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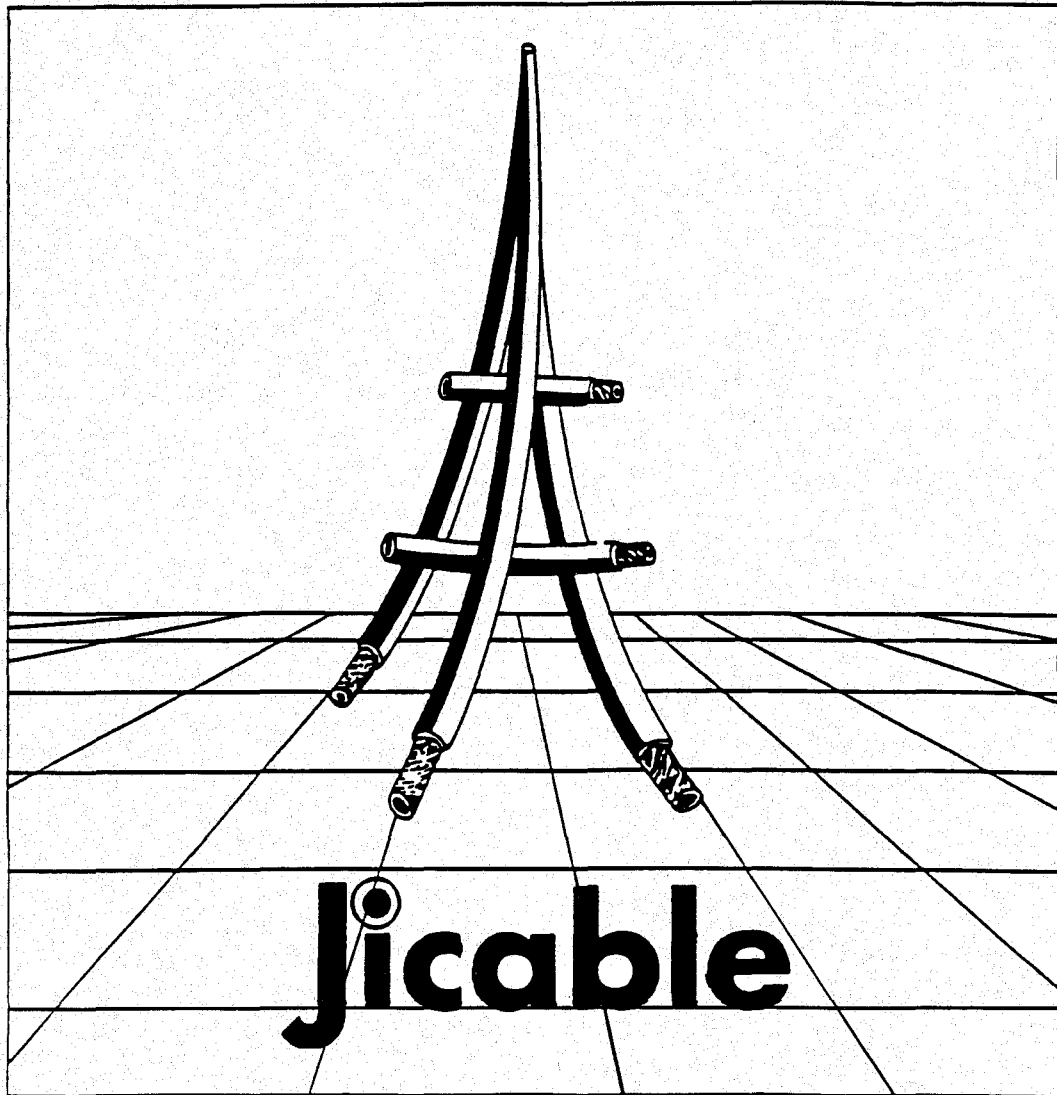
Topics :
Cable insulation
Ageing (material)
Transmission cables
Distribution cables
Extruded cables
Dielectric materials

June 1991

Proceedings : SEE/JICABLE
Workshop "Cable A91"
The Ageing of Extruded Cables

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WORKSHOP "CABLE A91"

Jicable

THE AGEING OF

EXTRUDED CABLES

WORKSHOP SEE/JICABLE

CABLE A91
THE AGEING OF EXTRUDED CABLES

Clamart, France
28 June, 1991

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SEE/JICABLE REPORT

WORKSHOP "CABLE A91"

THE AGEING OF EXTRUDED CABLES

Objective: Further progress in the understanding of the ageing mechanisms of synthetic insulation cables.

Summary: The "Cable A91" Workshop, organized by the SEE and JICABLE, was held on June 28, 1991 at CLAMART, FRANCE. Around 60 experts - research workers, operators and manufacturers - met on the occasion of the workshop to present their work on the ageing mechanisms of insulation, experimental techniques demonstrating these mechanisms, their diagnosis and feedback from experience.
Water and its influence were deliberately omitted from the topics discussed inasmuch as these aspects had been debated at length during JICABLE 91 and in other congresses.

The workshop, which was divided into three parts, was a continuation of the discussions between the various cable communities begun in SAINT PETERSBURG in 1989. The following points emerged:

- Fine and sensitive physico-chemical analysis is capable of evidencing the evolution of insulation characteristics and the role of pollutants.

- Work on ageing mechanisms demonstrate the presence of a threshold phenomenon (threshold field) below which the energy dissipated in the insulation does not lead to ageing. Validation of this hypothesis is currently under way.

- In the light of their 25 years experience, manufacturers and operators call our attention to the fact that cables are entirely satisfactory in service and will be interested to establish correlations between the physico-chemical characteristics of the material and the functional characteristics of the cable.

Keywords:

Cable insulation
Dielectric materials
Transmission cables
Extruded cables

Ageing (Material)
Distribution cables
Power plant cables

ABSTRACT

Following JICABLE 91, 60 experts, research workers, operators and manufacturers of cables met in CLAMART, FRANCE, for one day in a Workshop chaired by Professor M.MASHIKIAN, Director of Research on Electric Insulation at the University of Connecticut, STORRS, U.S.A.

In a spirit of continuity with the previous Workshop, organized under the patronage of JICABLE, EPRI and the CEA at SAINT-PETERSBURG BEACH, Florida, in 1989, the same topic "The Ageing of Synthetic Insulation in Energy Cables" was selected by the organisers.

However, inasmuch as the subject of water had been discussed at considerable length at other Conferences and in various Sessions of JICABLE 91, it was decided not to take this stress into consideration in order to focus discussion on other causes of the ageing of cable materials.

The importance of the subject justified its rediscussion two years later. Better knowledge of ageing should enable manufacturers to optimise materials dimensioning and to acquire the resources and models needed to calibrate type tests in terms of service life, while assisting users to diagnose the residual service life of installed systems, thus preventing incidents and providing a high level of service.

Discussions were divided into three parts.

The first part was devoted to the presentation of new experimental techniques enabling fine analysis of physico-chemical structure, composition and properties. Research workers presented the following topics:

- Various methods for the measurement of space charges. These charges are initiated by a pressure wave or by a diffusion process (heat wave).

The measurements carried out give an idea of field stresses, enabling the quantification and the determination of the local behaviour of the material as a result of the various stresses to which it has been subjected. Many applications were considered possible: selection of electrodes to avoid impurities, definition of structures to optimise interfaces, assessment of the influence of heat treatment etc. It should be possible to model behaviour.

- Infrared microscopy. Conducted under highly precise experimental conditions, this method enables the quantification of various parameters, whose evolution can then be monitored, the most important characteristics being crystallinity, degree of branching, and oxidation.

Films submitted to an electric field were checked by this method and it was shown that the combined effect of the field and of oxygen affects the insulation. It was also shown that there was a link between dielectric strength and oxidation.

