Report

Causes of Chemical Contamination in Edible Oil Poisoning Accidents

*By Yasuhiko Takeshita**

Synopsis: The cause of industrial chemical contamination in edible oil poisoning accidents, especially of human and poultrys' poisoning by PCB or its oxidized derivatives in rice bran oil in Japan, in 1968 was studied. An official report recognized that the source of PCB leakage from the heating coil of deodorizer might be pin-holes grown by split PCB, but the author and most engineers denied this hypothesis by calculation and practical experience. The local court accepted the pin-hole hypothesis in its decision. After about 10 years a foreman of the oil manufacturer confessed that the cause of leakage was a manually drilled hole of large size through an equipment converting process. Moreover, the contaminated oil was treated intentionally with poor evaporation, and sold to consumers. This error was kept secret from outsiders. Consequently, more than 1,000 persons and 400,000 chickens were poisoned or killed. Rice bran oil poisoning in Taiwan, 1979, and an olive oil accident by aniline derivative in Spain in 1981 were considered as industrial chemical poisoning, and avoidable edible oil manufacturing errors also recently occured.

要旨：1968年に西日本で起こったにわとりの大量斃死を来たし，人の中毒を生じた事件に次いで，1979年台湾でPCB中毒事故が発生し，1981年にはスペインでアニリン関連物質の食用油混入による大規模の中毒事件が発生した。これら3事件について，事故発生の化学的または機械的な原因を討論し，いずれも人為的で避けられる原因であることを報告した。

1. Introduction

The cause of industrial chemical contamination in edible oil poisoning accidents, especially of human and poultrys' poisoning by PCB or its oxidized derivatives in rice bran oil in Japan in 1968 was studied. An official report stated that the source of PCB leakage from the heating coil of deodorizer might be pin-holes grown by split PCB, but the author and most engineers denied this hypothesis by calculation and practical experience.

The local court accepted the pin-hole hypothesis in its decision. After about 10 years a foreman of the oil manufacturer confessed that the cause of leakage was a manually misdrilled hole of large size through a part converting process. Moreover, the contaminated oil was intentionally poorly evaporated, and sold to consumers. This error was kept secret from outsiders. Consequently, more than 1,000 persons and 400,000 chickens were poisoned or killed. Rice bran oil poisoning in Taiwan, 1979, and an olive oil accident by aniline derivative in Spain, 1981 were considered as industrial chemical poisoning, and avoidable edible oil manufacturing errors, also recently occured.

Specifically, in the Madrid district of Spain, in June 1981, an edible olive oil poisoning

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accident occured, and it was reported that more than 100 persons' died. The cause of poisoning might be aniline compound contamination in the edible vegetable oil refining process.

In March 1979, at the Shooka region in Taiwan, an edible rice bran oil poisoning accident happened by contamination with PCB.

In February 1968, before these accidents, a chick edema accident occured in the west of Japan, and it was reported that 924,212 chickens and 870,370 hens were poisoned, and 400,00 of them killed. After several months, it was reported that more than 10,000 persons suffered from the poisoning at the accident, however true sufferers might be about 1,200 persons.

The author, the leader of a non-official mission of investigation visited each area where the accident occured in the capacity of a rice bran oil processing first engineer.

He predicted PCB and deodorizing mistakes as the cause of poisoning. About the cause of PCB contamination, the author published three reports in Transactions of the Kokushikan University, Dept. of Engineering, **3**, 17 (1970); **6**, 20 (1973); **7**, 31 (1974). At the begining, the cause of the poultry killing accident was reported as oxidized substance of unsaponifiable matter in rice bran lipid by an official researcher.[1)]

However, after human poisoning chlorinated organic compound was pointed out and PCB was indicated as heat transfer medium, deodorizing equipment's defect was appointed as the source by the author, accordingly checked by a field investigation party.

About the cause of PCB contamination, Kyushu University's official investigating group reported that the cause of heat transfer medium PCB leakage might be the pin-holes grown by the split PCB corrosion. However, the size of the discovered pin-holes on heating coils were too tiny to leak an enormous volume of PCB, and most of the oil engineers including the author denied that hypothesis. The author had proposed a flange origin for leakage of large quantities of PCB in a short period, with the assumption that no human error concealed.

On the other hand, the staffs of Kanegafucikagaku Co. who were the developers and manufacturers of PCB, "KANECHLOR" disclosed the falsification of daily deodorizing record of rice bran oil in Kanemisooko Co., the manufacturer of poisonous oil, after eager calculation with computor.

