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(54) Method for replacing PCB-containing coolants in electrical induction apparatus with substantially PCB-free dielectric coolants.

(57) Method for replacing a coolant containing PCB in electrical induction apparatus having a tank containing the PCB-containing coolant and an electrical winding and porous solid cellulosic electrical insulation immersed in the PCB-containing coolant with a substantially PCB-free permanent coolant to convert said electrical apparatus into one in which the rate of elution of PCB into the PCB-free coolant is below the maximum allowable rate of elution into the coolant of an electrical apparatus rated as non-PCB, the porous electrical insulation being impregnated with said PCB-containing coolant. The method comprises the steps of: (a) draining the PCB-containing coolant from said tank to remove a major portion of the PCB-containing coolant contained by it; (b) filling the tank with an interim dielectric cooling liquid that is (i) miscible with PCB, (ii) sufficiently low in viscosity to circulate within said tank and penetrate the interstices of the porous solid electrical insulation, and (iii) capable of being readily separated from said PCB; (c) electrically operating the electrical induction apparatus for a period sufficient to elute PCB contained in the PCB-containing coolant impregnated in the porous insulation therefrom into the interim dielectric cooling liquid; (d) thereafter draining the interim dielectric cooling liquid containing the eluted PCB from the tank; (e) repeating the cycle of steps (b), (c) and (d), when the rate of elution of PCB into the interim dielectric cooling liquid exceeds 0.55 ppm of PCB per day based on the weight of the permanent dielectric coolant, a sufficient number of times until the rate of elution of PCB into the interim dielectric cooling liquid does not exceed the rate of 50 ppm PCB based on the weight of the permanent coolant after 90 days of electrical operation; and (f) filling the tank with a substantially PCB-free permanent coolant selected from the group consisting of high boiling, high viscosity, silicone oils, synthetic ester fluids, poly-alpha-olefin oils and hydrocarbon oils.

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BACKGROUND OF THE INVENTION

Field Of The Invention

This invention relates to electrical induction apparatus, e.g. electric power transformers, specifically to the dielectric liquid coolants contained therein and especially to those coolants consisting of or containing as a constituent, polychlorinated biphenyl, PCB. More particularly, the present invention relates to methods for converting PCB-containing electrical induction apparatus, e.g. transformers, into substantially PCB-free transformers in order to qualify said transformers as "non-PCB transformers" under U. S. government regulations.

Prior Art

Because of their fire resistance, chemical and thermal stability, and good dielectric properties, PCB's have been found to be excellent transformer coolants. US-A-2,582,200 discloses the use of PCB's alone or in admixture with compatible viscosity modifiers, e.g., trichlorobenzene, and such trichlorobenzene-PCB mixtures have been termed generically "askarels". These askarels may also contain minor quantities of additives such as ethyl silicate, epoxy compounds and other materials used as scavengers for halogen decomposition products which may result from potential electric arcing. ASTM D-2283-75 describes several types of askarels and delineates their physical and chemical specifications.

However, PCB's have been cited in the U. S. Toxic Substances Control Act of 1976 as an environmental and physiological hazard, and because of their high chemical stability they are non-biodegradable. Hence, they will persist in the environment and are even subject to biological magnification (accumulation in higher orders of life through the food chain). Accordingly, in the U. S., transformers are no longer made with PCB or askarel fluids. While older units containing PCB may still be used under some circumstances, it is necessary to provide special precautions such as containment dikes and maintain regular inspections. Transformers containing PCB's are at a further disadvantage since maintenance requiring the core to be detanked is prohibited, and the transformer owner remains responsible for all environmental contamination, including clean-up costs, due to leakage, tank rupture, or other spillage of PCB's, or due to toxic by-product emissions resulting from fires. To replace a PCB-containing transformer, it is necessary to (1) remove the transformer from service, (2) drain the PCB and flush the unit in a prescribed manner, (3) remove the unit and replace with a new transformer, and (4) transport the old transformer to an approved landfill for burial (or to a solid waste incinerator). Even then, the owner who contracts to have it buried still owns the transformer and is still responsible (liable) for any future pollution problems caused by it. Liquid wastes generated during replacement must be incinerated at special approved sites. Thus replacement of a PCB transformer can be expensive, but more importantly, since most pure PCB or askarel transformers are indoors, in building basements or in special enclosed vaults with limited access, it may not be physically feasible to remove or install a transformer, nor would it be desirable from an asset management perspective.

A desired approach to the problem would be to replace the PCB oil with an innocuous, compatible fluid. A number of fluid types have been used in new transformers as reported in Robert A. Westin, "Assessment of the Use of Selected Replacement Fluids for PCB's in Electrical Equipment", EPA, NTIS, PB-296377, March 1, 1979; J. Reason and W. Bloomquist, "PCB Replacements: Where the Transformer Industry Stands Now", Power, October, 1979, p. 64-65; Harry R. Sheppard, "PCB Replacement in Transformers", Proc. of the Am. Power Conf., 1977, pp. 1062-68; Chem. Week, 130, 3, 24 (1/20/82); A. Kaufman, Chem. Week, 130, 9, 5 (3/3/82); CMR Chem. Bus., October 20, 1980, p. 26; Chem. Eng., July 18, 1977, p. 57; Belgian Patent 893,389; Europ. Plastic News, June, 1978, p. 56. Among these are silicone oils, e.g., polydimethylsiloxaneoils, modified hydrocarbons (for high flash points, e.g. RTEmp, a proprietary fluid of RTE Corp.), synthetic hydrocarbons (poly-alpha-olefins), high viscosity esters, (e.g. dioctyl phthalate and PAO-13-C, a proprietary fluid of Uniroyal Corp.), and phosphate esters. A number of halogenated alkyl and aryl compounds have been used. Among them are the liquid trichloro- and tetrachlorobenzenes and toluenes and proprietary mixtures thereof (e.g. liquid mixtures of tetrachlorodiarylmethane with trichlorotoluene isomers). Liquid mixtures of the trichloro- and tetrachlorobenzene isomers are particularly suitable because of their low flammabilities (e.g., high fire points) and similar physical and chemical properties to askarels being removed. Other proposed fluids are tetrachloroethylene (e.g. Diamond Shamrock's Perclene TG) and polyols and other esters.

Of all the non-PCB fluids, silicone oils have been the most widely accepted. Their chemical, physical, and electrical properties are excellent. They have high fire points (>300°C), and no known toxic or environmental problems. These oils are trimethylsilyl end-blocked poly(dimethylsiloxanes):

$$(CH_3)_3SiO[(CH_3)_2SiO]_nSi(CH_3)_3 \qquad \text{Formula A}$$

wherein n is of a value sufficient to provide the desired viscosity, e.g., viscosity at 25°C of about 50 centistokes. Commercial silicone oils suitable for use are available from Union Carbide (L-305), and others. In addition, U. S. ~~Patent~~ A 4,146,491, British Patent 1,540,138 and British Patent 1,589,433 disclose mixtures of silicone oils with a variety of additives to improve electrical performance in capacitors, transformers and similar electrical equipment, and disclose polysiloxanes with alkyl and aryl groups other than methyl.

Replacement of PCB-containing askarels in older transformers with silicone oils or one of the other substitute fluids would seem to be a simple matter, but it is not. A typical transformer contains a great deal of cellulosic insulating material to prevent electrical coils, etc., from improper contact and electrical arcing. This material is naturally soaked with askarel, and may contain from 3 to 12% of the total fluid volume of the transformer. This absorbed askarel will not drain out, nor can it be flushed out by any known means, however efficient. Once the original bulk askarel is replaced with a fresh non-PCB fluid, the slow process of diffusion permits the old absorbed askarel to gradually leach out, and the PCB content of the new fluid will rise. Thus, the new coolant becomes contaminated.

For purposes of classification of transformers, the U. S. government regulations have designated those fluids with greater than 500 ppm PCB as "PCB transformers", those with 50-500 ppm PCB as "PCB contaminated transformers", and those with less than 50 ppm PCB as "non-PCB transformers". While major expenses may be entailed with the first two classifications in the event of a spill or the necessity of disposal, the last category is free of U. S. government regulation. To achieve the last classification, the PCB concentration must remain below 50 ppm for at least 90 days, with the transformer in service and sufficiently energized that temperatures of 50°C or higher are realized. This requires a 90-day averaged rate of elution of about 0.56 ppm/day. It is anticipated that most, if not all, states of the U. S. will adopt regulations which may be the same as, or stricter, than U. S. government regulations. More lenient regulations may be possible elsewhere.

