NATIONAL CONFERENCE ON POLYCHLORINATED BIPHENYLS

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CHLORINATED BIPHENYL DIELECTRICS - THEIR UTILITY AND POTENTIAL SUBSTITUTES

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Monsanto

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THEIR UTILITY AND POTENTIAL SUBSTITUTES

I. INTRODUCTION

In 1970, Monsanto voluntarily began its program of terminating sales of chlorinated biphenyls to open applications -- those which could result in losses to the environment. By late 1972, this program was fully implemented and Monsanto was selling these products only to manufacturers of sealed electrical equipment such as transformers and capacitors.

Major applications affected by our withdrawal were carbonless paper, fire resistant hydraulic fluids, heat transfer fluids, and plasticizers.

Sales for other miscellaneous minor applications were discontinued during the same period.

This action resulted in a reduction, in the use of chlorinated biphenyl, in areas where entry to the environment was less controllable, of some 45 million lbs. per year.

We decided at that time to continue supply to closed electrical applications because we believed that:

a) Entry of chlorinated biphenyl to the environment was limited and controllable;
b) A more biodegradable, lower chlorinated homolog had been developed which the capacitor industry could use;
c) Withdrawal would have brought to a halt production of equipment essential to the safe and efficient distribution and use of electrical energy because there was no known satisfactory replacement for chlorinated biphenyl dielectrics.

Today we continue to sell chlorinated biphenyl observing the following policy:

1. We supply only to manufacturers of sealed electrical equipment such as capacitors and transformers.

2. We supply lower chlorinated homologs, Aroclor 1016, to the capacitor industry.

3. We offer an incineration service for liquid PCB wastes.

4. We continue to work with ANSI Committee C107 and other bodies to establish appropriate handling and control procedures for equipment containing chlorinated biphenyl.

5. We allocated increased research resources in 1969 to seek and develop effective replacements. This program continues.

6. In seeking possible replacements, we will ensure that differences between Aroclor and candidate fluids from our program are widely reviewed in order that the potential impact of any compromises is fully evaluated.

The implementation of these and other programs both by ourselves and electrical equipment manufacturers was prompted by the utility of this dielectric family and the difficulties inherent in developing substitutes to effectively and fully replace it.

II. UTILITY OF CHLORINATED BIPHENYL IN CAPACITORS

1. Fire Resistance

The adoption of chlorinated biphenyls in 1929 as capacitor dielectrics stemmed from their superior dielectric properties compared to mineral oil. However, recognition of the fire resistant character of the fluids influenced system and equipment design and standards over the subsequent 45 years. It is probably true that today many people find it difficult to assess potential capacitor fire hazard purely because Aroclor has been used for 45 years.

Particular examples where fire resistance in a capacitor is of benefit include:

a) fluorescent lighting ballasts;
b) air-conditioner motor capacitors;
c) television capacitors;
d) large power capacitors where high fault currents can cause rupture and ejection of fluid from pole mounted units close to people and buildings;
e) industrial furnace capacitors.

2. Stability

The persistence of chlorinated biphenyl in the environment is associated with the high degree of thermal, chemical, oxidative, and hydrolytic stability which permits capacitor manufacturers to supply to the exacting reliability requirements which exist today.

3. Dielectric Constant/Dielectric Strengths

These properties are important in determining the size of a capacitor. In a mixed dielectric system, e.g., Paper/Aroclor or Paper/Polypropylene/Aroclor, the dielectric properties of Aroclor permit optimization of stress distribution between the components making up the dielectric layer.

This has enabled capacitor manufacturers to reduce paper and film volumes for a given capacitance. I shall discuss under the heading of "potential substitutes", the impact that this could have on:

a) paper/film availability and usage;
b) design of equipment containing capacitors.

III. UTILITY IN TRANSFORMERS

Chlorinated biphenyl transformers represent less than 15% of transformers in service. Their use is associated with the need to limit fire hazard in installations.

1. Railroad Transformers

   Multiple unit cars as used in rapid transit systems have transformers mounted beneath each car. By nature of the type of service, involving high passenger density, safety is essential.

2. Urban Power Substations (e.g., Underground Vaults)

   These designs need to take account of city center space limitations and, also, the safety of the public and maintenance crews. Fire resistant liquid transformers are helpful to all these objectives.

