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The Degradation of Polychlorinated Benzenes in Electrical Equipment

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THE DEGRADATION OF POLYCHLORINATED BENZENES IN ELECTRICAL EQUIPMENT

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The current legislation governing polychlorinated biphenyls (PCBs) was precipitated by the Yusho incident in southwestern Japan in 1968. Approximately 1300 people ingested an average of about 2g each of PCB fluid from a leaking heat exchanger. The first contaminant of the rice oil to be identified was PCB, and the symptoms of the poisoning were therefore blamed upon PCBs as the causative agent.

Subsequent analysis[1] of the Yusho oil has revealed that the apparent toxicity of the askarel is likely to have been due to the presence of PCB degradation products such as polychlorinated dibenzo furans (PCDFs).

In 1970 Vos et al[2] showed a correlation between the toxic effects of European PCBs and the concentration levels of PCDFs. The major PCDF components contained in Yusho oil were the highly toxic 2,3,7,8-tetra-CDF and 2,3,4,7,8-penta-CDF. The relative concentrations of the PCDF isomers present in Yusho oil and in two samples of used heat exchanger PCBs (Kanechlor KC 400 and Mitsubishi-Monsanto T 1248) were found to be strikingly similar.[3] This fact underscores the findings of other workers in this field that there is a connection between the toxicity of degraded PCB fluids, including tri-/tetra-chlorinated benzene/PCB blends, and the concentration of PCDFs. The overall toxicity of the fluid may then be attributable, as Vos indicates, to the two particular components mentioned earlier.

(1) H. R. Buser, C. Rappe and A. Garå; "Polychlorinated Dibenzo Furans Found in Yusho Oil and in Used Japanese PCB"; Chemosphere 7, 439 (1978).

(2) J. G. Vos, J. H. Koeman, H. L. Van der Maas, M. C. Ten Noever de Braun and R. H. de Vos; "Identification and Toxicological Evaluation of Chlorinated Dibenzofuran and Chlorinated Naphthalene in Two Commercial Polychlorinated Biphenyls"; Fd. Cosmet. Toxicol. 8, 625 (1970).

(3) M. Kuratsune, Y. Masuda and J. Nagayuma; Proceedings of the National Conference on Polychlorinated Biphenyls, Chicago, November, 1975; EPA-560/6-75-004.

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Buser has shown that the pyrolysis reactions of chlorobenzenes in the presence of air yield tetra- to octa- CDFs and tetra- to octa-CDDs.[4] The experimental conditions used in his laboratory study were intended to provide easily determined concentrations of degradation products (approximately 1%) within a short period of time. The fluid temperature inside a faulting transformer is not likely to reach 600°C for a sufficient length of time to cause the formation of PCDFs, but there may be hot-spot temperatures of 300°C for significant periods. It is of concern that heating PCBs in air at 300°C for only one week is sufficiant to generate PCDFs[5] in the ppm concentration range.

Chlorobenzenes with a higher degree of chlorination than the compounds used for pyrolysis were observed in each reaction mixture. These must have been formed by a chlorination process from components of the mixture containing less chlorine. However, the formation of chlorobenzenes with less chlorine than the compounds used for pyrolysis was not observed. This may indicate that once the chlorobenzene molecule has become reactive by the removal of a chlorine atom the product formed will depend upon the concentration of interactive molecules in the system. In any case, the partially dechlorinated chlorobenzene does react, probably with oxygen, and transmutes to a stable form which is not a chlorobenzene. For example, the reaction mixtures were found to contain chlorophenols in addition to PCDFs and PCDDs. It was therefore suggested that the reaction of chlorophenol with chlorobenzene could lead to polychlorinated diphenyl ethers (PCDPEs) which are known to form PCDFs upon pyrolysis. This mechanism does not seem probable, however, because PCDPEs were not detected.

PCDFs and PCDDs can be formed from chlorophenols in three ways.
(1) The dimerization of chlorophenates.
(2) The cyclization of PCDPEs.
(3) The cyclization of polychlorinated phenoxy phenols termed "pre-dioxins".[6]

The dimerization of chlorophenates is likely to be bimolecular and therefore the products formed should be highly dependent upon the chlorophenate concentrations. The PCDD isomers formed in the system, and their quantities, will depend upon the relative kinetics of the alternative reaction routes. It would be expected that the relative importance of the bemolecular mechanism would decrease with the concentration of chlorophenates.

