CAPACITOR ASKARELS & THE ENVIRONMENT

by

H.A. Vodden

(Monsanto, Europe)

INTRODUCTION

Polychlorinated biphenyls (PCBs) have enjoyed an enviable reputation as impregnation liquids for power frequency capacitors for several decades. The combination of thermal and chemical stability, coupled with excellent dielectric properties and a very high degree of fire resistance, has resulted in extensive use of these Askarels for impregnating paper and mixed dielectric capacitors in the medium and high voltage range.

In recent years, however, PCBs have also become well-known as environmental pollutants. The functional properties of these chemicals, which range from colourless mobile liquids to wax-like solids, were ideal for numerous other applications in heat transfer systems, hydraulic systems, adhesives and resins formulations and in carbonless reproducing papers. It was probably the expanding use of these substances in such a variety of applications which caused their widespread distribution in the natural environment. The physical and chemical properties were such that many PCBs were preferentially extracted from the aquatic and marine environments by living organisms and either directly, or through some food chain mechanism, accumulated in higher animals such as fish and birds. There is no doubt that PCBs are widespread in nature and have attained levels which are significant - in fish from waters near industrial regions and have been surprisingly high in some species of fish-eating birds. This subject has been reviewed very extensively (1), (2), (3) .

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Owing to the concern expressed by environmentalists at the possibility of harmful effects from a growing accumulation of these PCBs in the environment, actions have been taken in many countries to limit the uses of PCBs to applications where gross contamination of the environment can be avoided. The use of PCBs in capacitors and transformers is considered to be acceptable in this context. Indeed the OECD nations have agreed to actions which will still allow these uses (4). In the USA, a task force was appointed to study the situation and has accepted that PCBs should continue to be used in electrical transformers and capacitors where they fulfil an essential need (5). The OECD recommendations, however, differentiate somewhat between large and small capacitors; whilst allowing the use of PCBs in large power factor correction capacitors, indefinitely, it is suggested that member nations should work towards the elimination of PCBs in small capacitors, such as those for ballast and motor run. It is this latter recommendation which has caused concern among capacitor manufacturers who have, at present, no economic alternative to the use of PCB impregnants in medium and high voltage capacitors (> 300 volt working). The OECD Sector Group paper supporting the main OECD document, however, in a foot-note, anticipates that less persistent PCBs may be permitted as replacement products. It is this aspect of the use of Askarels in capacitors which will be reviewed in this paper.

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CHARACTERISTICS OF ASKARELS

In order to appreciate the problem and discuss possible solutions, it is necessary to consider something of the chemistry and manufacture of commercial PCB products. When biphenyl is chlorinated by direct chlorination, one or more hydrogen atoms in the molecule may be replaced by chlorine. From one to ten substitutions are possible, leading to the general formula $C_{12}H_nCl_{(10-n)}$, where -n- is any integer from 0 to 9. Thus there are ten possible homologues of chlorinated biphenyl, with chlorine numbers ranging from 1 to 10. Within each homologue several isomeric arrangements are possible and the total number of possible homologues and isomers exceeds 200. Commercial products are manufactured by direct chlorination of biphenyl and are normally characterised by the degree of chlorination. They will, therefore, consist of numbers of homologues and isomers, rather than being specific chemical compounds. Products which have commonly been used on a large scale include, for example, those containing 42%, 54% and 60% of chlorine by weight. These particular products contain, on average, about three, five and six chlorine atoms per molecule, but, as already indicated, will also contain other homologues. Analysis of such products by high resolution gas/liquid chromatography shows that each may contain more than 40 - 50 components (6). Products containing 42% and 54% chlorine were analysed and, typically, had compositions approximately as follows :

No of chlorine atoms	1	2	3	4	5	6	7	8
Percentage by weight (42%)	1%	14%	55%	24%	5%	1%	-	-
Percentage by weight (54%)	-	-	1%	22%	48%	23%	6%	-

Askarels are chemically inert and thermally stable. They are miscible with oils and fats but relatively insoluble in water. This combination of properties

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enables water-borne PCBs to accumulate in the lipid or fatty content of aquatic plants and animals from where they may pass through a food-chain mechanism to higher animals.

At this point it is necessary to consider the differences between the different PCB components. These components may behave differently in the environment due to differences in structure, chemical stability, water solubility, etc. Indeed it has been observed from analyses of wildlife specimens that the most commonly occurring PCB residues are those containing five or six chlorine atoms. The overall use pattern of PCBs, until recently was such that lower chlorine compounds would have been expected to contribute at least as much environmental pollution as those with five or six chlorines; since this is not so, it seems clear that differences between the different components can make a major difference to their accumulation.