In spite of approaching the true cause of the leakage, the court accepted the

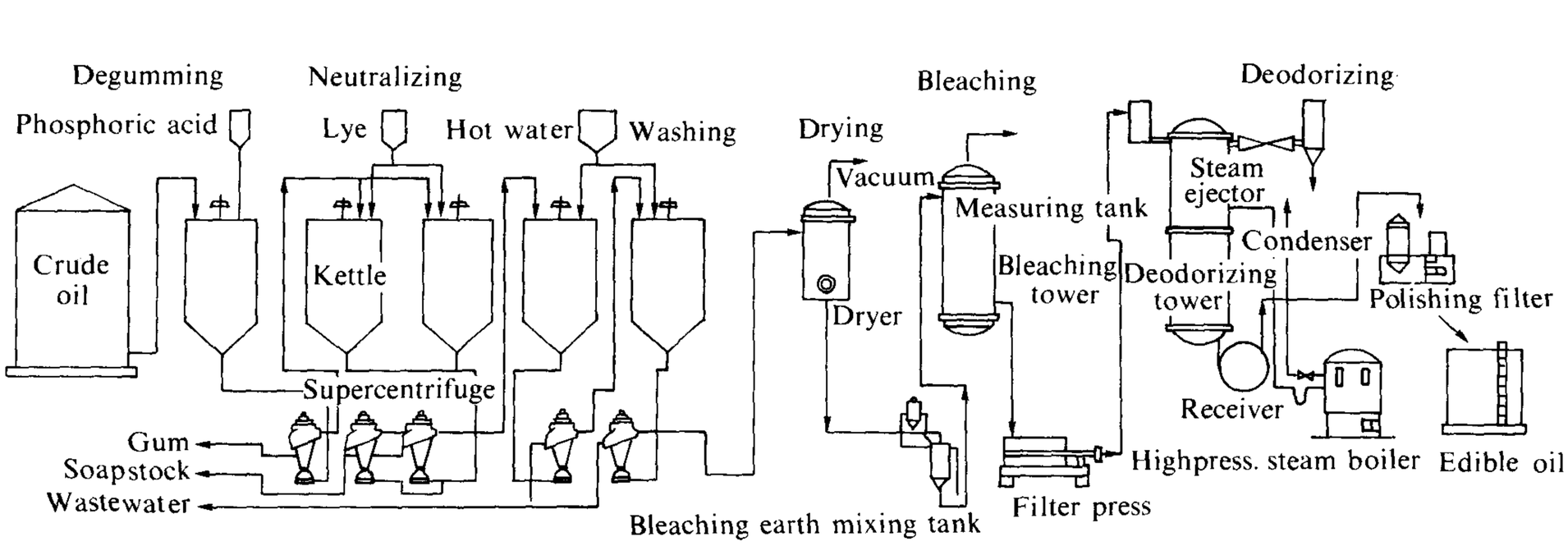


Fig. 1. Flowsheet of Semi-Continuous Oil Refining System.

unreasonable pin-hole hypothesis in the decision.

About 10 years after the happening, the foreman of refining factory of Kanemisooko Co. who engaged to produce poisonous oil, confessed that the cause of PCB leakage was a large sized manually drilled hole penetrated at an equipment converting process. Moreover, contaminated oil treated intentionally with poor and insufficient PCB evaporation, and sold to the consumers in the west of Japan generally.

This unfavorable news was kept secret from outsiders. Consequently, the serious poisoning accident enlarged, but it might be avoidable oil manufacturing error and ignorance induced an accident of food additives.

Compared to chronic toxic property of PCB, the oxidized, polymerized or split substances are known as more poisonous matter.[13)]

Edible vegetable oil and fat are important foods for mankind, however the industrial chemicals contaminant may be not always safe, and introduced here are three accident cases of teaching the prevention against food poisonings.

2. Outline of Accident in the West of Japan

From February 20, 1968 to early in March, at western Japan, chickens, raised by the feed containing Kanemisooko's rice bran dark oil (acidurated soapstock) 0.5～4.5%, caught chick edema after 4～6 days.

Among 700 thousand chickens, about 400 thousand were killed and 830 thousand hens dropped egg laying ratio. Kobanawa et al.[1)] reported the poisoning materials of this case would be any oxidized lipid.

Before this accident, in USA, 1962 and 1967～'68, chick edema occured, and McCune[2)] and Anita Huang[3)] researched chick edema factor. They discovered chlorinated biphenyl or chloronaphthalene as the cause of edema, if large quantities of them are applied.