(4) H. R. Buser; "Formation of PCDFs and PCDDs from the Pyrolysis of Chlorobenzenes"; Chemosphere, 8, 415 (1979).
(5) H. R. Buser and C. Rappe; "Formation of Polychlorinated Dibenzofurans (PCDFs) from the Pyrolysis of Individual PCB Isomers"; Chemosphere 8, 157 (1979).
(6) C. Rappe, S. Marklund, H. R. Buser, H. -P. Bosshardt; "Formation of PCDDs and PCDFs by Burning or Heating Chlorophenoles"; Chemosphere 7, 269 (1978).

The pyrolysis of PCDPEs follows two competitive reaction pathways viz., reductive dechlorination or ring closure to dibenzofurans.[7] This is not likely to be an important route in the laboratory pyrolyses because of the apparent absence of PCDPEs.

The cyclization of pre-dioxins is a molecules reaction caused by heating. The final concentration of dioxins in the heated chlorobenzene system should ultimately be dependent upon the concentration of polychlorinated phenols which are formed.

The presence of chlorobenzenes and chlorophenols in the product mixture which contain a higher degree of chlorination than the chlorobenzenes in the starting mixture indicates the probability of free redical reactions.

Louw, Rothuizen and Wegman[8] have interpreted the pyrolysis of chlorobenzene as a radical chain reaction involving $\cdot C_6H_4Cl$, $\cdot Cl$ and $H\cdot$ as carriers. The authors discuss a radical reaction sequence which explains the observed product pattern, including the formation of PCBs.

The pyrolysis of PCBs occurs intramolecularly by four alternative reaction routes to yield different isomeric PCDF products.[9] The extent to which the free radical reactions yield PCBs and the extent to which the eventual cyclization of the PCBs contributes to the overall yield of PCDFs is probably small. Indeed, the quantities of PCBs detected were small.

The formation of polychlorinated naphthalenes in Buser's experiments (Ref. 4) can be explained by either invoking the formation of benzyne intermediates or the re-arrangement of intermediates formed between an ortho-chloro phenyl radical with a chlorobenzene. The overall effect of radical reactions on the product distribution in a pyrolysis reaction will be effected by both temperature and the availability of oxygen. No work has so far been done to examine the effects of these parameters on the total quantity of PCDFs produced.

(7) A. Norström, K. Andersson and C. Rappe; "Studies on the Formation of Chlorodibenzofurans by Irradiation or Pyrolysis of Chlorinated Diphenyl Ethers"; Chemosphere, 241 (1977).

(8) R. Louw, J. W. Rothuizen and R. C. C. Wegman; "Vapour Phase Chemistry of Arenes. Part II. Thermolysis of Chlorobenzene and Reactions with Aryl Radicals and Chlorine and Hydrogen Atoms at 500°"; J. Chem. Soc. Perkin Trans., 2, 1635 (1973).

(9) H. R. Buser and C. Rappe; "Formation of PCDFs from the Pyrolysis of Individual PCB Isomers"' Chemosphere, 8, 157 (1979).

Morita[10] and Nagayama[11] have determined the concentrations of PCDFs in "Yusho oil" and in new European and Japanese PCB samples. The combined concentration of the different isomers identified in the unused PCB samples was from 1-24 ppm, while in Yusho oil, the concentration was reported as 2700 ppm in Ref. (10) and 5000 ppm in Ref. (11). The concentrations of PCDFs in new and used PCBs is shown in Table (1). The PCDFs in the unused PCBs were probably formed by the chlorination of dibenzofuran as an impurity in the original biphenyl. Chittim, Clegg, Safe and Hutzinger have analyzed unused North American askarels (Interteen, Pyranol and Chlorextol) and found[12] that they contained less than 0.05 ppm. As stated earlier, Vos et al have found[2] that the toxic effects of PCB based fluids could be correlated with the levels of PCDFs contained in them. It is therefore of considerable concern that, in Ref. (12), it was determined that the level of tetra-CDF in an askarel was found to increase as the time since the transformer was installed increases, see Fig.(1). The small number of samples tested were insufficient to obtain a definite correlation between kVA and oil volume, manufacturer and fluid type or TCDF concentration and transformer loading. While the results indicated that transformer load is probably a major factor in the formation of PCDFs, the effects of discharging or arcing appeared to be negligible.

