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The effect of organic additives on the breakdown and gassing properties of mineral oils

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Abstract. The effect of organic additive content on the direct voltage breakdown strength of degassed transformer oil and liquid paraffin is reported for a wide range of concentration of additives known to be effective gassing inhibitors. Their effect on the breakdown strength of oils saturated with hydrogen, nitrogen and oxygen is also reported. Measurements of the gassing properties of the oils were carried out for the same extended range of additive concentrations. The observed breakdown and gassing versus concentration characteristics indicate the presence of maximum and minimum points at concentrations which are independent of the matrix liquid and of dissolved gas and gas phase. There is a remarkable degree of correlation between the breakdown and the gassing properties of the liquids tested. This and other relevant observations indicate that gas generation is an intrinsic part of the breakdown process and strongly support the bubble theory of breakdown. This forms the basis for the discussion of the results.

1. Introduction

Of the various factors that are known to affect the breakdown strength of insulating liquids, the influence of organic additives seems to have received least attention. A small number of workers (Zaky and Hawley 1973) have reported that weak concentrations of aromatic additives improve the electric strength of insulating oils and that there is an optimum additive concentration that results in a maximum increase in the breakdown strength. Recent work by the present authors (Evangelou et al 1973) has shown that the breakdown voltage varies with additive concentration in a complex manner. The characteristics obtained for a very wide range of additive concentrations indicated that there could be more than one optimum concentration. The present paper forms an extension of the preceding investigation and gives the experimental results of the effect of additive content on the breakdown strength of degassed mineral oils (transformer oil and liquid paraffin) and oils saturated with hydrogen, nitrogen and oxygen. The effect of the additives on the gassing properties of the oils with hydrogen, nitrogen and oxygen as gas phases has also been investigated. The choice of additives (naphthalene, tetralin and quinoline) was based on the fact that these have already been extensively used to determine their effect on the gassing properties of mineral oils (Nederbragt 1936, Clarke and Reynolds 1963).

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As far as the mechanism of electric breakdown of dielectric liquids is concerned, there is substantial experimental evidence in support of the theory that the breakdown process, particularly in the later stages, is governed by the presence of a gaseous phase (Tropper 1961, Krasucki 1966, Singh *et al* 1972). Some investigators have held the view that there is a correlation between the breakdown strength and the gassing properties of insulating liquids (Zaky and Hawley 1973). If such a correlation exists, then one should expect some parallelism between the breakdown voltage and the gassing properties of an oil as a function of additive concentration. This has been confirmed experimentally for a number of organic additives over a limited range of concentrations (Angerer 1965, Zaky and Megahed 1972). By considerably extending this range, the present results indicate a remarkable degree of correlation between the effect which an additive has on the breakdown and on the gassing properties of an insulating oil. These results provide direct experimental evidence that the breakdown of an insulating liquid is initiated and governed by a gaseous discharge inside gas bubbles formed in the liquid.

Although it is difficult to account for all the observed effects, it is possible, by drawing from relevant results of other workers in the field and with a reasonable amount of speculation, to provide a satisfactory qualitative explanation of the main features of the present results.

2. Experimental apparatus and procedure

The apparatus used to carry out the breakdown tests consisted of two completely closed and interconnected liquid and gas systems in which the test cell formed an integral part. The procedures adopted for cleaning the apparatus, preparation of the electrodes and the test samples were identical to those described by Angerer (1965). In the present case, however, $0.3 \mu m$ Millipore filters were used in the system. For experiments carried out on liquids with gases in solution the required gas was allowed to bubble slowly into the degassed liquid which then remained in contact with the gas at atmospheric pressure for 16 h before the sample was admitted into the test cell. The gas was drawn from a large settling tank lined with silicone grease to minimize the entrainment of particles; it was dried by passing through a 70 cm column of silica gel and then filtered.

