Conference Paper

Industrial Organic Chemicals As Alternative Dielectric Fluids

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Substituted aromatic compounds prepared from benzene and diphenyl ether have a variety of properties that make them attractive as dielectric fluids. Like commercial fluids, they can be purified by distillation and clay treatment. They exhibit good stability, the proper combination of physical properties and excellent electrical properties, particularly low electrical losses. The dielectric strengths of the compounds is usually >30 KV. Even though some of these materials have relatively low dielectric constants, they deserve serious consideration as alternatives to polychlorinated biphenyl.

Product Stewardship[31]

Persistence, Toxicity and Selection of Candidates

"Product Stewardship" as used in Dow is a program to make sure that our products don't become environmental problems after they are in the hands of our customers. Our goal is to maintain our leadership in environmental affairs by protecting man and the environment from hazards associated with chemicals manufactured by Dow.

In research, product stewardship requires examination of four parameters. Stability of a chemical as measured by microbial, photochemical, or chemical degradation. Movement of a product in the environment is measured by examining its relative affinity for air, water, and soil. Bioconcentration of organic compounds as measured by comparing a product's relative solubility in fats or oils with its solubility in water. Toxicity is measured by representative species that may come in contact with the chemical.

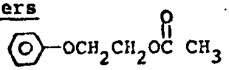
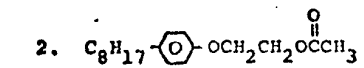
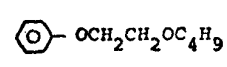
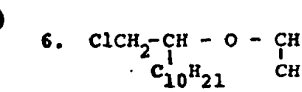
As described in the Introduction, the evaluation of environmental characteristics and toxicity data at an early stage is a critical feature of our dielectric fluid research program. The synthetic studies and subsequent screening of electrical properties, described above, demonstrate that several compounds are available that show promise as new dielectric liquids. At this point in our research, we were mainly concerned with microbial degradation and general toxicity of our potential new fluids. The selection of inexpensive, rapid, and meaningful test methods is the key to using this kind of data in a screening program. This section of the paper will describe our approach to the use of this information as a selection guide and will summarize pertinent test results.

Certain value judgments and general statements of what is desirable must be applied to evaluating preliminary biodegradation and toxicity data. Our goal is a biodegradable nontoxic fluid. Since compounds that can be considered as dielectric liquids need high boiling points, are chemically unreactive, and are largely insoluble in water, certain conclusions can be reached concerning their environmental characteristics. Chemically unreactive materials usually have low oral acute toxicity. Compounds with low water solubility are only available to microorganisms in water at very low concentrations. Also, microbial degradation for these types of compounds will be relatively slow. However, as long as a degradation route is available, a long-term build up in the environment would not be expected. In addition to the biological degradation already mentioned, chemical degradation, such as oxidation or hydrolysis can also play a role in removing chemicals from the environment.

The effect of chemicals on the environment and their ultimate fate is a complex question. Although many tests have been devised, the lack of standardized methods tends to magnify the complexity of the question.[32]

To study the environmental impact of potential new dielectric liquids, three bio-oxidation methods were employed. The first of these is the Biochemical Oxygen Demand (BOD) test.[33] In this procedure, several dilutions of the test compound in water are mixed with a dilute acclimated microorganism seed in nutrient solution which is saturated with oxygen, sealed and incubated at 20°C. The depletion of oxygen is measured at various time increments, e.g., 5, 10, and 20 days. Typical results from this test are given in Table X.

Biodegradability by the BOD Test*

Compound	Oxygen Demand 5 day	10 day	20 day
Esters			
1. 	B	A	A
2. 	water solubility ~1.4 ppm	Compound not detected after 5 days	
3. Di-n-butylphthalate	A	A	A
4. Di-octylphthalate	C	C	C
Ethers			
5. 	B	B	A
6. 	B	B	B
7. Methoxymethyldiphenyl ether	B	B	B
Substituted Aromatics			
8. 1,2,4-trichlorobenzene	C	A	A
9. 4-bromodiphenyl ether	B	B	A
10. Monochlorodiphenyl ether	B	A	A

*TOD = Theoretical Oxygen Demand or equivalents of oxygen required for complete conversion of compound to CO_2 and H_2O.