There are a number of commercial retrofill procedures on the market including those described in "The RetroSil PCB Removal System", Promotional literature of Dow Corning Corp., #10-205-82 (1982), and trade literature of Positive Technologies, Inc. on the Zero/PC/Forty process. These utilize initial clean-out procedures of as high efficiency as possible during which the electrical apparatus is not in operation. Most include a series of flushes with liquids such as fuel oil, ethylene glycol, or a number of chlorinated aliphatic or aromatic compounds. Trichloroethylene is a favorite flush fluid. Some processes, such as the Positive Technologies, Inc. Zero/PC/Forty process use a fluorocarbon vapor scrub alternating with the liquid flushes. When the initial clean-out procedure is complete, the transformer is filled with silicone fluid. As effective as these elaborate flushing procedures might have been expected to be, they cannot remove PCB adsorbed into the interstices of the cellulosic material. Consequently, the PCB content of the silicone coolant gradually rises as the residual PCB leaches out while the transformer is in use. Therefore, if one wishes to reach a PCB-free state ("non-PCB" as defined by U. S. government regulation), it is necessary to either periodically change-out, or continually clean up, the silicone fluid until a leach rate of less than 50 ppm for 90 days is reached.

Periodic change-out is very expensive, and because both the silicone and PCB are essentially non-volatile, distillation cannot be used to separate them is not practicable and other methods of separation are expensive or ineffective. Dow Corning in its RetroSil process uses a continual carbon filtration to clean up the fluid("The RetroSil PCB Removal System", Promotional literature of Dow Corning Corp., #10-205-82 (1982); Jacqueline Cox, "Silicone Transformer Fluid from Dow Reduces PCB Levels to EPA Standards", Paper Trade Journal, Sept. 30, 1982; T. O'Neil and J. J. Kelly, "Silicone Retrofill of Askarel Transformers", Proc. Elec./Electron. Insul. Conf., 13, 167-170 (1977); W. C. Page and T. Michaud, "Development of Methods to Retrofill Transformers with Silicone Transformer Liquid", Proc. Elec./Electron. Insul. Conf., 13, 159-166 (1977)). Westinghouse in U. S. ~~Patent~~ A 4,124,834 has patented a transformer with a filtration process for removing PCB from the coolant, while RTE in European Patent 0023111 has described the use of chlorinated polymers as an adsorbing media. However, the filters used in these processes are very expensive and the removal of PCB is very ineffective, due both to lack of selectivity and the very low concentrations of PCB being filtered. In lieu of filtration, procedures have been proposed involving decantation (U. S. Patent 4,299,704) which is impractical due to solubility limitations, and only good at high concentrations; extraction with polyglycols (F. J. Iaconianni, A. J. Saggiomo and S. W. Osborn, "PCB Removal from Transformer Oil", EPRI PCB Seminar, Dallas, Texas, December 3, 1981) or with supercritical CO_2 (Richard P. deFilippi, "CO_2 as a Solvent: Application to Fats, Oils and Other Materials", <u>Chem. and Ind.</u>, June 19, 1982, pp. 390-94), and chemical destruction of the PCB's with sodium (British Patent 2,063,908). None of these schemes have been found to be economically or commercially practical for askarel transformers. However, the filtration scheme could be a reasonably effective, though expensive, procedure if it were not for the fact that the leach rate is so slow that it could take many years to reduce the residual PCB to a point where the final leach is reduced to an acceptable value (Gilbert Addis and Bentsu Ro, "Equilibrium Study of PCB's Between Transformer Oil and Transformer Solid Materials", EPRI PCB Seminar, December 3, 1981).

The problem and its cause are discussed in L. A.

Morgan and R. C. Ostoff, "Problems Associated with the Retrofilling of Askarel Transformers", IEEE Power Eng. Soc., Winter Meeting, N.Y., N.Y., Jan. 30 - Feb. 4, 1977, pap. A77, p. 120-9. The solubility of a typical silicone oil in PCB is practically nil (<0.5%) at temperatures up to and over 100°C, while the solubility of PCB in the silicone ranges from only 10% at 25°C to 12% at 100°C. While this limited solubility does not restrict the bulk silicone from dissolving the available free PCB, it does restrict the ability of the PCB to diffuse from the pores or interstices of the cellulosic matter.

Within any given pore filled with PCB, diffusion of PCB out must be accompanied by diffusion of silicone in. At some point within the pore there must exist an interface between the PCB and the silicone, across which neither material can very rapidly diffuse. Because the PCB is more soluble in the silicone than the reverse, the PCB will slowly diffuse into the silicone while the interface advances gradually into the pore. The limited solubility restricts the rate of diffusion and while this mechanism can eventually clean the pore of PCB, it is orders of magnitude slower than if the two fluids were miscible. The high viscosity of the silicone (and many other coolants) is also an inhibiting factor. The result is a long drawn-out leach period of perhaps several years, during which the silicone must be continually filtered or periodically replaced to remove PCB's from it. Thus, the slow leaching of PCB's out of the solid insulation by the silicone is worse than no leaching at all since the dangers of a spill of PCB-containing materials will persist over a period of years. Experimental studies by Morgan and Osthoff showed, for example, that effective PCB diffusivities into a typical silicone oil were only 1/10 of those into a 10 centistoke hydrocarbon oil. Although one might prefer, then, to retrofill with such a hydrocarbon oil, if it were not for the fire hazard of hydrocarbons, there still also is the problem of separating the PCB from the contaminated hydrocarbon oil which is high boiling like the PCB and like the silicone oil.

The present invention is based on the fact that there are suitable cooling fluids which are more suitable than silicone oil for operation over a limited time while leach is being accomplished. They are reasonably volatile for distillation from PCB, readily miscible therewith, and of relatively low viscosity for rapid diffusion into the pores of the insulation. The other constituents of askarel, i.e., trichlorobenzene and tetrachlorobenzene, are found to be ideal fluids for this purpose. They can be used as temporary or interim, leaching, cooling fluids where fire may be a potential hazard, while light hydrocarbons could be used if fire is not a hazard.

No prior art has been found to disclose the concept of producing a substantially PCB-free transformer by removing, flushing and eluting askarels from transformers containing same with an interim dielectric liquid or the steps of filling the transformer tank with an interim dielectric cooling liquid that is miscible with the PCB contained by the transformer tank, capable of penetrating said electrical insulation and capable of being separated from the PCB or the step of electrically operating the transformer while eluting PCB with an interim dielectric liquid and continuing the electrical operation for a period sufficient to elute the PCB impregnated in the solid insulation into the interim dielectric cooling liquid, draining the PCB-laden interim coolant, repeating the cycle of filling with fresh interim coolant, electrically operating and draining a sufficient number of times until the elution rate of PCB drops below the rate of 50 ppm, based on the weight of the permanent coolant to be used, after 90 days electrical operation, whereafter the coolant then is drained from the transformer and thereafter separated from the PCB contained by it thus permitting filling of the tank with a PCB-free permanent dielectric cooling liquid which remains substantially PCB-free during subsequent electrical operation.

SUMMARY OF THE INVENTION

The present invention is based upon the use of a suitable temporary or interim cooling liquid as a substitute for PCB-containing coolants in electrical induction apparatus, e.g. transformers, having a vessel (e.g. tank) containing the coolant and an electrical winding and porous solid cellulosic electrical insulation immersed in and impregnated with PCB while electrically operating the transformer for a sufficient period of time to elute the PCB from the solid electrical insulation contained in the transformer. During the period of operation, the interim dielectric cooling liquid is changed to speed up the elution process, the preferred goal being to elute so much of the leachable PCB that the transformer can be operated for 90 days and not exceed 50 ppm PCB content in the permanent coolant intended for the transformer. After the amount of leachable PCB in the transformer has been reduced to this desired degree, the interim dielectric cooling liquid is removed from the tank and the tank is then filled with a PCB-free permanent dielectric cooling liquid compatible with the transformer. The following describes a procedure according to this invention by which a PCB-containing fluid in a transformer is replaced with a permanent PCB-free liquid coolant:

(1) The transformer is shut down (de-energized) and the PCB-containing fluid drained and disposed of in accordance with environmentally acceptable procedures. The transformer may be flushed with a flushing fluid, e.g., trichlorobenzene or trichloroethylene, liquid or vapor, to remove "free" PCB fluid.

(2) The transformer is filled with a temporary or interim cooling fluid, such as, trichlorobenzene, TCB, or a mixture thereof with tetrachlorobenzene, which is miscible with or dissolves PCB and is capable of penetrating into the pores of the electrical insulation and which is also capable of being readily separated from the PCB, and electrical operation is restored.

