CIGRE STUDY COMMITTEE NO. 15

Working Group SC 15/WG 02

"Askarels"

Minutes of Meeting held at KEMA in Arnhem, Holland, on 2 June 1971

PRESENT:

Mlle. B. Bouvier	France
Mr. P.L. Boyer	Switzerland
Mr. C.A. Bozzini	Belgium
Mr. C.R. Coleman	UK (Secretary)
Dr. T.W. Dakin	USA
Mme. B. Fallou	France
Mr. R. Fourme	France
Mr. G.A. Gertsch	Switzerland
Mr. G. Groslambert	Belgium
Mr. P. Jay	France
Dr. E. Knust	Germany
Mr. Z. Krasucki	UK
Prof. T. Leardini	Italy
Mr. A. Matsuoka	Japan
Mr. G. Martin-Vallas	France
Dr. R. Muller	Germany
Mr. H.O. Nerf	Sweden
Mr. A. Rein	Norway
Mr. E.H. Reynolds	UK (Chairman)
Mr. J. Schober	Switzerland
Mr. E. Serena	Italy
Mr. N. Shito	Japan
Dr. R. Syderius	Netherlands
Mr. K. Tangen	Norway
Mr. Trubacher	USSR
Dr. J. Vermeer	Netherlands
Mr. L.T.G. Virsberg	Sweden
Dr. R. Wilputte	Belgium

The Chairman opened the meeting and welcomed the delegates.

The Chairman requested that he be notified of any corrections to the membership list which he had circulated.

Titles and official reference numbers of documents circulated to delegates are listed in the Appendix to these Minutes.

The Chairman said that Professor Beyer had, after the previous meeting, forwarded a copy of the thesis of a member of his staff. Due to the length of this document and its specialist appeal, the Chairman had thought that it would not be apt to issue it generally, but copies could be supplied to those who requested them. In addition, a precis had been prepared by a member of his staff and a few copies of this were available on request.

1. MINUTES

The Minutes of the 5th Meeting held in Paris on 29 August 1970 were approved.

The Chairman thanked Mr. Bozzini for carrying out the welcome task of translating the Minutes into French.

2. ASKARELS (CHLORINATED DIPHENYLS)

Mr. Jay presented his paper 15-71 (WG-02) Jay-1 on "A new blend of chlorinated biphenyls for the impregnation of polypropylene and mixed dielectric capacitors". The new liquid, referred to as Pyralene 2000, was specially developed for the impregnation of polypropylene film and polypropylene/paper capacitor dielectrics. Pyralene 2000 does not crystallize at any temperature, has the same chlorine content as di-chlorobiphenyl, has the same permittivity as trichlorobiphenyl (TCB), is less viscous than TCB but its vapour pressure is higher than that of TCB. Wettability and penetrability characteristics of Pyralene 2000 with respect to polypropylene are better than those of TCB. No deleterious effects in mechanical properties of polypropylene film were observed after immersion in Pyralene 2000 at 100°C for 5 hours. Life tests carried out on experimental polypropylene/paper capacitors (dielectric: 2 x 12 μm Maurylene, 10 μm paper, impregnated with Pyralene 2000) at 1980 V (ie 56.5 V/μm) and at 90°C showed that no breakdowns occurred due to thermal instability. The dissipation factor at 90°C, 1300 V, after ageing for 700 hours was slightly higher for Pyralene 2000 capacitors ($\tan \delta = 0.00059$) than for TCB impregnated capacitors ($\tan \delta = 0.00051$). D.C. breakdown tests carried out on 30 Pyralene 2000 - impregnated polypropylene film (single thickness of 12 μm Maurylene) capacitors showed that the average breakdown voltage was 4.42 kV. The corresponding voltage for 30 TCB - impregnated capacitors was 3.92 kV.

In answer to questions Mr. Jay said:

Pyralene 2000 cannot be regarded as incombustible but the same applies even to TCB.

Mixed polypropylene/paper capacitors impregnated with Pyralene 2000 and with TCB both had the discharge inception voltage of 2800 V.

The width of polypropylene film used for making the experimental capacitors was 60 mm and the diameter of the windings was 30-32 mm.

Pyralene 2000 is similar to Aroclor 1232 except that its permittivity is the same as that of TCB and its wettability characteristics for polypropylene are better.

