DEVELOPMENT OF A NEW ELECTRICAL INSULATING FLUID

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ABSTRACT

One of the results of worldwide attention on environmental effects produced by synthetic organic chemicals was an accumulation of evidence that Polychlorinated Biphenyls, PCB's, are widely dispersed in the environment and that they exert both adverse toxicological and ecological effects. Since PCB's are widely used in the capacitor and transformer industry, in late 1970 a study was began to develop a suitable electrical insulating fluid without these adverse properties. This study culminated in the development of diisononyl phthalate (ENJ-2065) as a dielectric fluid for the capacitor industry. It is now in commercial use in the U. S. A.

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MONS 082209

Introduction

Polychlorinated biphenyls, PCB's, have been in commercial use as electrical insulating fluids for over forty years. They gained prominence in capacitors and transformers because of the property and performance advantages they showed over the hydrocarbon dielectric fluids. PCB's are non flammable, have a reasonably high dielectric constant, and a high degree of stability. These properties enabled manufacturers to produce relatively non-flammable smaller size capacitors and transformers with longer life performance than could be obtained with conventional hydrocarbon fluids. Over the years, more than 90 percent of the electrical utility and smaller industrial type capacitors have been impregnated with PCB's[1].

Commercially, PCB's are manufactured by chlorination of biphenyl. This procedure results in a complex mixture of isomeric chlorobiphenyls with varying chlorine content.

Trace quantities of PCB's were reported present in environmental samples in 1966[2]. In following years, PCB contamination was found to be widespread including human milk and adipose tissue[3]. Definitive toxological properties, as regards humans, remain poorly known. A detailed bibliography of the current status of toxicological data are given in[1].

As a result of the environmental and toxicological considerations, the use of PCB's has recently been either limited or banned altogether in many countries. So far in the U.S., PCB usage has been limited to those systems which are closed, e.g. capacitors and transformers, to minimize or eliminate environmental exposure. In May 1972, Japan totally banned the use of PCB's in any product either produced or imported into their

country. Member European countries in the Organization for Economic Cooperation and Development (OECD) reached an agreement in 1973 to recommend the restricted use of PCB's.

Physical and Electrical Properties of Insulating Fluids

Electrical insulating (dielectric) fluids are important as impregnants in tranformers, capacitors and other electrical devices. In addition to their electrical functions, the fluids may also be used for cooling and arc quenching. For use in capacitors with cellulose paper as a dielectric, the important properties of the fluid are:

1. High Dielectric Constant. A desirable dielectric constant is one which closely matches that of the paper dielectric. A close match reduces electric field inhomogeneites, increases dielectric strength and thus improves the useful life of the unit. Although liquids with dielectric constants greater than six would be desirable to reduce the size of the capacitor purifying such liquids of conducting impurities, such as water, is extremely difficult. A dielectric constant in the range of four to five appears to be a good compromise to maintain purity while permitting a reduction in unit size.
2. Low Dissipation Factor. This factor is known to be primarily a function of purity but molecular geometry may also influence it. A low value is important to reduce energy loss and damaging heat buildup in a capacitor.
3. High Dielectric Strength. High values are required to improve the service life of the units by permitting exposure to short periods of abnormally high stresses without breakdown.

4. Low Gassing Tendency. Low values are desirable to avoid the production of gases, such as hydrogen, which can lead to the buildup of pressure in sealed units. In practice of aromatic molecules has been found to be beneficial in reducing gas evolution[4].

5. High Chemical and Thermal Stability. The equilibrium concentration of water present in cellulosic paper and the normal operation of capacitors at elevated temperatures demand a high order of stability of these fluids to prevent or minimize failure of capacitors in use.

6. Low Viscosity. For ease of complete impregnation and filling of capacitors, a low viscosity fluid is desirable to eliminate voids of air pockets.

7. Low Degree of Toxicity. This property is mandatory to overcome objections of governmental, environmental protection organizations, and other private agencies.

