Contamination of rice bran oil with PCB used as the heating medium by leakage through penetration holes at the heating coil tube in deodorization chamber

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(Summary)

From February to March, 1968, a mysterious sickness causing difficulty in breathing occurred in poultry farms in a wide area of western Japan, resulting in the death of over 400 thousand birds. These chickens had been fed the dark oil produced at Kanemi Co, mainly composed of fatty acids, which is one of the byproducts of the deodorization process in the rice bran oil refining processes. From June to August, 1968, effects on human began to appear successively in western Japan as symptoms of skin rash and the internal organ diseases. These effects were generically called "Yusho". In October, 1968, one of the patients gave a sample to the local government health center of the rice bran oil made by Kanemi Co. that the patient had been using at that time. From the results of researches and investigations by scientists at the faculty of medicine, Kyushu University, and at the department of health, Fukuoka Prefecture, the cause of the diseases was determined to be the rice oil that was found to be contaminated with PCB. When an abnormal decrease in amount of the circulating PCB occurred in the deodorization process of the Kanemi Co., from the end of January to the beginning of February, 1968, the operation staff replenished the PCB desultorily without investigating the reason. This action resulted in the contamination of the rice oil product with as much as 280 kg of PCB. To make matters worth, even after the facts were clarified, they did not dispose the three drums of contaminated recovered oil but instead reused it by mixing the contaminated oil to the normal product after only by re-deodorizing the mixture. The recorded number of patients reached to 14 thousands. The actual reason for the heath diseases has recently been postulated to be the dioxins that are produced through the deterioration of the PCB, rather than PCB itself.

1. Event

The leakage occurred through two routes that happened at the almost same time. One was a pin-hole that had been formed by inter-granular corrosion. The other was a hole that had been made accidentally by a mistake during a welding operation.

[Route 1: the pin-hole formed by corrosion]

In the No.6 chamber out of a total of six chambers, inter-granular corrosion occurred at the heat affected zone of the seam weld line on the heating coil made of Type 316 stainless weld tube (40mm diameter, 2 mm thickness), which caused a pin-hole to open. The pin-hole had been plugged by a polymerized oil product until the time of the leakage, but a shock during the repair works made an open pit. The heating coil tubes in the other five chambers, which had been used for a longer period, were made of

Type 316L stainless weld tube. Therefore, inter-granular corrosion did not occur in the other heating coil tubes.

[Route 2: the hole formed by welding mistake]

In the No.1 chamber, a welding worker made an open hole in the adjacent heating coil tube by a mistake during welding, during a small welding operation for a sheath pipe of a thermometer.

2. Course

In the factory, the deodorizing process was conducted by using six vacuum chambers in a batch configuration (Figure 1). This configuration is different from the continuous longitudinal multi-tray vacuum column that is usually used at most large scale edible oil producing factories.

[Route 1]

The seam welded tube used for the No. 6 deodorization chamber was made of a high carbon containing Type 316 stainless steel. Solution heat treatment had either been insufficient, e.g. under too low a temperature, or not provided at all in the tubing process at the steel maker's shop. Therefore, the sensitized zone along the weld line suffered from the inter-granular corrosion caused by the combination of hydrochloric acid formed by decomposition of PCB with a coexisting trace amount of water. The inter-granular corrosion, which propagated after five or more years of operation, formed defects and pits along the grain boundary. The pits had been plugged by some polymerized oil until the time of the leakage, but a shock during the repair work and re-installation conducted on January 1, 1968, caused to break through the open pit. The leakage of PCB occurred through the pits after re-starting operation, contaminating the edible oil.

[Route 2]

On January 29, 1968, one of the maintenance workers of Kanemi Co., conducted a small welding operation to expand a hole at the top of a thermometer sheath in the No.1 deodorization chamber. At that time, the worker made an open hole at the adjacent heating coil tube by a mistake during the welding. Through the hole, a large amount of PCB leaked into the part of the facility that contained the edible oil, causing the contamination. The amount of leakage of PCB via route 2 was estimated to be much larger than that via route 1.

However, even after the leakage and contamination was found, the managers in the factory did not recognize the seriousness of the problem, so they did not isolate or abandon the contaminated oil, but instead they sold it to consumers.

In legalistic standpoint, the main cause of the contamination was determined by judicial decision to be the leakage via route 2, because the amount of PCB leakage was larger than that via route 1.

3. Cause

Route 1: Pin-hole formed by inter-granular corrosion in a high carbon containing stainless steel tube.

Route 2: A hole created by a mistake during a welding operation.

