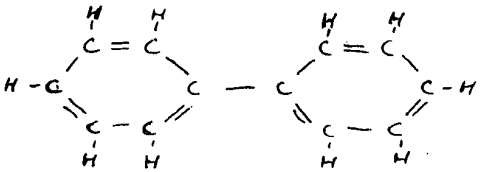
P.C.B.

Biphenyl is an aromatic hydrocarbon consisting of twelve carbon atoms and ten hydrogen atoms. The carbon atoms are arranged in two rings of six, each joined by alternate single and double bonds, the two rings being joined by a bond from a carbon atom of one to a carbon atom of the other. Each of the remaining ten carbon atoms is bonded to a hydrogen atom. The structural formula is:



One or more hydrogen atoms may be substituted by chlorine to form a polychlorinated biphenyl or P.C.B. Since from one to ten chlorine atoms may be substituted, there are ten

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homologs possible and for each homolog, of given chlorine number, several different arrangements, or isomers, of the molecule can be

The following table shows the number of isomers theoretically possible for each homolog group, making a total of 210 isomers.

Homologs No. of Cl atoms per biphenyl molecule	0	1	2	3	4	5	6	7	8	9	10
Theoretical number of isomers	1	3	12	24	42	46	42	24	12	3	1

Commercial PCB products, of which Aroclors are examples, are produced by direct chlorination of biphenyl, the degree of chlorination being chosen to provide desired properties. As the degree of chlorination is increased the products vary from mobile liquids to more viscous and finally to waxes and solids. Both boiling-point and fire resistance also increase with increasing chlorination. In all cases, however, the products consist of mixtures of homologs and isomers; indeed many of the desirable functional properties arise because

MONS 034497

they are mixtures. These materials are inert, chemically-resistant and readily soluble in most common organic solvents. They distill in the range 275°C to 450°C and are, in the classical sense, water insoluble.

The most widely used of the series have average chlorine contents of three, five or six chlorine atoms per molecule. Because they have high dielectric strength and dielectric constant and are fire resistant non-flamable they are used to insulate capacitors and transformers. Their thermal stability leads to their use as heat transfer fluids. Good viscosity and lubricity characteristics made them useful as hydraulic fluids and lubricants, whilst solvent power and compatibility with resultical in their selection as plasticisers and solvents for carbonless copying papers.

MONS 034498

All of these uses are essentially because of their resistance

of significant toxicity to ~~[illegible]~~ man or animals except in rare instances of massive & prolonged exposure.

Other fluids ~~can~~ have been substituted for PCBs for heat transfer, hydraulics, lubrication and ~~of~~ plasticizer applications and as solvents in carbonless ~~carbon~~ copying paper. ~~solvents~~ However, the PCBs have a unique combination of properties which satisfy our needs as capacitor insulating fluids and for transformers where risk of fire must be minimized. No other known materials ~~have~~ fill our needs in these areas.

Our present way of ~~the~~ living depends for its existence on the efficient generation, transmission, ~~and~~ distribution and use of electrical power. Transformers and capacitors are essential for the last three of these.

MONS 034499

Because large electrical generators are rotating machines, they must operate in a gaseous environment. This limits their output to relatively low voltages, whereas efficient transmission over long distances requires high voltages. Electrical step-up transformers are required for this service, but are usually oil-filled since they can be located out-doors and away from people. In some cases, to further improve the efficiency the power is converted to direct current for transmission. This requires the use of large banks of capacitors. Near the point of use the power is converted from direct to alternating current requiring more capacitors. For local distribution, the power is stepped down to lower voltages at substations which again use oil-filled transformers since they also are located out-doors. Most of the power

MONS 034500

used is for electric motors, which are inductive, capacitors are used to raise the power factor to avoid high line losses. Distribution transformers are often located inside buildings and in crowded areas. Here fire resistance is necessary to minimize the hazard to people. Conversion of electrical power to mechanical power for operating appliances, such as furnace blower motors, refrigerators, air conditioners, pumps for compressed air and to supply water from wells, usually involves capacitor start-run motors. Capacitors are required in fluorescent lights and high powered mercury vapor lamps for street lighting and for many other purposes.

No other type of fluid other than chlorinated biphenyl with as many chlorine as hydrogen atoms mixed with trichlorobenzenes or mixtures of tri and tetra chlorobenzenes gives

MONS 034501

a transformer insulating fluid which does not burn or form flamable or explosive gases when an arc is struck within it. Fluids of this type called Askarels ~~fulfil~~ fulfil a vital safety need where transformers must be located in close ~~proximity~~ proximity to people.