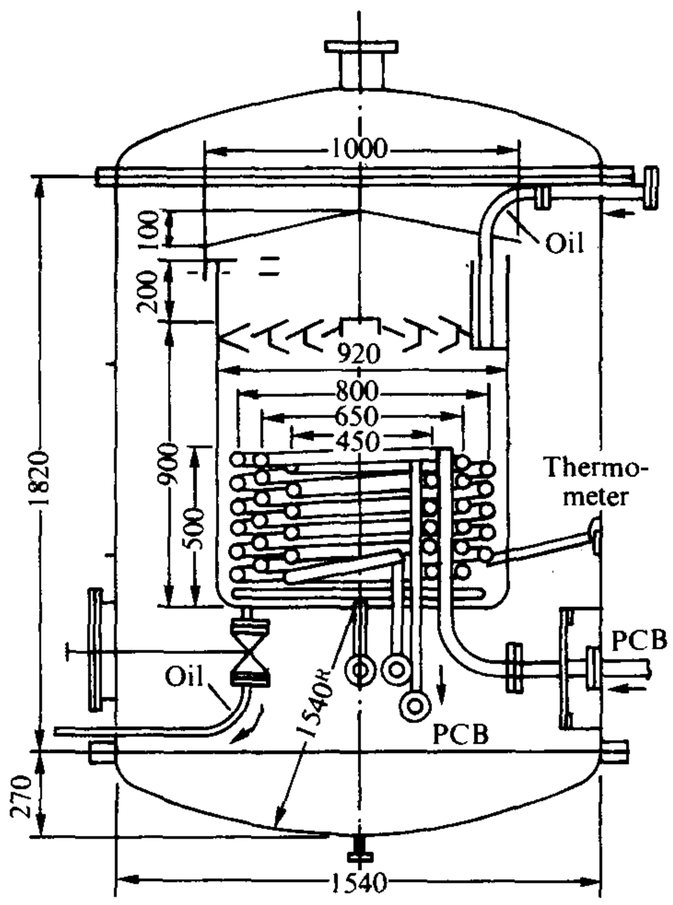


Fig. 2. Deodorizer of Kanemi Style.

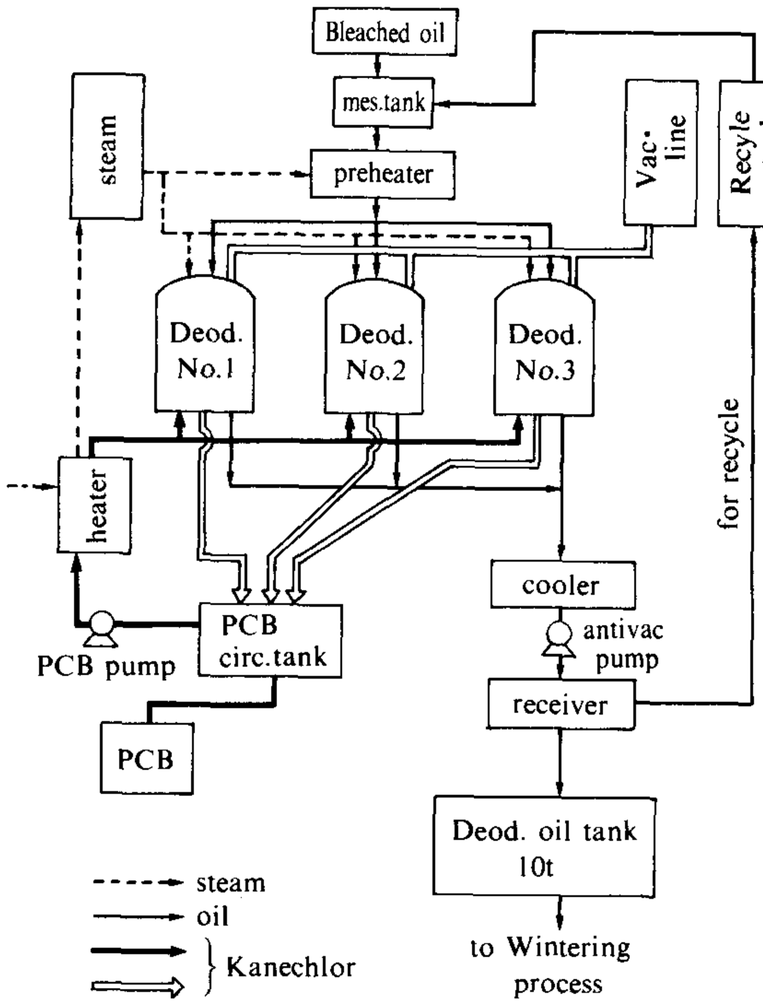


Fig. 3. System of 3 Deodorizers.

D .Firestone[4] reported the review about the relation of chick edema factor and residue of insecticides. In these steps, hexachlorophenanthrenes and hexachlordibenzodioxin were noticed as the cause.

After the chick edema in Japan, on July 15, 1968, a meeting of Agricultural Ministry and Japan Rice Bran Oil Manufacturing Association was held.

In this meeting, Kanemisooko's Kato asserted that even if the cause of poisoning concerned dark oil, it would be no single factor, but be complex one with other source.