Pyralene 2000 passes the ASTM stability test.

Additives used for improving wettability characteristics of Pyralene 2000 are not removed by Fuller's earth treatment.

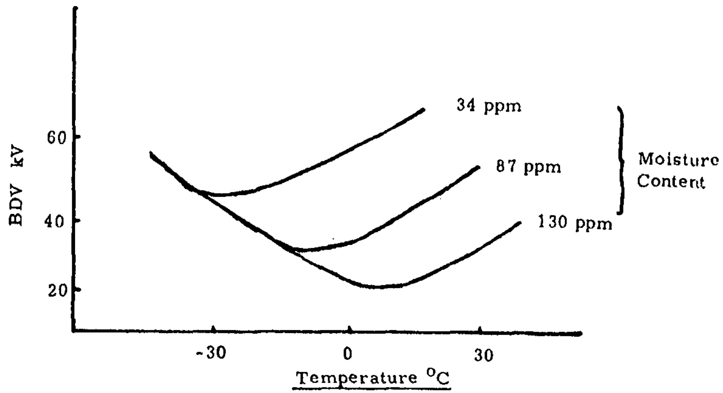
Effects due to ionizable impurities are more pronounced in Pyralene 2000 than in TCB for reasons of lower viscosity. At low measuring stresses tan δ of Pyralene 2000 impregnated capacitors may be higher by a factor of 5 than that of TCB - impregnated capacitors.

A patent has been taken out for Pyralene 2000 but there should be no problems in using the liquid in any part of the world.

When Pyralene 2000 is used in conventional impregnation plants, the impregnation temperature should be lowered and vapour traps should be used.

It is not known whether the lower chlorine content in Pyralene 2000 will make it more acceptable as the impregnant from the pollution point of view.

Mr. Matsuoka summarized the document 15-70 (WG-02) Nakamuta-1 on "The effect of water and temperature on the breakdown strength of different types of askarels" by A. Matsuoka and E. Namekawa. He also presented additional information on the dependence of breakdown strength of Kanechlor 1100 containing 34 ppm, 87 ppm and 130 ppm of moisture on temperature between -45°C and 40°C (approx.). The dependences obtained are illustrated in the following figure.



Dependence of breakdown voltage of K 1100 on temperature.
Electrode gap = 2.5 mm. Pour point = -45°C.

Mr. Jay asked for an explanation for the unexpected increase of breakdown voltage with decreasing temperature at low temperatures. Dr. Nakamuta will give a reply in writing.

Mr. Schober said that one must distinguish between saturation equilibrium and constant partial pressure of humidity in air above the liquid, since solubility decreases with increasing temperature. Dr. Nakamuta will supply further details about the experimental conditions used.

Mr. Krasucki asked on what basis the formula $V_{2.5} = V_{1.5} + 22$ (kV) was derived and whether its validity was checked over the whole range of conditions (nature of askarel, temperature, humidity, etc.) used in experiments reported in 15-70 (WG-02) Nakamuta-1. Mr. Matsuoka will provide a written justification for the formula.

Dr. Dakin commented that there is a certain similarity between the reported dependences of breakdown voltage on temperature and dependences of corona threshold voltage in capacitors on temperature.

Mr. Fournie summarizing his paper 15-70 (WG-02) Fournie-1 said that the paper was theoretical and dealt with dissociation of ions in askarels.

If B = askarel

$A = I_2$, $SbCl_5$, etc.

then $B \xrightarrow{e} A$ leads to $\left[A^- B^+\right]$, which can dissociate in an askarel.

In an askarel

$$A_rI_2 \rightleftarrows A_r^+ + I_2^-$$

with the equilibrium constant $K = \dfrac{\left[Ar^+\right]\left[I_2^-\right]}{\left[ArI_2\right]}$

In an electric field $K = K(E)$.

Presence of ionic space charges can be studied using the Kerr effect.

Dr. Dakin commented that it has been established by Onsager and others that a high degree of dissociation is possible in low permittivity liquids when one of the ions is of large diameter (eg., ammonium ions).

Mr. Krasucki, referring to the views expressed at the IEE Conference held at Lancaster in 1970, questioned the validity of the assumption that significant field emission occurs at fields above 200 kV/cm.

