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SUBJECT : NEW DIELECTRIC FLUIDS

REFERENCE :

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The attached discussion of the ABC's of Electrical Insulating Fluids describes the need for such materials, the required properties and gives a summary of the more important types of fluids which have been used or considered for this use. It also considers the basic molecular structural criteria which must be met by a satisfactory fluid dielectric.

The requirements for a good fluid are numerous. To a large extent they are conflicting. For these reasons they are hard to meet.

Aroclor 1242 has been considered and would still be considered one of the two best except for the growing possibility that it may cause environmental pollution to an unacceptable extent.

As is stated in the attached discussion, our sales of dielectric fluids are largely for transformers and for capacitors.

I believe that we could develop a synthetic hydrocarbon fluid which would have advantages over transformer oils now in use. We would seek to make it more resistant to oxidation and sludging. We should also seek to make it less likely to gas under electrical stress and cause bubbles of gas in the insulation which lead to dielectric breakdown. Since it would be synthetic, it would be more uniform in quality.

I doubt that we could develop a fire resistant transformer fluid which would be accepted by the industry. However, we should examine the properties of all our fire resistant fluid types to make sure none of them would be acceptable. They should have low dielectric constant. The requirements on resistivity and power factor are not nearly as severe as for capacitor fluids. Long time stability is a major requirement. Perhaps properly inhibited chloro alkanes would be usable. Perhaps tetra alkyl silicate esters would be worth considering now that transformers are sealed.

The development of a suitable capacitor fluid is just as difficult although the requirements differ. The capacitor fluid must have a dielectric

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constant in the 5-6 range or higher if possible. Its resistivity and power factor must be very good for paper-fluid dielectric systems. Somewhat poorer power factor and resistivity could perhaps be tolerated in plastic film type capacitors. Fire resistance is desirable but not necessary. Extreme stability is essential.

As is stated in the attached discussion, to secure high dielectric constant, we must have unsymmetrical charge distribution in the molecule. This must be done with constituent groups which themselves have the minimum possible ionic character. These must be located in structures such that the high charge groups do not promote ionization of adjacent atoms. This rules out the use of many groups such as $-\text{OH}$, $-\text{C}\equiv\text{N}$,

$-\text{O}_2\text{S}=\text{O}-$, $-\text{NO}_2$, $-\text{COOH}$, $-\text{CONH}_2$ and other similar groups. Some of

these ionize readily, others such as the $-\text{O}_2\text{S}=\text{O}-$ group promote ionization of adjacent hydrogens although they themselves do not ionize. We should consider whether such groups could be made useful by substitution for the ionizable hydrogens atoms such as chlorine or fluorine which would be less ionizable.

Ordinarily halogenated aliphatic side chains are not considered desirable. We should consider $-\text{CF}_3$, $-\text{CClF}_2$ and $-\text{CCl}_2\text{F}$ groups as substituents on diphenyl to see if good dielectric fluids would be produced. The first of these would be best but the second and third might be adequate due to the stabilizing effect of the F.

Preliminary tests have shown that halogenated diphenyl thio ethers have acceptable electrical properties. This lead should be followed up.

Oxy ethers should also be investigated. This would include halogen substituted diphenyl ethers and the possibility of partial substitution of the chlorine of Aroclor 1242 by $-\text{OCH}_3$ to reduce the amount of chlorine so that the material will biodegrade while still hopefully retaining good dielectric properties.

We should establish as soon as possible whether or not the lower chlorinated biphenyls are sufficiently biodegradable to permit their use. If they are, we should alter the distillation of Aroclor 1242 to fractionate out the tetra, penta and higher chlorinated material.

Finally, since the above is largely the thinking of one man, this problem should be put before one or more of our consultants who are expert in theoretical organic chemistry to see if they could make more suggestions.

R. H. Munch

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THE ABC'S OF ELECTRICAL INSULATING FLUIDS

The purpose of this discussion is to help us to develop new dielectric fluids. To do this, we must understand the requirements involved in the fluid use.

The basic reasons for using fluids as dielectrics are the following:

- 1) They have higher dielectric strength than gases.
- 2) Their fluidity permits them to conform to the structure and displace all gas.
- 3) They aid heat transfer since they have good thermal conductivity and permit convective heat transfer too.
- 4) In some uses a higher dielectric constant than is provided by gases is desirable. Fluids can have a wide range of dielectric constant.