K. Matano, the chief researcher in the Ministry of Health & Welfare noticed the influence of chick edema to human health, and he proposed to get some samples of poisoned feed. However his effort did not succeed officially. Fortunately, O. H. M. Wilder,[5] the director of technology of N.R.A. visited Japan to lecture about feed fat and chick edema factor. He said that in the U.S.A., March 1957, chick edema occured for the first time, and in October '57 repeated. After these accidents, the cause was confirmed, and it was known that the cause was not sickness but was a poisoning by toxic matter in U.S.M.. Also, the chlorinated hydrocarbon was pointed out. The accident in '57 occured by animal fat, but in '59, cottonseed dark oil in biological test shown typical chick edema factor.

In 1960, animal fat containing vegetable oil byproducts of edible refining, chick edema occured industrially. In 1961, a paper was published as an U.S.A. official report which

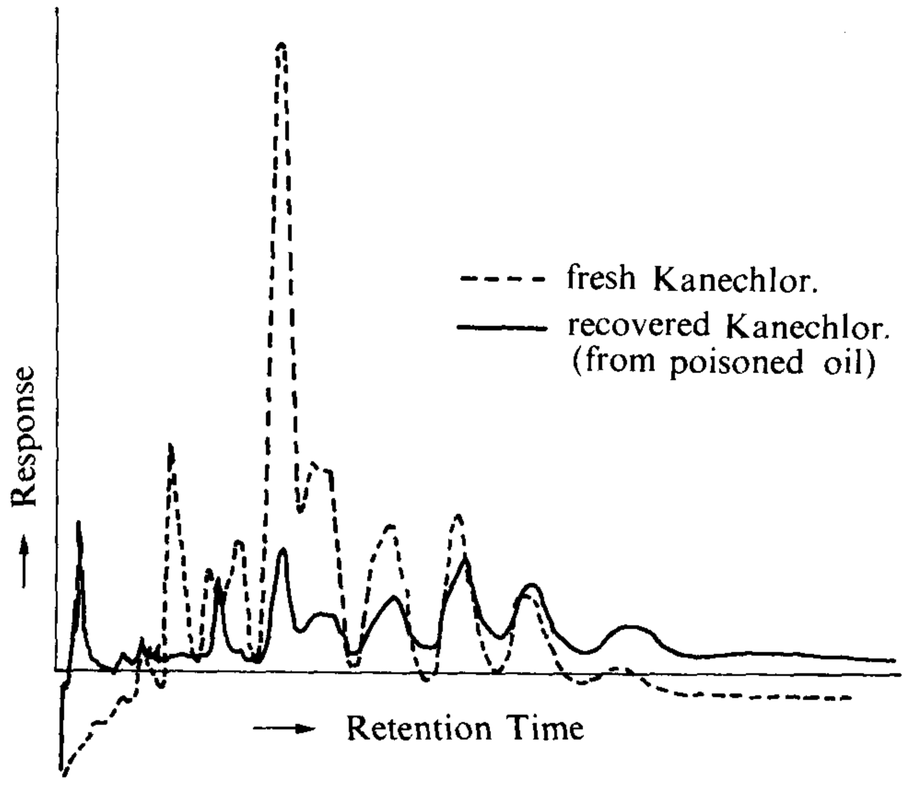


Fig. 4. GLC Curve of Kanechlor.
(by Health & Welf. Ministry)

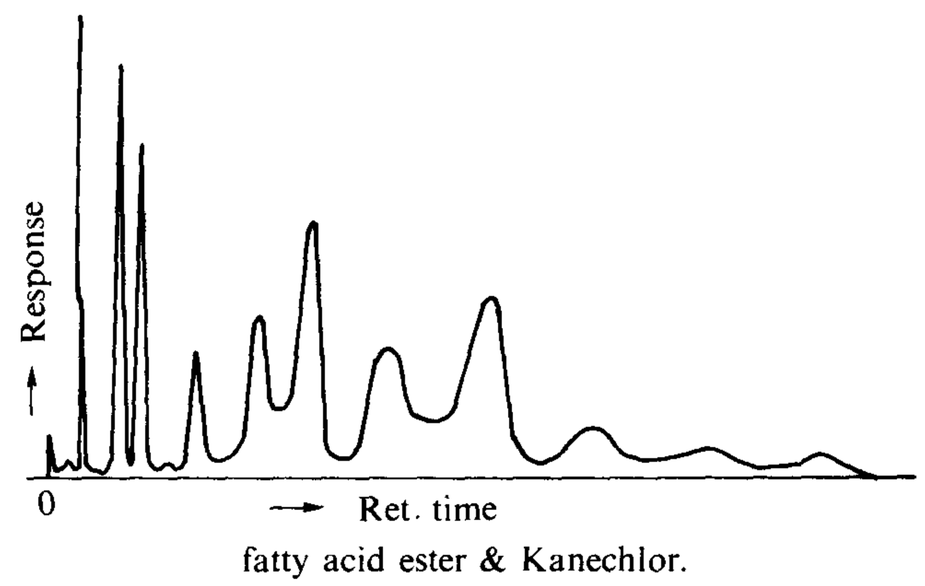


Fig. 6. GLC Curve of Rice Bran Oil+Kanechlor.