The electrode arrangement in the test cell was horizontal. Spherical 5 mm diameter hard chrome plated and mechanically polished electrodes were used in all tests. A new set of electrodes was used after each breakdown run with a given liquid sample and for a given gap setting. Stabilized direct voltage and a diverter circuit were used in all tests. The test sample was prestressed for 2 h at about 60% of the expected breakdown voltage. After each breakdown the voltage was reduced to the prestressing value for one minute and then increased at a constant rate of about 10 kV min⁻¹. Each breakdown voltage reported was the mean of 20 breakdowns. The coefficient of variation for all breakdown measurements varied between 4 and 8%.

The gassing experiments were carried out on a second independent test rig in which the procedure for the preparation of the oil samples was identical to that used for the breakdown measurements. The gassing cell and the measuring technique have been described in detail elsewhere (Zaky and Megahed 1972).

The transformer oil used in the experiments was Shell Diala B oil complying with British Standard 148–1959. The density of the oil was 0.88 gm cm⁻³ and its chemical constituents were as follows: paraffin, 24.6%; naphthenic paraffin, 16.4%; aromatic naphthenics, 37.6%; aromatics 21.4%. The liquid paraffin used had a density of

0.83-0.87 gm cm⁻³. The dielectric constant of the liquid samples tested was measured and compared with that of the additive-free liquid. At the highest concentrations used naphthalene had no effect whereas quinoline and tetralin produced an increase of 7%.

3. Experimental results

3.1. Breakdown measurements

Figure 1 shows the relationship between additive concentration and breakdown voltage for degassed transformer oil at atmospheric pressure and a 200 μ m gap. With quinoline and tetralin as additives the concentrations corresponding to the maximum and minimum points of the characteristic were the same as those reported previously (Evangelou *et al* 1973) for degassed oil at a few Torr hydrostatic pressure and a 125 μ m gap. With



Figure 1. Breakdown voltage against additive concentration for degassed transformer oil: N, naphthalene; Q, quinoline; T, tetralin. 200 μ m gap, atmospheric pressure. The horizontal line indicates the breakdown voltage of plain oil.

naphthalene as additive, however, the characteristic showed a new peak and minimum at concentrations of 0.05 and 0.1 molar respectively. It was at first thought that the second peak was fortuitous. However, its presence was confirmed not only by repeating the experiment, but also by its appearance in tests carried out with oil samples having different gases in solution (figure 2). Since each experimental point was obtained with a new set of electrodes and a fresh liquid sample, any element of fortuity can be disregarded.

Figure 2 shows the effect of varying naphthalene concentrations on the breakdown voltage of degassed transformer oil and oil saturated with oxygen, nitrogen and hydrogen. The characteristics indicate that the maxima and minima in the breakdown voltage appear at the same concentrations whether the oil is degassed or gas-saturated and in the latter case irrespective of the kind of gas. The only curves which show an increase in breakdown voltage over the whole range of concentrations examined, when compared with additive-free oil, are those for degassed oil and for oil saturated with hydrogen. However, all the characteristics lie above that for the degassed oil; this was also found to be so with quinoline as additive (Evangelou *et al* 1973). It is apparent that for additive-free oil the most effective of the dissolved gases is oxygen and the least effective hydrogen.



Figure 2. Effect of dissolved gases on the breakdown voltage of transformer oil with varying concentrations of naphthalene: Dg, degassed oil. 200 μ m gap, atmospheric pressure. The horizontal lines indicate the breakdown voltage of plain gas-saturated oil samples.



Figure 3. Effect of dissolved gases on the breakdown strength of transformer oil with varying concentrations of tetralin. Test conditions same as for figure 2.

Figure 3 shows the effect of dissolved gases on the breakdown voltage of transformer oil with varying concentrations of tetralin. In this case all the characteristics lie above that for oil saturated with nitrogen. As with naphthalene, the best overall characteristics are also those for degassed oil and oil saturated with hydrogen. It is interesting to note that in the latter case the increase in the breakdown voltage is almost independent of the additive concentration. With oxygen in solution the presence of the maximum and minimum points in the characteristics are brought sharply into focus.