Class A = 40-70% of TOD - most or all of compound degraded
Class B = >0-40% of TOD - compound partly or slowly oxidized
Class C = No oxygen demand detected

MONS 040614

To obtain meaningful results in the BOD test, a compound must be soluble in water to at least 2 mg/l (2 ppm). In the examples given, the oxygen demand is reported relative to percent of the theoretical oxygen demand (TOD). In compounds that bio-oxidize, the oxygen demand will usually reach about 60 - 70% of the TOD since about 30 - 40% of the compound has nutritional value for the microorganisms and, therefore, is not converted to CO_2 and water. This is considered to be complete biodegradation.

In the compounds presented, Esters 1 and 3 bio-oxidize quite readily in this test. Ester 2 has low water solubility and no meaningful oxygen demand can be detected, however, the parent compound cannot be detected after five days indicating bio-oxidation may have taken place. The two phthalate esters (Compound 3 and 4) demonstrate a marked effect of the alcohol chain length even though these compounds have similar water solubilities. There are several possible explanations for the lack of oxygen demand observed for di-octylphthalate. The first is that this compound does not bio-oxidize in this system or it is bound and is not available for degradation. Secondly, the test may not have been run long enough to allow the microorganisms to become acclimated to this compound. Thirdly, this compound may be toxic to the microorganisms or may inhibit their growth. Finally, degradation routes that do not require oxygen may be occurring.

The ethers (Compound 5, 6, and 7) bio-oxidize in this test but the rates and extent of oxygen demand are significantly different. Molecular weight and water solubility may be

factors in this difference between Compound 5 and 6, in that, the lower molecular weight Compound 5 (M.W. = 194) is more readily oxidized than the, presumably less water soluble, higher molecular weight Compound 6 (M.W. = 297).

Trichlorobenzene (Compound 8) shows evidence for an acclimation period. No oxygen uptake is detected after five days of exposure while a major percentage of the TOD is consumed between five and ten days. The two monohalogenated diphenyl ether compounds both bio-oxidize in this test. The monochloro compound appears to oxidize faster than the brominated analog but the extent of oxygen demand for both compounds is similar at the end of a twenty day test.

The second method used is the Oxygen Probe Test for Biodegradability.[34] In this test, a sample (500 ml) of settled activated sludge (allow to settle for one hour prior to taking sample) is diluted with water to make a total volume of 1000 ml. An oxygen probe connected to a recorder is inserted in the sludge and the system is aerated and stirred until a stable dissolved oxygen level of 3 - 4 ppm is recorded. The material to be tested is added at an initial loading of 1 mg/l up to 100 mg/l and the change in dissolved oxygen level is noted. A sample of phenol at a loading of 1 mg/l is used as a reference material. The initial slope in the oxygen curve is recorded. Results are compared to phenol and reported as follows:

Fast (F) - slope greater than or equal to phenol
Intermediate (I) = slope >1/3 of phenol
Slow (S) = <1/3 of phenol
Not detected (N.D.)

Selected results from this procedure are reviewed in Table XI.

TABLE XI

Biodegradability by the Oxygen Probe Test

	Compound	Result
1.	Phenol	Fast
2.	Diphenyl ether	Intermediate
3.	Biphenyl	Intermediate
4.	Sec-Butyldiphenyl ether	Intermediate
5.	1,2,4-Trichlorobenzene	Slow
6.	4-Bromodiphenyl ether	Slow
7.	Monochlorobiphenyl	Slow
8.	$ClCH_2\underset{C_{10}H_{21}}{CH} - O - \underset{CH_3}{CH} - CH_2Cl$	Slow
9.	Aroclor 1242 Fluid	Not detected
10.	Di-n-butylphthalate	Not detected
11.	Decyldiphenyl ether	Not detected

? degrades w. BOD Test

This test is less sensitive to compound water solubility than the BOD test but low water solubility can still contribute to negative test results. Diphenyl ether, biphenyl, and sec-butyldiphenyl exhibit oxidation rates in the intermediate range compare to phenol. Compounds 5 - 8 are oxidized slow compared to phenol. Compounds 5, 6, and 8 also show bio-oxidation in the BOD test (Table X). No oxygen uptake is detected for Compounds 9, 10 and 11. The reasons for no oxygen uptake in this test are similar to those described for zero oxygen demand in the BOD test. A combination of low water solubility and slow bio-oxidation can lead to oxygen uptake below the detection limit. This is probably the reason for the sharp contrast between sec-butyldiphenyl ether

(Compound 4) and decyldiphenyl ether (Compound 11). Increasing the alkyl chain length from four carbons to ten reduced the water solubility and oxidation rate sufficiently to cause negative results for Compound 11. Other causes for no oxygen uptake include the microorganisms not being acclimated to the compound and inhibition of the microorganisms by the compound. Positive results in the above tests are a good indication that a compound will biodegrade, however, negative results do not necessarily preclude biodegradation of a compound.