Replying Mr. Fournie said that the first part of the paper is a literature survey and does not represent his own views.

Mr. Reynolds stressed the effects of space-charge phenomena in liquid-solid insulation for high voltage d.c. systems. Mr. Fournie said that the study of space charges in impregnated paper is much more difficult than in pure liquids.

3. DIELECTRIC LIQUIDS OF HIGH PERMITTIVITY OTHER THAN CHLORINATED HYDROCARBONS

Mr. Krasucki summarized his paper (15-71 (WG-02) Krasucki-1) on "High permittivity liquids as capacitor impregnants". The data available indicate that the impulse electric strength of high permittivity liquids, eg., nitrobenzene (ε = 34.8), is of the order of 1 MV/cm and, therefore, from their strength point of view, the liquids must be regarded as adequate as impregnants for capacitor dielectrics. The main advantage of using high permittivity impregnants is the lowering of stress concentration of the edges of electrode foils with the consequent expected increase in the discharge inception stress. These advantages are offset in paper capacitors by the existence of regions in the dielectric where the paper may be subjected to considerable overstressing. No similar overstressing is expected in polypropylene film capacitors impregnated with highly polar liquids. With mixed polypropylene/ paper capacitors high local stressing at thin spots in the paper will be much less than in the all paper system.

Mr. Martin, referring to Fig. 3 of the paper, questioned the method used for measuring the distribution of thicknesses in capacitor tissue paper and commented that Hg electrode test indicates presence of holes rather than that of very thin places in paper. Replying, Mr. Krasucki said that the method used for measuring thicknesses had been described and discussed in CIGRE paper No. 112, 1966. He also said that results presented in Fig. 3 did not refer to capacitor tissue paper of current production.

Mme. Fallou commented on the importance of dissolved gases in breakdown strength measurements and said that the effects may be greater in high permittivity liquids. Mr. Krasucki explained that the gas content in liquids referred to in Fig. 1 was not known.

Mr. Jay said that to achieve satisfactory levels of tan δ when nitrobenzene is used as an impregnant, constant purification of the liquid must be employed. Some tests carried out with nitrodiphenyl showed that at $100^{\circ}C$ its tan δ was increasing rapidly with time. It is also important to have a high degree of chemical stability as an impregnant for capacitor dielectrics.

Mr. Boyer presented his document 15-71 (WG-02) Boyer-1. Liquids of permittivity higher than 7 tend to have poor tan δ characteristics and the increase in capacitance resulting from their use as capacitor impregnants is negligible. From the point of view of capacitor development, and especially when plastic film dielectrics are considered, the factors of primary importance are wettability of the films and of Al foils by the impregnant, swelling of the films caused by the impregnant, and satisfactory control of winding conditions.

Mr. Reynolds said that in choosing the impregnant one must optimize the capacitance increase, discharge inception voltage increase and ensure that capacitor characteristics remain satisfactory under temperature cycling conditions. During manufacture of capacitors, the winding tension must be kept constant. Swelling has been studied for polypropylene-paper laminates in oils for cables. Maximum amount of swelling occurs with liquids whose structure is similar to that of the polymer.

Mr. Reynolds gave an account of their work, carried out between 1949 and 1960 and also recently on high permittivity liquid impregnants. The following classes of liquids were considered:

(i) Polyglycols (ε = 9 to 12)

Liquids were purified by fractional distillation and percolation through alumina. With methoxy-polyethylene glycol 350 (ε = 12), the attainable resistivity was 2×10^{10} ohm-cm (20°C) and tan δ of capacitors impregnated with the liquid was about 0.25.

(ii) Amines (ε = 2.5 to 5.4)

The best results obtained with diethylaniline (ε = 5.4) were: resistivity = 5×10^{11} ohm-cm and tan δ = 0.2.

(iii) Specially synthesized fluorocarbons (ε = 4.5 to 9.6 and higher)

None of the liquids considered can compete with chlorinated diphenyls in metal foil-plastic systems. A summarizing document, 15-71 (WG-02) Reynolds-1 would be circulated.