3. Industrial Load Centers

   Efficient system designs for large, power intensive, manufacturing plants (e.g., automotive assembly, steel production) often incorporate transformers close to the electrical load centers. The use of Aroclor transformers at these centers, in the heart of the plants, or overhead in roof structures, protects both employees and plant.

4. Transformer/Rectifiers

   Programs to reduce the emission of particulate matter from stack gases, for example in fossil fuel generating plants, include installation of electrostatic precipitators. The transformer/rectifiers energizing the precipitator field must be located close to the electrodes. In many designs, the multiple transformers are located in a penthouse above the precipitator.

A fire in the penthouse could lead to close down of the precipitator and thus, the generating plant, if pollution control is to be maintained. A fire resistant fluid is of obvious benefit in this application.

In each of these applications, Aroclor protects the system from:

a) Initiation of a transformer fluid fire, by an electrical fault beneath the liquid level;
b) Electrical breakdown of the fluid causing emission of flammable gases;
c) Propagation of fire if the transformer liquid content is involved in an external fire.

IV. POTENTIAL SUBSTITUTES IN CAPACITORS

1. Research Objectives

In seeking potential substitutes, our research objectives, of necessity, related to those properties which gave Aroclor its value. Equally, we recognized the need that an Aroclor replacement should eliminate environmental concerns.

Desirably, a replacement should operate across the full range of current Aroclor capacitor applications while requiring minimum changes in design of capacitors and equipment utilizing capacitors.

The use of chlorinatad biphenyl is worldwide. Monsanto manufactures chlorinated biphenyls both in America and Great Britain. We supply to the capacitor industry of many countries. We sought potential replacement products that could be made available with the consistent quality control applied to Aroclor on a worldwide basis.

We referred earlier to availability of co-dielectric components in capacitors. A solution which required substantial changes in availability of polypropylene film (quantity or quality) or a major increase in short-term availability of capacitor paper, we considered unsatisfactory. If in 1974, such increased quantities had been required, they would not have been available. Capacitor production would have fallen short of demand, further jeopardizing efficient power supply.

Our research objectives can be broadly summarized in the following Table 1.

TABLE 1

POTENTIAL SUBSTITUTES

CAPACITORS

RESEARCH OBJECTIVES

1. MATCH OR EXCEED AROCLOR 1016 CAPABILITY.

   A) DIELECTRIC CONSTANT - USAGE OF OTHER COMPONENTS
      DIELECTRIC STRENGTH - CONVERTABILITY

   B) STABILITY - RELIABILITY
      POWER FACTOR

   C) FIRE RESISTANCE - SAFETY

2. GOOD ENVIRONMENTAL COMPATIBILITY.

3. A) SPAN EXISTING APPLICATIONS - COMPLETE SOLUTION.

   B) INTERNATIONALLY AVAILABLE - NOT SOLELY U.S.A. SITUATION.

2. Non-PCB Candidates

The capacitor industry is currently examining two Monsanto non-PCB (candidate) dielectrics. These contain no chlorinated biphenyl and are not chlorinated products.

The two fluids are designated:

MCS 1238
MCS 1588.

Both of these products are blends of synthetic hydrocarbons with a high dielectric constant additive to give a dielectric constant equivalent to Aroclor 1016.

Table 2, on the following page, lists some of the properties of MCS 1238 and MCS 1588 compared to Aroclor 1016.

Corona inception and extinction voltages are more a function of capacitor design than of the liquid, itself. Preliminary industry results demonstrate results in capacitors equivalent to Aroclor 1016. Further full scale work is required before final conclusions can be drawn.

Dielectric constants relate closely to those of Acorlor 1016 over the temperature range of capacitor operation.

Hydrolysis stability is mentioned because of work carried out on earlier candidates based on esters which gave concern because of hydrolysis instability.

Hydrolysis was assessed by measuring the neutralization number of a sample with 0.5% water added, which had been heated for 168 hours at 210°F. in a stainless steel bomb along with an aluminum and a mild steel coupon.

TABLE 2

PROPERTY	AROCLOR 1016	MCS 1238	MCS 1588
DK 25°C	5.9	6.0	6.1
100°C	4.85	5.1	5.1
CORONA IV/EV*	-	-	-
HYDROLYSIS STABILITY* (NEUTRALIZATION NUMBER)	0.00	0.00	0.00
DISSIPATION FACTOR FLUID TAN δ 60 HZ. 100°C	0.0025	0.05	0.05
DISSIPATION FACTOR MODEL PAPER CAPACITOR AT 90°C	0.0032	0.0039	0.0035

* SEE TEXT

3. Fire Resistance

Neither MCS 1238 or 1588 is fire resistant. This deficiency versus Aroclor 1016 must be closely considered.