With oxygen in solution it was found that for all the additives used, a small additive



Figure 4. Effect of small quinoline concentrations on the breakdown voltage of transformer oil saturated with oxygen. Test conditions same as for figure 2.

concentration lowered the breakdown strength of the oil to values below that of the additive-free oil. This was especially pronounced in the case of quinoline (Evangelou *et al* 1973). The low breakdown values obtained at concentrations less than 0.1 molar indicated that the breakdown voltage would have to rise by about 2 kV as the molar concentration dropped from 0.025 to zero. Breakdown tests on samples with very low quinoline concentrations have confirmed this; the continuous curve in figure 4 shows that with decreasing concentrations the breakdown voltage increases and tends asymptotically to that of plain oxygen-saturated oil.



Figure 5. Breakdown voltage against additive concentration for degassed liquid paraffin: N, naphthalene; Q, quinoline; T, tetralin. 125 μ m gap, a few Torr hydrostatic pressure. The horizontal line indicates the breakdown voltage of plain oil.

Figure 5 shows the relationship between additive concentration and breakdown voltage for degassed liquid paraffin at a few Torr hydrostatic pressure and a 125 μ m gap. All the characteristics show the same trend as that reported earlier for transformer oil under identical test conditions. For a specific additive the concentrations at which the maxima and minima appear in the characteristics are the same as in the case of transformer oil.

Figure 6 shows the effect of dissolved gases on the breakdown voltage of liquid paraffin with varying concentrations of tetralin. Again the general trend of the character-

istics is the same as in the case of transformer oil under similar conditions (figure 3). However, for liquid paraffin the maxima and minima are well defined for all the four cases examined.

For a 125 μ m gap the breakdown voltages of degassed oils were found to be independent of the hydrostatic pressure. It may thus be inferred that although with gases in solution the breakdown strength may be pressure dependent, the concentrations at which the breakdown maxima and minima occur are independent of pressure. Except for the additional peak observed with naphthalene, these concentrations are also independent of the gap.



Figure 6. Effect of dissolved gases on the breakdown voltage of liquid paraffin with varying concentrations of tetralin. Test conditions same as for figure 2.

3.2. Gassing measurements

Additive-free transformer oil and liquid paraffin, as well as pure quinoline and tetralin, were gas-evolving under hydrogen and nitrogen and gas-absorbing under oxygen. In general the presence of additives reduced gas evolution under hydrogen and increased gas absorption under oxygen; under hydrogen the characteristics changed with time from gas evolving to gas-absorbing. However, in all cases the shape of the gassing versus concentration characteristics were independent of the gassing time. Of the numerous gassing characteristics obtained we are giving only a few which are representative of the general trend shown by all of them.

Figure 7 gives the gas evolution/absorption versus tetralin concentration characteristics for transformer oil under different gas phases and a maximum stress of 60 kV cm⁻¹. As in the case of breakdown, the characteristics pass through minima and maxima points at certain concentrations. The fact that the same additive concentration which gives a maximum in the breakdown characteristics gives a minimum in the gassing characteristics and vice versa indicates a very strong correlation between breakdown strength and gassing properties.

Figure 8 shows the gassing versus concentration characteristics for transformer oil with different concentrations of quinoline and oxygen as the gas phase for three different



Figure 7. Gassing against tetralin concentration for transformer oil under various gas phases and a stress of 60 kV cm⁻¹.



Figure 8. Gassing and breakdown voltage against additive concentration characteristics for transformer oil with quinoline under oxygen. A, 64 kV cm^{-1} ; B, 44 kV cm^{-1} ; C, 36 kV cm^{-1} ; --- breakdown characteristic for oil saturated with oxygen; ... breakdown characteristic for degassed oil.

stresses. The breakdown characteristics obtained from earlier experiments are also shown on the same figure. Here again the parallelism between gassing and breakdown is evident.