- Monitoring of membrane voltage. This evidences the migration of impurities through a solid dielectric (presence of carriers) by determining the circulation of ions between two compartments containing electrolyte solutions of different strengths.

- Calculation of parameters Go (breakdown gradient) and Gs (Threshold gradient) according to Weibull's 3-parameter Law. 80 platelets of insulation taken from cable insulating jackets, were taken to breakdown under AC voltage and the results statistically processed, to improve the experimental reliability. Ageing is seen in the deviations between gradients for new and aged cables.

- Thermally stimulated spectroscopy. This enables analysis of molecular mobility, showing whether the material has been destroyed after stressing. This test characterises structural units of 4 to 25 Å.

- Chemiluminescence. This identifies the presence of oxidation through the emission of photons which is the origin of the phenomenon. This technique enables the study of oxidation reaction mechanisms and their associated kinetics.

- Measurement of complex low frequency permittivity and capacitance. The time spectroscopy obtained allows us to follow the phenomena accompanying the change in materials characteristics.

The second part of the Workshop dealt with mechanisms liable to deteriorate insulation characteristics, the type of stress considered being variable:

- Oxidation kinetics controlled by the circulation of oxygen or another product were commented on.

In a thick object, two areas should be focussed on: the outside, which is in direct contact and where the rate of oxidation is independent of concentration; and the inside, where the rate will be proportional to the concentration and will thus be dependent on circulation. This follows Fick's Law, modified by reaction consumption. In the case of a EHV insulator, the majority of its volume may not be subject to oxidation.

- Three research workers presented the results of their studies on the mechanism of ageing in an electric field.

A steep gradient lowers the energy barriers and dissipating phenomena inducing electroluminescence are observed in areas having a heavy concentration of carriers. At energy levels of 0.2 eV for some and of 4 eV for others, areas of local structural modification are noted with the creation of microvacua in the amorphous parts. Both oxygen and ionic impurities stimulate this phenomenon. The threshold field where this phenomenon begins was quoted and was hotly challenged by the manufacturers.

- The influence of pollutants on the deterioration of insulation characteristics was demonstrated. Pollution invariably reduces dielectric strength. However the effect increases with the degree of smoothness of the occlusion and renders adhesion to the insulation difficult. Thus glass has the greatest influence in this respect.

In the third part, Manufacturers and Operators call our attention on an over 25 years experience, during which cables in service had always provided total satisfaction.

In conclusion one can say that to explain the ageing mechanisms and to know the state of cables in service present much interest and justify the very important work completed for a few years.

On the one hand, more and more sophisticated analysis methods allow to detect microscopic characteristics evolutions of insulating material; The following table summarize their principles, the informations they give and the concerned material properties. On the other hand, the synthetic insulated cables in service do not present today faults ascribable to internal causes of ageing.

The links between the noted microscopic characteristics evolutions of materials and the behavior of cables in service still remain to establish. In the same time the concept of threshold where would be initiated the ageing mechanisms remains to be deepened.

Chairman MASHIKIAN thus invites the scientists, the manufacturers and the operators to continue their work in collaboration in order to, in a long term, bring a supported answer and to develop more powerful tools to perfect the dimensioning of cables insulations.

DESIGNATION	PRINCIPES	CATCHED INFORMATIONS	CONCERNED PROPERTIES
SPACE CHARGES	After polarization, apply a pressure or a thermal wave to move ions and electrons	Distribution charges and the values of internal electrical fields	Electrical stresses overestimated by the change of electrical field.
IR MICROSPEC-TROSCOPIE	IR absorption spectra determination of an insulating sheet	Cristallinity rate Short branchings distribution Presence of carbonyl radicals or insaturation	Physical and chemical characteristics of the material
MEMBRANE JUNCTION VOLTAGE	Measurement of voltage betweeen two different cells separate by the sample and measurement of an ionic conductivity	Ions permeability caused by organic sites present into the material	electrical characteristics influenced by the ions migration
VOLTAGE BREAKDOWN	Apply a gradual gradient to insulating samples up to breakdown	Breakdown and threshold gradient of the insulation	Electrical insulation withstand under alternative field
THERMALLY STIMULATED SPECTROSCOPIE	Evaluation of material molecular mobility by applying a shear stress to a sample of material	Structural changes of the material	Mechanical and electrical properties
CHEMILUMI-NESCENCE	Measurement of the photon light emited by oxidised organic material submitted to an electrical field	Presence of trapped radicals and hydroperoxydes in the bulk of the material	Electrical characteristics and influence of polar molecules on them
LOW FREQUENCY DIELECTRIC LOSSES	Using a single impulse determination of the complex capacitance and permittivity	Insulation ability to be polarized and to waste electrical energy	Electrical characteristics ,rise of losses generating a detrimental heating

CONTENTS

FOREWORD

The Cable A91 Workshop of 28 June 1991 was the fifth organised by the SEE and JICABLE following those held on:

- Cable HT84 the 8-9 March 1984 at CLAMART on the "use of synthetic insulation cables at high temperatures"

- Cable HT87 the 24 September 1987 at CLAMART on the "increase of the electric field in cables"

- Cable F87 the 25 September 1987 at CLAMART on "fire behaviour of electric cables"

- Cable A89 the 2-3 November 1989 at SAINT PETERSBURG BEACH, Florida, on the "ageing of extruded insulation cables".

This Workshop dealt with the same topic, "ageing", and was the continuation of the SAINT PETERSBURG Workshop.

By way of a preamble to the Work Session, Mr DESCHAMPS recapped the essential points of the previous Workshop, after first pointing out that this type of event was perfectly in line with the action program decided by the SEE (Society of Electrical and Electronic Engineers) and that it was complementary to the JICABLE 91 Conference, enabling a specific subject to be delved into in depth.

Mr DESCHAMPS announced that another Workshop, Cable T92, was being planned in Indonesia in June 1992 on the "behaviour of cables in tropical environments".

1. RECAPITULATION OF THE SAINT PETERSBURG WORKSHOP

Organised under the patronage of JICABLE, EPRI and the SEE, the Workshop comprised 60 Experts, Research Workers, Operators and Cable manufacturers, from ten countries who exchanged views on the definition of ageing and considered the possible internal and external factors responsible for the phenomenon, the sole way to acquire the knowledge required being tests and very long duration tests to bring out the mechanisms including the effects of direct factors and of interactions between factors.

Discussions were conducted on the basis of Experts' replies to a Questionnaire listing factors influencing ageing, such as the environment (dry or damp), temperature etc.

Accessories were also considered.

The work was divided up between three groups who later met together to draw joint conclusions.

The first group considered materials ageing mechanisms and, in particular, the importance of interfaces. In the presence of humidity, electrical strength is the parameter the most affected. In a dry environment, oxidation is preponderant. Research has continued and today new methods enabled a better understanding of the phenomena.

The second group considered service gradients:

- MV

- HV with gradients (G) from 5 to 10 kV/mm

- EHV with gradients (G) equal to or greater than 10 kV/mm

and proposed certain limits for the main factors considered to be important in ageing.

Examples:

a) Influence of water:

- if G > 5 kV/mm   Barrier not indispensable

- if G ≥ 10 kV/mm   Watertightness mandatory

- if 5 kV/mm >G >10 kV/mm   No clear position, opinions being divided

b) Influence of impurities:

This varies with the material, the size limit proposed being:

- for PE   20 to 30 μm

- for XLPE   200 μm.

The group discussed permissible temperatures and agreement was reached on 105°C as the overload temperature for XLPE.

The third group tackled service experience, in situ testing and diagnosis.

It emerged that:

- Weibull and Arrhenius' laws were useful but probably insufficient, thus requiring caution in their interpretation.

This was due to the fact that the materials are not always identical due to the effect of external factors such as water.