(3) The fluid temperature is monitored, and if the electrical loading of the transformer does not provide sufficient fluid temperature to provide the desired rate of PCB elution, thermal lagging or even external heating can be provided. Circulation of the fluid through an external loop and pump for the purpose of heating same, or for augmenting the internal circulation, may also be provided.

(4) The rate of PCB elution into the interim cooling fluid can be determined by periodic sampling and analysis. The accumulated PCB is periodically removed by removing the interim cooling fluid containing the PCB and distillation of the interim cooling fluid, e.g., trichlorobenzene (TCB) from the PCB. This may be done by shutting down, de-energizing, the transformer, draining the old fluid for distillation, and replacing with fresh interim cooling fluid, e.g., TCB. Alternatively, the transformer may be left operational while fresh interim cooling fluid, e.g., TCB, is added and old TCB removed via a slip stream or circulation loop.

(5) The PCB-contaminated TCB fluid is distilled to provide an essentially PCB-free TCB distillate, and a bottom product of PCB contaminated with TCB. The PCB may be disposed of according to approved U. S. government procedures, e.g., by incineration.

(6) When the elution rate of PCB reaches the desired level, preferably less than 50 ppm PCB based on the weight of the intended permanent coolant for a period of 90 days (e.g., an elution rate of 5/9 ppm per day), the permanent retrofill may be accomplished. The transformer is shut down (de-energized), drained, and filled with the silicone oil or other permanent cooling

fluid compatible with the transformer. It is then returned to service.

(7) In order to meet U. S. government regulations for "non-PCB" transformers, analysis should show a PCB content of less than 50 ppm PCB (based on the weight of the intended permanent coolant) after a period of 90 days, after which the transformer is reclassified as PCB free, (i.e. "non-PCB").

With respect to the flushing step, while efficient draining and flushing techniques should be used, these do not in themselves constitute the invention, but are a part of all heretofore known retrofill procedures. They are a prelude to the most efficient embodiment of the invention itself, but their value heretofore has been overrated, in that it is the slow leach rate, not the efficiency of flush which has been found to limit the rate of PCB removal. A wide variety of solvents may be used in the flushing step, including hydrocarbons such as gasoline, kerosene, mineral oil or mineral spirits, toluene, turpentine, or xylene, a wide range of chlorinated aliphatic or aromatic hydrocarbons, alcohols, esters, ketones, and so forth. However, from a materials handling standpoint and PCB separation logistics, it is practical to avoid using any more chemical types than necessary, so that the use of the intended temporary leach fluid, e.g., TCB or mixtures thereof with tetrachlorobenzene, as the initial flush is most practical.

Fluids other than normally liquid trichlorobenzene, TCB, or a mixture thereof with tetrachlorobenzene, can be used. The preferred interim fluid has the following characteristics: (a) it is compatible with PCB (i.e. preferably dissolving at least 50% of its weight of PCB, more preferably, at least 90% of its weight of PCB and, most preferably, being miscible in all proportions with PCB); (b) it is of low enough molecular weight to have good molecular mobility to be able to enter the pores or interstices of the solid insulating material and it promotes rapid mutual diffusion, preferably, having a viscosity at 25°C. of 10 mm^2/s (centistokes) or less and, more preferably, 3 mm^2/s (centistokes) or less; (c) it can be easily separated, e.g. distilled, preferably, having a boiling point of 275°C. or less and, more preferably, 260°C. or less, from PCB; (d) it is presently considered environmentally innocuous; and (e) it is compatible with typical transformer internals. While TCB, or mixtures with tetrachlorobenzene, is preferred, a number of alternatives, as above-mentioned can be used. These would include modified and synthetic hydrocarbons, and a variety of halogenated aromatic and aliphatic compounds.

There are also a variety of liquid trichlorobenzene isomer mixtures. The preferred TCB fluid would be a mixture of these isomers with or without tetrachlorobenzene isomers. The advantage lies in the fact that such a mixture has a lower freezing point than do the individual isomers, thus reducing the chance of it solidifying within the transformers in very cold climates. Further, the mixtures are often the normal result of manufacture and hence can cost less than the separated and purified individual isomers.

Because the preferred objective here is to leach out the PCB at the fastest practical rate, the preferred embodiment involves operating the transformer to obtain the fastest possible diffusion rates as specified in step (3) above. When used at its full rated loading, a transformer should automatically provide enough heat for this purpose. However, since many transformers are operated below their rated loading, and below the rated safe temperature, sufficiently elevated temperatures (e.g. at least 50°C) might not be achieved without thermal lagging or external heating. While this thermal control represents a preferred embodiment of this invention, it is optional and not an essential requirement, there being many transformers for which such lagging or heating may be impractical. Leaching at lower temperatures, even ambient, is workable but will take longer.

Fluid circulation as specified in step (3) is optional but is an advantageous embodiment in that such circulation will prevent the build-up of concentration gradients which can act to retard diffusion. Since elution is a slow process, the circulation rate need not be very rapid. Violent circulation, of course, is to be avoided in order to avoid damage to the internal structure of the transformer. It is recognized that many transformers may not, by their construction or placement, be readily modified to utilize a circulation loop, and such circulation is not considered a necessary aspect, but only one embodiment of this invention to increase elution rates. In most transformers, natural thermal gradients alone will induce sufficient circulation especially in those cases where a relatively low viscosity, mobile coolant, such as TCB, is used.

As the PCB content in the TCB or other interim coolant in the transformer builds up, it can eventually reach a point where diffusion no longer serves to leach PCB from the cellulosic pores or interstices of the insulation within the transformer tank. A reduction in elution rate as determined by sample analysis, is a clue that this may be occurring. If it is determined that this is occurring, it may become necessary as specified in step (4) to replace the PCB-laden interim dielectric cooling fluid with fresh PCB-free fluid. This is most easily accomplished by shutting down the transformer, draining out the contaminated leach fluid (interim dielectric coolant), and replacing it with fresh fluid. As a practical matter, instead of monitoring the elution rate to determine when diffusion no longer serves to effectively leach PCB from the pores or interstices of the electrical insulation, it is more practical to schedule the transformer for regular coolant changes. If a non-PCB transformer is desired, coolant changes are made after selected periods of electrical operation, until the coolant fails to elute 50 ppm of PCB per 90 days operation. Periods of electrical operation between coolant changes can be selected to be 20 days to 1 year (or more, if the transformer owner's needs prevent shutting down the transformer except at rare specified times, e.g., special holiday periods, such that there may be more than one year between shutdowns and possibly shutdowns can take place only every other year.), preferably 30 to 120 days and most preferably 45 to 90 days.

The contaminated leach fluid may then be distilled off and condensed for re-use to leave a PCB bottom product which is incinerated or otherwise disposed of pursuant to U. S. government regulations. While a complete change of interim coolant is preferred, it is possible that the inconvenience of additional shutdowns predicates a different procedure, i.e., that of simultaneously introducing new fresh fluid and removing the old contaminated fluid while the transformer remains in operation. It is less efficient because the fresh fluid mixes with the old in the transformer, and fluid of reduced PCB concentration is actually removed. Thus to eliminate all the PCB, more leach fluid will have to be removed than for the preferred procedure. This penalty can be reduced if one takes pains to avoid excessive mixing. For example, new chilled TCB or other interim dielectric cooling fluid can be introduced into the bottom of the transformer, while old, warm, PCB-laden interim dielectric cooling fluid is removed from the top. The density difference will retard mixing. Regardless of the method used, the process will require repetition until the desired PCB level, e.g., less than 50 ppm in silicone oil coolant can be maintained for at least 90 days.

While distillation is the preferred method for separating TCB or other interim dielectric coolant and PCB, other methods may be feasible, especially if fluid other than TCB is chosen as the temporary fluid.

There is some concern that TCB itself, or other chlorinated interim dielectric coolant, such as TTCB and the halogenated solvents, may eventually become suspect as a health hazard, and that the transformer, though free of PCB, will be contaminated with TCB or other potentially objectionable interim fluid. The further advantage of the procedure of this invention is that such contamination can be easily rectified if necessary, since the interim TCB or other fluid is more volatile than the silicone or heavy hydrocarbon fluids, or other relatively high viscosity permanent coolant used in the transformer and can be distilled therefrom. Accordingly, the chlorinated portion of the coolant can be replaced and the old batch sent to a still for easy purification. Two or three such changes over a period of several months will give a substantially halogen free system, if one is desired.