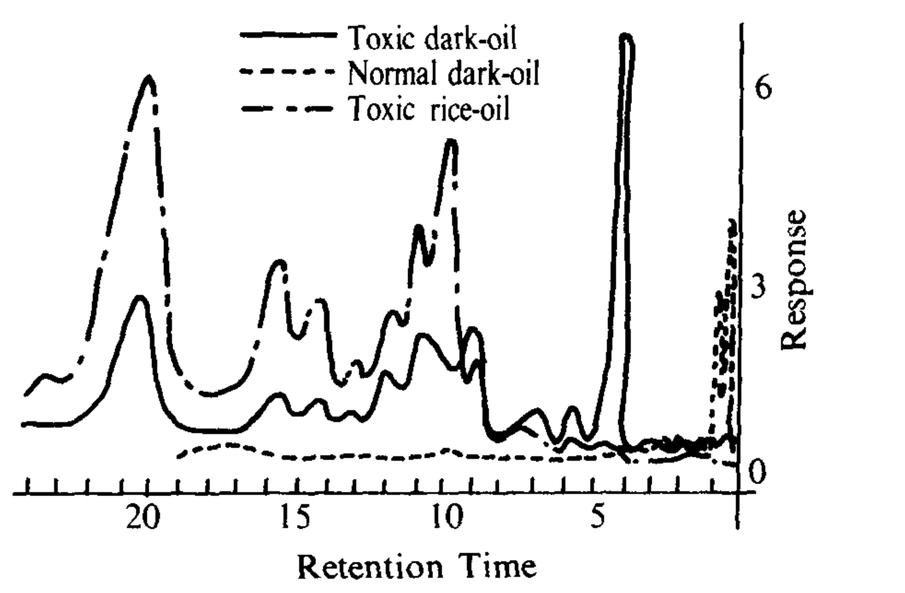
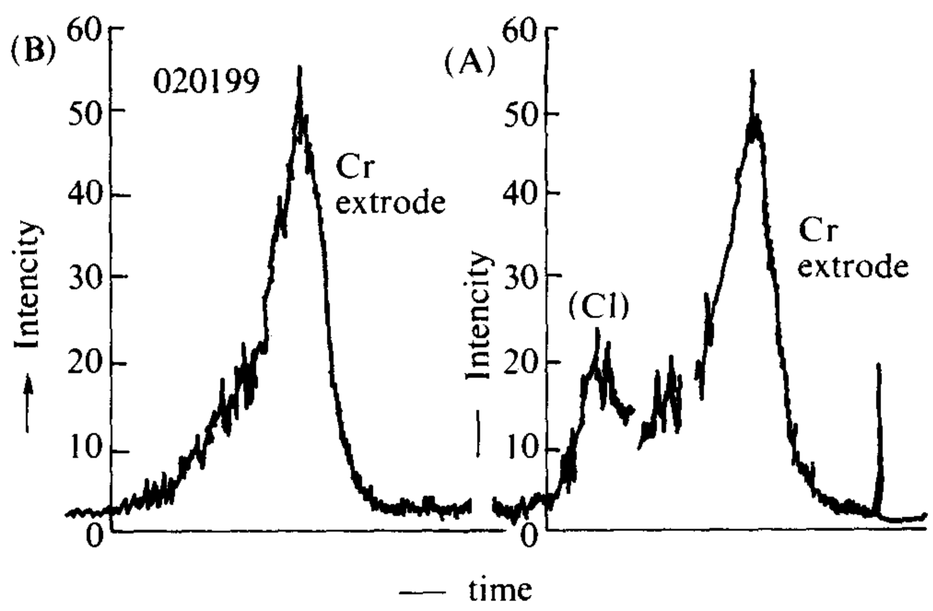


Fig. 5. GLC Curve of Toxic Edible Ref. Oil, Normal Dark Oil and Toxic Dark Oil. (by Agric. Ministry)



X-ray Fluor. Method. Cl Check
[A] Troubled Rice Bran Oil
[B] Contrast, Normal edible R. B. Oil

Fig. 7. X-ray Analysis of Oil.[14]

issued that the b.p. of toxic matter was near to b.p. of oleic acid, though the residue was also toxic. In 1962, Friedman[7] reported that the toxic matter had effect on monkeys, dogs and swines. Modified Lieberman Burchard reaction was effective for checking chick edema factor.