It is perhaps less essential that capacitor fluids be fire resistant, but still desirable since failure of a small capacitor could start a fire in a large building with many human occupants. In addition to being fire resistant, PCBs have a higher dielectric constant than other suitable fluids and permit manufacture of smaller capacitors for a given rating which have larger life. Conservation of electrical ~~power~~ energy, ~~through the~~ by using ~~of~~ transformers and capacitors in its distribution and use, ~~of electrical~~ [illegible]

MONS 034502

to decreased pollution because of more ~~efficient~~ efficient use of energy converted to electricity.

In 1966, Jensen[1] demonstrated by mass spectrometry that the unknown substances, appearing with organo chlorine insecticides during analyses of environmental specimens for organochlorine insecticides by gas/liquid chromatography, were PCBs. Since then, considerable analytical evidence, including much from Monsanto Laboratories using increasingly sophisticated techniques (Appendix) has accumulated in support of the view that PCBs are widespread in nature and may reach levels which are significant in many aquatic animals and in some species of fish-eating birds.[2-8] The combination of chemical and physical properties necessary for accumulation through a food chain, principally resistance to oxidation and lipid solubility, are characteristic of the chlorinated biphenyls. It is not too surprising that quite low levels in water, perhaps less than 1 part in 10^{12}, can be magnified to more than 1

MONS 034504

in 10^6 when passing through a food chain of aquatic species to predatory birds. The commercial PCB products like Aroclors are not single chemical species, but consist of quite large numbers of homologues and isomers (9), which although similar are not identical in chemical and physical properties. We might expect, therefore, to find variations in the extent to which these various components accumulate in wild-life and, indeed, many of the published data indicate a predominance of certain homologues, principally those containing 5 or 6 chlorine atoms, in wildlife residues (5, 6, 9, 10).

Aroclors are not particularly toxic to small mammals. Acute oral LD_{50} values for rats range from about 6 to 11 g./kg. (11) For some marine species dietary toxicity may be more serious; LC_{50} values ranging from 0·3 to 10 ppm have been reported

MONS 034505

for brown shrimp (crangon crangon) (12) and even lower concentrations have been reported to be lethal to the Gulf Shrimp (13). In the present context, where accumulation over long periods may be envisaged, the chronic toxicity of Aroclors is probably more relevant. Feeding trials over periods of two years have indicated that in small mammals (rats and dogs) significant effects are not observed at levels of 1 and 10 ppm in food. At levels of 100 ppm liver enlargement has been noted with more highly chlorinated Aroclors (14). In birds there is evidence that breeding success may be affected by PCBs and feeding trials with Aroclors have indicated the possibility of interference with calcium metabolism leading to thin shelled eggs and poor hatchability (4, 8, 14, 15).

MONS 034506

Generally, however, direct evidence that the present levels

of PCBs in the environment are biologically harmful has not been established. There is reason for concern, though, that a continued accumulation of PCBs could, eventually generate harmful effects in many species, particularly those near the top of a food chain of aquatic origin.

There have been suggestions that some of the PCB found have originated from biological or photo-chemical synthesis of other organic substances present in the environment. It is possible, for example, that DDT can be converted to PCB by such a mechanism (22, 23), although it seems probable that only the 4-4' dichlorobenzophenone would be formed in this way - this is not present in significant quantities in the environment.

MONS 034507

The fear ~~of~~ that ~~the~~ unpredictable consequences ~~of allowing~~ might follow indefinite accumulation of PCBs in the environment ~~at an ever increasing~~ ~~rate~~ has caused many ecologists to ask how this may be prevented. Some action appears to be necessary, although ~~of~~ opinion ~~will~~ may be ~~sharply~~ divided on how drastic ~~this~~ action should be.

A simple solution, apparently, would be ~~to legislate against~~ a total withdrawal ~~the [illegible]~~ of production and use of PCB products. To be effective, such ~~legislation~~ a ~~this~~ policy would need to be applied universally and experience shows that ~~international~~ multilateral ~~agreements~~ negotiations for introducing such measures can be long and protracted. Further, the complete withdrawal of these products would have serious consequences for some industries and the effects on the [illegible] distribution of electrical power for

MONS 034508

example could produce serious ~~social~~ problem. It is important to balance the social benefits arising from the continued use of such products against the threats posed by the ~~environm~~ environmental pollution problem. We believe that a satisfactory solution can be achieved by a combination of actions designed to limit the extent to which accumulation can occur, whilst retaining the use of ~~such~~ these products in essential applications. The level reached ~~depends~~ depends on ~~occurs because of~~ a combination of factors including resistance to degradation, lipid solubility and rate of input into the ecosystem. The present situation has arisen because the rate of degradation of residues is lower than the corresponding rate of input; ~~which~~ the high rate of input was ~~largely~~ due ~~to~~ largely ~~[illegible]~~ to the numerous applications ~~from which supplies have been withdrawn~~ previously discussed & which are not ~~[illegible]~~ regarded as essential.