To study compounds with bio-oxidation rates below the detection levels of the BOD and Oxygen Probe Tests, it is necessary to prepare radioactively labeled compounds (usually ^{14}C is used) to attain sufficient analytical sensitivity. These labeled compounds are tested in the so-called Activated Sludge Batch Die-Away Biodegradation Test.(32) Degradation of the compound is usually followed by trapping $^{14}CO_2$ in the system exit gases and obtaining a material balance with the ^{14}C compound remaining in the sludge system. This approach dramatically increases the complexity and the cost of the experimental procedure. In our studies, substituted aromatic compounds, such as dibromoethylbenzene and chloroalkyldiphenyl ether compounds require ^{14}C labels to evaluate environmental persistence. Studies are in progress to establish that compounds of the above types are biodegradable even though their water solubility is very low. It should be noted that trichlorobiphenyl, the main component in Aroclor 1242 and Aroclor 1016 brands, shows no evidence for biodegradation by any of the above test methods using either labeled or unlabeled compounds.

Our initial mammalian toxicity studies considered the effects of candidate fluids on experimental animals in

four basic areas. These are ingestion, eye contact, skin contact, and vapor inhalation. Specifically, ingestion refers to acute oral lethality obtained by administration of single relatively large doses of chemical to test animals. Eye irritation is evaluated by placing the compound in an animal's eye and observing both the animal and its eye for toxic effects and irritation. Skin contact is considered both in relation to skin damage, such as a chemical burn, and absorption of chemical through the skin leading to toxic effects. In this test, it can be important to observe contact with both covered areas, and skin that is exposed to the air. The toxicity of fluid vapors is usually evaluated by subjecting test animals to the vapors generated by passing air over the surface of fluid heated to 100°C. In addition to inhalation toxicity, this test may also give useful information on eye irritation caused by fluid vapors. Information from the above tests provides important guidance concerning the toxicity characteristics anticipated for a new compound and also contributes to the safe handling of experimental materials. The fluids selected for toxicity evaluation in this study exhibit low oral acute toxicity and low vapor toxicity. Minor eye irritation is observed in some cases. Skin contact is not a serious problem for minor exposures, however, prolonged or repeated contact, particularly on covered skin can lead to a reddening of the skin, swelling, and a moderate chemical burn. We have not observed toxic effects resulting from absorption of fluid through the skin. From the standpoint of our fluid development program, fluids which give satisfactory results in the above toxicity screening can be considered as candidates meriting additional study.

On a limited basis, we have also explored the acute fish toxicity of our compounds using polychlorinated biphenyls as a

reference point. Our studies indicate compounds such as tetrachlorobiphenyl are lethal to fish (fathead minnows) at levels well below 1 ppm (50% kill at 0.5 ppm). In contrast, monochlorodiphenyl ether is not lethal to fish at 0.5 ppm in this test. Also, the alkylated diphenyl ether compounds tested show no acute fish lethality because the compounds have very low water solubility (probably <0.5 ppm) and the fish are not in intimate contact with the chemical.

The test methods described above represent the initial screening phase of our product stewardship studies. Although these tests provide information to assess the environmental impact of our chemicals, more extensive tests are usually necessary. The use of ^{14}C labeled compounds early in this program is very expensive, but can pay dividends in reliability and time savings. Most of the studies that follow the screening phase can best be done using labeled compounds and the ease and quality of the associated analytical work is enhanced by using the labels. Situations have developed where laborious studies using unlabeled compounds have had to be redone using labeled materials as a result of unresolved analytical questions in the initial work. Laboratory evaluation of the environmental impact of chemicals can be part of new product research. Its benefits are measured in terms of minimizing the effect of chemicals on the environment and assuring their safe handling and use.

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