Biological tests with chicken succeeded in checking this matter. Crude toxic matter 0.8 γ initiates the symptoms, and LD_{50} was 5.4 γ per 1 chick. Between 8–9 years after those accidents, chick edema did not occur. However, in 1967, Cantrell *et al.* identified the toxic matter as 1, 2, 3, 7, 8, 9 Hexachlorodibenzo-*para*-dioxin.

AOAC official analytical method[8] proposed at p. 489–490, GLC Microcoulometric system. Inorganic chlorine compound and insecticide which was chlorine compound, were confirmed about no chick edema factor, by cooking process adding chlorinated insecticides. The effect of excess NaCl (in 1957, nonpublished experiment), and McCune et al.'s[2] report in 1962, PCB as plasticizer of epoxy-resin paint was checked, discovered that the poisoning effect was enphasized by Cl ion.

In the accident in 1968 in Japan, following chick edema, human poisoning occured.

In that step, hystorical study of chick edema by the author contributed much to discover the cause of poisoning.[9),10)]

Kanemi Rice Oil Poisoning Accident, retarding to the chick edema accident, in May '68 appeared. In that poisoning, skin disease patient visited the Kyushu University's Hospital and after several months, the cause of the disease was discovered as Kanemi Rice Oil which was produced by Kanemisooko Co., Ltd., the rice bran oil mill.

This disease was secretly treated as a medical doctor's researching theme. However, on October 10, the accident was broadcasted by Japanese National Broadcasting Association.

Immediately, the author who was the chairman of the Rice Bran Oil Manufacturing Technical Committee in Japan, started to investigate the cause of poisoning. The author got a small quantity of edible rice bran oil, distributed in the north Kyusyu, which had poisoned people.

Kumazawa et al.[11] analysed the poisoning oil by combustion flask and Mohl's process, and Cl content was confirmed as 980 ppm. By cleaning up and column chromatography, 670 ppm of Cl was also confirmed.

The author officially reported that the cause was not original contamination in crude rice bran oil, but it was contaminated in the refining step, and so the accident was concerned with only one factory though some persons thought that general rice bran oil in Japan might be poisonous. The author also announced that other rice bran oil mills' products had no relation to that accident.

The numbers of registered poisoned person are shown in next **Table 1..**

3. Cause of Contamination

The author and Inagami of Kyushu University supposed and confirmed that contaminating chemicals might be Poly-Chlorinated-Bi-Phenyl, PCB, which was used as the heat transfer medium in the deodorizing equipment.[12),13),14)]

Table 1 Registered Poisoned Chickens & Persons in each Prefect.

Item / Name of Prefecture	Poisoned by Feed (Spring, 1968)		Reported & Consulted Patients		
	Broiler	Hen	Reported	Consulted	Typical Poisoned
Aichi	—	—	2	—	—
Mie	—	—	7	—	—
Shiga	—	—	6	—	—
Kyoto	—	—	33	—	—
Ōsaka	—	—	430	—	—
Hyogo	—	—	91	—	—
Nara	—	—	14	—	—
Tottori	4,100	17,500	33	—	—
Shimane	57,775	0	249	—	—
Okayama	10,000	155,340	325	129	5(5)
Hiroshima	28,000	154,100	672	—	5(9)
Yamaguchi	63,977	149,215	1,108	—	(6)
Tokushima	71,327	16,350	458	—	—
Kagawa	1,800	2,100	74	—	—
Ehime	122,353	66,200	84	—	—
Kōchi	9,560	22,300	232	—	
Fukuoka	121,430	56,960	6,481{2,842}	2,708{116}	{15} 292{325}
Saga	100,130	0	772	309	16{70}
Nagasaki	—	—	834	667	109{281}
Kumamoto	78,318	91,000	50	50	1
Ōita	99,675	105,300	329	—	—
Miyazaki	23,853	5,000	210	68	0
Kagoshima	112,395	21,827	135	57	3
Total	924,212	870,370	12,629{13,300}	3,622	412{644}

However, the route of contamination was not clear. Several hypothesisses were proposed. Sakakura, one of the consultants of Kanemi Sooko Co., appealed the human handling, and the author proposed PCB-leakage from the flange of heating coils.[18)]

H. Shinohara *et al.* supposed officially that pinholes of coils by chemical corrosion.

However the pinhole hypothesis was not reasonable, because discovered pinholes were too small to pass such large quantities of PCB.

Most experts of the oil industry did not believe the pinhole hypothesis, but the regional court approved pinhole leakage by pyrolysis of PCB.

The author *et al.* made an effort to verify that the pinhole hypothesis was not true, and to support the flange leakage theory. The data will be shown in next **Table 2** and **Figures 1** ~ **9**.[18)]

Between many steps of the court decision, hypothesis of pinhole leakage of PCB was completely denied by the staff of Kanegafuchi-kagaku Co.,.

