Conference Paper

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Aliphatic Chloro, Siphatic Oxo Cl

Industrial Organic Chemicals As Alternative Dielectric Fluids

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ABSTRACT

A modern dielectric fluid must possess a unique combination of electrical characteristics and physical properties while minimizing toxicity parameters and adverse environmental effects. Existing commercial liquids fulfill these requirements with varying degrees of success. A notable deficiency is the environmental persistence and toxicity characteristics of products derived from chlorinated biphenyl. In addition to electrical and physical properties, our studies have considered the environmental behavior of various types of common organic compounds. This evaluation has shown that certain types of relatively simple organic compounds are biodegradable and possess electrical and physical characteristics essential to their functioning as dielectric fluids in transformers and capacitors.

INDUSTRIAL ORGANIC CHEMICALS AS ALTERNATIVE DIELECTRIC FLUIDS

Introduction

A modern dielectric fluid must possess a unique and complex combination of electrical and physical properties. In addition to the performance requirements imposed on existing products and new dielectric liquids, today's situation makes it imperative that consideration be given to a variety of other parameters, such as environmental persistence and toxicity. Information of this kind has become increasingly important to electrical equipment manufacturers in determining methods for safe handling, use, and disposal of dielectric fluids and equipment.

The study described in this paper was conceived to explore types of organic chemicals that could function as dielectric liquids giving consideration to both the performance requirements and the ecological characteristics that are an integral part of the dielectric fluid market of the 1970's. The phrase "industrial organic chemical" is used in this work to indicate organic compounds that are accessible by means of common chemical processing in contrast to those based on exotic raw materials or requiring complex multi-step processing. A treatment of fluid characteristics is presented with particular emphasis on capacitor impregnants and transformer applications.

Our dielectric fluid research program can be represented in four phases as shown in Figure 1. Specifically, our efforts in Phases I and II leading to the selection of new dielectric fluid candidates are the subject of this paper. In Phase I, our assessment of dielectric fluid requirements is given and

a brief survey of pertinent literature is included. The main thrust of our synthetic studies was to explore the relationship between chemical structure and dielectric constant in several series of related compounds and to attain a match of physical and electrical properties in promising compounds. A critical feature of our program is the incorporation of toxicity and environmental evaluation at an early stage in the research. It is essential that any candidate selected for development work in Phase III have acceptable toxicity and environmental characteristics, in addition to meeting dielectric fluid performance requirements. Conclusions concerning the most promising compounds identified and the relative advantages of each type are discussed.

Figure 1

NEW DIELECTRIC FLUID RESEARCH PROGRAM

Conception: six - eight
possible types of fluids

Exploratory Identify Fluid Requirements Literature Survey Accessibility - Raw Materials and Chemistry Preliminary Screening of Fluid Types	Phase I Select three types of fluids	Product Stewardship Chemically Inert Low Water Solubility (High Partition Coefficients) Select Test Methods
Laboratory Synthetic Studies Physical Property Screening Electrical Property Screening Purification Techniques	Phase II Select <5 Candidates	Biodegradability - Yes or No Animal Acute Toxicity Fish Acute Toxicity Partition Coefficient Movement in the Environment
Developmental Process Definition Fluid Evaluation by Equipment Manufacturers Pilot Plant Production of Fluid	Phase III Produce 1 or 2 Fluids	Develop Analytical Methods (^{14}C) Toxicity - Chronic - Aquatic Species & Animals Metabolism Studies Environmental Half Life Bioconcentration
Commercial Semi-Plant & Full Scale Production Facilities Substantial Sales Volume	Phase IV	Fish Taste EPA & OSHA Limits Fate in Air Soil Water

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Dielectric Fluid Characteristics

General

A. Physical Properties

The fluid must have a wide liquid range.[1] Boiling points should be above 300°C to reduce vapor losses during processing under reduced pressure at elevated temperatures and to minimize vapor losses in operating equipment. In the case of flammable liquids, a high boiling point will also contribute to higher flash and fire points. The fluid should have a pour point in the -30 to -40°C range to insure functioning of the fluid under winter conditions. The viscosity of the liquid should be relatively low through the equipment operating temperature range with 5 - 10 cps at 30 - 60°C being desirable values. The low temperature viscosity of the liquid is indicated by its pour point. The viscosity will usually reach 5,000 - 10,000 cps at temperatures near the liquid's pour point. The flash point of the fluid should be sufficiently high so that processing at elevated temperatures does not lead to a fire hazard. In a practical sense, this means that a flash point of 300 - 350°F (150 - 180°C) should be adequate. The specific role of fluid flammability will be discussed in more detail later.

B. Stability

The fluid should be chemically inert, stable at elevated temperatures (up to 200°C) for extended periods of time and stable when subjected to electrical stress. It should be noncorrosive. These stability parameters favor aromatic compounds over aliphatic and favor unreactive groups such as alkyl, halogens, or the ether linkage over functional groups that have a readily available degradation route, i.e., ester hydrolysis or oxidation of activated methylene groups. The fluid should also be

compatible with common construction materials used in electrical equipment components.

C. Biodegradability and Toxicity

The modern dielectric liquid should biodegrade in a short period of time. A major factor in the search for new biodegradable dielectric fluids derives from the environmental shortcomings of the polychlorinated biphenyls (PCB). A short fluid life in the environment largely eliminates the potential for the problems associated with bioconcentration of chemicals. Fluid biodegradability has the effect of minimizing the possibility of problems associated with long term chronic toxicity and reducing the likelihood of fluid or equipment disposal restrictions. In addition, toxicity evaluation of such areas as fluid ingestion, vapor inhalation, and skin absorption must show the material can be handled safely.

