed by GC-FID and GC-MS (GC 9AM-FID, and QP-1000S with GC 14A, Shimadzu, Kyoto, Japan). The analytical column used was a fused silica capillary column (30 or 50 mL × 0.25 mm ID, Ohio Valley Specificity Chemical, Inc., Marietta, Ohio, or Shinwakako, Kyoto, Japan).

In the second method of thermal degradation (method II), the paint material (2–5 mg) was decomposed for 5–10 s in a quartz microfurnace (Pyr 2A, Shimadzu, Kyoto, Japan) equipped with a temperature controller, and the combustion products were directly carried to the GC-MS. Helium was used as carrier gas under non-oxidative condition. Two meter glass column packed with Gaskuropak 54 (porous polymer, GL science, Tokyo, Japan) was used for analyses of thermal degradation products. Both resin samples from the old bridge and newly prepared one were directly extracted by CS<sub>2</sub> and the extracts were also analyzed by GC-FID and GC-MS, to discriminate tar and solvent constituents from pyrolysis products. The thermal degradation products and tar constituents were identified on the basis of mass spectra and/or retention time of the reference compounds. The mass spectrometric analyses were obtained by electron impact mode (70 eV). The solution of trimethylchlorosilane and hexamethyldisilazane (TMS-HT), and N-trimethylsilylimidazole (SIM) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan), and used for the derivatization of thermal degradation products.

RESULTS

Figures 2 and 3 showed tar constituents in CS<sub>2</sub> extract and thermal degradation products obtained by method I combustion. There were a great number of tar components in CS<sub>2</sub> extract of the paint sample from the old bridge structure (Fig. 2b). The most abundant components were identified as groups of polyaromatic hydrocarbons according to GC-MS analysis. In addition to the peaks of tar components, three main peaks were observed in pyrolysis products, and two of them (Figs. 2a and c, peak 4 and 7) were identified as phenol and p-isopropylphenol (IPP) by comparing the retention time and the mass spectrum of the respective reference compounds. The third compound (peak 8 in Figs. 2a and c, and in Fig. 3) was assumed to be p-isopropenylphenol (IPEP) by mass spectral datum (Fig. 4), and derivatization chromatograms with TMS-HT or SIM. The mass spectrum of the product (Fig. 4) could not be compared with an authentic sample, but with bibliographic mass spectral data on the prominent fragment ions and their relative abundance.<sup>5</sup> The derivatization of the product indicated that the compound contained hydroxyl group(s) reactive with TMS-HT and SIM. The other presumptive evidence was the more unstable nature of the peak than that of IPP peak, especially in a solution diluted with CS<sub>2</sub>. In the thermal degradation products, some minor peaks were observed and identified as cresols, xylenols, toluene and xylenes. A small peak of bisphenol A (Figs. 2a and 3) that is an essential component in epoxy resin, is observed in thermal degradation products. The chromatograms (Figs. 2c and d) of thermal degradation products and of CS<sub>2</sub> extracts from experimentally cured tar epoxy resin which is currently used in the same workshop are essentially the same with those of the samples obtained from old bridge structures (Figs. 2a and b), although the newly cured resin contains relatively larger amounts of toluene and xylenes that originate from paint solvent.