Other preferred coolants of a permanent nature that can be used in place of the final fill of silicone oil include dioctylphthalate, modified hydrocarbon oils, e.g. RTEmp of RTE Corp., polyalphaolefins, e.g. PAO-13-C of Uniroyal, synthetic ester fluids, and any other compatible permanent fluid. It is also preferred that the permanent dielectric fluid be characterized by a high boiling point compared to said interim dielectric solvent so that the interim dielectric solvent can be separated from the permanent fluid if the need arises and also to avoid releasing permanent fluid due to volatilization in the event the transformer tank is ruptured.

While the following have been suggested, and in some cases used, as permanent dielectric fluids, they are less preferred than the relatively high viscosity, high boiling permanent dielectric fluids: tetrachlorodiaryl methane with or without trichlorotoluene isomers, freon, halogenated hydrocarbons, tetrachloroethylene, the trichlorobenzene isomers and the tetrachlorobenzene isomers. The trichlorobenzene isomers, the tetrachlorobenzene isomers, and mixtures thereof have high flammability ratings and other physical properties similar to askarel and therefore are preferred amongst the less preferred permanent fluids.

The following examples are presented. In the examples, the following abbreviations have been used.

TCB	trichlorobenzene
TTCB	tetrachlorobenzene

TCB mix	30-35 wt. % tetrachlorobenzene, TTCB, in trichlorobenzene, TCB (containing an effective amount of a chlorine scavenging epoxide-based inhibitor)
PCB	polychlorinated biphenyls
ppm	parts of PCB or TCB mix per million of coolant based on weight
Askarel	Askarel Type A, 60 wt. % Aroclor 1260, 40 wt. % TCB
Aroclor 1260	polychlorinated biphenyl containing 60 wt. % chlorine
L-305	A silicone oil within the scope of formula A above, having a viscosity of 50 mm^2/s (centistokes) at 25°C.

A "cycle" is the period of time between changes in the coolant. A "part" of a cycle is a portion of a cycle where the leach rate into the coolant is markedly different from the rate in the earlier or later portion of the cycle.

Examples 1, 2, A, B and C

Each of the four transformers identified in Table I were drained, rinsed and filled with the coolant designated for Cycle 1 in each case in Table I.

In each case of Examples A and 1; the coolant in the transformer prior to draining and rinsing was mineral oil (Exxon Univolt inhibited oil, transformer grade) containing the initial PCB concentration shown in Table I. Transformer #459 and #461 of Examples A and 1 at one time had been askarel-filled transformers that had been previously switched to mineral oil and respectively contained 9,150 and 7,800 ppm PCB. Transformer #459 of Example A was drained, spray rinsed with mineral oil and then filled with fresh mineral oil. Transformer #461 of Example 1 was drained, spray rinsed with TCB mix and then filled with fresh TCB mix. The transformers were operated at about 80°C. for the time periods listed in Table I. In Example 1, the transformer was drained of TCB mix and refilled with TCB mix 2 ~~two~~ more times to provide two complete cycles and one ongoing cycle.

In Examples 2, B and C, each respective transformer was a member of a bank of three identical Westinghouse transformers having a rated capacity of 333 KVA each. Each of these transformers contained about 719 ℓ (190 gallons) of type A askarel that was a coolant having a 60/40 wt. ratio of Aroclor 1260 (PCB) and trichlorobenzene. These ~~three~~ 3 transformers were all tied into the same three-phase bank and were all operated at the same capacity and otherwise encountered the same conditions except as hereinafter designated. The normal service of the transformers of Examples 2, B and C, was far below their rating and the annual average operating temperature was around 40°C. except as otherwise designated. Transformer #669 (Example 2) and transformer #667 (Example C) were drained of askarel, spray rinsed twice with TCB mix and subsequently refilled with TCB mix. Transformer #668 (Example B) was drained, spray rinsed twice with silicone oil (L-305) and subsequently refilled with silicone oil, L-305. All transformers were reenergized and liquid samples were taken periodically to check the PCB content.

All ~~five~~ 5 transformers were operated and PCB concentrations were determined at the end of the various day intervals indicated in Table I and the daily rate of ppm of PCB increase in the coolant was calculated and converted to a silicone oil coolant basis (if not already on such basis) as designated in Table I.

In Example 2, transformer #669 was operated for 96 days then drained, spray rinsed with TCB mix and refilled with TCB mix and operation was continued in Cycle 2 and the same sequence was repeated for Cycles 3 and 4 for the transformer. In Example 2, at the end of Cycle 4 in the case of transformer #669, the transformer was drained and spray rinsed with TCB mix and thereafter filled with TCB mix and it continued to be electrically operated. The day intervals, PCB concentrations at the end of the day intervals and overall rate of elution and converted rate of elution in terms of ppm per day are given in Table I in respect to each cycle.

In Example B, transformer #668 was initially drained of askarel, spray rinsed twice with L-305 and filled with fresh L-305. At the end of the 390th day the transformer was again drained, spray rinsed with L-305 and subsequently filled with fresh L-305 and continued to operate in Cycle 2. The day intervals, PCB concentrations at the end of the day intervals, and the overall rates of elution in ppm per day are correspondingly listed in Table I.

Transformer #667 (Example C) was initially drained of askarel, spray rinsed twice with TCB mix and filled with TCB mix. At the end of the 96th day, it was drained, spray rinsed and filled with fresh TCB mix. Subsequent cycles are as indicated in Table I.

TABLE I

Description	Initial PCB conc. ppm	Solvent (coolant) used	Temp. °C	Day Interval start	Day Interval end	PCB conc. at end, ppm*	Overall Rate (On L-305 Basis) ppm/day*
Transformer # 461	7,800	mineral oil					
Cycle 1, 1st part		TCB mix	85	0	25	650	25.97
Cycle 1, 2nd part		TCB mix	85	25	68	820	4.01
Cycle 2		TCB mix	85	68	164	1,140	3.29
Cycle 3		TCB mix	85	165	213	80	1.64
ongoing							
Transformer # 669	600,000	askarel					
Cycle 1, 1st part		TCB mix	40	0	50	11,300	226.50
Cycle 1, 2nd part		TCB mix	40	50	96	13,000	36.03
Cycle 2		TCB mix	20	96	161	680	10.45
Cycle 3		TCB mix	55	161	225	830	12.98
Cycle 4		TCB mix	85	225	294	390	5.69
Cycle 5		TCB mix	85	294	438	500	3.46
ongoing							
Transformer # 459	9,150	mineral oil	85				
Cycle 1, 1st part		mineral oil	85	0	115	440	3.83
Cycle 1, 2nd part		mineral oil	85	115	213	475	0.36
Cycle 1, 3rd part		mineral oil	85	213	220	n/a	n/a
Cycle 2		L-305	85	220			
ongoing							

TABLE I (CONT'D)

Description	Initial PCB conc. ppm	Solvent (coolant) used	Temp. °C	Day Interval start	Day Interval end	PCB conc. at end, ppm*	Overall Rate (On L-305 Basis) ppm/day*
Transformer # 668	600,000	askarel					
Cycle 1, 1st part		L-305	40	0	28	8,650	308.93
Cycle 1, 2nd part		L-305	var.	28	392	11,700	8.38
Cycle 2		L-305	85	392	438	650	14.13
ongoing							
Transformer # 667	600,000	askarel					
Cycle 1, 1st part		TCB mix	40	0	50	12,000	241.60
Cycle 1, 2nd part		TCB mix	40	50	96	14,600	55.87
Cycle 2		TCB mix	55	96	161	1,200	18.58
Cycle 3		TCB mix	85	161	225	600	9.44
Cycle 4		TCB mix	85	225	336	530	4.76
Cycle 5		L-305	40, 85	336	390	180	3.33
Cycle 6		L-305	85	390	438	60	1.25
ongoing							

Var. = irregular variation between 20 and 40°C. (Fall, winter and spring operation).

* converted where necessary to an L-305 basis.

n/a = not available

For Example A, transformer #459, the leach rate had been reduced to an average PCB leach rate of 0.36 ppm/day in the second part of the first cycle. This was below the 0.55 ppm/day or 50 parts per million in 90 days required for reclassification as non-PCB. Accordingly, at day 220, the mineral oil was drained and replaced with the permanent L-305 silicone coolant. As can be seen from Table I the total PCB removed during Cycle 1 was equivalent to 475 ppm in the volume of coolant held by that transformer. This is less than the 1220 ppm removed during the same interval of time by TCB mix in #461, a similar size and type of transformer, and indicates that the mineral oil had not been as effective a leachant as TCB mix.