- the inhomogeneous nature of qualification tests, termed long term tests, was evidenced.

Examples:

- The EDF test, which lasts 6000 hours at 3 Uo.

- The ENEL test which lasts a few hours at 3 or 4 Uo.

Nevertheless, the growing practise of the long-term tests showed the sure interest of this kind of tests.

- There was a radically different approach between the Operator, who desires reliable results, and the Manufacturer, who requires short duration tests.

2. OUTLINE OF THE CABLE A91 WORKSHOP

Mr DUCHATEAU then outlined the scope of the Workshop.

Ageing was defined as a negative change of characteristics. The sole factor to be considered was the intrinsic deterioration of materials. Defects or weak points were not to be taken into account.

The preparatory document circulated in advance is recalled below together with the aims and the three parts adopted to serve as a guide to discussions.

2.1 PURPOSE OF AGEING STUDIES

They should enable:

- Manufacturers to optimise the dimensioning of materials and to acquire equipment and models for the calibration of type tests in terms of service life.

- Users to diagnose the residual life of equipment installed on the system (after a fault, for example, or as part of a renewal policy ...).

2.2 AIM OF THE WORKSHOP

The aim of the Workshop was to enable participants to exchange views on the phenomena which cause deterioration of insulating properties of synthetic insulation used in power cables and on methods to assess ageing. It was to cover both materials and the cable in its entirety.

Special attention would be devoted firstly to correlations between micro and macroscopic phenomena and, secondly, to the relationships between deterioration mechanisms and the methods of diagnosis used.

Inasmuch as the treeing phenomenon had been discussed at length during the plenary session of JICABLE 91 and CIGRE 1990, no discussion would be held on ageing due to the accidental penetration of water. Consideration would be focussed on the overall change of materials characteristics when submitted to thermal and electric stressing.

Ageing is taken to mean any change decreasing the capacity of the material to respond to the function assigned to it. Discussion would not be confined to thermoplastic or cross-linked polyethylene. Other synthetic insulating materials could also be examined provided that their mode of ageing was comparable to that of polyethylene and that the methods of analysis were similar.

The following questionnaire contains a certain number of questions concerning ageing mechanisms, experimental techniques and methods of diagnosis. Its purpose is to guide discussion on the various topics.

2.3 QUESTIONNAIRE

2.3.1 Ageing mechanisms

Theoretical and phenomenological studies of ageing have already been the subject of a considerable volume of work and various models using parameters as varied as impurities, filler injections, gradients and temperature have been prepared.

Questions:

- By avoiding any water penetration, is the humidity trapped during manufacture liable to decrease cable service life? (is it an ageing factor?)

- Does ageing affect the entire insulation or is it localised at interfaces?

- What is the influence of pollutants (organic and mineral impurities) on the deterioration of the insulation dielectric properties?

- According to what mechanisms can morphological variations (vacuoles, type of crystallinity, degree of branching) be interpreted as ageing?

- What is the influence of electric gradient and of temperature on the rate and mode of ageing? Do certain phenomena only appear beyond a given threshold?

- Can such ageing mechanisms be categorised by the development of models? Have such models been validated on materials and/or on cables and if so with what degree of reliability?

- Are the heat and electric stresses used for qualification (accelerated ageing) representative of natural ageing in the system and are burn-in tests harmful to the cable.

2.3.2. Experimental techniques

A wide variety of analysis techniques is available for the assessment of the electrical and morphological characteristics of cable synthetic insulation.. Ranging from the most traditional to the most sophisticated, these techniques should make it possible to conduct a "post-mortem" of the insulation and of the interfaces between the semiconductors and the insulation itself

Questions:

- What techniques have you tested or which you know to be best suited to the study of cable ageing and what is their degree of reliability?

- Which methods can be considered complementary and which redundant, i.e. providing similar information?

- How can these methods be linked to the service life of materials and equipment?

2.3.3. Diagnosis and feedback from experience

Based on an experimental study, the understanding of deterioration phenomena can lead to the construction of kinetic models and the identification of characteristic indicators of ageing. The Operator of an energy system is highly interested in such studies which can provide valid diagnostic tools and assist in defining his replacement criteria.

Questions:

- What are the most promising current techniques for the future diagnosis of the condition of cable?

- Has research and development testing made it possible to diagnose the condition of a system and to define a replacement policy?

- What do Operators currently use as a basis for the diagnosis of the condition of their system? Do they have a clearly defined policy?

3. DISCUSSION

The Chairman, Mr MASKIKIAN, then opened the discussion.

He expressed the strong desire that this Workshop would lead to the establishment of links or bridges explaining electrical faults on the basis of changes in physico-chemical properties.

He considered it inadequate to consider the material and its electrical behaviour separately, as has often been the case up to now.

He had taken cognizance of the abstracts of the contributions proposed by participants and attempted to establish a logical order for communications which he would direct as far as possible.

Participants' contributions to discussions are to be found in Appendix 1.

3.1 EXPERIMENTAL TECHNIQUES

3.1.1 SPACE CHARGES

Communication by Mr TOUREILLE (cf Appendix 1)

The measurements of space charges by the thermal shock method

According to Mr TOUREILLE, the reliability and ageing of an insulation appeared to be correlated with the onset and development of space charges, hence the interest of a method showing charge distribution and the value of the electric field inside the cable insulation.

He recalled the method he had developed at the MONTPELLIER Electrotechnical Laboratory, based on the principle of the diffusion of a thermal front to create the charges and the application of this method to MV and HV cables.

To illustrate his point, he showed the results obtained on the same cable, new and aged in laboratory, polarised at 65 kV at 70°C for 89 hours.

By comparing the curves obtained, different behaviour was observed between the two cables. On the cathode side of the aged cable, the positive charge density amplitude was twice the value whereas on the anode side the density was low.

By comparing the curves thus obtained, it is observed that the two cables behave differently. On the cathode side of the aged cable, the positive charge density amplitude is twice as great, while on the anode side the density is low.

Communication by Mr BERDALA (cf Appendix 1)

Application of the thermal shock method by a Manufacturer

M.BERDALA agreed with Mr TOUREILLE and considered that the accumulation of space charges led to a distortion of the electric field which was harmful to dielectric strength. Distribution therefore played an essential role. Accumulation might be due to the material utilised but it also had effects on the behaviour of the material in time and under stress.

He had calculated that the residual field in an aged cable was 2 to 3 times greater than the field applied and he had had the rare opportunity to observe the charge density distribution in a plane model shortly before puncturing occurred.

The field which would normally be 6 kV/mm or at most 10 kV/mm, dependent on the voltage applied, actually rose to 100 kV/mm.

Thus the accumulation of space charges was distinctly predominant and the stress observed was close to the breakdown voltage of a cable insulation.

Communication by Mr LEWINER (cf Appendix 1)

Application of space charge measurement to cable insulation.

Mr LEWINER made a very general comment showing that knowledge of space charges enabled an excellent evaluation of a product or material and, in particular, to assess its ageing, in the sense defined by Mr DUCHATEAU.

His contribution covered four points:

- justification of the interest in space charges,

- description of the two current principles,

- comparison between methods using these two principles,

- future prospects for these methods.

a) Interest in the measurement of space charges,

Space charges might be a good or a bad thing inasmuch as the changes they effect could be harmful or favourable. Several phenomena contribute to this. Due to the effect of free charge carriers (electrons or ions) could migrate and create a homogeneous space charge. Intrinsic dipoles may be oriented and create divergent polarity, equivalent to a charge density superimposed on the previous one. This results in a distortion of the internal field which, in certain areas of the insulation, may be vastly greater than the field applied and lead to breakdown. By knowing charge distribution, it is possible to monitor the physical process leading to this breakdown.

b) Presentation of the principles used and the corresponding techniques

Two techniques are possible, using different principles. They both make use of the nonhomogeneous disturbance of the charges to be measured and generated by:

- heat diffusion

- propagation of a pressure wave.