Apart from the solubility, which could affect the initial uptake of the compound from the aquatic phase, the factor which is likely to be most important in any biological system is the stability of the compound towards biodegradation and this aspect will be considered in more detail.

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BIODEGRADATION

It is often stated that PCBs are persistent, non-biodegradable, chemicals. This is a generalisation which is not universally true. It is true that some PCB compounds will not degrade very rapidly, as the accumulation in wild-life demonstrates, but, there is substantial evidence in the literature to show that many PCB compounds can be degraded by enzymes. The metabolism of PCBs in pigeons and quail has been studied by Bailey and Bunyan (7), who found that compounds with a relatively low degree of chlorination were metabolised fairly rapidly, unlike more highly chlorinated compounds. Grant et al (8) and Benthe et al (9) have studied metabolism in rats and mice and report that tissue residues from lower chlorinated components are significantly less than the more highly chlorinated ones. Analyses of tissues from rats, dogs and leghorn chickens, following two year feeding trials with various commercial PCB products, have been reported by Tucker et al (10) who report similar findings.

It is also well established that many PCB compounds can be degraded by micro-organisms. Ahmed and Foch (11) have reported degradation by a species of achromobacter, and Baxter et al (12) have reported an extensive study of the effects of two biphenyl-degrading organisms on a number of chloro-biphenyls. In this latter work, studies were made of the degradation of several single PCB compounds as well as on commercial mixtures and estimates of the appropriate rate constants were made. The particular organisms studied have been described by Lunt and Evans (13) who also postulated metabolic pathways for the microbial degradation of biphenyl. The results of this work indicated quite clearly that many PCB compounds, especially those containing three or less chlorine atoms per molecule, could be degraded quite rapidly by microbial action. The work also showed that some individual PCB compounds degraded more easily when present in a

mixture than if present alone. Thus the components of a commercial mixture may be much less persistent than work on single isomers might indicate. Although it is not possible to indicate exact values for degradation rate constants, since these will be dependent on many factors like temperature, nature of organisms and concentrations of other biologically active materials, it seems likely that mono and dichlorobiphenyl can be degraded to half concentration in one or two days, trichlorobiphenyls in about five days and tetrachlorobiphenyls in about twenty days. Although in favourable circumstances some penta and hexachlorobiphenyls can be degraded by micro-organisms, meaningful rates for these components have not been determined .

Rates of degradation of PCB compounds in the organs of animals will depend on the body temperature; it is likely that warm-blooded animals like birds and mammals these rates will be generally faster than those indicated for micro-organisms. For cold-blooded animals, such as fish, the rates will depend on the ambient temperatures, but, even in fish, there is evidence that the residues found are mainly of higher chlorinated components (14).

ENVIRONMENTAL RESIDUES

As an indication of the possible effects of contaminating the environment with Askarels it may be instructive to consider a few simplified examples. It will be assumed that the major factor influencing the degradation of Askarels will be enzyme catalysed hydroxylation, which is the mechanism by which most biological systems degrade organic materials. For simplicity, a first order reaction will be assumed with a rate constant, D. The equilibrium concentration arising from a rate of input, R , will then be $C = R / D$. Supposing that an animal eats food contaminated with Askarel and that it consumes its own weight of food in ten days. The maximum equilibrium concentration which could be reached in the animal could be calculated from the knowledge of the original composition of the Askarel and of the degradation rate constants of the components. Crude calculations based on the analyses given for Askarels containing 42% and 54 % chlorine indicate that, if the original concentration in the food is w ppm, the distribution of concentrations of components will be as follows :

No of Cl atoms	2	3	4	5	6	7
ppm (42% Cl)	$\frac{0.014\,w}{D_2}$	$\frac{0.055\,w}{D_3}$	$\frac{0.024\,w}{D_4}$	$\frac{0.005\,w}{D_5}$	$\frac{0.001\,w}{D_6}$	-
ppm (54% Cl)	-	-	$\frac{0.022\,w}{D_4}$	$\frac{0.048\,w}{D_5}$	$\frac{0.023\,w}{D_6}$	$\frac{0.006\,w}{D_7}$

where D_2, D_3, etc. are the degradation rate - constants for the various components.