8. Ecological Compatibility. This requires an acceptable fluid to be readily biodegradable by microorganisms in soil and water. If biodegradation to carbon dioxide and water is not complete, the degradation products should be relatively nontoxic or no more toxic than the parent fluid.

The above requirements apply primarily to capacitors. In practice PCB's have also found use as dielectric fluids in transformers particularly in those used indoors where limited flammability is an important requirement. In these transformer applications the magnitude of the dielectric constant is of less importance than the fluid's heat transfer ability.

The search for a suitable dielectric fluid to replace PCB's in capacitors has been undertaken in many laboratories. Organic esters, fluorocarbons and silicones have received much attention[1,7]. The organic esters studied generally had either low dielectric constants, showed poor dielectric strength or were either hydrolytically or thermally unstable. The esters which received the most attention were derived from either straight chain alcohols, e.g. butyl sebacate or mono-branched alcohols e.g. di(2-ethyl hexyl) phthalate (DOP). Esters from these type alcohols would be expected to have a lower hydrolytic stability in capacitor applications since a higher degree of branching in the alcohol is believed to improve hydrolytic stability[7e]. The fluorocarbons were generally more volatile and expensive than PCB's, and decomposition products are expected to be toxic. Silicones have the disadvantage of low dielectric constant and some deteriorate rapidly under electric arcing.

With these general considerations in mind, it is possible to focus on the myriad of possible ester types of polar dielectric liquids. As will be shown in the following sections, we believe the choice is limited to a few types of compounds, with special emphasis on esters from branched chain alcohols if one is to stay within the realm of readily available, stable and economically practical materials.

Experimental

The fluids used in this study were either experimental materials prepared in the laboratory or were supplied by the Exxon Chemical Company U.S.A. (see Table 2). The sample of PCB (42% Cl) was obtained from the Monsanto Chemical Company. In the preliminary screening studies, they were used as prepared or received (see Table 1A, 1B). In the later stages

of this investigation, the samples were carefully purified (see Table 1) and the preferred purification method will be described later.

A. Dielectric Measurements

The dielectric measurements were carried out in two types of cells. When evaluating liquids alone, a Balsbaugh cell, Type LRC-1 (manufactured by Balsbaugh Labs, South Hingham, Massachusetts and conforming with ASTM D150) was used, together with a GE built high voltage bridge (Direc Read Capacitance Bridge) capable of operating at up to 5000V. For the evaluation of the interaction of the liquids with capacitor-grade paper a glass cell having flat parallel platinum electrodes with cell constant 0.1 (manufactured by Beckman's Industrial Instrument Division as Cell A01) was used. This cell was supplied with a ground glass joint so that the liquid and paper could be sealed in the cell for the duration of any test. All dielectric measurements reported in subsequent sections represent the average of measurements on at least three different samples. Constant temperature of the cells was maintained in an oven into which dry nitrogen was circulated. The temperature in the oven could be controlled to within $\pm$ 1°C. The capacitor paper was always dried under vacuum at 90°C for at least 48 hours prior to impregnation with the liquids under study.

B. Physical Measurements

The physical properties of the fluids were determined according to ASTM methods unless stated otherwise. To evaluate the thermal stability of the fluids, a simple screening test procedure was developed. It consisted basically of an evaluation of the dielectric constant and loss factor at 25°C. Then, while still in the measuring cell, the samples were heated to 90°C. After two hours at 90°C, to reach thermal equilibrium,

dielectric properties of the fluid were determined. The system was allowed to cool to 25°C overnight. When thermal equilibrium at 25°C was reached, the dielectric properties were again measured. The data were evaluated according to the following criteria: The dielectric constant at 90°C had to be less than that at 25°C both before and after heating. The dielectric loss factor should not exceed 0.5 at 90°C and its value at 25°C should not change by more than a factor of two as a consequence of the heating cycle. As a rule, properly purified liquids were found to satisfy readily these requirements and their long term thermal stability was found to be quite satisfactory. The purification of these fluids is discussed in the following section.