To examine the effect of combustion temperature on the constituents of thermal degradation products, we used a specific pyrolysis apparatus, i.e. temperature-controlled furnace (method II). Figure 5 shows TIC (total ion chromatogram) profiles of thermal degradation products of the steel paint materials at varying temperatures. Table 2 indicates changes in amounts of 10 thermal degradation products, and also those in the relative area of IPEP peak. The production of IPP and IPEP decreases with rising in pyrolysis temperature. The highest production of IPP is observed at 550°C, and that of IPEP is between 550°C and 700°C. Phenol production is maximum at 700°C. The three main peaks almost disappear at 1,000°C. In contrast, the amounts of benzene and naphthalene increase at the temperatures more than 850°C, and the largest amounts of toluene are produced at 850°C. Max-
Fig. 2. Gas-chromatograms (FID) of thermal degradation products and extracts (a and c) of tar epoxy resin coating on the surface of old bridge steel plates, and those of experimentally cured epoxy resin (b and d), respectively. A fused silica capillary column (50 mL, 0.25 mm ID) coated with methylsilicone was used in a temperature programming mode from 80°C to 280°C at 5°C/min; the start temperature was maintained for 10 min and the final temperature for 60 min. Identified compounds were (1) Ethylbenzene, (2) m- and p-Xylenes, (3) o-Xylene, (4) Phenol, (5) Cresols, (6) Xylenols, (7) p-Isopropylphenol (IPP), (8) p-Isopropenylphenol (IPEP), (9) Naphthalene, (13) Anthracene, (14) Pyrene and fluoranthene, (15) Naphthacene and chrysene, (16) Benzpyrenes, and (17) Bisphenol A.
Fig. 3. TIC (total ion chromatogram) and ion chromatograms of thermal degradation products emitted from tar epoxy resin coating from old bridge steel plates. A fused silica capillary column (30 mL, 0.25 mm ID) coated with methyl silicone was used in a temperature programming mode from 40°C to 280°C at 5°C/min; the start temperature was maintained for 0.5 min and final temperature for 30 min. Compounds 1-18 were the same as shown in Fig. 2. 

The maximum amount of benzene and naphthalene are 9.6 and 1.2 g per square meter of steel plates burned at 1,000°C, respectively. Among nitrogen-containing compounds produced by thermal degradation, hydrogen cyanide continuously increases as pyrolysis temperature rises, while the peak production of acetonitrile and acrylonitrile is found at 850°C, and between 700°C and 850°C, respectively. About 2.4 g/m² of hydrogen cyanide are produced by thermal degradation of the paint materials at 1,000°C. Thus, the major products at low temperature are phenol, alkylphenol and alkenylphenol, while those at higher temperature are hydrogen cyanide, benzene, and naphthalene.

DISCUSSION

There are few reports on the occupational exposure to toxic and organic materials or fumes originating from heated steel plates, although inorganic fumes and particles originating from welding or flame-cutting has been extensively investigated. The profile of emitted organic contaminants may vary according to the temperature, types of paints, and techniques of heating, such as welding, flame cutting, and...
Fig. 4. Mass spectrum of peak 8 compound in Figs. 2 and 3.

Fig. 5. TIC (total ion chromatogram) of thermal degradation products of tar epoxy resin from old bridge steel plates at various temperatures. A glass column (2 mL, 2 mm ID) packed with porous polymer was directly attached to the furnace (method II). The oven was programmed for 40°C to 250°C at 10°C/min, and the final temperature was maintained for 60 min. (A) Hydrogen cyanide, (B) Acetonitrile, (C) Acetone, (D) Acrylonitrile, (E) Benzene, (F) Toluene, (G) m-Xylene, (H) Phenol, (I) p-Isopropylphenol (IPP), (J) p-isopropenylphenol (IPEP), and (K) Naphthalene.
straightening. The amounts of organic pollutants emitted in the straightening process were relatively larger than those in welding or frame cutting. Nakagawa and Tsuge reported that pyrolysis products of diglycidyl ether of bisphenol A at 600°C were identified as phenol, IPP, IPEP, and bisphenol A. Their chromatographic profiles coincided well with our data on the coated steel plates. Engstrom et al. identified major organic compounds emitted from welding steel coated epoxy resin; i.e. alkylated benzene, aliphatic alcohols, bisphenol A, phenol etc. Recently, Engstrom et al. determined the concentrations of organic pollutants in breathing zone air of welders during ship building: The concentration of bisphenol A was 0.22–0.37 mg/m³, and that of phenol was 2–10 times of bisphenol A. Naphthalene and methylnaphthalene (0.1–2.8 mg/m³) were often detected among the emission products of epoxy tars, while the concentrations of polyaromatic hydrocarbons, such as benzo(a)pyrene were at or below detection limits (0.0002 mg/m³).