Mr. Jay described his studies on aryl-alkyd-sulphone, which is a viscous liquid with permittivity of 20 to 22. The liquid was considered as a possible impregnant of paper energy storage capacitors. It was found that even with a very thorough purification of the impregnant (zone-melting), tan δ of the capacitors increases and their IR decreases during heating at 80°C. A drift in electrical properties is observed even in a 10 per cent solution of sulphone in trichlorodiphenyl. When used in metallized capacitors, the liquid improves the self-heating properties.

Mr. Bozzini said that sulphones are used by Westinghouse for impregnation of the inexpensive capacitors for the air conditioning systems. The dielectric is low-density paper. The permittivity of the dielectric decreases with increasing temperature.

Referring to castor oil, Mr. Reynolds said that the liquid is mainly used for impregnation of high voltage (up to 100 kV) energy storage capacitors. The solid dielectric is high density paper. Castor oil is not particularly attractive for impregnation of polyolefin film capacitors.

4. COMPATIBILITY

Mr. Reynolds summarized his document (15-71 (WG-02) Reynolds-4) on "Compatibility of polypropylene with Askarels" by K.W. Plessner. The document describes a novel method where compatibility is studied by measuring tan δ of the polypropylene film after it has absorbed the askarel from the vapour phase.

Replying to questions asked by Mr. Krasucki, Mr. Reynolds said that absorption of askarel vapour in polypropylene film is completed within 48 hours and that the dependence of low-stress tan δ on temperature has not yet been studied.

Mr. Jay asked whether the reported difference between loss angles of films A and B could not have been due to differences in the swelling characteristics of the films. Mr. Reynolds explained that the method has been primarily developed to provide a quick screening test for different makes of polypropylene film and a detailed analysis of the results obtained has not so far been made.

The Chairman invited comments on the question of as to whether compatibility is still to be regarded as an outstanding problem. Mr. Boyer expressed the view that compatibility was no longer a problem and that the main causes of failure were faults in the technology of manufacture of askarel-impregnated polypropylene film capacitors. Mr. Fournie agreed that handling of materials during manufacture of capacitors was the main cause of failures.

The Chairman then asked whether any experiences could be reported with pure polypropylene film capacitors. Mr. Krasucki said that work being done at the ERA was directed towards establishing conditions under which satisfactory discharge inception stress characteristics can be attained in trichlorodiphenyl-impregnated polypropylene film capacitors. The results obtained showed that capacitors made with 6 inch wide film were at least as good as those made earlier with 1 inch wide film and discussed in CIGRE paper No. 15-01, 1970.

5. STABILIZATION

The proprietary nature of information relating to the use of stabilizers in askarel-impregnated capacitors made it impossible for the subject to be discussed at the meeting and the Chairman ruled that the subject will not be raised in the future unless specific requests to the contrary are made by the delegates.

6. IEC 10B

Referring to test cells used for measuring tan δ of askarels, Mr. Schober said that in any recommended method, account should be

In view of the fact that test cells used for measuring mineral oils may be unsuitable for askarels, Mr. Reynolds asked the delegates to communicate to him their views on the best cell and method to be used for measuring tan δ of askarels. He also said that after the IEC 10B meeting he will circulate to the delegates a document on the subject of test cells.

7. PRECAUTIONS

Professor Leardini suggested that an article on the subject of hazards relating to the use of askarels should be written and published, for example, in the CIGRE journal Electra.

Mr. Reynolds agreed on the desirability of such a publication and asked the delegates to submit to him any documents which they might have on precautions to be used when handling askarels and on national rules concerning askarels.

8. DATE OF NEXT MEETING

The next meeting of the "Askarels" Working Group will be held in August 1972 in Paris.

APPENDIX

List of Working Documents Circulated

1. 15-71 (WG-02) JAY-1 on "A New Blend of Chlorinated Biphenyls for the Impregnation of Polypropylene and Mixed Dielectric Capacitors".

2. 15-71 (WG-02) KRASUCKI-1 on "High Permittivity Liquids as Capacitor Impregnants".

3. 15-71 (WG-02) BOYER-1.

4. 15-71 (WG-02) NAKAMUTA-1 on "High Temperature Performance of Askarel".

5. 15-71 (WG-02) VIRSBERG-1.

6. 15-71 (WG-02) REYNOLDS-1 (in preparation).