4. Discussion

The complex character of the variations of the electrical strength and gassing properties of mineral oil with aromatic additive content shows that there is no simple correlation between the chemical constitution of the liquid and these properties. However, the strong correlation between breakdown and gassing, revealed by the additives, provides direct evidence that the breakdown of an insulating liquid is initiated and governed to a large extent by a gaseous discharge inside gas bubbles. This will serve as a basis for the present discussion.

A number of results indicate that the aromatics present in the transformer oil tested are not effective gassing inhibitors. These results are: (a) there is no significant difference between the breakdown strength of transformer oil and of liquid paraffin either when degassed or with gases in solution; (b) saturating either of these liquids with hydrogen produces no significant difference in the breakdown strength compared to that of the degassed liquids; and (c) the variation of breakdown strength with additive concentration is similar for both liquids. This last result indicates that the action of the additive is independent of the matrix liquid. Result (b), as well as the increased strength with dissolved nitrogen, suggests that the process of bubble formation per se does not necessarily lead to breakdown. Although bubbles may form more readily and at lower stresses in a gas-saturated liquid, such bubbles are likely to be expelled from the high-field regions, either by electrostatic forces or by electrohydrodynamic motion of the liquid, before conditions in the gap are ripe for the initiation of a gaseous discharge inside a bubble.

4.1. Effect of bubbles on the breakdown process

The fact that the maximum and minimum points on the breakdown versus additive concentration characteristics are apparently independent of the gap, indicates that the additive effect is not a bulk liquid one but is principally determined by conditions in the vicinity of one of the electrodes. Because of the inevitable build-up of space charges the gap will be non-uniformly stressed. Positive and negative space charges will enhance the fields in the cathode and anode regions respectively: it is therefore more likely that a discharge will be initiated inside a bubble formed in one of those regions rather than in a bubble formed in the bulk liquid. The region in the vicinity of the cathode is considered to be the most favourable one. Evidence in support of this is available from various sources. The phenomena of luminescence and electroluminescence in insulating liquids is closely related to the appearance of bubbles and bubble spraying (Singh et al 1972, Takahashi and Ohtsuka 1975). There is evidence that electroluminescence is produced by excited molecules and that the excitation is electronic in nature (Darveniza 1963); the fact that electroluminescence always appears first at the cathode region irrespective of the electrode geometry (Smith et al 1966, Kao and Rashwan 1974) indicates that this region is rich in energetic electrons which have the cathode as source. The results of Croxford (1973) on the electric strength of plastic films having punched holes and impregnated with mineral oil with varying concentrations of trichlorodiphenyl showed that the impulse strength of the composite was strongly sensitive to the additive content only for those specimens containing holes adjacent to the negative electrode.

The phases leading up to breakdown may be outlined as follows: (a) the formation of gaseous hydrogen bubbles in the vicinity of the cathode; (b) the initiation of a discharge inside a bubble; (c) the growth of this bubble and its development into a gas channel; and (d) the propagation of the gaseous channel. The onset of the first two phases need not necessarily lead to breakdown but they constitute a necessary prelude to it. Once a discharge has been initiated inside a bubble, its growth will be determined by conditions at the interface between the bubble, which represents the gas phase, and the liquid. Phase (c) is thus governed by the gassing properties of the liquid and will therefore be

strongly dependent on additive concentration. Phase (d) will determine the ultimate breakdown strength. The transition from phase (c) to phase (d) will depend on the field in the bulk liquid; if it is not propitious for the propagation of the gaseous channel, the bubble may disintegrate into several smaller ones (Schmidt 1960).

All the above four phases will be influenced by the presence of space charges. The presence of a positive space charge at the cathode will aid phases (a), (b) and (c), whereas the presence of space charges at both electrodes will oppose phase (d) by reducing the field in the bulk liquid and thus inhibiting the extension of the gas channel across the gap. These two contrary actions of the space charges may minimize their overall effect so that the influence of the additives will predominate.