Ultimately, it may be desirable to use radioactively labeled compounds to establish the fate of products of this type in the environment.

D. Processing Characteristics

In many electrical applications highly purified liquids are required to attain the desired levels of equipment reliability and performance. Standard purification techniques, particularly distillation and clay treatment should be applicable to new materials. Contaminants

such as acid, water, and ionic species need to be controlled and removed by whatever fluid purification scheme is selected.

E. Electrical Properties

The electrical properties desired in a dielectric fluid are usually selected to give the best combination of high dielectric constant and low dielectric losses.[2] Generally, the dielectric constant will be <6, with 4 - 6 being the most useful range when alternatives to chlorinated biphenyl are being explored. Values below six are more of a practical limit than a theoretical one in that the electrical losses often become prohibitive at dielectric constants greater than six. High dielectric constant liquids are more difficult to purify to low electrical losses and their purity is more difficult to maintain since they tend to leach ionic species from materials the fluid comes in contact with.

The electrical losses, expressed as dissipation factor or power factor (%), must be low to minimize energy losses in operating electrical equipment and particularly to avoid the generation of excessive heat that results in reduced equipment life. Typically, when measuring the electrical losses of a liquid sample, (60 - 100 Hz at 25°C) values of <0.01 dissipation factor (<1.0% power factor) should be easily attainable. Similarly, the resistivity of a candidate fluid should be $>10^9$ ohm to merit serious consideration. Guidelines on desired dielectric strength value can be drawn from existing commercial products. Common dielectric strengths are in the range of 30 - 40 KV minimum (25°C, 0.1 inch gap).

Capacitor Fluid Requirements

A. Flammability - Flash and fire point

Although much of the experience with capacitor fluids is derived from the use of polychlorinated biphenyl, non-flammability does not appear to be an essential property of a capacitor fluid. A variety of naturally occurring fluids such as castor oil have been employed and synthetic hydrocarbons, esters and ethers are identified as capacitor fluids in the patent literature (see literature review section). Presumably, all of these fluids have flash and fire points. From a practical standpoint, the flammability of a capacitor fluid is of concern mainly during manufacture of the capacitor when the liquid is handled at elevated temperatures under vacuum. The risk of fire from the fluid in an operating capacitor seems a remote possibility even when the unit is ruptured. Therefore, the flash point of the fluid should be higher than any temperature encountered in processing and higher than any temperature that can realistically be anticipated during the use of the capacitor. In this context, a flash point of >300°F should be adequate for a new capacitor fluid and compares closely with existing capacitor fluid products (Aroclor* 1016 polychlorinated polyphenyls - flash point 338°F, minimum). In a flammable fluid, the fire point will lie somewhat above the flash point; for example, a fluid with a 325°F flash point might exhibit a fire point in the 350-400°F range. As noted above, these temperatures are not likely to be encountered in capacitor

*Aroclor is a trademark of Monsanto Chemical Co., St. Louis, Mo.

operations so the fire hazard associated with such a fluid will be slight.

B. Impregnation

An important characteristic of a capacitor fluid relates to the ease with which capacitor dielectric materials such as paper or an organic film can be impregnated with the fluid. This property is difficult to quantify in simple laboratory tests and often can only be evaluated by the success or failure experienced in building and testing capacitor test units.

Transformer Fluid Requirements

A. Fluid Flammability

There are two areas for consideration of fluid flammability in transformers. One relates to mineral oil usage while the other pertains to the fire resistant polychlorinated biphenyl based fluids. Since mineral oil can burn at high temperatures, new liquids in this area need to have a flash point at least as high as mineral oil (typically 300 - 400°F). When considering alternatives to transformer fluids derived from polychlorinated biphenyls or blends of polychlorinated biphenyl with chlorinated benzene, a complex dilemna is encountered. These fluids are essentially nonflammable which means they are stable to chemical oxidation even at elevated temperatures, i.e., no fire point below the boiling point. Unfortunately, stability to chemical oxidation is often accompanied by comparable stability to biological oxidation.[3] Although a variety of nonflammable liquids can be

considered for use in transformers, only in rare instances are these materials biodegradable. One notable exception is 1,2,4-trichlorobenzene which biodegrades after a period of time during which the microorganisms become acclimated to its presence. However, trichlorobenzene itself is not a suitable transformer fluid because of its narrow liquid range (freezing point 16°C, boiling point 214°C).[4] A potential nonflammable biodegradable transformer fluid will be described in a later section of this paper.

B. Products of Decomposition in an Arc

In addition to the apparent contradiction between biodegradability and nonflammability in a transformer fluid, the situation is further complicated by consideration of the decomposition products formed when the fluid is subjected to arcing. Historically, chlorinated fluids were selected because they gave a noncombustible mixture of products, mainly HCl, from arcing.[1,5] The original intent of attaining the noncombustible gas mixture was to minimize the explosion hazard in transformers filled with fire resistant fluids. In this context "Askarel fluids" are defined as nonflammable synthetic liquids which when decomposed in an electric arc evolve only nonflammable gases. This definition is used in safety standards and codes, especially the National Electrical Code and for product listing by Underwriters' Laboratories. Structurally, noncombustible arc-formed gases require that the fluid molecule contain ~1/1 mole ratio of hydrogen to chlorine.

The events which occur during arcing and subsequent rupture of a transformer are difficult to describe quantitatively; however, it appears that three situations might occur.