Although it is not possible to assign exact values to these rate - constants, the work of Baxter et al (12) gives some indication of likely ranges of values for the different groups of PCBs. For warm-blooded animals, it seems reasonable to assign values, in reciprocal days, approximately as follows :

$D_2 \simeq 1$ $D_3 \simeq \frac{1}{3}$ $D_4 \simeq 1/10$ $D_5 < 1/50$ $D_6 < 1/100$

The compositions of the residues in the animal can then be calculated as :

No of Cl atoms	2	3	4	5	6	7
42% Cl (ppm)	0.01 w	0.16 w	0.24 w	0.25 w	0.01 w	-
54% Cl (ppm)	-	-	0.22 w	>2.4 w	>2.4 w	>1.2 w

The total concentration of the Askarel residue arising from feeding on food contaminated with 42% chlorine Askarel would then be about 0.6 w ppm, but its composition will tend to contain the more highly chlorinated components. It should be noted that the concentration in the animal will be less than in the food, whereas, if an Askarel containing 54% chlorine were the cause of contamination, the residue concentration could be more than 6.0 w ppm, which is several times greater than in food.

Similar selective processes will take place in a variety of environments. In soil or mud, for example, bacteria may cause degradation, as in the experiments described by Baxter et al. Thus some selection may have occurred before material enters a potential food chain. A food chain mechanism would accentuate this selectivity and the distortion of the composition could be much more extreme than the simple example might indicate. Further selectivity of components could also arise from selective absorption and excretion of components.

The evidence in support of the preceding hypothesis is extensive and there are numerous references in the literature to the fact that the PCBs found in wildlife consist mainly of those containing five or more chlorine atoms (15) (16) (17).

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It seems evident that the risk of causing environmental contamination is much less with Askarels containing 42% chlorine than with those containing higher levels of chlorine. It also follows, from the previous argument, that this risk can be further reduced by limiting the content of the highly chlorinated components, particularly those containing five or more chlorine atoms. For this reason it has been suggested that capacitor Askarels should be restricted to those based on trichlorobiphenyl, rather than more highly chlorinated materials and that the percentage of components containing five or more chlorine atoms should be minimized. It has been found that the level of these highly chlorinated components can be reduced to less than 3.5% without affecting the functional properties, or imposing too great an economic penalty : Askarel manufacturers will impose such a limit on capacitor Askarels.

With these restraints and the knowledge that the accumulation of such Askarels in living systems is unlikely to be high, it seems reasonable to expect that their use as capacitor impregnants will be allowed to continue, even for small units. The eventual disposal of small capacitors is unlikely to cause massive pollution and disposal along with household refuse will normally impose a restraint on their entry into water ways. The slow leaching with water, which might eventually disperse the Askarel, will allow time for degradation ; fortuitously, the more water-soluble components are those which are more susceptible to oxidation through enzyme catalysis.

For large capacitor units, where more serious local pollution could arise from uncontrolled disposal, it would be prudent, and possibly mandatory, to dispose of the capacitor, or its contents, either by proper incineration or at a site approved for toxic wastes.

REFERENCES

1) Risebrough, R.W., Rieche, P., Peakall, D.B., Herman, S.G., and Kirven, M.N., Nature, 220, 1098, (1968).

2) Anon, BIBRA Bulletin, 11 (7), 323, (1972).

3) Edwards, R., Chemistry and Industry 47 1340, (1971).

4) OECD Document A ('73) 3 , (February 1973).

5) Interdepartmental Task Force on PCBs, Washington, (May 1972), p.4 .

6) Sissons, D., and Welti, D., J. Chromatogr., 60, 15, (1971).

7) Bailey, S., and Bunyan, P.J., Nature, 236, 34, (1972).

8) Grant, D.L., Phillips, W.E.J., and Villeneuve, D.C., Bull. Environ. Contam. & Toxicol., 6 (2), 102, (1971).

9) Benthe, M.F., and Schmoldt, A., Arch. Toxicol., 30, 207, (1973).

10) Tucker, E.S., Presentation to Interdepartmental Task Force on PCBs, Washington (May 1972).

11) Ahmed, M., and Focht, D.D., Can. J. Microbiol., 19, 47, (1973).

12) Baxter, R.A., Gilbert, P.E., Lidgett, R.A., Mainprize, J.H., and Vodden, H.A., Biochemical Journal In press.

13) Lunt, D., and Evans, W.C., Biochem. J., 118, 54, (1970).

14) Helminen, M., Karpanen, E., and Henriksson, K., PCB Conference II, Stockholm, p. 19, (1972).

15) Koeman, J.H., Ten Noever de Brauw, M.C., and De Vos, R.H., Nature, 221, 1126, (1969).

16) Risebrough, R.W., Florant, G.L., and Berger, D.D., Canadian Field Naturalist, 84, 247, (1970).

17) Prestt, I., Jefferies, D.J., and Moore, N.W., Environ. Pollut., 1, 3, (1970).

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