Chittim et al have concluded that the PCDFs found in the oil were probably produced during the normal operation of the transformer and that a number of different variables all contribute to the formation of PCDFs. In particular, it was observed that the samples which contained the most polychlorinated benzenes also had the higher TCDF concentrations. Thus, the presence of certain polychlorinated benzenes may be the major contributer to the formation of PCDFs in transformer askarels.

The results of different studies on the formation of PCDFs in chlorobenzene/PCB fluids are shown in Table II to IV. A list of the reactions involved in the formation of toxic products is given in Table V.

(10) M. Morita, J. Nakagawa, K. Akiyama, S. Mimura and N. Isono; "Detailed Examination of PCDFs in PCB Preparations and Kanemi Yusho Oil"; Bull. Environ. Contam. Toxicol.; 18, 67 (1977).

(11) J. Nagayama, M. Kuratsune and Y. Masuda; "Determination of PCDFs in Kanechlors and Yusho Oil"; Bull. Environ. Contam. Toxicol. 15, 9 (1976).

(12) B. G. Chittim, B. S. Clegg, S. H. Safe and O. Hutzinger; "Chlorinated Dibenzofurans and Dibenzo-p-Dioxins: Detection and Quantitation in Electrical Equipment and their Formation During the Incineration of PCBs."; Report prepared for Fisheries and Environment Canada, under Contract No. 05578-00067; September 1979.

TABLE

PCB	Polychloro Dibenzo Furans			Total
	Cl_4	Cl_5	Cl_6	
NEW:				
Aroclors 1254, 1260[11]				< 0.05
Clophen A-60[13]	1.4	5.0	2.2	8.4
Phenoclor DP-6[13]	0.7	10.0	2.9	13.6
T 1242[9]	2.3	2.2	-	4.5
T 1248[9]	0.5	2.3	-	2.8
T 1254[9]	0.1	3.6	1.9	5.6
T 1260[9]	0.8	0.9	0.5	2.2
Kanechlor 300[9]	6.7	1.6	-	8.3
Kanechlor 400[9]	12.2	10.4	0.9	23.8
Kanechlor 500[9]	1.7	1.1	3.1	6.1
Kanechlor 600[9]	0.2	0.5	0.4	1.1
USED:				
T 1248[9]	5.8	5.6	0.7	12.4
Aroclor 1254[11]				0.55
Aroclor 1260[11]				1.1
Yusho Oil PCB (KC400)	520	1330	810	2680

(13) G. W. Bowes, M. J. Mulvihill, B. R. T. Simoneit, A. L. Burlingame and R. W. Risebrough, Nature, 256, 305 (1975).

TABLE II

Chlorobenzene Pyrolysis

Chlorobenzene Studied	Process	Product(s)	Yield	Ref.
Mixture of tri-/tetra-chlorobenzene; pentachloro-benzene	Pyrolysis in air	PCDD, PCDF, PCB, higher chlorinated benzenes, Cl phenols	2,000 ppm	4
Monochlorobenzene	Pyrolysis in N_2	Mono- and di-Cl biphenyl	50 ppm	8
Monochlorobenzene	Pyrolysis	di-Cl biphenyl	10%	14

(14) C. F. Cullis and J. E. Manton: Trans. Faraday Soc. 54. 381 (1958)

TABLE III

Chlorophenol Pyrolysis

Chlorophenols Studied	Process	Product(s)	Yield	Ref.
Various tri-, tetra- and pentachlorophenols	Pyrolysis	Various PCDDs	3-10%	15
Trichlorophenol	Pilot scale combustion on wood chips	Mainly TCDDs	230 ppm	16
Tetrachlorophenol		Mainly HCDDs	350 ppm	
2,4,5-Trichlorophenol	Pyrolysis	2,3,7,8-TCDD	1%	17
2,4,6-Trichlorophenol		2,4,7,9-TCDD	up to 15%	
2,3,4,6-Tetrachlorophenol		1,3,4,6,8,9-HCDD	30%	