MONS 034509

Degradation may occur in many ways, but the principal

mechanisms affecting the ~~[illegible]~~ environmental situation are probably biological and photo-chemical. Evidence for photo-chemical breakdown of PCBs is scanty, but U.V. photolysis of some highly chlorinated PCBs has been reported. (16). Evidence for the biodegradation of PCBs through enzyme catalysed hydroxylation is, however, ~~[illegible]~~ substantial. Studies of biological degradation arising from exposure of single isomers and commercial mixtures to micro-organism cultures are discussed later & detailed ~~reported~~ in Appendix 2

These studies show that biodegradable PCB ~~prod~~ products are feasible; and that virtually complete degradation can ~~Aroclor 1242 can be degraded virtually completely~~ be achieved ~~reported~~ in selected products.
and: ~~Aroclor 1242 shows very substantial degradation~~. Several authors report the results of feeding PCB products to various animals, coupled with tissue analyses (5, 14, 17, 18)

MONS 034510

These show substantial metabolism of many of the PCB isomers,

especially those with 2 and 3 chlorine atoms per molecule. ~~[illegible]~~

The use of products which contain only these less intractable isomers, by increasing the rate of degradation, should reduce the level of residues arising from a given rate of input to the environment. If the rate of input can also be reduced by restricting the applications ~~of~~ to those such as in the Electrical Industry, where tight control can be exercised, there is every prospect that the trend to increasing residues can be reversed and that the level of residues in ~~wit~~ the environment ~~should~~ will fall. Monsanto has already restricted sales of ~~its~~ products to ~~of~~ those applications which are controllable and is (~~planning to supply~~ [illegible]) more degradable products where they are functionally acceptable. These actions seem appropriate to meet the situation and it is interesting to note that this

MONS 034511

is regarded as satisfactory and realistic by Government representatives in the United States (19) and United Kingdom (20). [For such a policy to be successful, co-operation between the industries involved is important to ensure that pollution arising from manufacturing processes and disposal of wastes is minimised. Some of the steps taken to ensure this are discussed in the next section.]

In Sweden, where legislation to control the use of PCBs has been introduced, it is important to realise that although indiscriminate use has been banned, a licensing system permits use in well controlled applications such as in electrical capacitors. Similar policies are expected to be adopted in Finland, The Netherlands & other countries.

MONS 034512

Part of the overall policy for controlling the ~~[illegible]~~ level of PCB in the environment is to establish a system which effectively limits the rate of entry. It has been emphasized that many of the applications for which PCB products were used formerly were, by their nature, allowing most of the product to find its way into the environment, through ~~[illegible]~~ effluent, inadequate incineration, and, generally, indiscriminate disposal methods. For many of these applications substitute products are now available. For example in plastics, rubber, adhesives, carbonless papers, hydraulic ~~[illegible]~~ & heat transfer ~~[illegible]~~ systems and miscellaneous smaller uses, these products, although desirable, are not essential since alternatives ~~[illegible]~~ can be used, sometimes ~~[illegible]~~ at some ~~[illegible]~~ penalty in cost/performance

MONS 034513

~~[illegible]~~. In some applications effective control over the

rate of leakage to the environment is feasible. Electrical transformers ~~are an example~~, for example, are constructed so that the dielectric/cooling fluid is contained in a steel tank and in operation there is no reason for leakage to occur. In fact, in order to prevent the ingress of water, which ~~would~~ could impair the ~~dielectric~~ electrical properties of the system, they are designed to make leakage very unlikely. They also have a very long life, 20 years or more, and at the end of this period it is possible to dispose of the fluid safely. ~~can be removed and safely disposed~~ In the event of the fluid becoming damaged through electrical faults in the system the fluid can be removed, reclaimed and re-used in a similar system.

MONS 034514

The ~~electric~~ application of the product in electrical transformers also happens to be a very essential one, as explained earlier

and we see no reason why this application should not continue satisfactorily using relatively intractable PCB fluids, which are necessary to provide the functional & fire resistance properties.

A similar argument can be applied to the application of fluids in large power-correction capacitors which are large sealed units which can be kept well controlled. For small capacitors, ~~which~~ some difficulties may be experienced in establishing absolute control since their numbers are relatively large and ~~their~~ average lives much shorter. For such applications we insist that ~~the use of~~ less intractable fluids ~~is~~ like Arochlor 1016 ~~is~~ must be used, so that a ~~small~~ ~~margin is allowed~~ some leakage can be accepted without the level of residues building up significantly. Coupled with general capacitor manufacturing, plant-keeping and cleanliness

MONS 034515

effective control over the disposal of waste capacitors we consider that the use of PCBs for this application can be allowed to continue.