In contrast, transformer #461 was leached with TCB mix. At day 68 the TCB solvent was drained and reintroduced into the same transformer. At day 165 the TCB mix was drained and replaced with fresh TCB mix. While the overall rate for Cycle 3 was 1.64 ppm per day, the rate decreased during the cycle and as of day 245 the PCB elution rate was reduced to 0.05 ppm per day which was well below the target rate of 0.55 ppm PCB per day. Accordingly, the fluid can at this point be replaced with a permanent silicone coolant.

Transformer #669 (Example 2) was originally filled with askarel. Hence, it had much more PCB in the insulation than #461 (Example 1) to be leached. Therefore, it required many more cycles and a considerably longer period of time to leach to an acceptable level. When the rate of leach falls below the target rate of 50 ppm in 90 days then the TCB mix can be replaced by silicone. The rate figures in the last column of Table I show a continual decrease with time, and the target rate should be reached around day 600. It should be pointed out that transformers #667, #668 and #669 were expected to be among the most difficult to leach. They are spiral wound transformers in which the paper insulation, and hence diffusional path length, can be several inches in depth. In contrast, many transformers are of the "pancake" design in which path lengths will be less than an inch.

Examples B and C, transformers #668 and #667, are comparative examples because in Example B the initial coolant used was silicone oil, and in Example C, the change over to silicone oil was made before the elution reached 0.55 ppm PCB per day.

Transformers #667 and #669 were filled initially with askarel which was replaced with TCB mix, while transformer #668 was filled initially with askarel which was replaced with L-305 silicone oil. Figure 1 compares

PCB analyses for the first cycle of these three transformers. The data have been converted to the total actual grams of PCB removed. While about 60,000 to 70,000 grams of PCB were quickly removed (within the first 28 days), subsequent removal was much slower, and the rates are indicated by the straight lines drawn through the points. It is presumed that the major quantity of PCB held up in the looser insulation is easily extracted regardless of solvent, but that it is the PCB held up in the tighter wound paper and pressboard insulation which is limiting to the process, and in this case the effectiveness of the eluants differs. Figure 1 shows this difference. While the data points are somewhat scattered due to the difficulties of precise PCB analysis, it appears that the silicone takes 400 days to remove the same quantity which the TCB mix can remove in 60 days. A comparison of the slopes of the lines shows the TCB mix to be about 8.5 to 9.0 times as effective a leachant as L-305. The key point in this invention is that the ratio of effectiveness is so high. Thus, a process which might take 5 to 10 years with silicone alone could be carried out in a much shorter time with an interim coolant such as TCB mix.

Figure 2 illustrates the effect of the transformer temperature on the rate of PCB elution. Both #667 and #669 were at about 40°C during the first cycle. They were changed out to fresh TCB mix after 96 days. Because winter was approaching and the transformers were not utilized to that capacity required to keep their temperatures high, it was anticipated that low temperatures might interfere with the leaching. Accordingly, #667 was artifically heated by applying heat to the cooling fins. Transformer #669 was left unheated for comparison. The temperature of #667 averaged about 55°C , while that of #669 averaged about 23°C. Again, the data points are quite scattered, but it is clear that the warmer transformer eluted PCB faster than the colder one by a factor of 1.6. This factor may not be linear, and, consequently, the rate gain may not be as dramatic for higher temperatures. Further leaching was carried out at 85°C when possible, and thus most leaching listed in Table I was done at this higher temperature.

By way of further example the following illustrative cases of Example 3-5 are presented. While they do not represent results from actual transformers, they are based upon the performance to be expected from the process of this invention under the conditions outlined below for each example as applied to transformers from which it is relatively easier to elute PCB by the process of this invention than those transformers used in Examples 1, 2, A, B and C.

In each of Examples 3-5 there is used a transformer of (200 gallon) 757 ℓ fluid volume capacity, the internals of which hold up to 6 gallons in the cellulosic materials, i.e., the paper insulating the coils, and which contains (200 gallons) 757 ℓ, more or less, of an askarel of 50% PCB (500,000 ppm), except for Example 4 wherein the transformer contains (200 gallons) 757 ℓ, more or less, of mineral oil containing 10,000 ppm PCB.

Figures 3 through 5 are plots of concentration of PCB in ppm in interim dielectric fluid (TCB) in the transformer plotted on a vertical logarithmic scale versus days elapsed (or soak time) and graphically illustrate the anticipated results sought to be obtained by this invention.

Example 3

In Example 3, the transformer is first deenergized. Then it is drained of its askarel, the latter being ultimately disposed of in an approved manner. The transformer is flushed out with a small quantity (e.g. 95 ℓ 25 gallons) of trichlorobenzene, so as to reduce the residual askarel in the free fluid system to 0.5% of its initial value. The system is then logically inspected for leaky bushings or other physical problems which may require repair at this time.

Then the transformer is filled with 200 gallons of trichlorobenzene, TCB, (or, alternatively, a trichlorobenzene-tetrachlorobenzene mixture), is sealed up, and, after appropriate testing, is reenergized. Because the flush is not totally thorough, the initial PCB level in the new fluid in the transformer is anticipated at 2500 ppm, i.e. 0.5% of the initial PCB levels. It is assumed that the PCB held up in the cellulosic materials leaches out at a rate varying from 0.001 to 0.01% per day. While these values may appear, arbitrary, they are probably attainable in easy-to-leach transformers, and higher or lower rates will only affect the length of time required to accomplish the total leach, not the basic procedure. The uppermost curve plotted on the graph marked Fig. 3 shows the concentration (on a logarithmic scale) of PCB that can be expected to be found in the transformer fluid as a function of time. In actual commercial applications of the process one would not need to determine all these concentrations. However, one would want to sample the old fluid being replaced and determine its PCB concentration. This is shown by the open circles in Fig. 3. While the exact length of the leaching periods is arbitrary, experience with a given type of transformer will indicate the most practical period lengths in terms of overall process time and total number of fluid replacements. In this example, 60 day leach periods are used.

At the end of 60 days, the transformer is once more deenergized, the fluid is drained, and a sample taken 95l for analysis. The system may be reflushed with about (25 gallons) of TCB, and the flush fluid, along with the bulk fluid, is taken to a site where the TCB may be recovered by distillation (and the residual PCB properly disposed of by EPA approved methods).

The transformer is refilled with TCB, and this time the intial expected PCB concentration (due to residual prior fluid) is about 83 ppm. Again the anticipated PCB concentration follows along the second highest curve in Fig. 3 for the next 60 days (to 120 days), whereupon the

TCB in the transformer is changed as before, with one exception. Since the drained TCB fluid has a concentration of PCB less than the initial value for the first fill, the drained fluid need not be sent to the still for separation, but instead can be used as the initial fill for a second PCB transformer to be converted to a non-PCB condition. This saves valuable distillation time and energy, as well as transportation or handling costs.

The refill process is repeated one more time. Table II gives a list of the anticipated analytical results which are represented by the circles on the graph of Fig. 3. It is clear from the data of Table II and Fig. 3, that the fourth refill will not rise above 50 ppm PCB content, the U. S. government cut-off value for the designation of non-PCB transformers. Therefore, at the end of 180 days, the transformer is refilled with its permanent fluid, a silicone oil, e.g., L-305. The PCB value expected to be reached after another 60 days (240 days) is only 16 ppm, and after the prescribed U. S. government 90 day period (270 days) it is anticipated to be at still only 18 ppm. Thus, the transformer may be reclassified as a non-PCB transformer.

Table II

Days Elapsed	Concentration PCB, ppm In Drained Fluid	 Initial In Refill
0	500,000	2,500
60	16,600	83
120	896	4
180 Silicone Refill	101	<1
240	(16) Not drained	
270	(18) Not drained	

Example 4

In Example 4, 60 day leach periods are used but flushing out of the transformers is eliminated. It is assumed that 98% of the fluid can be adequately drained, leaving 2% in the transformer. In this case the initial concentrations will be 2% of the previously drained fluids instead of the 0.5% of Example 3. The procedure of Example 3 is repeated in this example.

The results to be expected for Example 4 are given in Table III and are shown in the graph of Fig. 4. Note that the objective is still obtained and the system can be refilled with silicone or other permanent oil at 180 days. The lack of highly efficient flushing is expected to lead to slightly higher PCB contents in the final fluid, but this does not substantially change the achievement of the goal of a non-PCB transformer.