4.2. Effect of dissolved gases

Taking the breakdown strength of the additive-free oils as reference, the relative increases in strength for intermediate additive concentrations indicate that the additives are more effective in degassed oils and oils saturated with hydrogen than in oils saturated with oxygen or nitrogen. In the case of degassed oil and oil saturated with hydrogen the gas-inhibiting properties of the additive can be fully exploited due to the absence of any other sources of electron energy absorption. The electronegativity of the oxygen and the pulse quenching properties of nitrogen (Nosseir 1975), by raising the strength of the oil, reduce the effectiveness of the additive.

All the results indicate that for oils saturated with oxygen the presence of very small concentrations of additives produces a marked decrease in the breakdown strength (figure 4). This may be explained as follows. Both the additive and the oxygen act as electron scavengers $(X + e^- = X^-)$ and this process leads to a build-up of negative space charges at the anode. Space charge measurements by Forster (1967) have shown that for unsaturated hydrocarbons there always was an excess negative charge in the vicinity of the anode. Such space charges will intensify the local anode field and give rise to ionization of the liquid with a feedback of positive ions to the cathode (Swan and Lewis 1961). At the cathode we will have the following competing reactions:

$$RH_{2}^{+} + X^{-} = RH_{2}X \tag{1}$$

$$\mathbf{R}\mathbf{H}_{2}^{+} + \mathbf{e}^{-} = \mathbf{R}\mathbf{H} \cdot + \mathbf{H}.$$

$$RH_{2}^{+} + e^{-} = R \cdot + H_{2}.$$
(3)

At low additive concentrations reactions (2) and (3) predominate and these will facilitate the formation of a gaseous phase at the cathode. As the additive concentration increases not only will reaction (1) become more effective, but the additive will react with atomic hydrogen to produce stable nonvolatile molecules plus some stable free radical of low energy content. This should lead to a rise in the breakdown strength.

The experimental result that the additive concentrations corresponding to the maxima and minima in the breakdown characteristics are independent of the dissolved gas, strongly suggests that the gas phase associated with the bubble mechanism is hydrogen.

4.3. Effect of aromatic additives as gassing inhibitors

All the available data on the composition of the gases formed (evolved or dissolved in the oil) when an electric discharge is initiated above the surface of insulating oils indicate that hydrogen is the predominant gaseous product (Davies 1971, Zaky and Megahed 1972). Because the process $2H \rightarrow H_2 + 104$ kcal is highly exothermic, it is impossible

for two hydrogen atoms to recombine to form a diatomic molecule unless at the instant of recombination the excess energy is removed in a ternary collision between the atoms and a third body. This termolecular recombination process may be sufficient to cause excitation and dissociation or internal conversion of the third body, in this case a hydrocarbon molecule at the gas liquid interface of the gaseous phase (bubble). Now whereas energized alkane molecules appear to decompose very readily, energized aromatic molecules are very enduring. With mineral oil we are dealing with a mixture of more than one chemical species. In such a mixture both excitation transfer and ionization transfer may occur simultaneously (Manion and Burton 1952). In these processes ionization or excitation is transferred with a high probability from a molecule of higher ionization or excitation energy (A) to one of lower (B): $A^{\ddagger}+B=A+B^{\ddagger}$, where A^{\ddagger} and B^{\ddagger} represent both ions and excited molecules.

In accordance with the above charge or energy transfer mechanism, it would appear that the aromatic additive molecules are particularly effective in the dissipation of available energy and thus act as protectors or gassing inhibitors. The effectiveness of an additive may be due partly to its large cross-section for charge transfer and partly to the low energy of the deepest-lying triplet states. In the particular case of unsaturated molecules the low-lying triplet states are stable and the energy may thus readily be dissipated through normal quenching processes without decomposition. One must bear in mind that the presence of the additive will also introduce secondary effects involving reaction between one component (oil or gas) and free radicals produced from the second component (additive) or vice versa. Thus the free radicals produced from the oil will react with the additive giving rise to new compounds soluble in the oil whilst nascent hydrogen may hydrogenate the additive.

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