Situation I - Arcing occurs in a transformer filled with either mineral oil or a fire resistant fluid. No air is present in the transformer. The arcing produces hot gases faster than available pressure relief devices can dissipate the pressure, the pressure exceeds the pressurized capability of the transformer housing, and explosive rupture occurs with discharge of liquid to the surroundings.

Situation II - Similar to Situation I except air is present in the transformer and rupture can result from either pressure as in Situation I or combustion of arc-formed gases.

Situation III - A secondary event from combustible arc-formed gases mixing with air after the transformer rupture. Explosive combustion of arc-formed gases in the air outside of the transformer requires an explosive mixture in a confined space in the presence of an ignition source.

Situation I appears to be predominate over II and III. It should be noted that arcing leading to a transformer explosion is a rare but serious occurence.[6] Although data is largely lacking, it appears that explosions have occurred both in mineral oil and Askarel filled units. Air should not be present in the transformer housing, however, leakage can occur during the years a unit may be in service. The relative likelihood of occurence between Situation I and Situation II is not clear. Most transformers operate under positive pressure at elevated temperatures and may even show a slight vacuum at ambient temperatures. If the transformer body is intact and air is absent, then Situation I will prevail.

Situation II can take place but in many cases may be indistinguishable from the primary event.

The ambiguity of the emphasis on noncombustible arc-formed gases from nonflammable transformer liquids is magnified if today's commercial fluids are examined. The blends of pentachlorobiphenyl (Aroclor 1254 brand) with tri- and tetrachlorobenzene are still available but are under severe attack due to the environmental persistence of the polychlorinated biphenyls. These fluids form HCl in an arc and fit the definition of an Askarel fluid. Other current products range from tri- and tetrachlorobiphenyl (Aroclor 1242 brand) blended with chlorinated benzenes to trichlorobiphenyl alone. These products have a H/Cl ratio as high as 7/3 and must form substantial quantities of combustible gases when decomposed in an arc. Also, Aroclor 1016 brand of trichlorobiphenyl is listed by Underwriters' Laboratories[7] without comment concerning the combustibility of arc-formed gases. In the present studies, we have concluded that nonflammability is an essential property of an Askarel-like transformer fluid. However, the role of the combustibility of the arc-formed gases is unclear in the face of existing commercial products, the use of the Askarel definition in codes and standards, and the sequence of events presumed to occur during a transformer rupture. The possibility exists that gas combustibility plays a minor role in the already disastrous conditions of a transformer explosion, if a nonflammable liquid is involved.

Alternative Dielectric Liquids - What Type?

Literature

A survey of the literature reveals a considerable variety of synthetic dielectric liquids. These, as would be expected, are dominated by chlorinated aromatic compounds, especially polychlorinated biphenyls. Other chlorinated compounds include pentachlorodiphenyl ether, pentachlorodiphenyl ketone, hexachlorodiphenyl methane, polychlorinated aliphatic hydrocarbons, highly chlorinated benzenes or alkylbenzenes, pentachlorophenyl benzoate, chloronaphthalenes and tetrachlorodiphenyl sulfide.[1,6,9] All of these materials are similar in that they are nonflammable, have relatively high dielectric constants (5 - 8), and form mainly HCl when decomposed in an arc. Presumably they are also similar to polychlorinated biphenyl in the respect that they are persistent in the environment. More recently, a variation on chlorinated biphenyl has been reported.[10] Biphenyl or terphenyls containing one to three chlorines are alkylated with from 1 - 12 carbon alkyl groups and up to 2.5 alkyl groups per biphenyl or terphenyl. These fluids are identified as capacitor fluids and an improvement over chlorinated biphenyl itself. Blends with chlorinated biphenyl are also proposed.

Organic esters emerge as a second major class of dielectric fluid. Abundant examples of esters, particularly as capacitor fluids, can be found in the patent literature and published sources. Naturally occurring esters, such as castor oil, have been used commercially but it appears that synthetic esters have not reached major commercialization.[11] In an extensive study of organic esters, Romans and Singleterry[12] have explored the relationship between dielectric constant and chemical structure for common types of esters and have extended their conclusion to a series of nonflammable fluorine containing

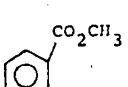
esters.[13] From dipole moment arguments, these authors conclude that the dielectric constant of an ester can be increased by using the shortest possible alcohol chain, the lowest molecular weight dibasic acid, or an aromatic acid that falls within the constraints of physical property requirements such as volatility. Introduction of a second ester group into a flexible molecule will increase the dielectric constant (ε).

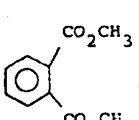
Methyl acetate

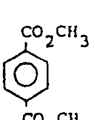
Dimethyl malonate

ε	6.8	10.4

In a rigid molecule, introduction of a second ester group in a structurally complimentary position will increase the dielectric constant, i.e., methyl benzoate versus dimethyl phthalate. In contrast, the ester groups in





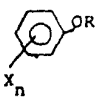


	Methyl Benzoate	Dimethyl Phthalate	Dimethyl Terephthal
ε	6.6	8.5	~7

dimethyl terephthalate interact to reduce the dielectric constant.[14] It is also shown in studies of dissipation factor versus temperature and time that selected esters are

less stable thermally than polychlorinated biphenyl. In patents by F. M. Clark, esters of tetrahydrofurfuryl alcohol, in particular the oxalate, are identified as high dielectric constant (ε = 10 - 12) capacitor impregnants.[15] Jaffe has studied phthalate esters, especially dicyanoethyl phthalate, as high dielectric constant dielectric fluids.[16] More recently, Eustance has identified a capacitor impregnant consisting of an aromatic ester, in particular dioctyl phthalate, stablized by an epoxide additive such as the diglycidyl ether of bisphenol A.[17] In an effort to retard hydrolytic degradation of ester derived capacitor fluids, Ross and Finkelstein have described fluids with alkyl substituents α to the carbonyl and β to the ether linkage.[18] Structures of these types effectively prevent hydrolytic attack on the ester by water or hydroxide ion.