4. Environmental Considerations

The environmental/health evaluation of capacitor replacement fluids must be related to:

a) Degradation - If some quantity enters the environment, at what rate and through which mechanism will it degrade?

b) Tissue Accumulation

c) Toxicity - Occupational Safety
Environmental Compatability

5. Degradation

Biodegradation has been studied using a semi-continuous activated sludge technique. Forty-eight hour exposure of Aroclor 1254, Aroclor 1016, and MCS 1238 dielectric fluids to activated sludge using a semi-continuous procedure resulted in the following percent biodegradation rates and 95% confidence limits:

TABLE 3

MATERIAL	48 HOUR % BIODEGRADATION	FEED CONCENTRATION, PPM
Aroclor 1254	15 $\pm$ 38	1
Aroclor 1016	33 $\pm$ 14	1
MCS 1238	70 $\pm$ 10	3

For the polychlorinated biphenyl (PCB) materials, the level of chlorination appears to be the most significant factor in their relative biodegradability. The rate of biodegradation decreases as the number of chlorine atoms per biphenyl molecule increases. Chromatograms representing samples after exposure to activated sludge show significant alteration in the Aroclor 1016 isomer distribution, but little for Aroclor 1254. Degradation of the non-halogenated fluid, MCS 1238, proceeds much more rapidly than for the halogenated PCB fluids with no evidence of resistant components.

Methodology for this technique is described in Appendix B.

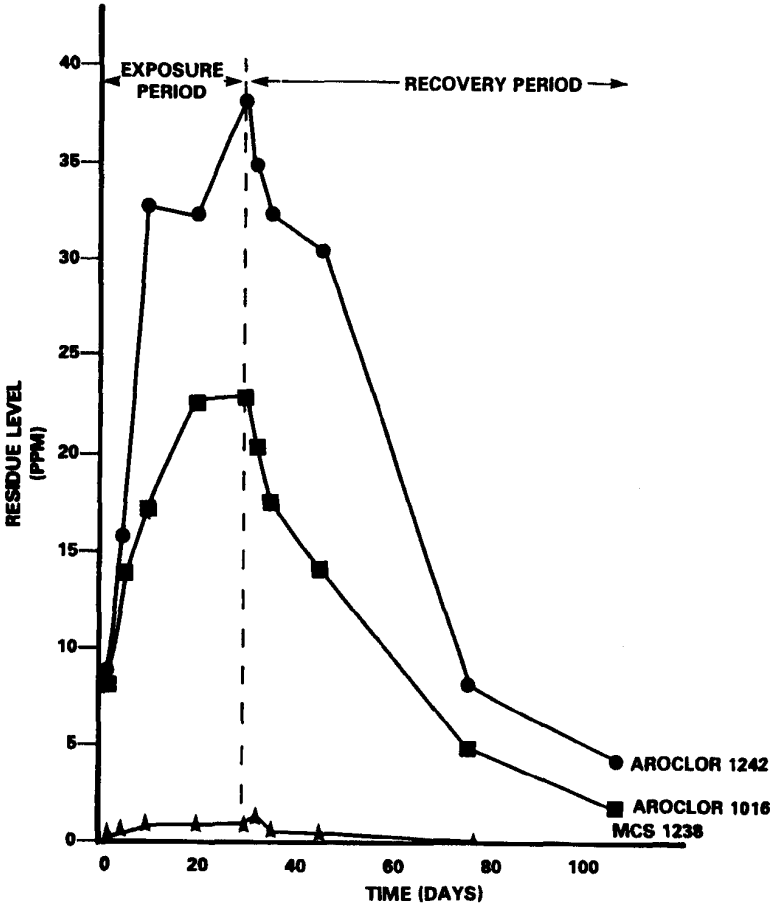
6. Tissue Accumulation

Table 4 (Graph) depicts the results of Rat Tissue Residue Level Studies vs. Time and compares Aroclor 1242, Aroclor 1016, and MCS 1238 (see following page).