The first technique may be implemented by:

- brief illumination of one of the faces of the specimen by a light impulse (thermal impulse method)

- illumination of one of the faces of the specimen by sine modulated light, the measurement being repeated at various frequencies (Light Intensity Modulation Method)

- placing one of the faces of the specimen in contact with a thermostat at a temperature different from ambient (thermal shock method presented by Mr TOUREILLE).

The second method also allows several implementations:

- mechanically, a pressure wave is created externally by the impact of an extremely short laser pulse on a target close to the specimen by applying an electric pulse to a piezoelectric transducer, which is also coupled to the specimen

- electrically, by applying a voltage step to the specimen itself. The electrostatic forces acting on the charges present in the material produce a local displacement of the atomic lattice. This local mechanical disturbance created within the material is propagated at the speed of sound, as in the previous case.

c) Comparative analysis

Methods using heat diffusion, which is a slow process, do not involve costly equipment. Recording of the signals generated does not require wideband equipment, but these signals require highly sophisticated digital processing to render them usable.

Pressure wave propagation methods have the drawback of being more expensive.The wave propagation is effected in an extremely short time and measurements must be made in a few fractions of microseconds, requiring the use of wideband equipment. They involve, without any mathematical processing, directly usable data making it possible to monitor changes in stressed materials.

The two principles described and the corresponding techniques which have been developed have their pros and cons. In conclusion, the two principles are more complementary than competing.

d) Prospects

When an insulation undergoes electrical stressing, the various phenomena described in the introduction may occur. Measurement of charge distribution and evolution enables the observation of either stabilisation or, on the contrary, divergence in local fields and therefore:

- the selection of materials and additives on the basis of small specimens:

    . Selection of electrodes to avoid the migration of impurities.

    . Definition of structures to optimise interfaces.

- evaluation of the influence of chemical impurities - beneficial or harmful

- assessment of insulation behaviour dependent on its structure after heat treatment.

Furthermore, based on these measurements it should be possible to consider modelling the behaviour of materials and structures.

Among future prospects, one could also include the search for correlations between local chemical properties and space charges inasmuch as a very small quantity of impurities can induce major problems.

Communication by Mr FAVRIE

Mr FAVRIE pointed out that space charges are observed after polarisation under DC voltage whereas energy systems are operated with AC. He considered that the behaviour of the dielectric is different in the two cases, based on the fact that nothing abnormal has been observed on cables in service so far.

There were two replies to this point:

Mr LEWINER explained that it was first necessary to validate the methods and agreed that in fact AC was more important.

Some preliminary measurements had already been made and with AC there was also an accumulation of space charges when a divergent field existed due to a local distortion.

Spatial resolution was probably necessary inasmuch as the protusions were of the order of one micrometer.

Mr LAURENT stated that the electric ageing of synthetic insulation under DC was certainly influenced by the spatial distribution of charges. However, current methods did not possess adequate spatial resolution to provide data on space charges liable to affect small volumes. If, then, ageing mechanisms were identical for AC and DC, ageing was controlled by mobile charges in small microscopic volumes.

Communication by Mr NAYBOUR

Mr NAYBOUR wondered whether a slightly conductive material should not be used.

Mr LEWINER replied that it was a question of compromise and recalled the Mr IKEDA (HITACHI) communication at JICABLE 91 and the studies by the TOULOUSE team to limit the field by varying resistivity.

3.1.2 INFRARED MICROSPECTROSCOPY

Communication by Mr MONTAGNE (cf Appendix 1)

Infrared microscopy applied to electric cable monitoring

The method presented had been developed relatively recently and work was currently ongoing to assess its applications to electric cables.

The experimental rig involving a microscope coupled to an FTIR spectrograph was presented and the procedure outlined.

Transmission analysis is performed on slides of around 100 μm thickness, it being possible to focus the spot to a diameter of 8 μm. However, the preferred working focus was 50 μm. The spot was moved by scanning and followed a radius covering the entire thickness of the insulation.

The following parameters could be quantified by this method:

- Proportion of crystalline phase

- Proportion of amorphous phase

- Short branching

- Vinylidene insaturation

- 1-2 vinyl insaturation

- 1-4 trans-vinylene insaturation

- Oxidation

- Presence of antioxidant

An example of the result is present at Appendix 1.

Several questions and comments followed this communication:

Mr MAYOUX observed that in the spectra presented oxidation appeared on the outer layers only.

Mr NAYBOUR, who had used the same technique, pointed out that the migration of certain cable components confused interpretation inasmuch as one could not be certain that the peaks were part of the insulation itself.

Chairman MASHIKIAN had also used this method in an area subjected to treeing and had detected the presence of water and of carbonyl radicals. It would probably be possible to link the results to those obtained by the measurement of space charges, which would provide the "bridge" to better understand stressing.

Communication by Ms GOSSE (cf Appendix 1)

FTIR microspectroscopic mapping applied to the AC ageing of a polypropylene film impregnated with an organic liquid

The experiment did not directly involve a cable insulation but polypropylene film impregnated with Butyl-Toluene and having a thickness of 1300 μm.

The films were placed between two electrodes of circular section and submitted to an electric field (see Figure 1)

Figure 1
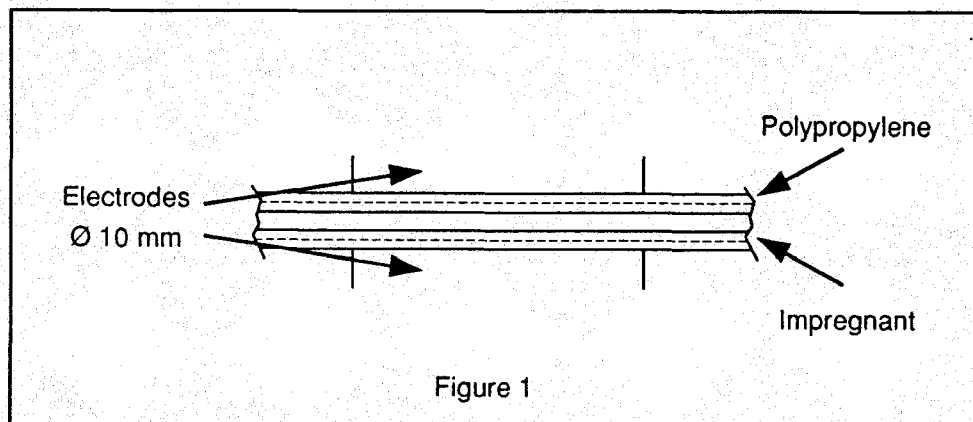
After stressing, bidirectional mapping of the films was performed using FTIR. Using an automatic platen, 6000 spectra (exploration area: 150 x 150 μm per spectrum) were recorded and processed with special software.

Three zones were highlighted (cf Figure 2):

1. Zone outside electric field

2. Zone within electric field, peripheral corona

3. Zone within central electric field

Figure 2
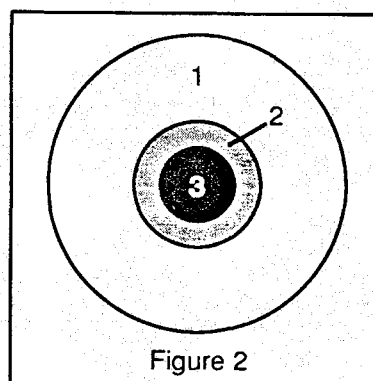
The corona was seriously deteriorated with the presence of carbonyl bonding (>C=0), absorption at 1718 cm^{-1} and 1018 cm^{-1}, whereas the centre was much less affected.

The result is thus very nonhomogeneous, demonstrating two specific types of deterioration (nonhomogeneous deterioration, oxygen diffusion).