Aromatic and aliphatic ethers of phenol and its derivatives appear in the patent literature as capacitor fluid. Munch and Thompson identified alkyl phenyl ethers of the general structure (I).[19] In a similar example,



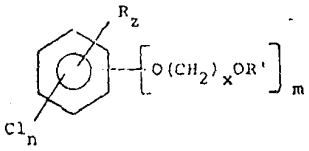
I

R = alkyl C, to C_{10}

X = Cl, Br, or F

n = 1 or 2

Dazzi has studied ethers with the general structure (II).[20] These compounds have

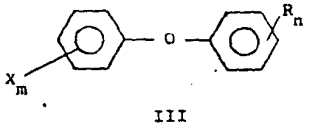


II

R = alkyl C_1 to C_5
z = 0 - 4
m = 1 or 2
R' = alkyl C_1 to C_8
x = 2 - 4
n = 1 - 4

dielectric constants ranging from five to seven and are reported to perform well in dielectric applications.

In addition to the pentachlorodiphenyl ether mentioned earlier, several other diphenyl ether derived compounds have been identified as dielectric liquids. Many of the compounds included in the general structure (III)



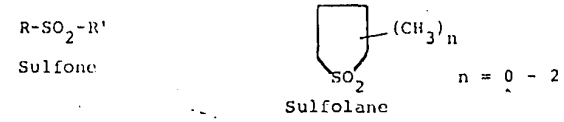
III

X = Cl or Br
m = 0 - 10
R = alkyl C_2 - C_6
n = 0 - 4

have been synthesized and characterized both individually and in combinations.[21] These compounds have good physical properties, dielectric constants from 3.5 to 5, low power factors, and dielectric strengths from 16 - 30 KV (25°C, 0.1 inch gap). Polyphenyl ethers with two to four ether linkages have been studied as high temperature dielectric liquids.[22] Their dielectric constants range from 4.4 to 6.0

with low electrical losses and d.c. resistivities of 10^{10} to 10^{12} ohms at room temperature.

Several sulfones and sulfolanes of the types indicated below have been studied as components in dielectric liquids.[23] The sulfones are blended with

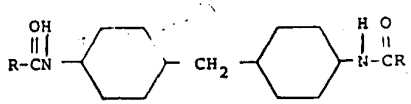


R and R' = phenyl, tolyl, xylyl, naphthyl, biphenylyl

polychlorinated biphenyl and various oils to form dielectric liquids for capacitors. Similarly, sulfolanes are blended with sulfones and other materials to obtain liquids with dielectric constants from 10 to 30. The electrical losses of these fluids are high at low frequencies with a minimum at 10^5 - 10^6 Hz.

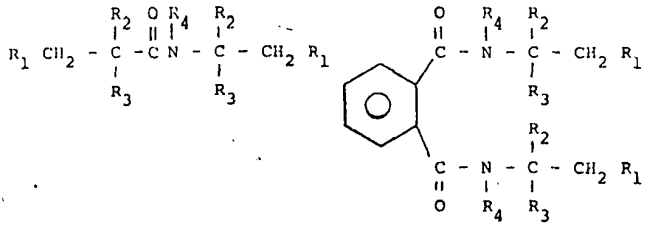
Several references to phosphate esters as dielectric fluids are also encountered.[24] Clark uses phosphate esters with alkyl groups up to four carbons in combination with mineral oil, castor oil, and chlorinated aromatics to obtain dielectric liquids with low viscosity, low pour points, and good lubrication characteristics.[25]

Finck in a German patent describes the reaction of fatty acids with amines to give compounds of the type indicated (IV).[26]



IV

The use of these waxy materials in capacitors is reported. Ross and Finkelstein describe amides as a class of compounds useful as dielectric liquids but lacking in hydrolytic stability.[27] These authors present many examples of amides that are stabilized against hydrolysis by alkyl substituents α to the amide functional groups. Two general examples are given below (V and VI). The steric



V VI

R_1 = alkyl C_1 to C_{18}

R_2 = CH_3 or C_2H_5

R_3 = CH_3 or H

R_4 = H, alkyl C_1 - C_{18}

effects introduced by the substituents effectively stabilize these compounds against acid or base catalyzed hydrolysis.

The use of a nitro compound as a capacitor impregnant was described by Clark in 1948.[28] Dichloro-α-nitro-naphthalene

blended with polychlorinated biphenyl gives fluids with dielectric constants up to 25 and when used in capacitor test units a power factor of <0.6% is attained through a wide range of fluid compositions.

Although the use of hydrocarbons in capacitors is restricted by low dielectric constants and limited stability, several recent patents report improved stability and life characteristics of hydrocarbon based fluid particularly in metallized paper or film and all film type capacitors.[29]

Selection of Compound Types for Further Study

In addition to a survey of the literature, our initial efforts in Phase I of this study included screening a wide range of compounds with the goal of selecting major types for detailed evaluation. Consideration was given to such factors as typical physical properties, accessibility in terms of a synthetic scheme, raw material requirements, stability characteristics, anticipated electrical properties, and the probability of attaining biodegradability and low toxicity. From this broad spectrum of compound types we determined that emphasis in Phase II on selected esters, ethers, and substituted aromatics would best facilitate the identification of potential new dielectric fluids.