FAT TISSUE RESIDUE LEVEL VS. TIME

Table 4

25 PPM FEED LEVEL FOR RATS



A fraction of the ingested Aroclor 1242 and Aroclor 1016 was stored in rats' lipid reservoirs. However, most of this residue was depleted after the rats had been on the basal laboratory diet for several weeks. During the course of the feeding study, residues of Aroclor 1016 accumulated more slowly and to a significantly lesser extent than those of Aroclor 1242. During the recovery period, these PCB residues decreased to lower values for Aroclor 1016.

The residue concentrations of MCS 1238 quickly reached a stable level well below the concentration in the feed. The residues did not increase with continued exposure. After feeding of the treated chow was ceased, the MCS 1238 residues were rapidly metabolized and/or excreted.

The tissue residue accumulation and depuration profile of MCS 1238 shown in Table 4 is markedly different than those of the Aroclor fluids, especially that of Aroclor 1242.

Methodology is given in Appendix A.

7. Toxicity

Before samples of MCS 1238 could be evaluated in the capacitor industry and within Monsanto, acute toxicity data was gathered:

a) Rat - Acute single oral dose LD_{50}: 3800 mg/kg.

b) Rabbit - Dermal LD_{50}: 5000-8000 mg/kg.

c) Rabbit - Potential eye irritation - A slight degree of irritation resulted when 0.1 ml. of undiluted MCS 1238 was placed in the conjuctival sac of the rabbit eye. The average maximum score recorded at one and again at twenty-four hours after treatment was 12.0 on a scale of 110.0. All eyes had regained normal appearance seventy-two hours after dosing.

d) Rabbit - Potential skin irritation - When undiluted, MCS 1238 was held in continuous twenty-four hour contact with intact rabbit skin, a moderate degree of irritation resulted. The maximum average score was 3.6 on a scale of 8.0.

Further programs are in process, or scheduled, to study the following:

a) Vapor Inhalation
b) Ultimate Degradation
c) 90-Day Pilot Feeding Study
d) Long-Term (2-Year) Feeding Studies
e) Fish Tissue Residues.

8. Conclusions

To summarize Monsanto research activities:

- A large number of single compounds and mixtures have been evaluated in terms of physical property data, environmental compatability, fire resistance, and model capacitor life testing.

- These have led us to conclude that:
  a) Aroclor 1016 may well be sufficiently degradable to remain in controlled use.
  b) MCS 1238 is a potentially acceptable replacement with the qualification that it is not fire resistant.

- Further programs must be completed with MCS 1238 in order to:
  a) Deepen our knowledge of its environmental compatibility.
  b) Permit complete evaluation by the capacitor industry across their range of applications.
  c) Enable utilities, capacitor users, and agencies to evaluate the significance of decreased fire resistance.

As a closing thought to this section, I would like to comment that since 1929 when Aroclor was first developed as a capacitor dielectric, normal commercial pressures have spurred efforts to find supperior replacements. The awareness of environmental accumulation of chlorinated biphenyls from other applications added further impetus for more intensive research in the chemical and electrical industries. Aroclor has defied 45 years of search for a superior replacement.

V. SUBSTITUTE TRANSFORMER FLUIDS

Neither Monsanto nor any other company, to our knowledge, has developed a transformer dielectric with equivalent fire resistance to that of Aroclor. The difficulties that we face in common with other workers in this field are two-fold:

1. Aroclor has become the reference standard for fire resistance in transformers because it works and has worked for 45 years. To establish standards to guide research effort, there is a need for objective evaluation of the fire hazard associated with the major sectors of transformer use.

2. The chemistry which imparts fire resistance tends also to produce stable molecules. Monsanto seeks replacement products that will provide protection against:

   a) Fire from transformer faults under the liquid surface;
   b) Fire from secondary ignition of gaseous arc decomposition products;
   c) Fire propagation if the transformer is involved in an externally initiated conflagration.

   We strive to accomplish this and produce an environmentally compatible product.

We have four candidates which are currently being evaluated by the transformer industry. These materials are in a sufficiently early stage of development that it would be premature to give detailed property data at this meeting.

APPENDIX A

Methodology For Feeding Study

Feeding and Sampling

Rat chow containing 25 ppm Aroclor 1242, Aroclor 1016, or MCS 1238 was prepared by mixing the products into Ralston Purina rat chow. The treated chow was fed ad libitum to adult albino rats for an exposure period of 30 days. Following the 30-day exposure period, all remaining rats were placed on the basal laboratory diet. At predetermined intervals during the exposure and recovery periods, five rats from each exposed set and a control set were sacrificed. Fat tissue was excised for analysis and composited for each group. Samples were quick-frozen and stored in glass containers with aluminum foil-lined caps to minimize risk of contamination.