CIGRE

WORKING GROUP SC. 15/WG-02

REPLACEMENT OF AROCLOR AS A CAPACITOR IMPREGNANT

1.0 INTRODUCTION

There have been several occasions in the past, when a search was made for Askarel substitutes. The reasons were varied - a belief that Askarels were insufficiently stable, high cost, poor performance in energy storage capacitors and their toxicity. Recent signs that Askarels have found their way into the environment and the stricter controls over pollution have prompted a renewed search for substitutes. This report summarizes the findings of past work in BICC and suggests new liquids for investigation.

2.0 LIQUIDS INVESTIGATED

Certain amines and some polyglycols were examined for a.c. applications, while work on both natural and synthetic esters was done in connection with energy storage capacitors. Fluorocarbons were studied by a member of the staff seconded to Birmingham University. More recently, an ester, a silicone fluid and liquid paraffin have been used to impregnate plastic film capacitors, some of them with vacuum metallized electrodes in place of solid aluminium foils.

2.1 Polyglycols

These had permittivities in the range 9 to 12 and it is not surprising that the difficulties in obtaining low conductivity were formidable. The best result obtained by vacuum distillation of triethylene glycol dimethyl ether, of permittivity 9.0, was a conductivity of 3.10^{-8} (ohm.cm)$^{-1}$. Rather better values resulted from purification of certain commercial polyglycols in a column of active alumina. A condensate of methoxy polyethylene glycol 350 with di-isocyanate was treated in this way and gave a conductivity of 5.10^{-11} (ohm.cm)$^{-1}$ in spite of a K as high as 12.

When small paper windings were impregnated with this liquid, a tan δ of 0.23 was measured at 50 Hz, a value much greater than expected from the parameters of the paper and liquid separately. It was ascertained that the polyglycol leached impurities out of the paper, so increasing its conductivity.

2.2 Amines

Although the amines investigated did not have such high permittivities, the highest value being 5.4, similar difficulties of purification were encountered. Diethyl aniline was purified by first distilling it and then passing it down an alumina column. A conductivity of 2.10^{-12} $(ohm.cm)^{-1}$ was achieved. On impregnating a paper winding, however, the tan δ value was again of the order of 0.2. An amine with lower permittivity (4.5) ethyl benzyl aniline gave a lower conductivity (4.10^{-13} $(ohm.cm)^{-1}$) and impregnated capacitors showed a tan δ of 0.010. The loss tangent, however, increased with applied stress.

2.3 Fluoro-dielectrics

Most of the work concerned the preparation of compounds with a permittivity between 5 and 7, the aim being a liquid with greater stability than Askarel. The most promising compound was trifluoromethyl diphenyl, whose loss tangent could be effectively reduced by treatment with alumina. The work was, however, discontinued at a rather early stage. The cost of fluoro compounds is bound to remain several times that of chlorinated compounds.

2.4 Natural Esters

Castor oil has been used very successfully in energy storage capacitors, where resistance to partial discharges is a prime requirement. Its use at 50 Hz stresses is normally prohibited by excessive losses and therefore it is not known how it would perform in a.c. power capacitors.

The only other natural ester, which has been tried in energy storage capacitors, is Tung oil. Its performance, in terms of the number of capacitor discharges from a given stress before failure, was decidedly inferior to castor oil.

2.5 Synthetic Esters

Both di-octyl phthalate (strictly, di-ethyl hexyl phthalate) and di-octyl sebacate were compared with castor oil in energy storage capacitors. The former emerged well, giving a very similar performance, while the latter gave considerably shorter lives. The conductivity of these liquids was reduced to about the same level as that of castor oil, i.e. about 10^{-13} $(\mathrm{ohm.cm})^{-1}$, which is adequate for energy storage but not for a.c. capacitors.

Di-iso-octyl phthalate was purified to a higher degree, using active alumina, such that its conductivity and loss tangent at 100°C fell within the specification for capacitor Askarel. It was found, however, that paper capacitors impregnated with this liquid had rather high losses at elevated temperature, even at working stress. An accelerated life-test on a.c. duty ended in premature failures, compared with Askarel capacitors, probably because of the high dielectric losses.

DiOP was also used to impregnate metallized polypropylene film capacitors. These performed well for many thousands of hours, but the stress used at the time this work was done would now be regarded as rather modest (about 30 MV/m).