Breakdown gradients, determined by the Weibull method, were also distinctly different and were weaker in the corona. For the breakdown test, the electrode was a small ball 1 mm in diameter.

There was therefore a relationship between dielectric strength and deterioration of the material due to oxidation.

Mr LEWINER asked Ms GOSSE if the carbonyl groups (>C=0) were the cause or the result of breakdown.

Breakdown occurred at the corona close to the ball and was therefore a consequence. Since the oxygen diffused from the outside to the inside of the electrode, its effect was initially felt at the corona.

Mr MAYOUX pointed out that the bi-oriented polypropylene films could be treated by "corona" discharges during production and before metallisation in order to improve the adhesion of the metal to the polymer. This treatment itself could already create carbonyl functions. Ms GOSSE stated that she did not know whether the specimens she had tested had been subjected to this treatment or not.

3.1.3 MEMBRANE VOLTAGE

Communication by Ms MONDIN (cf Appendix 1)

Measurement of membrane junction voltage

Ms MONDIN explained why she had developed this analysis technique. She considered that there might be a migration of impurities through the dielectric and she had realized the possibility of studying this migration by measuring variations in voltage between two cells separated by a thin film (40 μm) containing ionic solutions of varying concentrations (cf block diagram at Appendix 1).

The principle was as follows:

Take a polymeric membrane allowing ions to diffuse between a reference cell containing H^+Cl^- for example with a concentration of Co and a measurement cell containing H^+Cl^- at a strength C>Co.

Due to ionic conduction a voltage difference is established between the two cells, the difference dependent on concentration C according to the following law:

$$E = k + (2t^+ - 1) RT/F \log C_0/C$$

k being constant

t^+ being the ion transport number

C and Co being the concentration in each cell.

In the measurement cell different volumes of solution are added at concentrations $10^{-2}M$, $10^{-1}M$ and 1M. After each measurement there is a pause of 5 to 15 minutes to reach a state of equilibrium before reading the value of the membrane junction voltage.

To use theses measurements the curve of the membrane junction voltage is plotted as a function of the logarithm of the solution concentration:

$$E (mV) = f(\log C)$$

When the material is permeable to ions, a straight curve is obtained, the slope of which varies with the rate of diffusion linked to the number of organic sites on the membrane transporting the ions.

Mobility varies with the type of solution and hence with the type of ion.

For example: $H^+ \gg K^+ > Na^+$

When the material is impermeable to ions, no measurement is possible since the membrane behaves like a capacitor and the measurement circuit remains open (antenna behaviour, unstable voltage).

A result obtained on a cable withdrawn from service after 13 years is presented at Appendix 1.

Mr SCHÄDLICH asked whether the cable had proved faulty previous to this test. The cable in question was a 63 kV cable which had been removed (with no breakdown) due to changes in the routing of the link.

3.1.4 BREADDOWN GRADIENT

Communication by MM GALCERA and LAURENT (cf Appendix 1)

Determination of the dielectric strength of solid insulating materials in thin sections, statistical processing of data and problems of interpretation

Mr GALCERA outlined the following procedure to determine parameters:

- Go: breakdown gradient,

- Gs: breakdown threshold,

using Weibull's method.

The procedure was as follows :

- Preparation of 80 specimens, thickness 200 µm

- Conditioning: baking at 80°C under primary vacuum

- Voltage ramping at 4 kV/s

- Preparation of measurement cell

- Statistical processing of data using special software.

Mr LAURENT provided further details regarding the determination of Weibull parameters Go and Gs in particular. He stressed the need to perform the tests carefully but not to neglect the statistical treatment.

He recalled that the Weibull cumulative probability model contained three parameters:

- Eo: rated field

- Es: threshold field, which could be taken to equal 0

- α: shape parameter

If the results were recorded on a Weibull diagram and assuming the threshold field to be nil (2-parameter law), in general the points are not aligned but form a fairly regular curve, signifying that a threshold field not equal to 0 should be taken into account. The subsequent treatment consists in determining the most appropriate polynomial smoothing by applying the least square method and proceeding step by step until the best linear adjustment is obtained. This will determine parameter Gs.

By taking into account the shape parameter a straight curve is obtained. However, there still remained a gap between the linear plot and the experimental points. This must be justified by calculating the confidence interval and checked by a χ^2 test.

Mr LAURENT considered that the result was influenced by ageing. This might lead to a scattering of values and induce a dual slope due to the deterioration of certain areas. He considered there to be a "gateway" with Ms GOSSE's communication. He perceived the influence of another parameter: the incrementation of voltage ramping. Stressing of the insulation was more or less brutal.

Mr FAVRIE, referring to a communication during JICABLE 91 where the author, based on Weibull's theory, took into account the concept of volume to justify the decrease of dielectric strength (E average) with increasing insulation thickness, asked how it was possible to extrapolate the results obtained on thin layers to the performance of a cable with insulation corresponding to several tons of material per kilometre.

Mr VERDU put forward a reason. He considered the analysis to be complicated inasmuch as thin films and thick objects were not morphologically equivalent. Furthermore, thick objects had a "skin-core" structure due to their thermal insulation. This induced nonhomogeneous cooling at then end of the application.

3.1.5 THERMALLY STIMULATED SPECTROSCOPY

Communication by Ms LACABANNE (cf Appendix 1)

Thermally stimulated spectroscopy for the study of polymer ageing

Insulation materials were submitted to various stresses inducing modifications of their physico-chemical bonds and corresponding to structural changes.

To characterise this phenomenon use had been made of thermally stimulated spectroscopy, which enabled the analysis of dipolar mobility. Ms LABACANNE presented a thermally stimulated creep (TSC) method for the analysis of molecular mobility which was more sensitive for flexible chains. Since the most frequently used insulation materials were polyolefins (semi-crystalline materials with a metastable amorphous phase), this technique appeared particularly suitable to evaluate their ageing due to the characterisation of structural units of 4 to 25 Å in the absence of any external field at the very low frequency of 10-3 Hz.

She outlined the principle of the method:

Shear stressing is applied to a specimen placed in a twisting pendulum at temperature T for two minutes to enable the mobile units to be studied to orient themselves.

The specimen is then placed at temperature To, which is sensibly lower than T, in order to freeze the orientation. After stressing has stopped, a monotonous temperature rise (7°C/min) provides the requisite energy for the oriented mobile units to return to equilibrium.

Strain, strain rate and temperature are then recorded versus time.

Variation in strain rate (normalised versus the stress applied) as a function of temperature represents the complex FTS spectrum.

The analysis of complex spectra provides only comparative and qualitative data; it is therefore necessary to complement this study by analysing the fine structure associated with the complex spectrum.

By applying the experimental technique of fractionated stresses, the complex spectrum is resolved into elementary spectra, each of which is characterised by a lag time:

$$\tau_i = \tau_{oi} \exp(\Delta H_i / kT)$$

τ_{oi} being the entropic factor and

ΔH_i the activation enthalpy.

This set of $(\tau_{oi}, \Delta H_i)$ values enables us:

- firstly, to find the compensation diagram $\ln \tau_{oi}$ as a function of ΔH_i for the identification of the segments of polymeric chains responsible for molecular rearrangements in a given temperature range and, thereby, the quantification of any ageing effect versus time and temperature.

- secondly, to calculate the complex compliance versus frequency and temperature (after deducting the parameters of the fine analysis of the FTS spectra) and to obtain the classical micromechanical damping measurements (tanδ) and their evolution.

In the case of polyethylenes, which comprise various phases, three modes of compensation can be evaluated corresponding to 3 levels of order:

α   paracrystalline phase

β   amorphous phase influenced by branching

γ   amorphous phase not influenced by branching

Under the effect of stressing stimulated ageing occurs:

. through modification of physical bonds,

. through changes in chemical bonds,

the amorphous phases are affected and molecular mobility modified.