4. Countermeasure

(1) Dangerous substances must not be used in food processes even as materials only in indirectly contact with food products, such as heat transfer fluids. At that time, non-chlorine containing chemicals such as diphenyl or diphenyl ether (e.g. Dowtherm, etc.) were adopted as the heating fluids in various plants manufacturing edible oil. Recently, high temperature water or pressurized steam is mainly used as the heating fluid for food processes.

(2) In the construction of food refining plants construction, the equipment materials must be exhaustively checked and confirmed in order to avoid introduction of inappropriate materials, e.g. Type 316 stainless steel in place of Type 316L. Measures to increase corrosion resistance and reliability must be considered, for example adopting seamless tubes in stead of weld tubes.

(3) In the construction of new plants or the repair of existing equipments, supervision of activities in the field must be strictly enforced and skilled workers should be employed.

(4) Above all, maintenance of complete quality control and observation of good manufacturing practice must take highest priority in manufacturing foods for human consumption.

5. Knowledge

In manufacturing foods for human consumption, the following items should be noted;

(1) When new chemicals, substances, or materials are introduced to the processes, safety for human health must be evaluated and confirmed, regardless of whether the substances are in direct or indirect contact with the food products. Unconfirmed materials must never be introduced to the processes.

(2) Leakage in heat exchangers will happen sooner or later. Therefore, the following measures must be conducted comprehensively select safe heat transfer fluids, select highly resistant materials for the equipment, strictly enforce supervision of construction and repairing field work, and keep equipment completely maintained.

(3) Foods are taken by the mouth into human bodies freely without the control of medical doctors. The quality of foods, therefore, must be controlled and guaranteed even more rigorously than that of medicines.

6. Background

PCB is a colorless, oily liquid, with superior electric insulation property and thermal stability. PCB is used as an insulator for high-voltage transformers, condensers, and stabilizers for fluorescent lamp. PCB is also used as an additive for paints, a heat transfer fluid, and so on. However PCB is thought to have effects as an endocrine disruptor, in addition to causing direct health effects such as skin rush. In Japan, PCB was noted for its toxicity with the Kanemi Yusho incident in 1968, as a turning point. In 1972, the use of PCB in open systems was prohibited, and in 1974, the manufacture and the use of PCB were banned completely. The recovery of PCB from users has been conducted in earnest, but there is still a large amount of PCB in use, particularly in closed systems.

Manufacture of PCB was started in 1929 at Swan Co., USA. Immediately after that, the toxicity of PCB began to cause problems such as the chlorine pimple disease in laborers, which was confirmed by animal

experiments. However, because of the excellent properties of PCB, the production was expanded especially for military uses and we apon industries. The production of PCB i n Japan was start ed in 1954. Soon after that, the pollution pr oblems fro m PCB were fou nd a ll over t he w orld, such as cont aminated fee d for chickens in USA and environmental co ntamination i n Sw eden. T he K anemi Y usho i ncident i n Ja pan happened in 1968.

7. Sequel

Taking this PCB problem as an opportunity, in 1973 the Law Concerning the Evaluation of Chemical Substances and Regulation of the ir Manufacture, etc. (Chemical Substanc es Control Law) was enac ted in Japan. The L aw requir es prior evaluat ion of c ertain hazardous pr operties of new chem ical substances before manufacturing a nd/or im porting those su bstances. T he Law reg ulates (1) persis tent and h ighly bioaccumulative chem ical substa nces with lo ng-term toxicity o r ec otoxiticy (Spec ified Chemical Substances), (2) persistent but no t bi oaccumulative chem ical subst ances wi th certain ec otoxiticy (Monitored C hemical Substances), and (3) New C hemical Substa nces. R ecently, t he Law i ntroduced regulations fo r ev aluation not o nly of d amage t o human health by environmental p ollution, b ut a lso of damage to flora and fauna.

8. Discussion

The patients of "Yusho" had been recognized based only on the evaluated PCB concentrations that have persisted in t heir bodies. However, r ecently t he concentration of dioxin w as a dded to t he b ase (2 004), because high concentrations of PCD F (poly-chlorinated di-b enzofurane), a kind of dio xins t hat is form ed by the thermal decomposition of PCB, were detected in their blood.

Another w ell-known case of food co ntamination i n Japa n w as the contamination of pow der m ilk for babies with arsenic by Morinaga Co. The relief measures by Morinaga were more generous than those of Kanemi, in part because of the larger size of the Morinaga enterprise.