(15) H. R. Buser; "Separation and Identification of PCDDs by Gas Chromatography - Mass Spectrometry"; J. Chromatogr., 114, 95 (1975).
(16) B. Jansson, G. Sundstrom and B. Ahling; Sci. Total Environ. 10, 209 (1978).
(17) M. G. Langer, T. P. Brady and P. R. Briggs; Environ. Health Perspect. 5, 3 (1973).

TABLE IV

PCB Pyrolysis

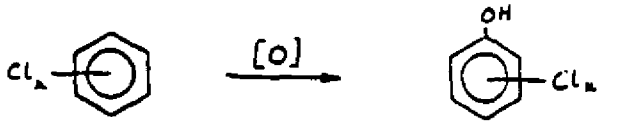
Chlorobiphenyl Studied	Process	Product(s)	Yield	Ref.
18 different chlorobiphenyls containing 4,5,6,7 and 8 Cl atoms	Pyrolysis in air	PCDF	0.1-1%	5
2, 2^1, 6, 6^1 - TCB	Pyrolysis in air	PCDF	2%	18
2, 2^1, 4, 4^1. 5, 5^1 - HCB		2,3,7,8-TCDF	2%	
2, 2^1, 4, 4^1, 6, 6^1 - HCB				
Arochlors 1248 and 1260				
Archlor 1248	Pyrolysis in air in O_2 in N_2	PCDF	300 ppm 1100 ppm 2 ppm	19

(18) H. R. Buser, H. P. Bosshardt, C. Rappe and R. Lindahl; Chemosphere, 7, 419 (1978).

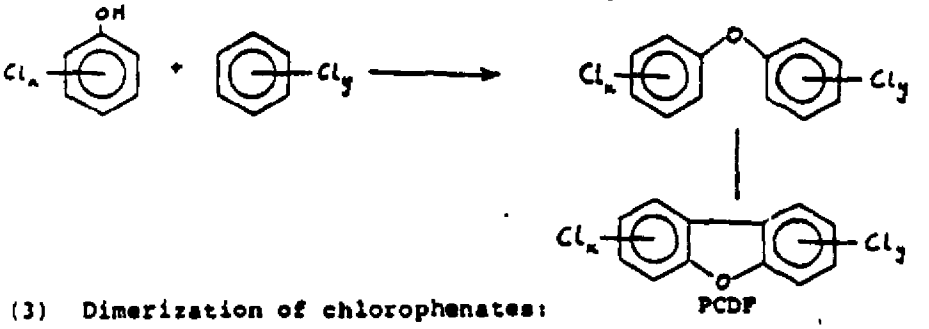
(19) M. Morita, J. Nakagawa and C. Rappe; Bull. Environ. Contam. Toxicol.; 19, 665 (1977).

TABLE V

(1) Formation of chlorophenols:



(2) Formation of polychlorinated dipehnyl ethers/PCDFs:



(3) Dimerization of chlorophenates:

(4) Cyclization of polychloro phenoxy phenols:

(5) Free radical formation of PCB from polychlorinated benzenes:

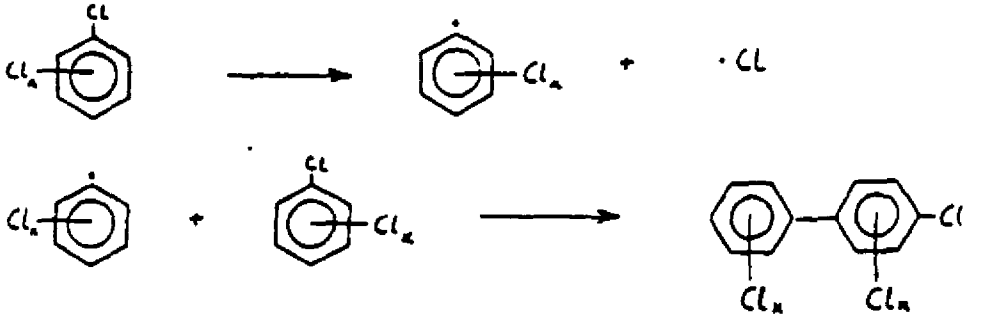


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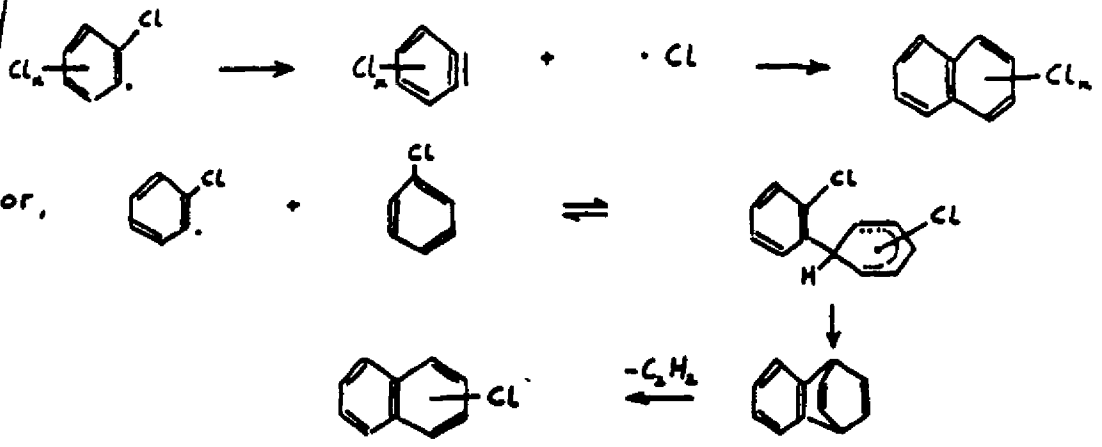
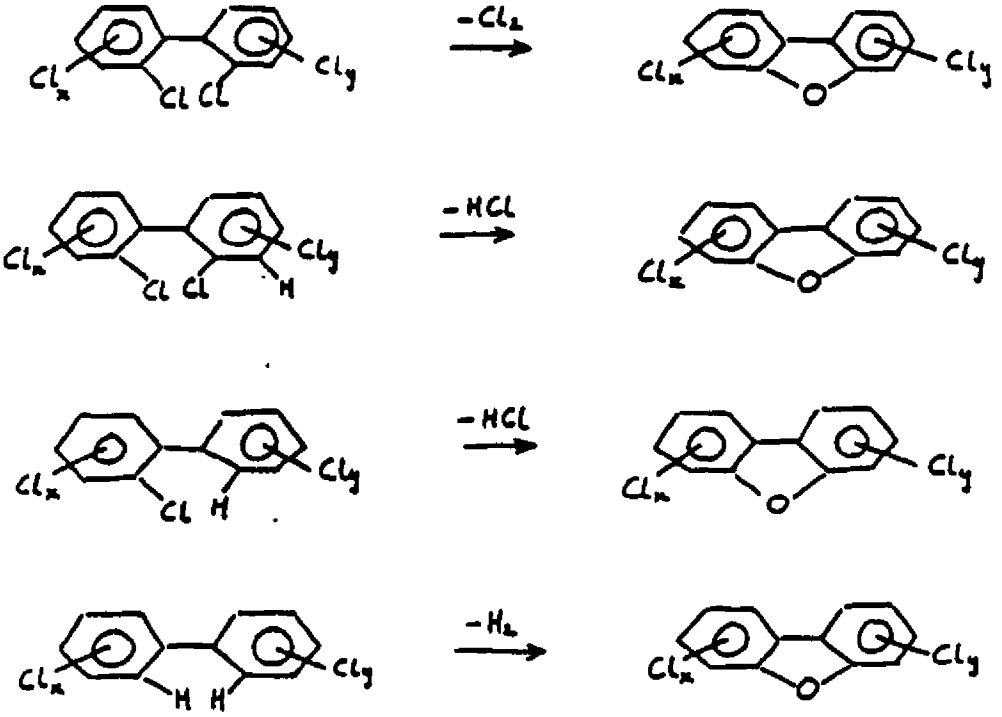
TABLE V (cont'd)