C. Purification

Esters, particularly those used in electrical applications require purification if they are to maintain their chemical and physical integrity. Such purification involves the removal of trace moisture, unreacted alcohol and organic acids as well as half (acid) esters and possibly catalyst residues, since their presence could adversely affect the dielectric fluid's stability and performance. Examples of the effect of residual alcohol and moisture on conductivity are shown in Tables 3 and 4 respectively. The efficiency of any purification process is usually determined by conventional macro- and micro-analytical techniques. When dealing with fluids for use in electrical equipment such as capacitors, these conventional techniques prove to be insufficient and experience has shown that electrical measurements are a more sensitive means for evaluating the state of purity of such liquids.

Various purification methods were evaluated but eventually the method involving percolation of the ester through a packed column was selected as the most convenient and efficient. As packing material, activated

Attapulgus clay (30/60 mesh) proved most effective. Activation of the clay was achieved by heating it to 250°C for a minimum of 12 hrs while flowing nitrogen through the column. The gas inlet and outlet were connected to bubblers to prevent back mixing of moist air during the cooling period. The liquid esters were gravity fed through the clay bed at ambient temperature while maintaining a dry inert atmosphere. In general the first 5% of fluid coming through the column was recycled. A typical example of a run is shown in Table 5. No attempt was made to optimize flow conditions. In Table 2 are summarized the electrical and physical properties of the various purified phthalate esters used in this study.

Results

In order to obtain a general understanding of the interrelation between molecular structure and dielectric properties a significant number of mono and dibasic esters were examined. Their dielectric constants as well as conductivities are shown in Tables 1A and 1B. Within a group of esters it was noted that generally both the dielectric constant and the ac conductivity decreased with increasing molecular weight. Exceptions to this trend were found among the aliphatic dibasic acid esters, which may be due in part to impurities in the various ester. In selecting some potential candidates for use as electrical insulating oils, thought was given to availability of the material, its physical characteristics as well as such special properties as gassing tendency under high electrical stresses. Since it is well known that aromatic compounds perform better than aliphatic ones in this latter aspect and to assure availability at reasonable cost, the selection was narrowed to the phthalate esters shown in Table 3. Among these six esters, diisononyl phthalate was the most promising candidate in terms of overall properties. Diisononyl phthalate

is manufactured in the United States by the Exxon Chemical Company U.S.A., under the trade name ENJ-2065. It is made from phthalic anhydride and isononyl alcohol. Isononyl alcohol is a homologous mixture of branched isomeric alcohols. Diisononyl phthalate, ENJ-2065, was selected as the final candidate for a more thorough and exhaustive study on the basis that it has (1) an advantage in its loss characteristics relative to the lower molecular weight dihexyl and dioctyl phthalates, (2) a higher dielectric constant than the higher molecular weight phthalates, (3) a relatively high flash point, and (4) a more highly branched ester group than dihexyl and dioctyl phthalates to improve hydrolytic stability. The other physical and electrical properties of ENJ-2065 also offer a good balance of performance characteristics.

It is well known that electrical insulating fluids have to remain chemically unchanged when subjected to temperature cycles. For this reason it is desirable first to know what effect certain contaminants might have on the stability of the material, secondly how one could remove these contaminants and thirdly what protective additives might be useful in enhancing its stability. To provide answers to the first point the effect of adding small amounts of alcohol and water on the material's conductivity was evaluated. The results shown in Tables 3 and 4 respectively indicate that less than 0.1 wt % of alcohol and less than 0.01 wt % of water could probably be tolerated without adversely affecting performance. To obtain an answer to the second point it was decided to use a percolation technique to eliminate these contaminants as well as others such as residual catalyst. In Table 5 are shown the results of such a purification process using activated Attapulgus Clay. Under the conditions used, the column could handle about 22 to 23 gallons before the clay lost its activity and breakthrough of

conducting impurities occurred. In search for a solution of the third point, it was deemed expedient to take a look at the additives used with polychlorinated biphenyls[6]. In general, it was noted that epoxide type compounds were compatible with ENJ-2065 and indeed imparted beneficial effects to its long term performance.