An important feature of this type of controlled application is that a relatively small number of responsible manufacturers are involved, and this is in fact the case with these two electrical applications.

MONS 034516

The concept that an ecologically acceptable PCB product is feasible stemmed originally from the observation that, whereas the case histories of PCB products covered a very broad spectrum of homologs, the analytic evidence from the literature (5,6,9,10) & Monsanto work indicated that most wild-life PCB residues were concentrated in the penta / hexa chloro region. This certainly implied that many of the other dominant isomers in the parent materials were not accumulating.

As part of a broad Monsanto study to elucidate the reasons for this, we have investigated the effects of micro-organisms on PCBs under aerobic conditions.

MONS 034517

Initially our studies were undertaken using activated sludge, taken from one of our biological effluent treatment

plants, and pre-adapted to degrade (Culture C_1) biphenyl. Although some evidence of degradation of certain single isomers and mixtures was obtained, difficulties were experienced in achieving reproducible results. We were aware that workers at University College, Bangor, N. Wales, had isolated from soil a biphenyl-degrading pure culture, reported to be a nocardium of the order actinomycetes (Culture C_2). The Bangor workers had studied the breakdown mechanism for biphenyl, using this culture and had demonstrated the metabolic pathway (21). Details of this have been included in Appendix 2.

Using this culture for degrading single isomers of chloro-biphenyls, we were able to establish a pattern of degradation broadly agreeing with the metabolic mechanism proposed by the Bangor workers for biphenyl.

Subsequently the Bangor workers isolated another biphenyl degrading organism in pure culture from a canal mud. This was reported as a strain of the (Culture C_3)

MONS 034518

pseudonomas family. The metabolic route for ~~this~~ degradation by ~~this~~ organism was ~~found~~ shown to be different from that of the ~~to~~ earlier culture. Subsequent studies of the degradation of chloro-biphenyl isomers ~~were~~ ~~showed~~ showed broadly ~~in~~ agreement with this proposed metabolic pathway and it was ~~[illegible]~~ demonstrated ~~[illegible]~~ that ~~[illegible]~~ most ~~[illegible]~~ ~~large proportion~~ of the lower chlorine isomers of PCBS (< hexta) ~~[illegible]~~ were susceptible ~~[illegible]~~ to degradation by ~~either~~ one or other of these micro-organism culture.

~~[illegible]~~ When commercial mixtures of isomers were subjected to attack by these pure cultures ~~it was established that~~ the analytical results indicated ~~that a~~ a different pattern of degradation ~~was emerging~~ than ~~that~~ ~~[illegible]~~ might have been predicted from the studies of single isomers. For example, the isomer 44' dichloro-biphenyl was not degraded by culture C_2 although it was degraded by culture C_3 in agreement with the

MONS 034519

proposed pathways. In admixture with other isomers, as in Aroclor 1242, however, the 4-4' dichlorobiphenyl was degraded by both cultures independently. This implied that in the presence of suitable levels of ~~[illegible]~~ ~~[illegible]~~ degradable isomers the organism could adapt to utilize some at least of the more intractable isomers as carbon sources. Certain isomer mixtures, of practical significance, such as Aroclor 1016, were prime targets of this study and the results indicated virtually complete degradation of this particular product with these two organisms. For Aroclor 1242, very substantial degradation of the significant isomers has been demonstrated and the evidence ~~[illegible]~~ suggests that ~~[illegible]~~ some of the more highly chlorinated penta + hexa chloro isomers in 1242 can also be degraded ~~in Aroclor 1242~~ through adaptation. More evidence for this is being sought in current experiments

MONS 034520

in which the more highly chlorinated components are ~~may~~ accentuated to establish better data.

In the work on single isomers it was established that the rates of degradation could be accelerated by including biphenyl itself with the isomer under test. The reasons for this have not been established, but one suggestion is that a mechanism of co-oxidation ~~may be~~ responsible (24) Most of the work done so far has therefore included biphenyl in the study and this does raise the question whether the conditions are too artificial for extrapolation to the natural environment. For single isomers this probably would be a valid criticism, although nature is well endowed with organic chemical structures not unlike that of biphenyl (23), which could induce similar mechanisms for degradation.

MONS 034521

For mixtures like Aroclor 1016, however, the adaptive mechanism which has been observed for both cultures C_2 and C_3 would probably ensure that ~~the~~ ~~[illegible]~~ adequate nutrient could be derived from the PCB products. Experimentation to confirm this point is currently in progress.

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