Esters

Our investigation of organic esters as dielectric fluids covered several types of esters with the goal of relating dielectric constant to chemical structure. Variation of both the acid and the alcohol portion of the ester was explored. The first type of ester considered is the diesters

derived from ethylene and propylene glycols of varying molecular weights and simple monobasic acids (Table I).

TABLE I

$$RCO\ (\text{alkylene oxide})_n\ OCR$$

R	Alkylene Oxide	n	Dielectric Constant (ε
CH_3	Ethylene oxide	2	9.6
C_3H_7	"	3	7 6
H	"	4	15.5
CH_3	"	4	11.3
C_2H_5	"	4	9.2
CH_3	"	9	10.3
CH_3	Propylene oxide	2	8.3
CH_3	"	4	7.5

From this family of esters it is apparent that the dielectric constant can be influenced by the alkylene unit chosen and by the molecular weight of the glycol and the acid. Two moles of propylene oxide versus two moles of ethylene oxide in the acetate diester differ in dielectric constant by 1.3 (9.6 versus 8.3); the substitution of two methyl groups on the glycol lowers the dielectric constant. This feature is more pronounced in the tetra glycol acetates; ethylene oxides (11.3) versus propylene oxide (7.5). The molecular weight of the acid has a dramatic effect on the dielectric constant of the tetraethylene glycol diesters; formate (15.5), acetate (11.3), and propionate (9.2). The values for ethylene glycol diacetates go through a maximum; 2 moles (9.6),

4 moles (11.3), and 9 moles (10.3). The butyrate of triethylene glycol further demonstrates the influence of acid molecular weight. The dielectric constant of triethylene glycol dibutyrate is similar to tetrapropylene glycol diacetate. The dielectric constants of the compounds in Table I are higher than existing chlorinated capacitor fluids, however, higher molecular weight acid could reduce the dielectric constants into a more useful range.

The second type of ester studied was that derived from a monobasic acid and a simple alcohol or an alcohol prepared by reaction of a simple alcohol with an alkylene oxide. (Table II). Variation of

TABLE II

$RO\ (\text{alkylene oxide})_n\ \overset{O}{\overset{\|}{C}}R'$

R	Alkylene oxide	n	R'	Dielectric constant (ε)
C_4H_9	Ethylene oxide	2	CH_3	7.1
"	"	2	C_2H_5	6.9
"	"	"	Phenyl	6.5
CH_3	"	1	Phenyl	7.3
CH_3	Propylene oxide	3	CH_3	7.1
Benzyl	-	0	CH_3	5.3
Benzyl	-	0	Phenyl	5.4

the acid, the parent alcohol, and the amount or type of alkylene oxide has a minor effect on the dielectric constant of this type of ester. The use of benzyl alcohol reduces the dielectric constant into the desired range.

The third type of ester is that derived from an alcohol or an alcohol reacted with an alkylene oxide followed by esterification with a dibasic acid (Table III).

TABLE III

Esters of Aliphatic Dibasic Acids

Acid	Alcohol	Alkylene Oxide (n moles)	Dielectric Constant
Oxalic	n-butyl	Ethylene oxide (2)	6.9
Maleic	"	" "	7.9
Cis-1,2,3,6-tetrahydro-phthalic	methyl	" (1)	8.6
Adipic	methyl	" "	8.3
Adipic	n-butyl	" (2)	6.8

Esters of Aromatic Dibasic Acids

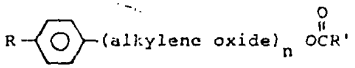
Phthalic	n-butyl	6.5
Phthalic	octyl	5.2
Phthalic	decyl	5.1
Isophthalic	ethyl	7.0
Isophthalic	n-butyl	5.8

The esters of aliphatic dibasic acids have dielectric constants somewhat higher than desired and appear to be particularly unstable to water or base. A higher molecular weight alcohol would probably reduce the adipate dielectric constant below six. For comparison, the dielectric constant of dibutyl sebacate is 4.6.[30] The esters of aromatic dibasic acids give good dielectric constants if a long chain alcohol is used (C_8 and C_{10} phthalates) or if the ester groups interact to reduce the dielectric constant (isophthalates). The environmental properties of long chain alcohol esters will

be discussed in a later section of this paper. In n-butyl phthalate the ortho groups produce a dielectric constant of 6.5 compared to meta ester functionality which gives n-butyl isophthalate a value of 5.8.