(6) Formation of polychlorinated naphthalenes from chlorobenzene:



(7) Formation of PCDFs from PCBs:



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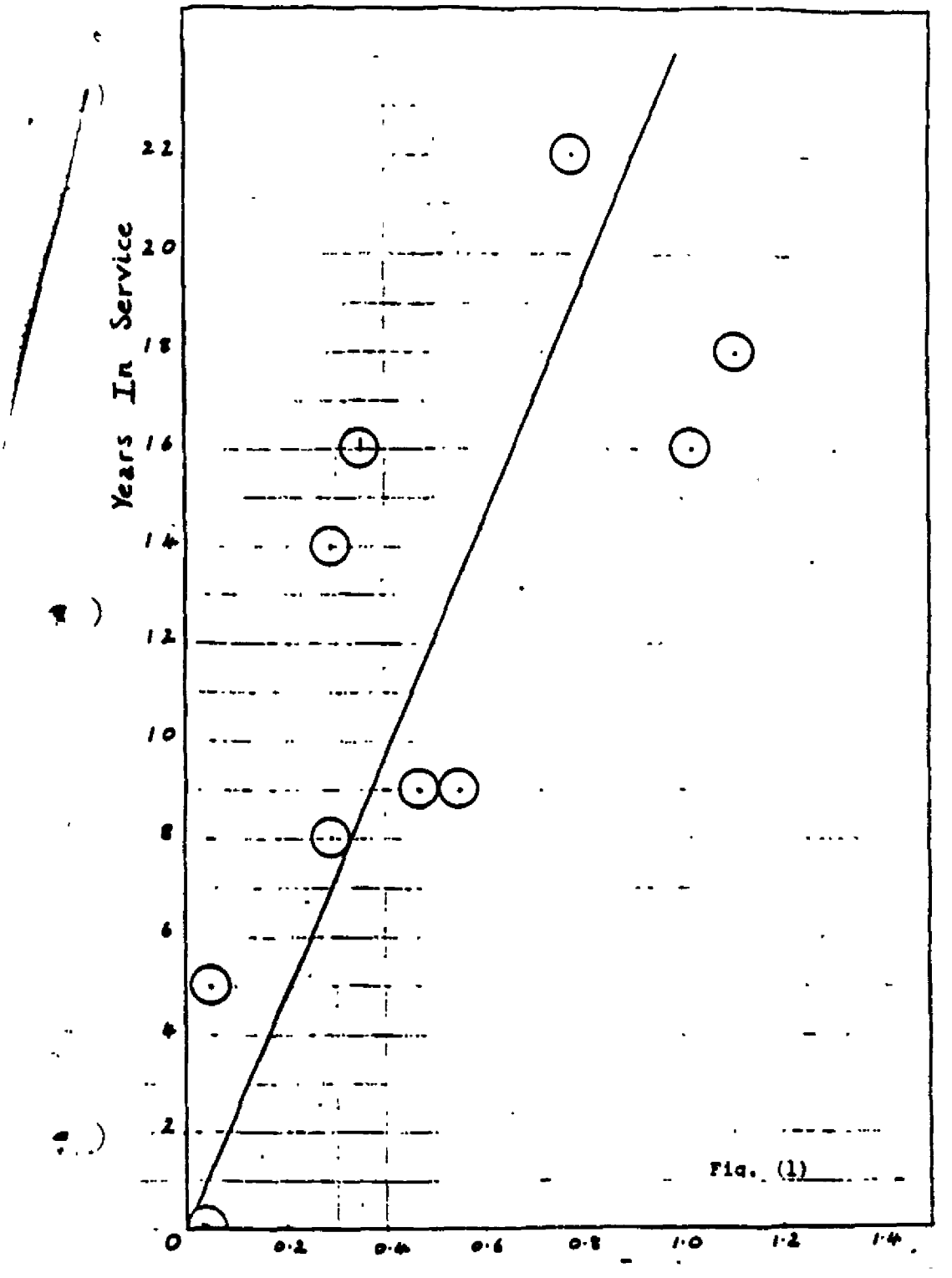

Fig. (1)

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