The staff discovered much artificiality in the factory operating report which was falcified by Kanemi Sooko Co.. For example, the record of manufacturing team in the period of accident was altered with bad will.[23)]

Table 2 Edible Oil Analysis, Refered to Accident.

Test Items \ Sample Kind & Deliv Route	Kanemi Sooko, Poisoned Edible Oil		Kanemi Sooko. →Osaka →Wakayama (16.5 kg×1)	Kozuma Oil Mill Rice Oil (Contrast)
	2×16.5 kg →Kusutake(1.8 *l*×5)	1×16.5 kg →Tanaka(1.8 *l*×3)		
Poisoned No. ⁄Cl / Checked ⁄+	5/5＼+	3/5＼+(X)	0/0＼−(X)	0/0＼−all.
Acid Value, P.P (AB-6B), (BTB)	1.06_2(BTB 0.37_4)	1.0(0.28)	〔0.53〕 0.66 (0.12)	0.66～0.62(0.05～0.03) 0.10 (0.03)
Peroxide Value	38.5	31.4	16	0～10
(133mm Lovi. Color R, Y)	5.1, 49 (R), (Y)	5.3, 46 (R), (Y)	4.4, 30 (R), (Y)	1.5～5.8, 15～47 (R), (Y)
Sap. Value	180.2(190+)	188.9	191	188～193
Iodin. No.	109.3	105.7	108.5	105.3～110
Flavor & Taste	bad smell	Flavor, Taste } bad	bad taste	good
Smoke pt. °C	not detected	not detected	202	244
PCB cont. etc.	much PCB Content.	(Cl Cont.) 670 ppm 980 〃	1968, Feb. Refined	1968 produced, not detected PCB

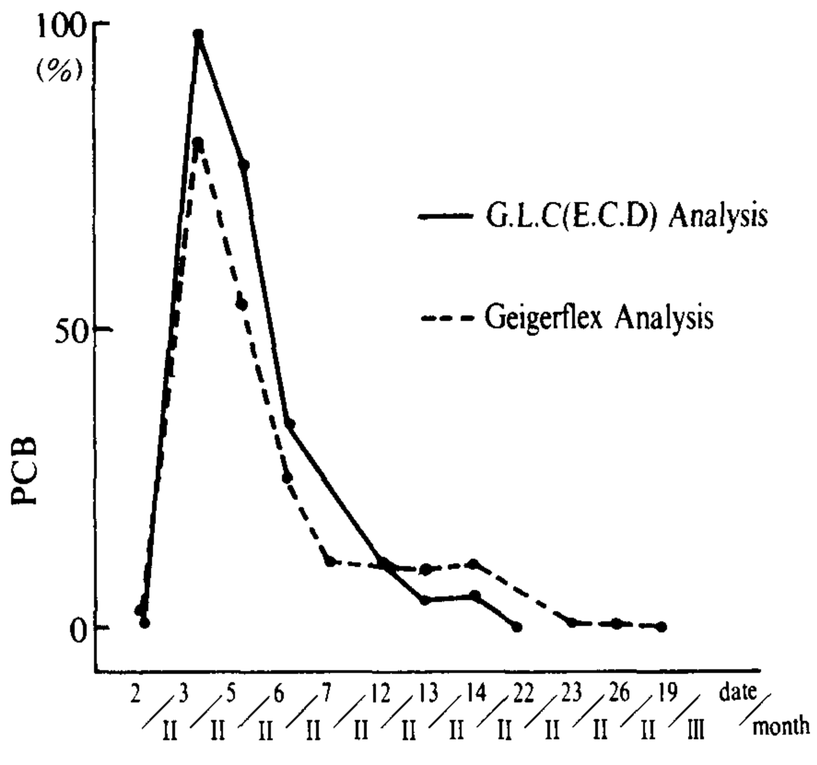


Fig. 8. PCB Contamination Rate about Manufactured Lot. (by Ogata[20])

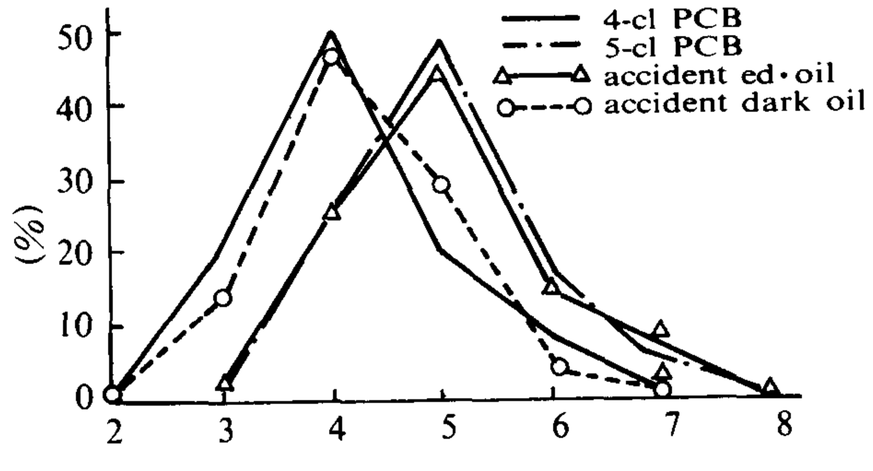


Fig. 9. Chlorinating Number of Recovered PCB and its Content.