Table III

Days	Concentration PCB, ppm	
Elapsed	In Drained Fluid	Initial in Refill
0	500,000	10,000
60	23,900	480
120	1,440	30
180 Silicone Refill	145	3
240	(21) Not Drained	
270	(23) Not Drained	

Example 5

The shapes of the concentration curves in Figs. 3 and 4 might lead one to believe that the fluid changes should be made more often, e.g., every 30 days instead of 60 days. Example 5 is identical to Example 4, except that 30 day leach periods are used. The expected analytical results are given in Table IV and the plots are shown in Fig. 5. The trend is obvious from the graphs of Fig. 5. The initial refill shows a reduction almost as good as that for Example 4, but subsequently the reductions start to curve off. The sixth refill can be made with the permanent fluid, and some time has been saved, about 30 days, at the expense of the two extra refills with TCB. This example illustrates the availability of a trade-off of time vs. number of refills, and the choice depends upon which is valued the most highly for the specific case at hand.

Table IV

Days Elapsed	Concentration PCB, ppm In Drained Fluid	Initial in Refill
0	500,000	10,000
30	15,800	316
60	1,260	25
90	310	6
120	120	3
150 Silicone Refill	50	1
180	(21) Not Drained	
240	(32) Not Drained	

The present invention is not limited to use in transformers but can be used in the case of any electrical induction apparatus using a dielectric coolant liquid including electromagnets, liquid cooled electric motors, and capacitors, e.g., ballasts employed in fluorescent lights.

PATENTANWÄLTE 42
WUESTHOFF-v. PECHMANN-BEHRENS-GOETZ
EUROPEAN PATENT ATTORNEYS

DIPL.-CHEM. DR. E. FREIHERR VON PECHMA
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EP-58 989

Claims

1. A method for replacing a coolant containing PCB in an electrical induction apparatus having a tank containing said coolant, an electrical winding and porous solid cellulosic electrical insulation immersed in said PCB-containing coolant with a substantially PCB-free high boiling dielectric permanent coolant to convert said electrical apparatus into one in which the rate of elution of PCB into said coolant is below the maximum allowable rate of elution into the coolant of an electrical apparatus rated as non-PCB, said solid porous electrical insulation being impregnated with said PCB-containing coolant, said method comprising the steps of:

(a) draining said PCB-containing coolant from said tank to remove a major portion of said PCB-containing coolant contained by it;

(b) filling said tank with an interim dielectric cooling liquid that is miscible with said PCB, is sufficiently low in viscosity to circulate within said tank and penetrate the interstices of said porous solid electrical insulation, and is capable of being readily separated from said PCB;

(c) electrically operating said electrical induction apparatus and continuing said electrical operation for a period sufficient to elute PCB contained in said PCB-containing coolant impregnated in said porous solid insulation therefrom into said interim dielectric cooling liquid;

(d) thereafter draining said interim dielectric cooling liquid containing said eluted PCB from said tank;

(e) repeating the cycle of steps (b), (c) and (d) when the rate of elution of PCB into said interim dielectric cooling liquid exceeds 0.55 ppm of PCB per day based on the weight of said permanent dielectric coolant; and

(f) filling said tank with a substantially PCB-free permanent coolant selected from the group consisting of high boiling, high viscosity, silicone oils, synthetic ester fluids, poly-alpha-olefin oils and hydrocarbon oils so as to reclasify said electrical apparatus to non-PCB status.

2. Method as claimed in claim 1 wherein the interim dielectric cooling liquid is trichlorobenzene, tetrachlorobenzene or mixtures of same and the permanent coolant is a dielectric silicone oil coolant.

3. Method as claimed in claim 1 or 2 wherein each step (c) is continued for 20 days to 1 year or 30 to 120 days or 45 to 90 days.

4. Method as claimed in claims 1 to 3 wherein, when carrying out step (d) of the previous cycle and step (b) of the next succeeding cycle, the interim cooling liquid is drained from the top of the tank while fresh chilled interim dielectric cooling liquid is fed into the bottom of the tank and while electrical operation of the apparatus is continued.

5. Method as claimed in claims 1 to 4, wherein the steps (d) and (f) are carried out by feeding the PCB-free permanent coolant into the bottom of the tank while removing the interim dielectric cooling liquid in the tank from the top of said tank, and while electrical operation of the apparatus is continued.

6. Method as claimed in claims 1 to 5, wherein the tank is provided with heat insulation in order to raise the temperature of the interim dielectric cooling liquid contained by it during each step (c) while electrically operating said electrical induction apparatus.

7. Method as claimed in claims 1 to 6, wherein the interim dielectric cooling liquid in the tank is heated during step (c) while electrically operating the

electric induction apparatus.

8. Method as claimed in claims 1 to 6 wherein during step (c) the interim dielectric cooling liquid is removed from said tank, heated and returned to said tank while maintaining sufficient interim dielectric fluid in said tank and electrically operating said electrical induction apparatus.

9. Method as claimed in claims 1 to 8 wherein the interim dielectric liquid is more volatile than the PCB and is separated from the contained PCB by distilling off the interim dielectric cooling liquid.

10. Method as claimed in claims 1 to 8 wherein the interim dielectric cooling liquid containing PCB eluted from the solid insulation is drawn off from the tank as a slip stream while electrically operating the electrical induction apparatus adding fresh interim dielectric cooling liquid substantially equivalent to the amount of PCB-containing interim dielectric fluid drawn off in the slip stream.

11. Method as claimed in claims 1 to 10 wherein the tank is flushed with a solvent for the PCB following step (a) and before step (b).

12. Method as claimed in claim 11 wherein the flushing solvent is the same liquid as the interim dielectric cooling liquid used in step (b).

13. Method as claimed in claim 11 wherein the flushing solvent and the interim dielectric cooling liquid is trichlorobenzene.

14. Method as claimed in claims 1 to 12 wherein the interim dielectric cooling liquid is 1,2,4-trichlorobenzene or a mixture of trichlorobenzene and tetrachlorobenzene.

15. Method as claimed in claims 1 to 14 wherein the permanent coolant employed to fill the tank is a silicone oil.

16. Method as claimed in claim 15 wherein the permanent coolant used in step (f) is a silicone oil having the following formula:

$$(CH_3)_3SiO\ (CH_3)_2SiO\ _nSi(CH_3)_3$$

wherein n is a number of such value providing a viscosity of about 50 mm²/s at 25°C.