There are three major types of electrical apparatus which use dielectric fluids:

- 1) Cables
- 2) Transformers
- 3) Capacitors

In the first two of these, fluid with a low dielectric constant is desirable while in the third, a high dielectric constant is desirable.

We have had virtually no sales to cable producers because our fluids have high dielectric constant and fire resistance is not a major requirement in this use. We have sold our fluids to the transformer industry primarily because they are fire resistant and in spite of the fact that they have a higher dielectric constant than would be desirable. Our fluids have been used in capacitors primarily because they have high dielectric constant and low dissipation factor. Fire resistance in capacitor fluids is usually one of the less important properties.

For all these uses, non-electrical physical properties such as boiling point, viscosity, pour point and cracking temperature are important. The fluids must be high boiling because vacuum degassing and vacuum impregnation are employed to eliminate air filled voids in the insulation. These must be eliminated because they are the cause of corona discharge which causes degradation

of the dielectric properties and leads to ultimate breakdown and failure of the equipment.

Dielectric fluids usually operate at temperatures up to about 100°C. This limit is set by the fact that cellulosic insulation begins to decompose too rapidly to give the 20-30 year life expected of transformers and capacitors. The lower limit of the operating temperature range is set by the use. For equipment installed indoors it may be 0°C. For outdoor installations, it depends on the location and may be -30°C for locations in most of our country. It may go down to -60°C for outdoor installation in places such as Labrador.

A table which gives a list of the desirable properties of a dielectric fluid for capacitor use is attached. If the requirement for high dielectric constant is eliminated this same list would apply to transformer and cable fluids. This list is adapted from one given to us by Westinghouse.

Economics are a primary factor determining whether or not a fluid will be used. This does not mean that the lowest cost fluid will be used but the one that leads to the best over-all economics for the apparatus manufacturer and the user of the apparatus. The apparatus manufacturer will be willing to pay more for a fluid which permits him to have an advantage such as smaller size, less weight, longer life, higher operating temperature or reduced costs for other components. Savings in installation costs, operating costs and insurance costs on the finished installation are also important.

Now let us consider the nature of products suitable for use as dielectric fluids. By definition, they must be non conductors. In other words, they must have as high resistivity and as low power factor as possible. Since conduction in liquids is ionic, this means that structures which offer minimum possibility of producing ions must be chosen. Also, ionizable impurities must be rigidly excluded.

Reasoning from these facts, we would say that a highly refined hydrocarbon oil should be a good dielectric fluid. This is indeed the case. Such materials are widely used in transformers, cables and to a limited extent in capacitors.

The reason that the use of hydrocarbons in capacitors is limited is that capacitors with oil impregnated paper insulation are inconveniently large and expensive. A capacitor can be reduced in size if the dielectric constant of the insulation between its plates is increased. The dielectric constant of hydrocarbon fluids is about 2.

To have a high dielectric constant, a liquid must have a molecular structure with an unsymmetrical charge distribution. Unfortunately, many such structures

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lead to the ability of the molecule to ionize. High dielectric constant also promotes ionization of impurities.

Thus it has been considered to be a fair generalization that materials will have increasingly poor resistivity and power factor as the dielectric constant increases and that the higher the dielectric constant the greater the degradation of resistivity and power factor by ionizable impurities will be.

Water with a dielectric constant of 80 and an ion product of 10^{-14} is a prime example of this situation. We cannot take advantage of it as a capacitor dielectric because the molecule itself ionizes and because acids, bases and salts ionize almost completely in it because of its high dielectric constant.

Aroclor 1242 has a dielectric constant of about 5. This is the result of an electrically unsymmetrical structure which does not involve any bonds which are ionizable to a significant extent. When uncontaminated by ionizable impurities it has excellent resistivity and power factor although not as good as hydrocarbon fluids. Because of its higher dielectric constant, the effect of dissolved impurities on its resistivity is much greater than is the case with hydrocarbon fluids. A few parts per billion of ionizable impurity degrade its resistivity and power factor so much as to make it impossible to make a high quality capacitor from it. It is thus more difficult for capacitor makers to use this material than lower dielectric constant materials but the economic advantage has made them learn to do so.

Attached to this discussion is a tabulation of dielectric fluids. The superscript numbers refer to notes at the end of the table and classify the materials roughly as to their usefulness as dielectric fluids.