Isolation

The dielectric fluid residues were isolated from the fat by solvent extraction. A weighed amount of fat was placed in an Erlenmeyer flask and homogenized three times with 25 ml of pesticide grade hexanes and anhydrous sodium sulfate using an ultrasonic homogenizer. The combined supernatants and washings were filtered through anhydrous sodium sulfate and diluted to 100 ml with hexane.

Lipid Weight Determination

A 5 ml aliquot of the extract solution was pipetted into a tared 50 ml beaker. After evaporation of the solvent under a stream of nitrogen, the beaker and residue were reweighed to obtain the lipid weight of the aliquot. All residue levels are reported as ppm on a lipid weight basis.

PCB Clean-Up And Measurement

Sample clean-up for the extracts containing Aroclor 1242 and Aroclor 1016 residues was accomplished by pipetting an aliquot of the extract onto a 5% deactivated alumina column and eluting with 125 ml of hexanes. The column eluate was collected in a Kuderna-Danish evaporative concentrator, a

3-ball Snyder condenser was attached, and the solution was concentrated to 5 ml. The residue levels in the extracts were measured by gas chromatography using an electron capture detector.

Non-PCB Clean-Up And Measurement

Sample clean-up for the extracts containing MCS 1238 residues required separation of the residues from the lipid by preparative scale gel permeation chromatography. Following the GPC separation, the extracts were further cleaned up on an alumina column, collected, and concentrated as above. The residue levels in these extracts were measured by gas chromatography using a flame ionization detector.

Calculations

Calibration curves for each product were prepared by plotting detector response (total peak area) versus nanograms of standard injected. Residue levels in the samples were determined by summation of the total area of peaks corresponding to peaks in the standard and use of the appropriate calibration curve. The calculations were done as follows:

$$\text{Residue(ppm)} = \frac{(N)(V_F)}{(V_I)(W)},$$

where N = amount of product from calibration curve (ng)
V_F = volume of final concentrate (ml)
V_I = volume injected (ul)
W = lipid weight of original sample (g).

APPENDIX B

Biodegradation Method

Since activated sludge is one of the most important agents for sewage treatment, test procedures evaluating its action are of great importance.

The semi-continuous activated sludge (SCAS) method has been extensively utilized in the development of biodegradable detergents. In our SCAS procedure, patterned after the Soap and Detergents Associations standard method (1,2,) mixed liquor (activated sludge and supernatant) from a local domestic sewage treatment plant is charged to magnetically-stirred glass vessels of 1.5 liter capacity. Means for aeration and sampling are provided. The SCAS unit is generally operated using a retention or aeration time cycle of 24 to 72 hours. At the beginning of each cycle, synthetic sewage (300 mg glucose, 200 mg nutrient broth, and 130 mg K_2HPO_4) and the appropriate test material in ethanol solution are added to the mixed liquor (2500 mg/liter suspended solids concentration). Aeration is maintained until the end of the cycle, at which time the sludge is settled and one liter of supernatant drained. The cycle is then re-initiated by the addition of tap water, synthetic sewage, and test material. Operation of the units can be continued for an indefinite period of time until consistent degradation rates are observed.

Sample Analysis

Biodegradation of the test material was determined during one cycle each week by analyzing 20 to 50 ml mixed liquor samples withdrawn after feeding and at the end of the aeration cycle. The mixed liquor analytical procedure involved extraction with three successive 25 ml portions of hexane, and drying combined extracts with anhydrous sodium sulfate. Extracts were concentrated in a Kuderna-Danish evaporative concentrator equipped with a 3-ball

Snyder condenser, and measured by electron, capture, or flame ionization, gas chromatography. Calibration curves for each product were prepared by plotting detector response (total peak area) versus nanograms of standard injected.

The percent biodegradation was calculated from the following equation: % Biodegradation = $(C_o - C_n)/C_o \times 100$ where C_o and C_n use the initial and final concentration of test material, respectively, on the mixed liquor.

References

1. J. Am. Oil Chem. Soc. 42, 986 (1965).

2. J. Am. Oil Chem. Soc. 46, 432 (1969).