Di-nonyl sebacate was purified sufficiently to lead to acceptable loss tangents in polypropylene film capacitors impregnated with this liquid. The capacitors were put in accelerated a.c. life-test, but did not perform well.

2.6 Silicone Fluid and Liquid Paraffin

Both these liquids have been used with polypropylene film capacitors, but their performance was inferior to that of Askarel. The use of silicone in a metallized film capacitor was more successful, although, again, the stress used was modest.

3.0 SPECIFICATION FOR AN IMPREGNANT

It is not difficult to enumerate the desirable properties, in addition to non-toxicity, of a potential impregnant. Even though both paper and film capacitors are involved, and though it might be thought difficult to use the same impregnant for a.c. and for energy storage capacitors, there is no conflict here.

The permittivity should be between 5 and 7. In paper capacitors a high K is desirable to make full use of the permittivity of the cellulose, while in film capacitors the reason lies in the stress in the liquid being lower for a high K. ERA work has shown that this tends to lead to a higher discharge inception stress. Values beyond 7 or 8 are bound to entail great difficulties in achieving and maintaining high purity as exemplified by the reference to the work on polyglycols.

The conductivity must obviously be low enough to avoid an appreciable contribution to the capacitor losses, even at elevated temperature. This requirement is more severe in paper capacitors, because of the larger volume fraction occupied by liquid, in addition to complications introduced by residual "impurities" in the paper (or film). Even though these solid dielectric components have been purified so as to be free of substances that contaminate Askarel, they may contain other substances that will dissolve in other impregnants with possibly very different solvent properties.

The liquid must withstand the effects of internal discharges without generating too much gas or breaking down into highly corrosive products, although additives may, of course, exist to render such products innocuous.

The viscosity must be low enough to allow impregnation and re-impregnation after temperature excursions. The vapour pressure must be low enough to avoid excessive distillation during processing.

The following is a list of the desirable attributes of an impregnant:

Permittivity	5 - 7
Low loss tangent	$\ngtr$ 0.005 at 90°C.
Gas absorbing	
Decomposition products due to discharges harmless or easily rendered so by an additive.	
Thermally stable (in vacuo) up to 150°C.	
Pour point	less than -20°C
Boiling point	greater than 250°C.
Vapour pressure at 20°C less than about 1 N/m^2.	
Swelling of polypropylene at 60°C less than 10% (vol).	

4.0 POSSIBLE CANDIDATES

It would be an impossible task to list all the liquids which satisfy the more easily ascertained of the above requirements, i.e. permittivity, melting and boiling points. Nevertheless, a survey of liquids with suitable permittivities listed in the 1951 NBS

"Table of Dielectric Constants of Pure Liquids" and in the annual digests of literature on dielectrics (NAS-NRC) between 1956 and 1968 has been made. The range was narrowed down by ruling out halogenated compounds as potentially toxic, amines as having been explored previously, alcohols as being too hygroscopic, and phenols as probably too conducting. This left a large number of esters, a ketone and polypropylene oxide.

The well known rule that straight-chain hydrocarbons tend to be gas-evolving, while aromatic compounds tend to be gas-absorbing, helped to eliminate sebacates, succinates, etc. as well as polypropylene oxide. A few liquids were also ruled out because of high cost.

The following table shows the liquids remaining:

Liquid	K	M. Pt. °C	B. Pt. °C
Benzyl acetate	5.1	- 51	215
Ethyl phenyl acetate	5.2	- 31	232
Glycerol triacetate	7.1	< - 40	260
Ethyl benzoate	6.0	- 34	213
Benzyl benzoate	4.9	18.5	324
Iso-amyl benzoate	5.0		262
n-butyl benzoate	5.1	- 22	242
o-hydroxy-2 naphthyl benzoate	6.0		
o-hydroxy-phenyl benzoate	6.7		
di-n-butyl phthalate	6.4	< - 10	340
di-iso-octyl phthalate	5.1	- 46	386
benzyl propionate	5.8		220
iso-amyl salicylate	5.4		276
n-heptadecanone	5.4	48?	320

Most of these liquids would have no special virtue for the present application; their appearance in the dielectric constant tables was simply due to someone having carried out an academic study. The task of selecting the best liquids for practical trials from this table may be prolonged and unrewarding.

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