The next type of ester considered was prepared from a phenol, an alkylene oxide and a monobasic acid. (Table IV)

TABLE IV



R	Alkylene oxide	n	R'	Dielectric Constant
H	-	0	CH_3	5.2[5]
H	Ethylene oxide	1	CH_3	5.5
H	"	2	"	7.9
H	"	1	C_2H_5	5.3
H	"	1	Phenyl	5.7
H	Propylene oxide	3	CH_3	6.7
C_8H_{17}	-	0	CH_3	3.6
"	Ethylene oxide	1	CH_3	4.3
"	"	2	"	5.1

All of the acetates can be considered derivatives of phenyl acetate. Alkylation causes a sharp drop in dielectric constant (5.2 versus 3.6). Introduction of one mole of ethylene oxide into phenyl acetate causes an increase in dielectric constant from 5.2 to 5.5 while two moles causes a sharp increase from 5.2 to 7.9. The acetate from phenol and three moles of propylene oxide has a dielectric constant

higher than phenyl acetate (6.7 versus 5.2), but lower than that formed from phenol and two moles of ethylene oxide. In these cases, the relationship between ethylene oxide and propylene oxide is similar to that observed in the polyglycol esters. Acetates prepared by introduction of ethylene oxide into the alkylphenol show increasing dielectric constants (0 moles, 3.6; 1 mole, 4.3; 2 moles, 5.1). Compared to the acetate derived from phenol and one mole of ethylene oxide, increasing the molecular weight of the acid by one carbon, propionic acid, causes a small decrease in dielectric constant (5.5 versus 5.3) while an aromatic acid, benzoic, enhances the value slightly (5.5 versus 5.7).

Several characteristics of esters such as those described above, make them attractive as dielectric liquids. They can be prepared from readily available raw materials by common chemical processing techniques. They can usually be distilled to give a high quality product and, as demonstrated above, the structure of an ester can be modified to give the desired dielectric constant. The necessary combination of physical and electrical properties can be attained in selected compounds. For example, in Table IV, the acetate from octyl phenol and two moles of ethylene oxide has the following properties:

Dielectric constant (25°C)(10^2Hz)	5.13
Dissipation Factor (10^2Hz)	0.007
Boiling Point	390°C
Pour Point	-29°C
Flash Point	360°F
Fire Point	375°F
Biodegradable	Yes

The main weaknesses of esters as dielectric liquids relate to stability, both hydrolytic and thermal, and processing characteristics. Since water is a product in the esterification reaction, esters usually contain a small amount of water. Residual acidity is also common. Typically, our esters contained between 100 and 1,000 ppm of water with <1.0 mg KOH/g of ester of acidity present. Under neutral conditions an ester and water will equilibrate to form the parent acid and alcohol as shown in Equation 1.

$$RCOR' + H_2O \rightleftharpoons RCOH + R'OH \qquad (1)$$

This equilibrium situation means that water present in an ester, whether from the esterification reaction or from atmospheric moisture, will ultimately lead to the formation of free acid and alcohol. Thermal or oxidative degradation of an ester can also lead to acidic products and water. The limited hydrolytic stability and potential for oxidative or thermal degradation are important in considering the electrical performance of an ester. Low electrical losses can be attained in many esters, however, the processing required is often laborious compared to that required for polychlorinated biphenyl or mineral oil. Once the ester is purified to a low power factor, it is often difficult to maintain low electrical losses and low acidity because of hydrolysis or degradation such as that described above. Scavengers or inhibitors can be used to minimize these problems, but the reaction products from the scavenger and free acid or alcohol can also contribute to increasing the power factor. In summary, while certain esters have the physical and electrical properties required for them to function as dielectric liquids, factors such as hydrolytic stability, acidity and processing

characteristics can significantly limit their utility. In addition, the ability of esters to stand up under heavy electrical stress is largely unknown. Their biodegradability will be discussed in a later section.

Ethers

Ethers are attractive as dielectric fluids because many opportunities are available to explore the relationship between dielectric constant and structure. The ether linkage imparts good stability and processing characteristics to these compounds, particularly when compared to the esters described previously. The major preparative route used in this study was the classical Williamson ether synthesis (Equation 2).

$$\underset{\text{Step 1}}{\text{ROH} + \text{NaOH} \longrightarrow} \; \text{H}_2\text{O} + \text{RO}^-\text{Na}^+ + \underset{\text{excess}}{\text{R'X}} \; \underset{\text{Step 2}}{\longrightarrow} \; \text{NaX} + \text{ROR'} \qquad (2)$$

$$\text{X} = \text{Cl, Br or I}$$

Since step 1 is reversible, it is necessary to remove the water to attain high conversion to the intermediate alcohol sodium salt. Step 2 is not reversible but it is usually heterogeneous. It is generally difficult to reach complete reaction to the ether even using an excess of the alkylating agent. Conversions of 70 ~ 95% are typical. In this situation, it is essential that the ether purification method remove unreacted alcohol. This can usually be accomplished by distillation or, in cases where the alcohol and ether have similar boiling points, selective adsorption techniques can be employed. When these compounds are free

of unreacted alcohol, the electrical losses are usually quite low. In this study, consideration was given to aliphatic ethers, alkyl-aromatic ethers and totally aromatic compounds. Representative aliphatic ethers are listed in order of increasing molecular weight in Table V.

TABLE V

Aliphatic Ethers

RO (alkylene oxide)$_n$ R'

R	Alkylene oxide	n	R'	Dielectric Constant	Carbon/Oxygen
C_2H_5	-	0	C_2H_5	4.0	4.0
C_2H_5	Ethylene oxide	2	C_2H_5	5.9	2.7
CH_3	"	2	$n\text{-}C_4H_9$	5.3	3
CH_3	"	2	$t\text{-}C_4H_9$	4.9	3
$n\text{-}C_4H_9$	"	1	$n\text{-}C_4H_9$	3.7	5
CH_3	Propylene oxide	3	$n\text{-}C_4H_9$	4.9	3.5
$n\text{-}C_4H_9$	Ethylene oxide	1	$n\text{-}C_8H_{17}$	3.2	7
$n\text{-}C_4H_9$	Propylene oxide	~19	CH_3	4.9	3.1

The dielectric constant of these compounds is determined by the size of alkyl groups and the number of ether linkages present. Increasing the carbon content reduces the dielectric constant while the value increases as ether linkages are added. In Table V, this relationship is expressed as the carbon/oxygen ratio for each compound. The dielectric constant decreases as the carbon/oxygen ratio increases. Even though the dielectric constants of these compounds lie in an attractive range, significant physical property limitations

exist. The low molecular weight materials are too volatile (low flash point), while the high molecular weight members are difficult to purify since they cannot be distilled and their viscosity makes clay treatment laborious. The middle members of this series have good physical properties and can often be obtained in high purity (low electrical losses) by distillation.