Monsanto has synthesized and tested many types of compounds as candidate dielectric fluids. The reports listed below cover most of this work:

- 1) Phosphate Division Final Report No. 2906, New Dielectrics 1951-53; R. J. Good.
- 2) CRD Progress Report Job No. 3101, June 1964, W. C. Hamman and R. M. Schisla.
- 3) Interdivisional transfer of technological developments Report TR-23 Aroclor 1242 with Improved Dielectric Properties dated October 15, 1959, by Harold Weingarten.
- 4) Exploratory Fluorination of Biphenyl Derivatives Job No. 2-02-750.01-3199, by H. L. Merten.

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- 5) New Compounds from Acrylo Nitrile Part VIII Acrylonitrile Derivatives as Dielectrics RD-57 Short form 1097 by S. A. Heininger.
- 6) St. Louis Research Report No. 2737

None of this work has lead to new commercially acceptable dielectric fluids. Our larger customer such as General Electric and Westinghouse and some of the other chemical companies such as DuPont and Hercules have also searched for a successor to Aroclor 1242 without success.

Much of this work was done rather blindly without recognition of the fact that many types of organic structural groups which are not ordinarily thought to ionize in fact do so to an extent sufficient to produce conductivity too great to allow use of compounds containing them as high quality dielectrics.

To succeed in developing useful dielectric fluids we will have to use modern theoretical organic chemistry to guide our efforts. The structures of our candidate fluids must be chosen to give an unsymmetrical charge distribution sufficient to give the desired dielectric constant. This must be achieved without use of structural groups such as nitrile or hydroxyl or sulfone or others known to be ionic in character or known to promote ionization of adjacent hydrogens.

Where the harm is done by promoting ionization of adjacent hydrogens, we might be able to block these positions with atoms which do not ionize.

There is some possibility that we might be able to use materials such as the ICI chloro alkanes which are poor compared to Aroclors by suitable purification and with a very active hydrogen chloride scavenger such as diphenyl mercury. The activity, both rate of reaction and completeness of reaction with hydrogen chloride, of this material is many orders of magnitude better than the best epoxy scavengers.

Because of the facts mentioned above we should not aim to produce a fluid of very high dielectric constant. We should look for one in the 5-6 range. For capacitor use it need not be fire resistant. For transformer or cable use the dielectric constant should be low. This might offer the possibility of producing a mixture and separating high dielectric constant isomers for capacitors and low for transformers. Transformer fluid must be fire resistant or at least oxidation resistant so that it will not sludge and resistant to gas formation under electrical stress so that it will resist electrical puncture of the dielectric in order to compete with hydrocarbon oils now used.

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DESIRABLE PROPERTIES AND/OR REQUIRED DATA
FOR APPLICATION OF NEW CAPACITOR DIELECTRIC FLUID

Property	Test	Value
I. <u>Electrical</u>		
A. Low Power factor at 400-1000 VPM, 60 cycles (-50° to + 150°C)	D150-59T	<.0001
B. High Resistivity	D257-58	
C. High Dielectric Constant (-50 + 150°C) (50 N 10 ⁴ N)	D150-59T	~ 5.0
D. High Dielectric Strength (-50 + 150)	D877-49	35 KV/.1 in
E. High Corona Starting Voltage (-50°, + 150°C)		
F. High Corona Extinction Voltage (-50 + 150°C)		
G. Stable Power Factor After Exposure to Corona		
Stable Dielectric Strength After Exposure to Corona		
Stable Life Expectancy After Ex- posure to Corona		
Stable CSV & CE _x V After Exposure to Corona		
H. Power Factor Stable in Presence of Low Concentrations of Contaminants: Salts, Oxides, H ₂ O, etc.		
I. Good Arc Extinction Characteristics		
J. By-Products of Arc & Corona Do Not Result in Tracking		
K. No A.C. or D.C. Electrochemical Reactions (Sludging etc.)		

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Property	Test	Value
II. <u>Physical</u>		
A. Usable Temperature Range		(-50, + 150°C)
B. Low Viscosity		(20 CS)
C. Viscosity vs. Temperature		(Req'd. data)
D. Low Pour Point		(-60°C)
E. Vapor Pressure vs. Temperature		(Req'd. Data)
F. High Flash Point	Cleveland Open Cup	(>200°C)
G. High Fire Point		
H. "Non-Flammable" Rating	Underwriters	
I. Low Coefficient of Expansion		(<.005cc/cc/cc).
J. Low Density		(<8#/gal.)
K. Low Specific Gravity		(<1.0)
L. High Specific Heat		
M. High Thermal Conductivity		
N. Distillation Range		(Req'd. Data)
O. Wet Paper, Films		(Req'd. Characteristic)
P. Solubility of Gases as Function of Pressure Temperature: O ₂ , N ₂ , H ₂ O, CO, CO ₂ , H ₂		(Req'd. Data)