At relatively low temperature (350°C), phenol, bisphenol A, alklyphenols, aliphatic alcohols as well as alkylbenzenes were reportedly the major degradation products of epoxy paints, while hydrogen cyanide was below detection limit. Hydrogen cyanide gas is well known to be produced in combustion of polyacrylonitrile, and its production increased, as the temperature rose. In the present experiments at the higher temperatures (1,000°C), larger amounts of hydrogen cyanide were found at lower temperature such as 450°C. The most important factor affecting the production of hydrogen cyanide in combustion of epoxy resin is the presence of nitrogen-containing curing agents used, which in the present experiments were described to be polyamides and tert-amine (Table 1). In the combustion of tar epoxy resin coatings on steel plates, the major toxic products were hydrogen cyanide, phenol, benzene, naphthalene, IPP, and IPEP. From 1 m² of the coated steel, 2.4 g of naphthalene were produced by heating at 1,000°C. At 700°C phenol and IPP productions were 3.7 and 0.57 g, respectively. If the concentrations of these substances in work atmosphere in question were estimated, the average concentrations of hydrogen cyanide, benzene, and phenol were, at least, 16 mg/m³ (14.5 ppm), 64 mg/m³ (21.3 ppm), and 24 mg/m³ (6.3 ppm), respectively, when the area heated was 0.34 m² (according to the two workers). These concentrations exceed the permissible limit levels in Japan (10 ppm of benzene, and 5 ppm of hydrogen cyanide and phenol). Additionally, actual concentrations in the breathing zone of workers might be several times higher than the above mentioned levels. Slight symptoms have been found after several hours of exposure to hydrogen cyanide at 0.04–0.06 mg/l. The symptoms observed in our cases partly agree with those in low dosages of hydrogen cyanide; weakness, headache, confusion, nausea and vomiting.

In the experiments with human volunteer,
Piotrowski described that phenol vapor inhaled at or below 20 mg/m³ (5 ppm) was completely eliminated within 24 h, and that there was no adverse effects. Urinary phenol concentrations (0.004–0.006 ppm) produced an increased sensitivity to light in dark-adapted subjects, and elicited the formation of conditioned electrocortical reflexes. In animals these effects were generally preceded by muscular twitching and severe clonic convulsions due to the action of phenol on the central nervous system motor mechanism. In the workers who were accidentally exposed to the vapor of cresol, phenol, and methylene chloride, such symptoms as nausea, dizziness, weakness and vomiting were reported. Some of the symptoms including peripheral neuropathy were found in our patients. Since benzene has no acute effects on human at less than 25 ppm, but produces headache, lassitude, and weariness at 50 to 150 ppm, it is considered that benzene is actually less toxic than hydrogen cyanide and phenol in our case. Although skin irritation, degmentation and contact dermatitis have been observed in workers handling alkylphenols including p-tert-butylphenol, the occurrence of IPP and IPEP in occupational environment and their toxicity have not been studies so far. Toxicity of these chemicals remains to be elucidated. From the results of present experiments alone the responsible agent for the patients' symptoms including disorders in peripheral nervous systems cannot be exactly described. The other toxic products such as carbon monoxide may be also involved in the development of present symptoms. At least, hydrogen cyanide, phenol, benzene, IPP and IPEP were produced in a relatively high amount by thermal degradation of coatings on steel plates, and sole or cooperative action of these chemicals may be related to some of the patients' symptoms.

REFERENCES


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タールエポキシ樹脂加熱作業により発生する毒性ガスの分析

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タールエポキシ樹脂塗料の加熱で発生するガスに曝露した2人の作業者に急性の末梢神経症候群がみられた。作業所の空気中ガス成分を推定するため，ガストロマートグラフ-質量分析計により加熱・燃焼ガス成分を分析した。エポキシ樹脂の加熱で発生する主要な毒性ガスはシアン化水素，フェノール類，ベンゼン，ナフタレンなどであった。タールエポキシ樹脂で表面塗装された鉄板 1 m² から 1,000°C で 2.4 g のシアン化水素，9.6 g のベンゼン，1.2 g のナフタレンが発生した。700°C ではフェノールとイソプロピルフェノールがそれぞれ 3.7 g，0.57 g 発生した。これらの結果と加熱した鉄板の表面積から計算すると，作業所の空気中のシアン化水素，ベンゼン，フェノール濃度はそれぞれ 16，64，24 mg/m³ となりうることが推測される。今回の作業者の症状の一部は末梢神経症候群を含めこれら化合物の単独あるいは複合した作用に関連すると考えられる。

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