Table VI lists a series of β-chlorinated aliphatic ethers that were prepared.

TABLE VI

β-CHLORINATED ALIPHATIC ETHERS

$$Cl - CH_2\underset{\underset{R}{|}}{CH} - O - CH_2 - \underset{\underset{CH_3}{|}}{CH} - Cl$$

R	Dielectric Constant
Phenyl	8.4
Tolyl	5.9
t-Butylphenyl	6.6
$n\text{-}C_8H_{13}$	6.4
$n\text{-}C_8H_{17}$	5.5
$n\text{-}C_{10}H_{21}$	5.2

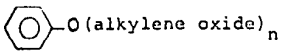
The compounds, especially where R = $n\text{-}C_{10}H_{21}$, showed promise in early stage evaluation. They have excellent physical properties, are readily prepared from common raw materials, and can be purified to exhibit low electrical losses. Additional evaluation showed that these compounds have limited

thermal stability and decompose under electrical stress. Degradation of these compounds produces HCl leading to corrosion problems and prohibitive electrical losses.

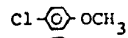
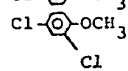
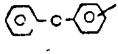
In Table VII selected alkylaromatic ethers are presented.

TABLE VII

ALKYLAROMATIC ETHERS



Alkylene oxide	n	R	Dielectric Constant
Ethylene oxide	1	CH_3	6.4
Ethylene oxide	2	CH_3	6.7
Ethylene oxide	1	$n\text{-}C_4H_9$	4.8
Propylene oxide	3	$n\text{-}C_4H_9$	4.2

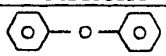
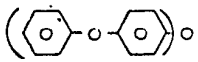
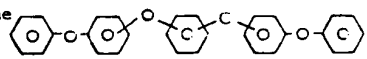
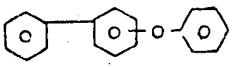
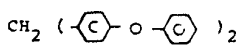
Anisole		4.3
4-chloroanisole		7.1
2,4-dichloroanisole		11.1
4,4'-dimethoxydiphenylmethane	$CH_2(C_6H_4OCH_3)_2$	4.5
methoxymethyldiphenyl ether		4.8

In the compounds incorporating ethylene oxide, the structural effects on dielectric constant are similar to those observed in aliphatic ethers. The propylene oxide derivative leads to lower values than any of the ethylene oxide based compounds. Chlorination of anisole leads to a sharp rise in dielectric

constant. 4,4'-dimethoxydiphenylmethane is essentially a dimer of anisole and has a dielectric constant similar to anisole (4.5 versus 4.3). This compound has attractive properties except for its 35°C freezing point. Methoxymethyldiphenyl ether isomer mixture is a particularly attractive candidate. This fluid has excellent physical and electrical properties and can be purified by clay treatment alone (no distillation is required) to exhibit low electrical losses (dissipation factor 0.002 10^2Hz, 25°C).

Representative aromatic ethers are presented in Table VIII.

TABLE VIII
AROMATIC ETHERS

Compound	Structure	Dielectric Constant
Diphenyl ether		3.7
bis (phenoxyphenyl) ether (isomer mixture)		4.4
bis (phenoxyphenoxy) benzene (isomer mixture)		4.4
Biphenylylphenyl ether (isomer mixture)		3.4
4,4'-Diphenoxydiphenylmethane		4.0

Aromatic ethers, particularly polyphenyl ethers, have excellent electrical properties and thermal stability. However, these compounds have high pour points, freezing points,

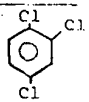
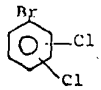
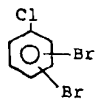
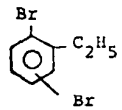
and viscosities such that they cannot be considered in applications where exposure to winter weather would be expected.

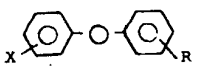
Substituted Aromatic Compounds

The compounds considered were derivatives of benzene and diphenyl ether (Table IX). Many derivatives of benzene, toluene, and xylene cannot be seriously considered in this study because they have a relatively narrow liquid range (high freezing point and/or low boiling point). A similar situation is encountered with naphthalene and biphenyl. In contrast, many compounds derived from diphenyl ether have good low temperature properties and high boiling points.