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1/5

FIG. I

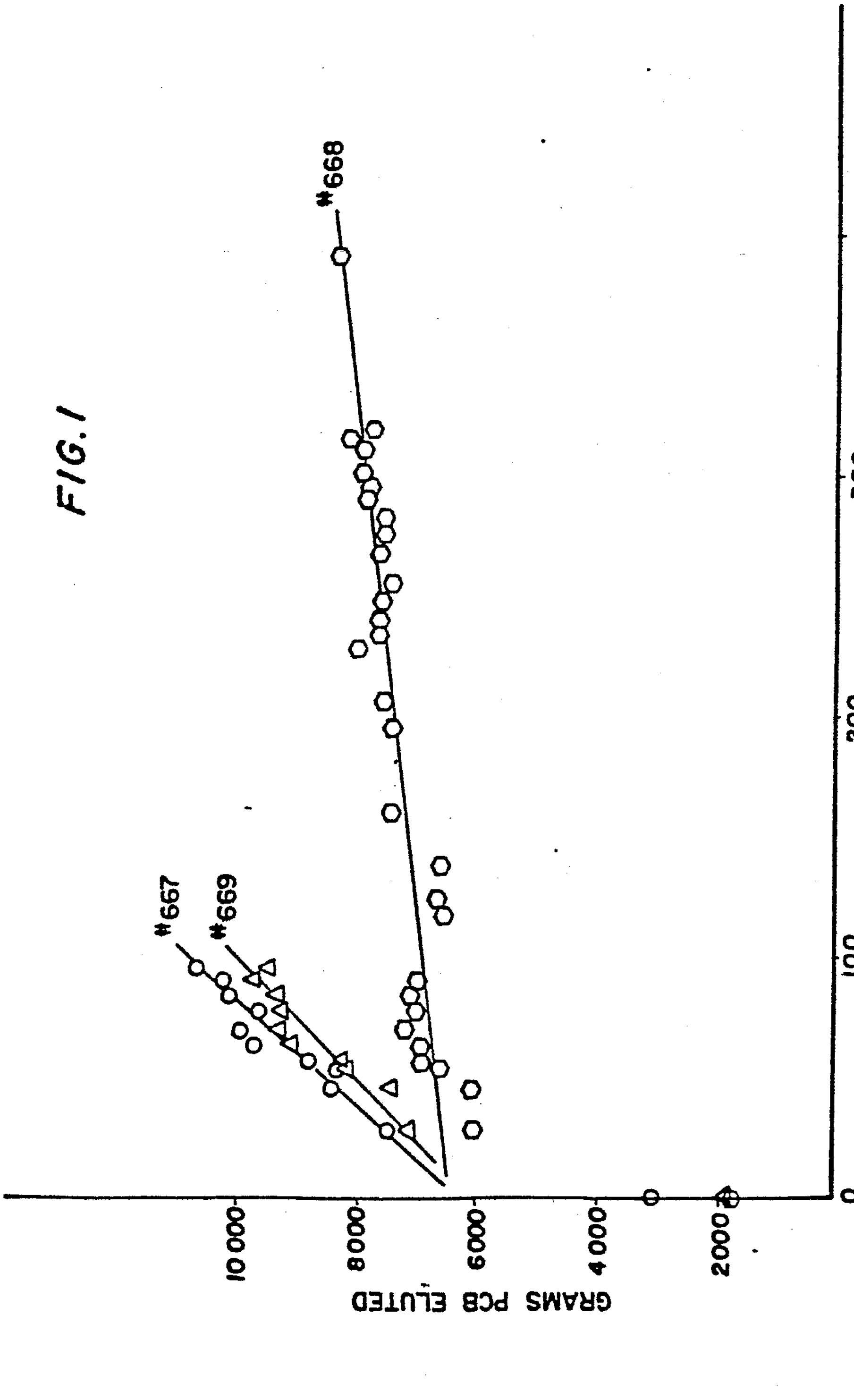
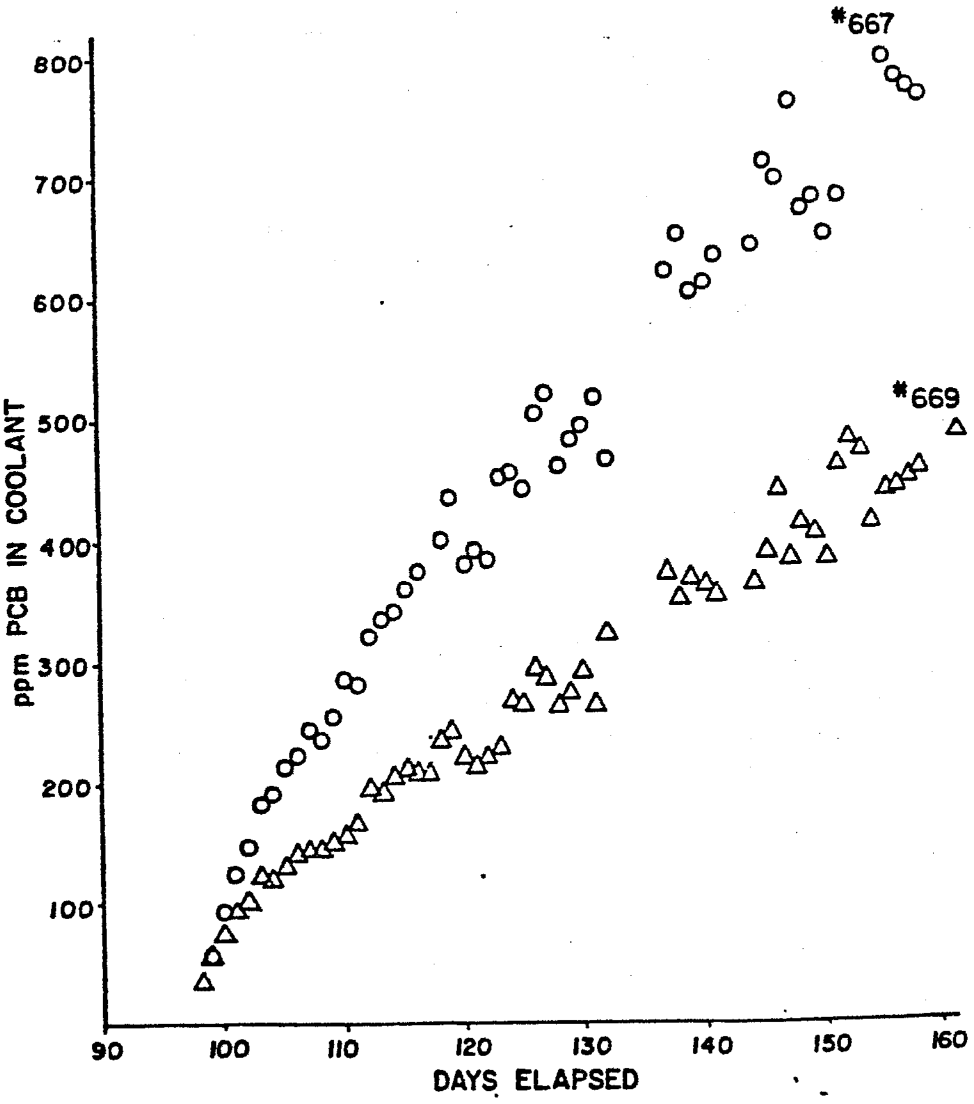
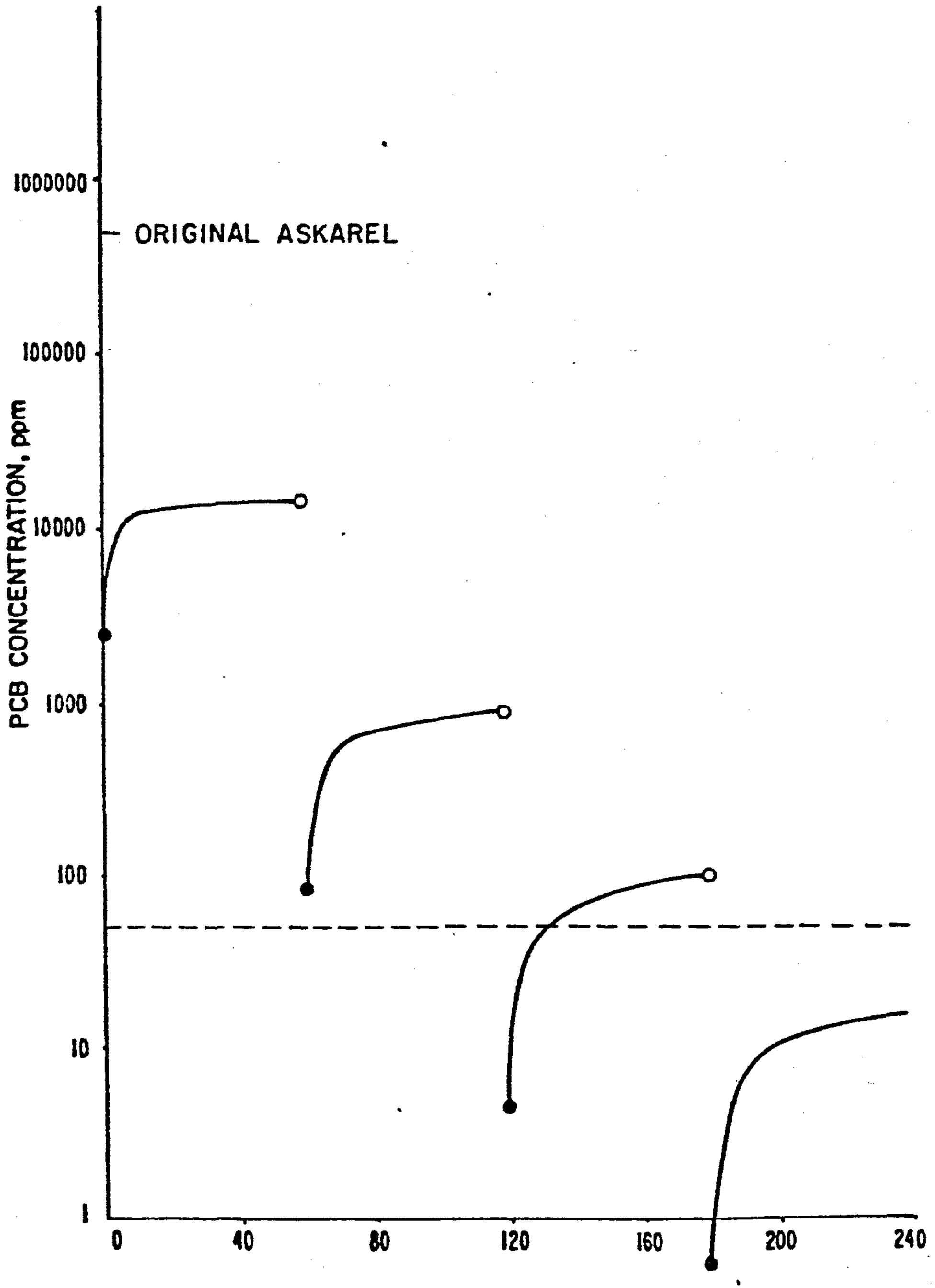