9. Information Source

(1) Y. Tokunaga; Netsushori, vol.19, No.4 (frontispiece) (1979).
(2) T. Sugimoto;"Considering PL in Japan", p.48, Chijin-shokan (2000).
(3) H. Kawana; "Verification of Kanemi Yusho incident", Ryokufu-shuppan (2005).
(4) h ttp:www.safe.go.jp/kasin.html.
(5) Asahi-shinbun, Morning Ed., December 18 (2003).

10. Primary Scenario

(1) Route 1 (pin-hole by corrosion)
01. Misjudgment
02. Narrow Outlook
03. Oversight of Intermixing Wrong Material (Type 316 stainless steel)

04. Lacked Research in Corrosivity of PCB
05. Production
06. Hardware Production
07. Production of Machine/Equipment
08. Heating Coil for Deodorant Column
09. High-C Stainless Steel (Type 316)
10. Lacked Inspection in Receiving Materials
11. Purchase of Sensitized Material
12. Failure
13. Fracture/Damage
14. Intergranular Corrosion
15. Contamination of PCB to Food Product
16. Bodily Harm
17. Sickness
18. Poisoning

(2) Route 2 (hole by welding miss)

01. Carelessness
02. Insufficient Precaution
03. Lacked Precaution in Worker
04. Welding Work
05. Usage
06. Maintenance/Repair
07. Make Hole by Welding to Adjacent Part
08. Failure
09. Fracture/Damage
10. Heating Coil for Deodorant Column
11. Make Hole by Welding
12. Lacked Inspection in Finishing Work
13. Contamination of PCB to Food Product
14. Bodily Harm
15. Sickness
16. Poisoning

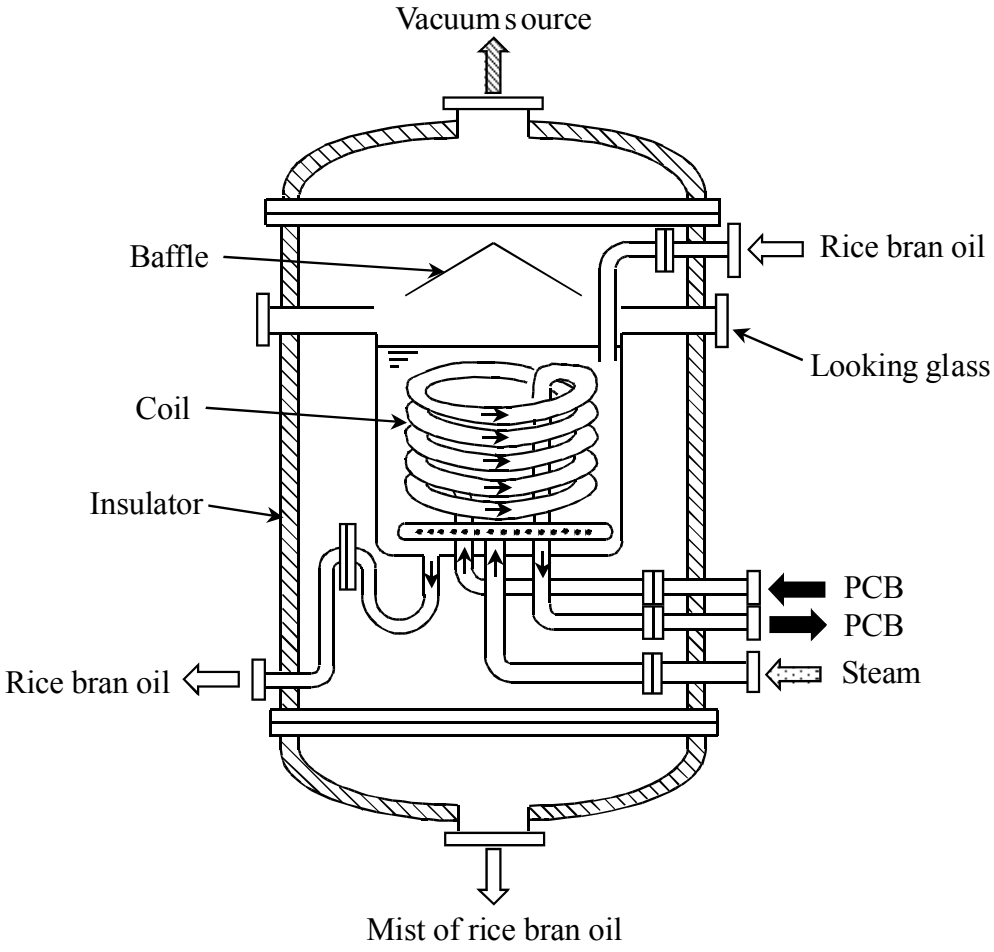

Fig. 1 Schematic diagram of deodorant vessel.