In the next phase of the study, the gassing tendencies of ENJ-2065 were evaluated and the results are shown in Table 6. Although its gas absorption tendency was not as good as that of a typical PCB capacitor fluid, it was judged sufficient for the intended purposes.

The preliminary test results indicated the suitability of ENJ-2065 for use in capacitors. Its compatibility with other components forming a capacitor needed to be evaluated. In Table 7, a comparison is shown of a long term stability test run in the presence of regular capacitor paper. Over the test period of 600 hours, the dielectric loss decreased and was considerably below that of the PCB. The presence of aluminum or nickel foil did not show an adverse effect on the long term stability of ENJ-2065.

For an overall evaluation, six capacitors designed for a nominal 30 μfd, 370 VAC in PCB (42% Cl) were impregnated with ENJ-2065 containing 0.3 wt.% epoxide stabilizer. Conventional techniques were used to dry and impregnate the units. The results of these tests are shown in Table 8.

A substantial amount of safety evaluation has been carried out on diisononyl phthalate. A summary of these studies is presented in Appendix 1 and its implications are discussed later on.

Discussion

The results presented in the preceeding section indicate that ENJ-2065 possesses all the necessary characteristics of a capacitor impregnating fluid. Although its dielectric constant is not as high as

that of typical polychlorinated biphenyls (PCB), it is sufficiently high to be useful in capacitors designed for use with PCB's and has the advantage of being ecologically acceptable. It may be argued that some lower phthalate esters have high dielectric constants but at the same time their conductivities are higher and their thermal stability and flash points are lower than that of ENJ-2065. The branched structure of the ester group in ENJ-2065 provides an increased measure of hydrolytic stability for improved service life of paper wound capacitors. Thus, ENJ-2065 represents a dielectric fluid with the best overall balance of physical and electrical properties for capacitor applications.

Another important aspect involves the potential danger involved in disposing of this material. Although much has been written about the biodegradation of phthalate esters, only recently have studies been carried out on neat phthalate esters[5]. Saeger and Tucker evaluated the biodegradation of phthalate esters using (1) a semi-continuous activated sludge test, and (2) a River Die Away test. Comparisons were made to controls including a readily degraded surface active agent, LAS, and a poorly degradable insecticide, DDT.

The test results of Saeger and Tucker "clearly demonstrated that the phthalate esters and their intermediate degradation products are all rapidly degraded by readily available bacteria in our environment. For this reason, these compounds should not be classified as persistent materials but rather as a class of industrial chemicals which are easily recycled by natural biological processes".

Phthalate esters also have been the subject of considerable toxicology studies. In the period 1971-72 much concern was voiced regarding their occurrence in the environment and in bank blood. As a

result of this concern, the National Institute of Environmental Health Sciences sponsored a meeting in Pinehurst, North Carolina, on September 6-7, 1972. The information presented at the meeting showed that there is a vast difference in degree in the types of problems presented by phthalates as compared with those related to polychlorinated biphenyls[1].

At the Pinehurst meeting after hearing papers on such diverse aspects of environmental consequences as "...Phthalate Esters in Aerospace Technology", "...Toxicity via Ingestion", and "Toxicology in Aquatic Organisms", Mr. Lloyd Tepper, Associate Commissioner for Science of the FDA commented in his review that we are in a "...clearly preferable position (over PCB's and mercury which were found to be the source of overt disease) of having an etiology which is searching for a disease".

A similar symposium in March 1973[8] reaffirmed the Pinehurst conclusion that phthalates present no immediate hazard to the public health. Although there are no data to suggest imminent hazard, more work should be preformed to insure that there are no long term in-house effects. An FDA fish-sampling study recently completed[9] gives cause for further optimism that phthalates are not accumulating in the environment since only 20% of the fish sampled contained phthalates and those at such a low level that the FDA abandoned further fish sampling.

In summary, ENJ-2065 represents a dielectric fluid with the best overall balance of physical, electrical, toxicological and environmental properties to meet the current needs for capacitor applications.