Kanegafuchikagaku Co. team discovered also that the troubled deodorizer was not No. 6 but No. 1. Formerly people believed the emergency had happened on January 31, at No. 6 unit, but the team discovered the accident initiated on January 28, at No. 1 unit.

On the other hand, the former foreman, Higuchi of Kanemisooko factory lettered and confessed that the hole leaking PCB was bored by erroneous operation of improving sheath of thermometer of deodorizer by iron works operator. As a result, the oil was contaminated by a large quantity of circulating PCB heat transfer medium, and was repaired by redeodorization with another deodorizer after cutting out the coil bored deodorizer. However, removing of PCB and its derivatives were not sufficient and especially polymerized or oxidized matters of PCB, which were highly toxic,[13] remained.

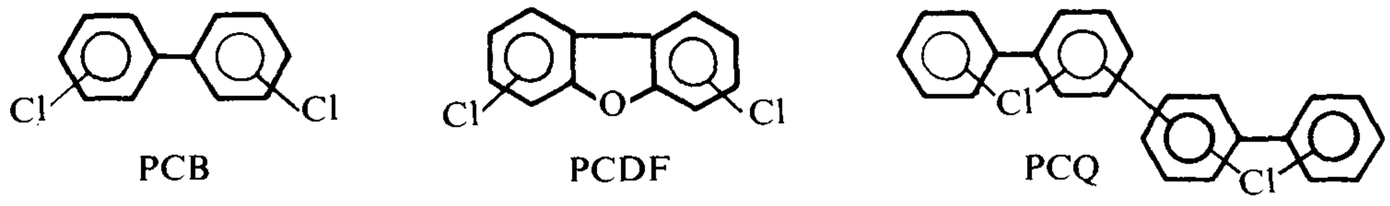


Fig. 10. Molecular Formulas of PCB, PCDF, PCQ.

The re-deodorized poisonous oil was delivered to consumers, and injured the health of many people, whose symptoms were *chlor-acne*, lever harm and other abnormal health.

Finally, it was researched that the main toxic matter was not PCB but PCDF and PCQ etc. which were oxidized or polymerized PCB. **(Fig. 10)**.

These derivatives were predicted by the author,[14] and after a few years identified by Kashimoto *et al.*.[22]

The pyrolyzed PCB at Kanemi factory was also analysed quantitatively and identified about chlorinating number by Kanegafuchikagaku Co.'s staff and the author's efforts. **(Fig. 9)**[18]

Step by step, the fact has been discovered, but material evidence was already eliminated and so the verification is very difficult.

In Japan, another accident of heat transfer medium occured in 1971,[19] however it was not harmful because the vapor type heat transfer medium, used for edible oil deodorizing, was completely evaporated. However, the damage of the factory was high, because indemnification was great to edible oil using factories.

4. Poisoning Accidents in Other Countries

In Taiwan, a PCB poisoning accident occured in 1979, and also injured many consumers of the Shooka district. The president of a company and factory manager were punished, but already released from prison.

At the time this accident happened, the author happened to visit those areas, and discussed with a chief officer of the government and regional engineer of Taichun. The cause of PCB contamination in this accident was not highly clear, but it might be the habitual blending of cheep components to expensive edible oil. It might be the artificial error or ignorance to hygiene at the edible oil distributing step.

As for the incident of edible oil poisoning in Spain, the author also was staying in Madrid and Valencia after the Congress of IUPAC at Belgium. In that accident, the cause of contamination would be artificial or mistaken operation. Aniline is used only for industrial purpose, and it is very rare to contaminate edible oil.

5. Discussion

Discussing the cause of those three or four accidents of industrial chemical contamination, some chemical engineering factors were proposed. But main causes are error or ignorance of worker's foreman, operator or manager.

In Japan, after these accidents, mainly high pressure steam, elctric heating and hot air indirect heating system were recommended, and PCB was prohibited for edible oil refining.

Dowtherm A etc. are not also adopted to edible oil deodorization in Japan, because it was also organic heat transfer medium.

6. Conclusion

Contamination by industrial chemicals of edible oil is mainly caused by artificial errors of processing operator and ignorance of foreman or manager.

Conscience and knowledge about hygiene are important for food manufacturers.

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