Two cases of ageing were presented:

- *in deionised water*: the amorphous phase is plastified and the para-crystalline areas restructured.

- *in an ionic solution at 75°C under G equal to 10 kV after approximately 1000 hours*: the amorphous phases are destructured while the characteristics had practically remained unchanged after the first 300 hours.

A comparative TSC study enables ε and tg δ to be linked with structural modifications as a function of temperature.

Mr LE GUENNEC posed the following question to Ms LACABANNE:

- What quantity of ions such as Cu^{2+} is required for there to be an effect?

The exact value was not specified, but it was very low for certain ions while for others, such as K^+, there was no effect.

- How do you explain the displacement of these ions in a non-polar material?

There appeared to be a possible relation between this characteristic and stimulated currents. The two phenomena coincided.

3.1.6 LIFE CURVE

Communication by Mr MENGUY (cd Appendix 1)

Rapid methods for the determination of the thermal endurance of insulation material

For various technical and economic reasons insulation materials are used beyond their thermal endurance limits. Mr MENGUY wished to obtain a rapid method to ascertain thermal endurance and thus assess how materials will withstand temperature.

IEC Standards 216, based on Arrhenius' law, require lengthy exposure of greater than 5000 hours at the lowest test temperature.

The underlying principle of the method proposed, which is moreover in agreement with the future IEC Standard 1026, consists in determining activation energy and on checking one point on the life curve after exposure to the high temperature. This is more rapid.

This method had been made possible by the sensitivity of analytical methods which were capable of evaluating the rate of reactions representative of deterioration in a short space of time.

LCIE adopted gas chromatography, the deterioration tracer gases being CO and CO_2. Ageing was conducted in sealed vials pressure at ageing temperature being atmospheric pressure.

The linearity of the curves obtained for Epoxy and Polyethylene terephtalate was quite good and energy activation measured by gas release was considered to be identical to that controlling the reduction of elongation strength.

Furthermore, sensitivity was such that the phenomenon did not change in nature between the point of measurement and service temperature.

Hydrogen and light hydrocarbons could be used as tracers.

There was excellent correlation with oxygen consumption in the vial and it was also possible to simulate humidity and oxidation.

In summary, the duration of testing was divided by 10 while the conclusions were more reliable.

Mr ROBERTS recalled the difficulties encountered when ageing was accelerated by temperature. The material tested is in a modified morphological condition, the crystalline phase has melted and the insulation is often of a rather different structure and more permeable to oxygen.

This being so, in the United Kingdom the REA was considering a method to measure residual anti-oxidant concentration in order to predict service life.

Mr MENGUY stated that he had good results as regards the reliability of the method he presented in the 60°C to 120°C temperature range.
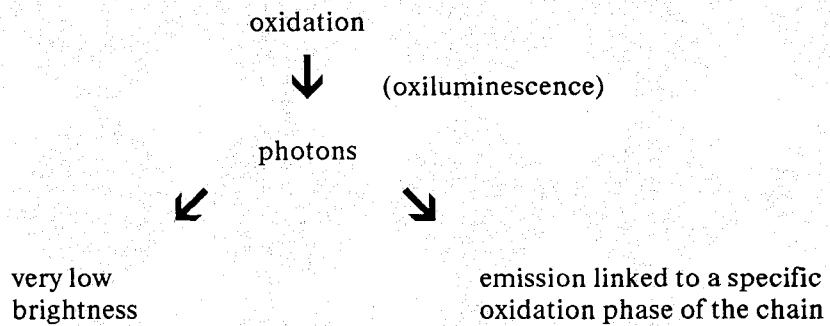
Gas chromatography (GC) measurements and the evolution of mechanical properties correlated well and one could be sure of behaviour for a period of 25 years.

3.1.7 CHEMILUMINESCENCE

Communication by Mr VERDU

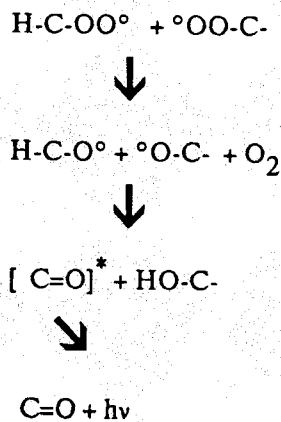*Chemiluminescence applied to the study of the ageing of polymers*

Mr VERDU briefly recalled the principles of chemiluminescence.

oxidation

$\downarrow$ (oxiluminescence)

photons

$\swarrow$ $\searrow$

very low   emission linked to a specific
brightness   oxidation phase of the chain

giving the overall view of the mechanism

$A + B \rightarrow [C]^*$: excited condition

$[C]^* \rightarrow C + h\nu$: phosphorescence

An organic material submitted to oxidation emits a very low light flux which can however be detected with a sufficiently sensitive sensor. It is generally agreed that the RUSSEL termination reaction is responsible for the emission of photons. The process can be shown schematically as follows

$H\text{-}C\text{-}OO^\circ \ + {}^\circ OO\text{-}C\text{-}$

$\downarrow$

$H\text{-}C\text{-}O^\circ + {}^\circ O\text{-}C\text{-} + O_2$

$\downarrow$

$[\ C{=}O]^* + HO\text{-}C\text{-}$

$\searrow$

$C{=}O + h\nu$

the two peroxide radicals interacting to give a cetone which emits a photon. He then showed the rig he utilised for his experiments (cf figure 3)

Figure 3
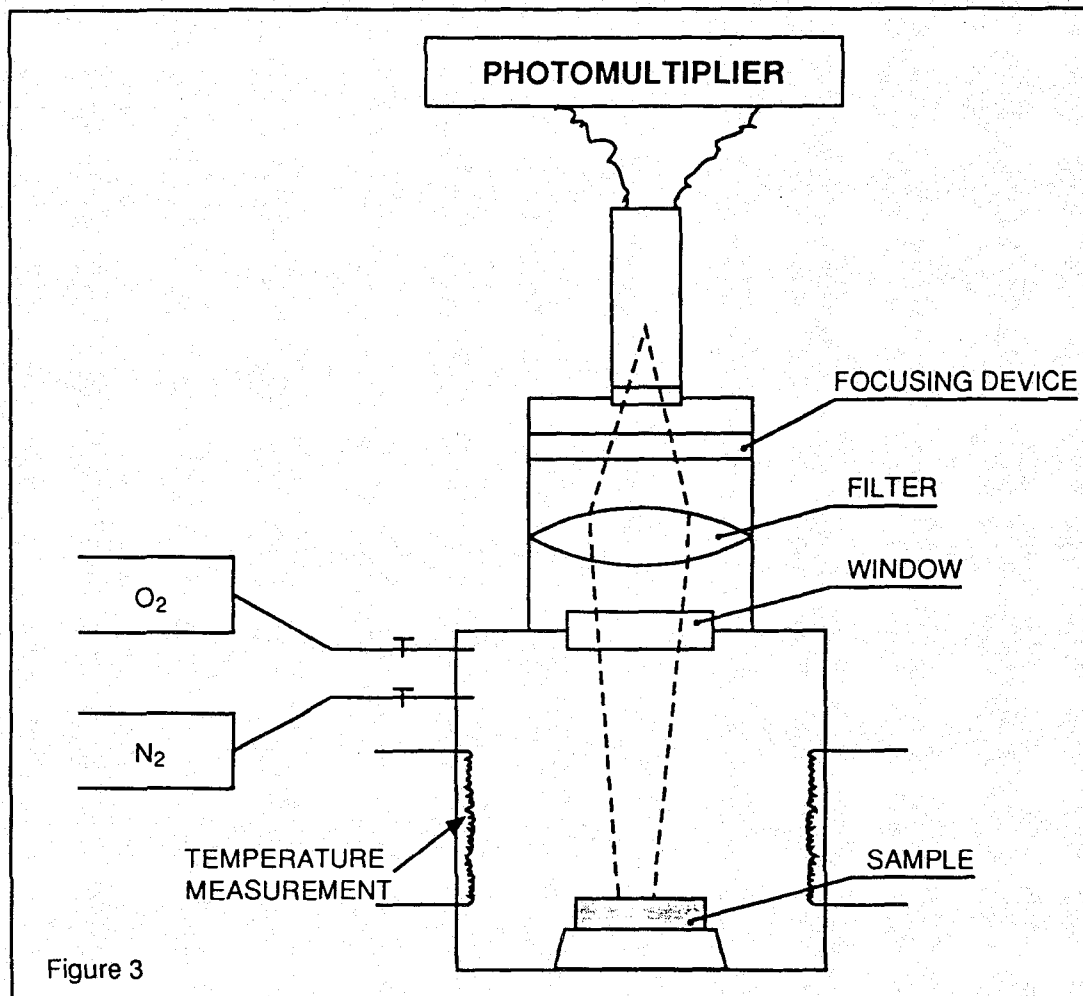
Three examples of use were given:

a) Fundamental research of oxidation reaction mechanisms and their associated kinetics by non steady state methods. The reactivity of the peroxide radicals is monitored versus time, passing from an O_2 oxidising medium to an inert N_2 medium.


Figure 4
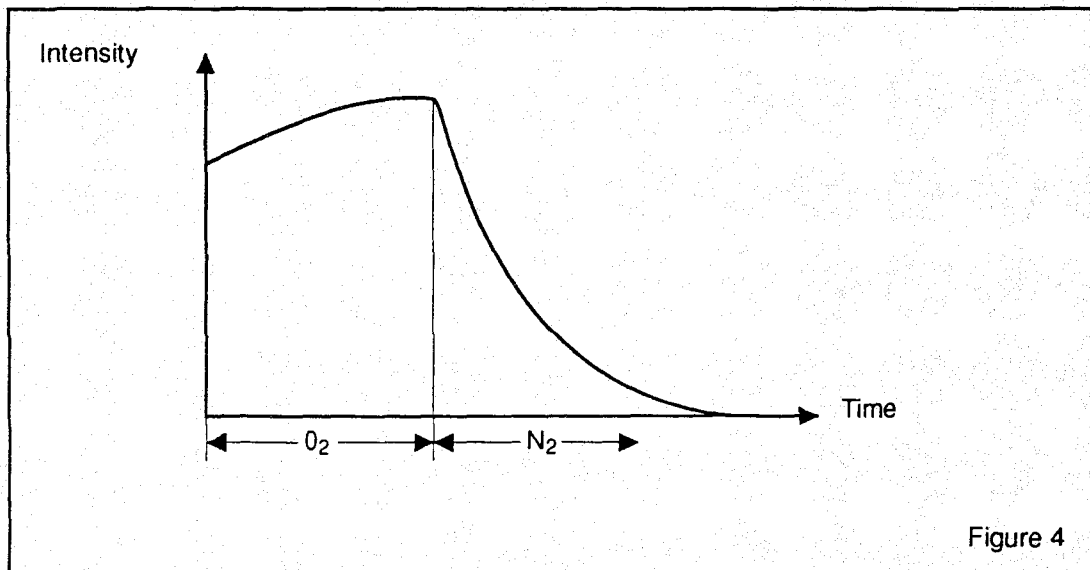
b) Efficacy of antioxidants by monitoring brightness versus time.

This is comparable to the use of DSC to monitor oxidation induction time, but is less sensitive and less costly. It may also be used at low temperatures and is more directly linked to oxidation mechanisms, particularly when photon counting is also provided.

Intensity

Non stabilised polypropylene

Stabilised polypropylene

Time

Figure 5
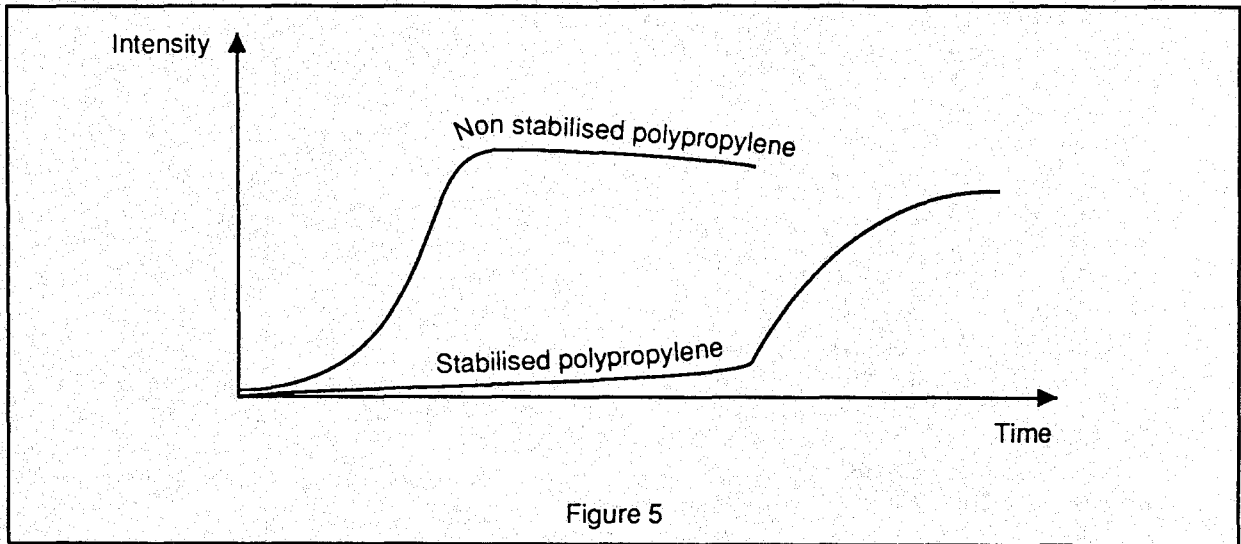
c) Study of the effects of UV radiation, γ and ß rays

This enables the detection of very slight effects of radiation inducing the formation of trapped radicals and of hydroperoxides.

Irradiated

Non irradiated

N₂   O₂

Figure 6
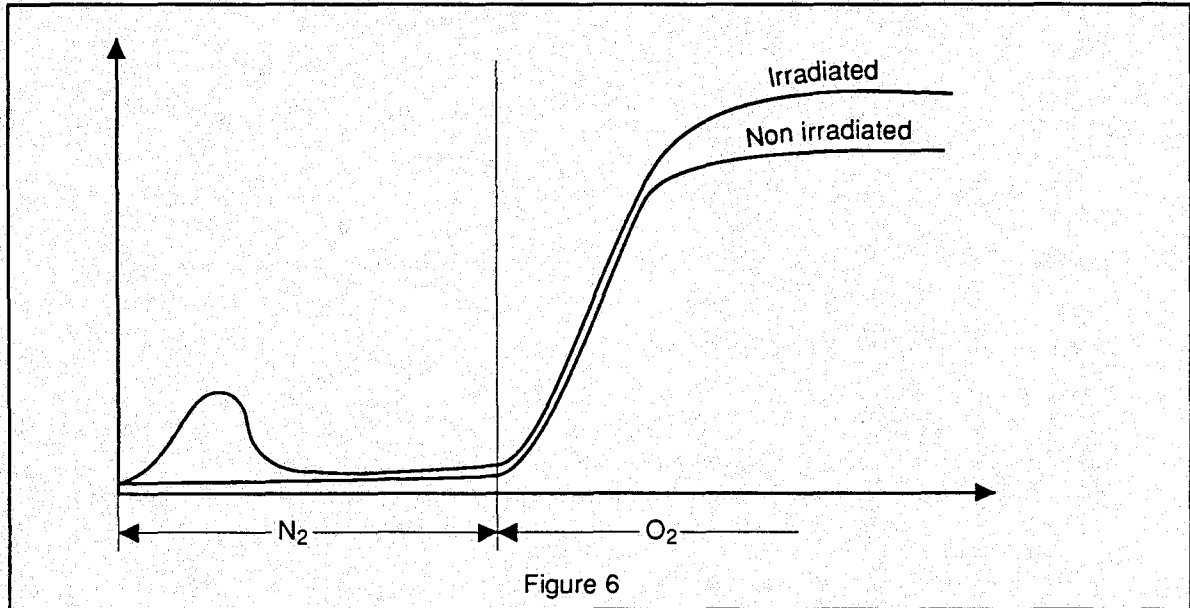
3.1.8 DIELECTRIC LOSSES AT LOW FREQUENCY