TABLE IX

Substituted Aromatic Compounds

Name	Structure	Dielectric Constant
1,2,4-trichlorobenzene		4.0
Bromodichlorobenzene (isomer mixture)		4.0
Chlorodibromobenzene (isomer mixture)		3.9
Dibromoethylbenzene (isomer mixture)		5.1



X	R	
H	H	3.7
Cl	H	4.7
Cl	Cl	5.7
Br	H	4.3
Cl	Sec-C_4H_9	4.5
Cl	Sec-C_6H_{13}	4.3
Cl	Sec-$C_{12}H_{25}$	3.6
Cl	Branched-$C_{12}H_{25}$	3.9
$CH_3C(=O)-$	H	6.0
H	Sec-C_4H_9	3.0
H	Cyclohexyl	3.2
H	Benzyl	3.4

Of the benzene derivatives considered, only dibromoethylbenzene is not limited by its freezing point. In addition to a low pour point (-40°C), this compound is nonflammable, has an attractive dielectric constant (5.1), and a relatively high boiling point (260°C). This combination of properties is very similar to those of polychlorinated biphenyl as used in nonflammable transformer fluids. Additional comparison of dielectric strength, resistivity, thermal stability and corrosion characteristics reinforced this similarity. With this background, we have used this fluid in several transformers in our plant in Midland. Although our experience is limited, we now have up to 1.5 years of normal operation in units using this fluid under a variety of load conditions. Studies are continuing to determine the potential of this compound as a nonflammable transformer fluid. It should be pointed out that this fluid is nonflammable but it can produce a combustible mixture of gases when decomposed in an arc (hydrogen/halogen = 4).

In the diphenyl ether derivatives, chlorination raises the dielectric constant sharply (Cl_0 ~ 3.7, Cl_1 = 4.7, Cl_2 = 5.7), however, as in the case of biphenyl, the level of chlorination is critically related to biodegradability. Monochlorodiphenyl ether biodegrades quite rapidly, while dichlorodiphenyl ether biodegrades significantly more slowly. This distinction led us to conclude that our studies should be limited to compounds containing a maximum of one halogen per diphenyl ether moiety. Alkyl derivatives of monochlorodiphenyl ether have dielectric constants lower than the parent compound and the dielectric constant generally decreases with increasing molecular weight of the alkyl substitutent, i.e., R = H, 4.7; R = C_4H_9, 4.5; R = $C_{12}H_{25}$, 3.6. Alkyl derivatives of diphenyl ether follow a similar pattern with dielectric constants ranging from the parent ether's value of 3.7 downward to ~3.0. The methyl ketone derived from diphenyl ether has a relatively high dielectric constant (6.0) but even after extensive purification, this compound exhibits excessive electrical losses.

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.

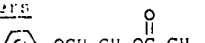
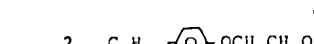
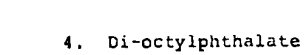
In research, product stewardship requires examination of four parameters. Stability of a chemical as measured by microbial, photochemical, or chemical degradation. Movement of a product in the environment is measured by examining its relative affinity for air, water, and soil. Bioconcentration of organic 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.

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

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.

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.	$ClCH_2\underset{C_{10}H_{21}}{\underset{\vert}{CH}} - O - \underset{CH_3}{\underset{\vert}{CH}} - CH_2Cl$	Slow
9.	Aroclor 1242 Fluid	Not detected
10.	Di-n-butylphthalate	Not detected
11.	Decyldiphenyl ether	Not detected

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.

Experimental Procedures

The acetate esters were prepared by reacting acetic anhydride with the appropriate alcohol. Other esters were formed by reaction of acid and alcohol in toluene solution. The water of reaction was removed by azeotropic distillation. Ethers were prepared by the Williamson Synthesis. The alcohol was reacted with sodium hydroxide and the water formed was removed by azeotropic distillation. The resulting sodium alkoxide was reacted with excess alkyl halide to yield the ether. Chlorination and bromination of diphenyl ether or benzene was carried out using Lewis acid catalysts such as stannic chloride or ferric chloride. Alkylation reactions were catalyzed with aluminum chloride.

The compounds reported were usually purified by distillation and clay treatment. The clay used was 80 - 200 mesh material from the Hilliard Corporation, Elmira, New York.

Electrical measurements were made on a General Radio Model 1615 A capacitance bridge. Dielectric constants were run at 10^2 Hz and 10^4 Hz. A stainless steel capacitance cell having a liquid capacity of ~10 ml and a cell constant of 54.7 pF was employed with the bridge.

Summary and Conclusions

In our dielectric fluid research program, Phase II studies on esters, ethers and substituted aromatic compounds have identified compounds in each class that show promise as new dielectric fluids. In each type of compound, the proper selection of a fluid can give a combination of good physical properties, stability, biodegradability and the desired electrical properties. The remaining question is comparison of the strengths

and weaknesses of these three types of fluids to arrive at the best candidates for developmental studies in Phase III. The accompanying table represents some of our conclusions:

	Synthesis	Purification	Dielectric Constant	Electrical Losses	Stability
Esters	+	-	+	±	-
Ethers	-	±	+	+	+
Substituted Aromatics	+	+	±	+	+

Synthetic routes to esters are readily available. Purification of esters can be difficult if water or residual acid is present. Purity and electrical losses are related in that low losses may not be attained if purification is a problem. The most significant weakness of esters is their susceptibility to hydrolysis and thermal degradation. Hydrolysis or degradation leading to water, acidity and poor electrical performance can significantly limit the utility of these compounds.

The major shortcoming of ethers is the inefficiency of synthetic routes to these compounds. Incomplete reaction in ether preparations leads to difficulties in purification if the ether and the parent alcohol are not readily separable. The electrical properties and stability of ethers are excellent.

Substituted aromatic compounds derived from benzene and diphenyl ether are accessible synthetically. These compounds can be purified to low electrical losses and are characterized by excellent stability. In our work, these compounds are limited to dielectric constants of ~5 or less.

In conclusion, it is our position that the history of aromatic compounds as dielectric fluids and the results of our studies point to substituted aromatic compounds, particularly those derived from diphenyl ether, as our best candidates for Phase III developmental studies.

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