FIG. 2


*667
*669
ppm PCB IN COOLANT
800
700
600
500
400
300
200
100
90
100
110
120
130
140
150
160
DAYS ELAPSED

3/5


1000000
ORIGINAL ASKAREL
100000
PCB CONCENTRATION, ppm
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1000
100
10
1
0
40
80
120
160
200
240
DAYS ELAPSED

FIG.3

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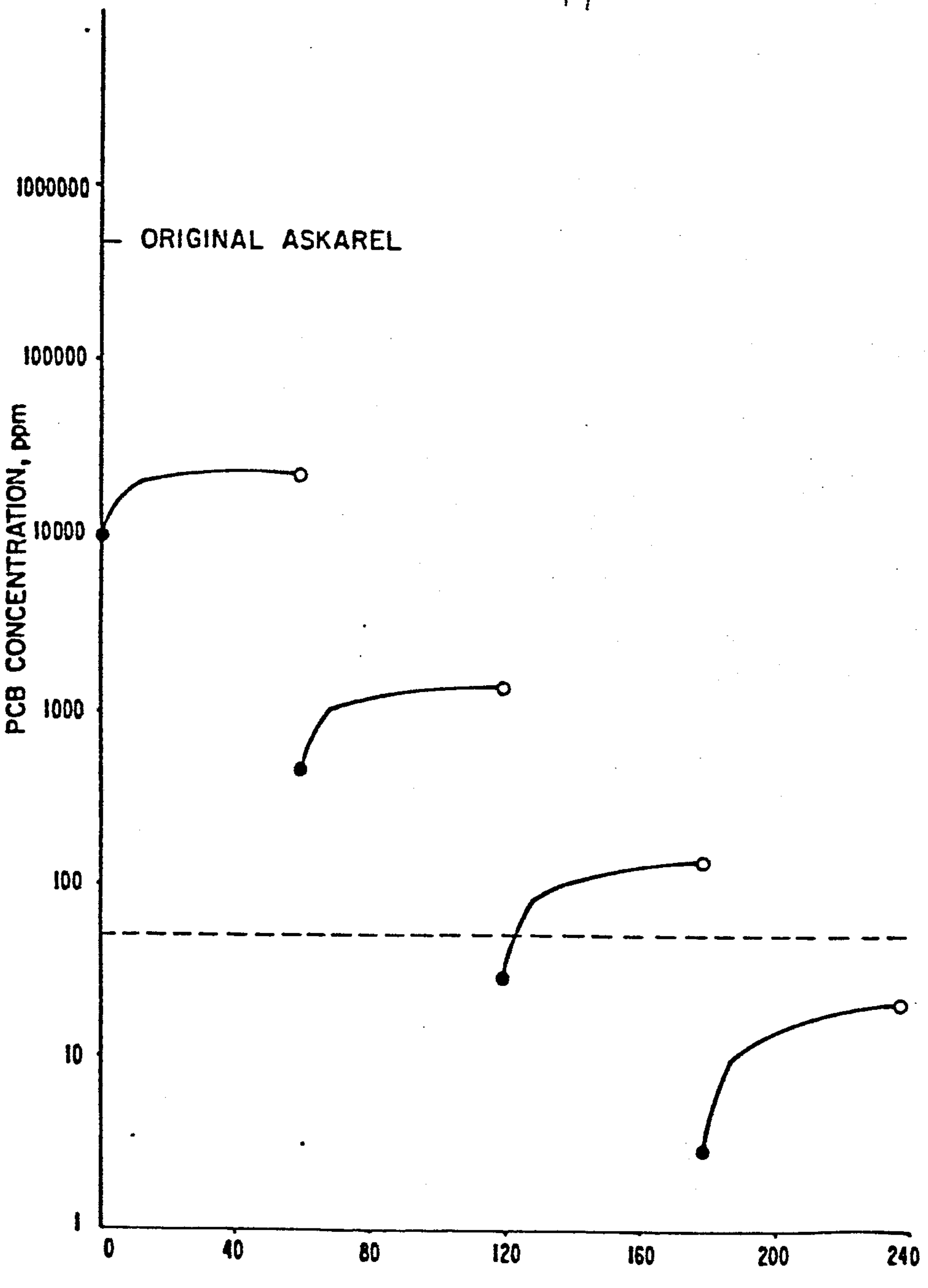
PCB CONCENTRATION, ppm
1000000
100000
10000
1000
100
10
1
ORIGINAL ASKAREL
0
40
80
120
160
200
240
DAYS ELAPSED

FIG.4

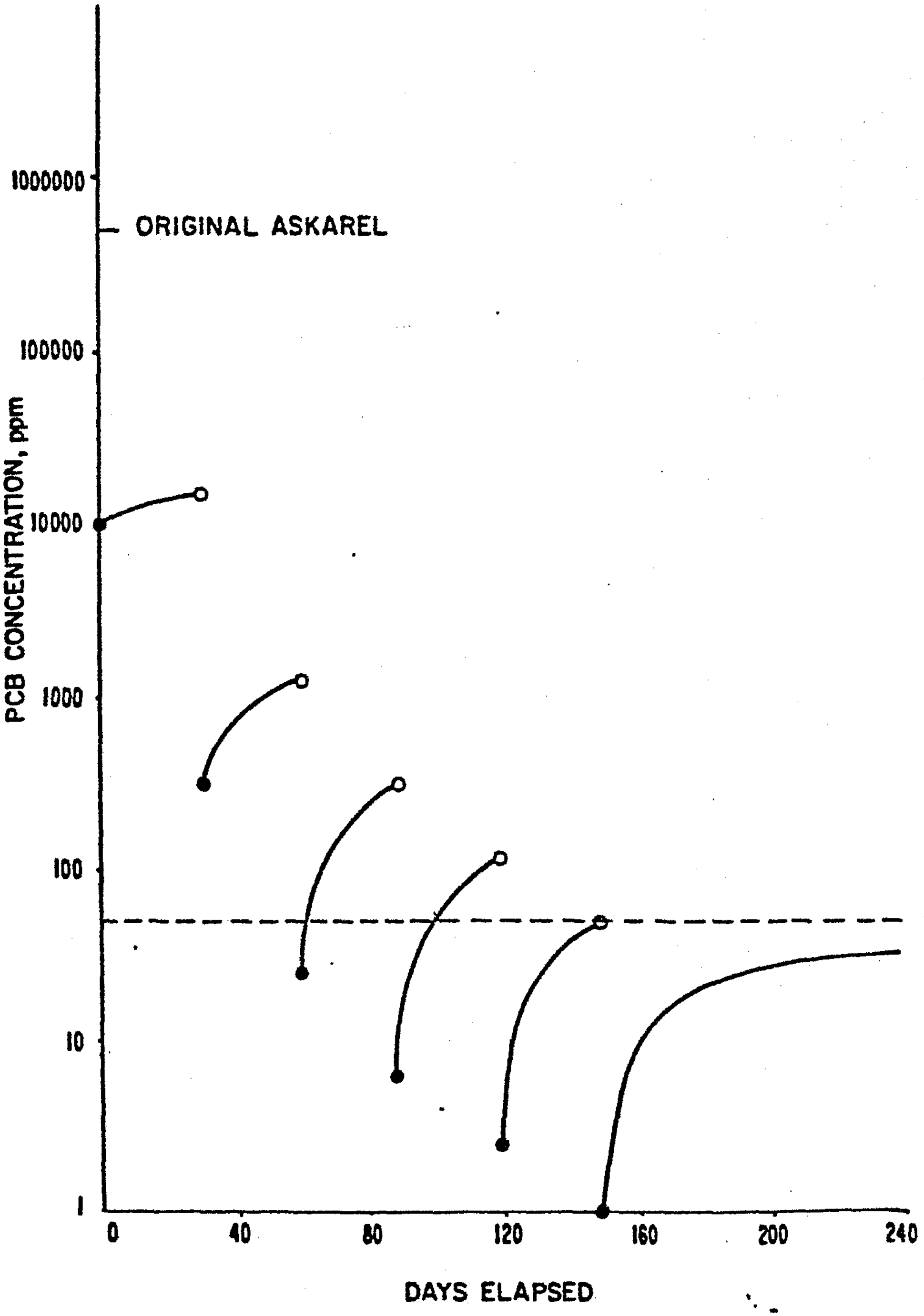
1000000
ORIGINAL ASKAREL
100000
10000
1000
100
10
1
PCB CONCENTRATION, ppm
0
40
80
120
160
200
240
DAYS ELAPSED

FIG. 5