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	Property	Test	Value
III.	<u>Chemical</u>		
A.	Stable (-50, +150°C) in the presence of high electric field, metals and dielectrics (listed below), light, minor concentrations of contaminants.		
B.	Compatible with plastic films, kraft paper, gasket materials, steel, aluminum, solder, copper, flux.		
C.	Non toxic (liquid and vapor) to either humans or wild life.		
D.	Non acidic		
E.	Products of Electric Arc should be (1) dielectrics, also (2) non-gaseous (or readily soluble gases), (3) non toxic.		
F.	Non Reactive (Electrochemically) to A.C., D.C., in presence of materials above (B).		
G.	Dissolved by low-cost, safe solvents.		
IV.	<u>Handling & Treating Properties:</u>		
A.	Purification or reclaiming should be possible by simple treatment (Vacuum spray, clay treatment, etc.)		
B.	Readily handled and controlled by pumping, valves, piping, etc.		
C.	Simple and safe cleaning methods for spillage metal preparation for painting, shop cleanliness, etc.		
D.	Permit solder sealing of leaks.		
E.	Permit limited exposure to air, light.		
F.	Low vapor pressure at elevated temperature (to permit vacuum impregnation).		
G.	Medium viscosity change with temperature.		
H.	Biodegradable		

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V. Economics

- A. Estimate cost and availability as function of activity and years of usage.
- B. Compare costs on Functional Basis, with existing dielectric fluids: Transformer oil, Aroclors, Castor Oil, Polybutene, etc.

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DIELECTRIC FLUIDS

I. Hydrocarbons

A. Mineral Oils Refined from Petroleum

- ¹1. Transformer oils
- ¹2. Capacitor oils
- ¹3. Cable Oils

¹B. Poly isobutenes

C. Alkyl benzenes

- ²1. DDB
2. DDB hi boilers

D. Alkyl biphenyls

1. Isopropyl biphenyl

E. Cyclo aliphatics

1. Isopropyl bi cyclohexyl

F. Mixed aromatic-cycloaliphatics

1. HB40

II. ⁴Halogenated alkanes

III. Halogenated Aromatics

A. Chloro benzenes

- ¹1. Tri chlorobenzene
- ¹2. Tri tetra chlorobenzene mixtures
3. o dichlorobenzene

B. Chlorinated Napthalenes

- ¹1. Halowaxes

C. Halogenated biphenyls

- ¹1. Aroclors 1242, 1248, 1254, 1260
2. Bromo chloro biphenyls

D. Chlorinated phenyl indane

IV. Halogenated Aromatic Ethers

A. Chlorinated diphenyl ether

- ²mono, di, tri etc.

B. Bromo chloro thio ethers

V. Perfluorinated Compounds

- ²1. Flutecs
- ²2. 3M fluids

VI. Partially fluorinated compounds

1. Trifluoro methyl substituted biphenyl
2. Difluoro chloro methyl substituted biphenyl

VII. Mixed halogenated methoxy substituted biphenyls

VIII. ²Silicones

IX. Esters

- ²1. Silicates
 - a. OS-59 etc.
2. Carbonates
- ⁵3. Carboxylates
 - ²a. di 2 ethyl sebacate
 - ²b. Castor oil
- ⁵4. Phosphates

X. ⁵Amides

XI. ⁵Nitriles

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XII. Nitro compounds

- ⁵1. o ethyl nitro benzene
- ⁵2. o nitro chlor benzene
- ⁵3. Nitrobenzene

XIII. Sulfones

- ⁵1. Tolylylyl sulfone

XIV. Aliphatic esters

XV. ⁵Alkanols

XVI. ⁵Phenols

XVII. ⁵Water

XVIII. Liquified elemental gases

N₂
H₂
HC

- ¹ Materials which are used commercially.
- ² Materials which have been used or are used to a small extent for specialty uses. Use limited by high price or marginal electrical properties or both.
- ⁴ Materials which decompose under use conditions to give impurities which degrade electrical properties to an unacceptable extent.
- ⁵ Materials known to be inherently too ionic to be useful for capacitors where low power factor is a requirement.

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