Statement by Chairman MASHIKIAN (cf Appendix 1)

The Chairman added to the communications of the first part of the Workshop by providing some information on the possibilities of analysis offered by the very low frequency measurement of tanδ.

Ageing is shown by a variation in chemical, mechanical or electric characteristics under the influence of various stresses.

To evaluate the evolution tan δ had been measured on aged cables and, in particular, at very low frequencies such as 10^{-3} Hz.

This provided a time spectroscopy enabling the phenomena to be monitored. Using a single impulse it was possible to determine complex capacitance and permittivity.

The results obtained on cables which had undergone accelerated ageing in contact with oils are presented (mineral oil for impregnation) at Appendix 1. Measurements were made at ambient temperature.

Questions were put to the Chairman.

Mr LEWINER asked whether the tangent measurements at low frequency had been correlated with conductivity measurements.

This had not been done but should be done.

Mr BERNSTEIN wished to know the reason for the increase in tangent on the new cable. Also, referring to EPRI studies, he considered it necessary to correlate the findings of the studies on materials presented during this Workshop with the actual dielectric strength of cables which have shown a measurable evolution of their characteristics for the overall objective remained the ability of the cable to perform correctly in service.

Finally, he asked what type of cables had been tested. The cables tested were for nuclear use, most of them being LV but a few MV cables had also been tested.

Mr NAYBOUR had applied a similar technique to synthetic insulation cables, both new and aged. He recommended the utmost caution in the interpretation of results inasmuch as charges could appear at barrier level. He had published his results some ten years ago.

Mr KATZ also requested details on the cables tested and the manner in which measurements had been made. Were the cables complete with their sheaths?

Was the influence of interfaces not so preponderant that it could mask the intrinsic evolution of the materials?
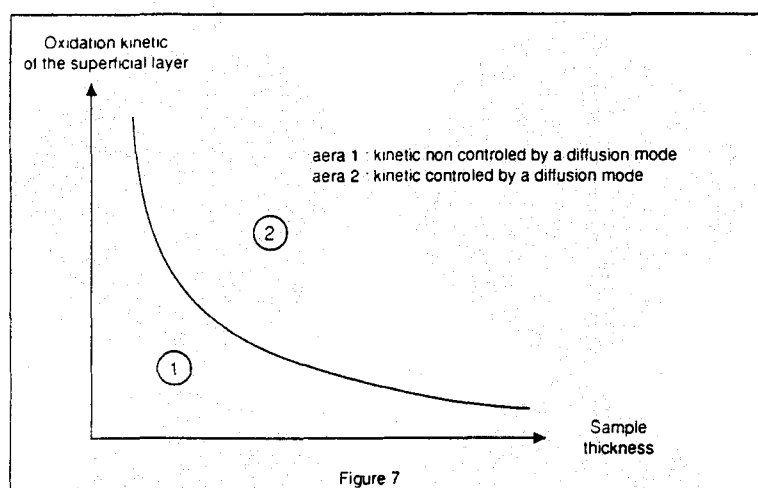
3.2 DETERIORATION MECHANISMS

3.2.1 OXIDATION

Communication by Mr VERDU (cf Appendix 1)

Oxidation kinetics controlled by diffusion

Mr VERDU demonstrated how oxygen acted on a product dependent on the latter's thickness. He distinguished two zones governed by two different processes as shown in the diagram below.

Figure 7

The profile of oxidation rates and hence of the concentration of oxidation products after a specified time can be predicted if we know the oxidation kinetics characteristics (effect of oxygen concentration, C) and the oxygen diffusion properties (oxygen concentration at equilibrium, $C\infty$, and diffusivity, D).

It is possible to write that the variation of O_2 concentration in an elementary slice of material is equal to the diffusion contribution minus the quantity consumed by the reaction or:

FICK's law modified by the oxidation reaction consumption:

$$\partial C/\partial t = D\partial^2 C/\partial x^2 - r(C)$$

with

$D\partial^2 C/\partial x^2$: term relating to O_2 diffusion

$r(C)$: term relating to O_2 consumption by oxidation

In steady state:

$\partial C/\partial t = 0$ hence $C = f(x)$

corresponding to oxygen concentration.

Two cases were considered:

First case: Reaction of zero order. Oxidation rate is independent of O_2 concentration.

$r(C) = r_0$ et TOL $\simeq \sqrt{D S/r_0}$

with:

D	=	Diffusivity	$m.s^{-1}$
S	=	Solubility	$mol.m^{-3}$
ro	=	Reaction rate	$mol.m^{-2}.s^{-1}$
TOL	=	Thickness of oxidised layer	

Second case: First order reaction. Reaction rate is proportional to O_2 concentration.

$r(C) = kC$ et TOL $\simeq \sqrt{D/k}$

with

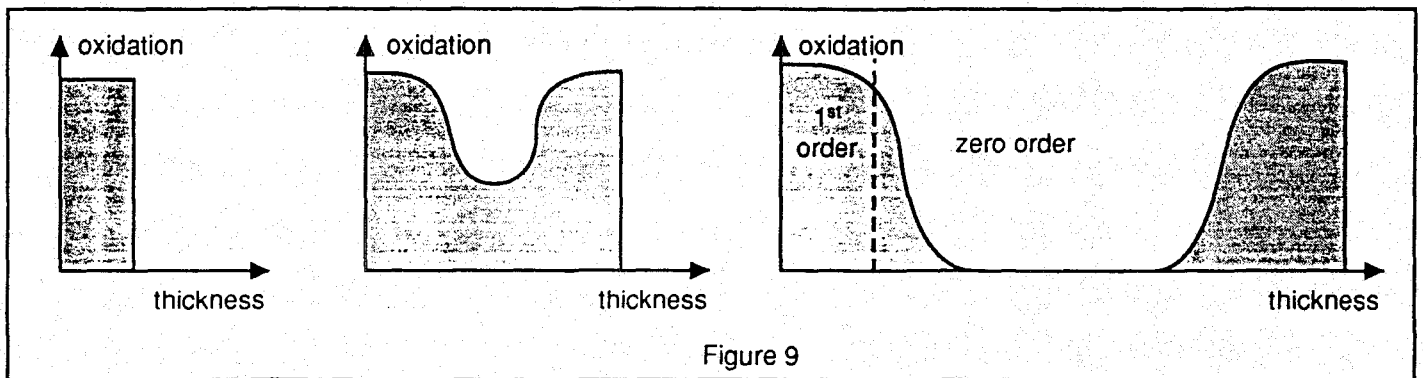|			
D	=	Diffusivity	$m.s^{-1}$
k	=	First order rate constant	s^{-1}
TOL	=	Thickness of the oxidised layer	

Two examples of oxidation rate distribution are given.

For a resin epoxy cross-linked by an anhydride as a function of depth, at 180°C and after various time intervals:
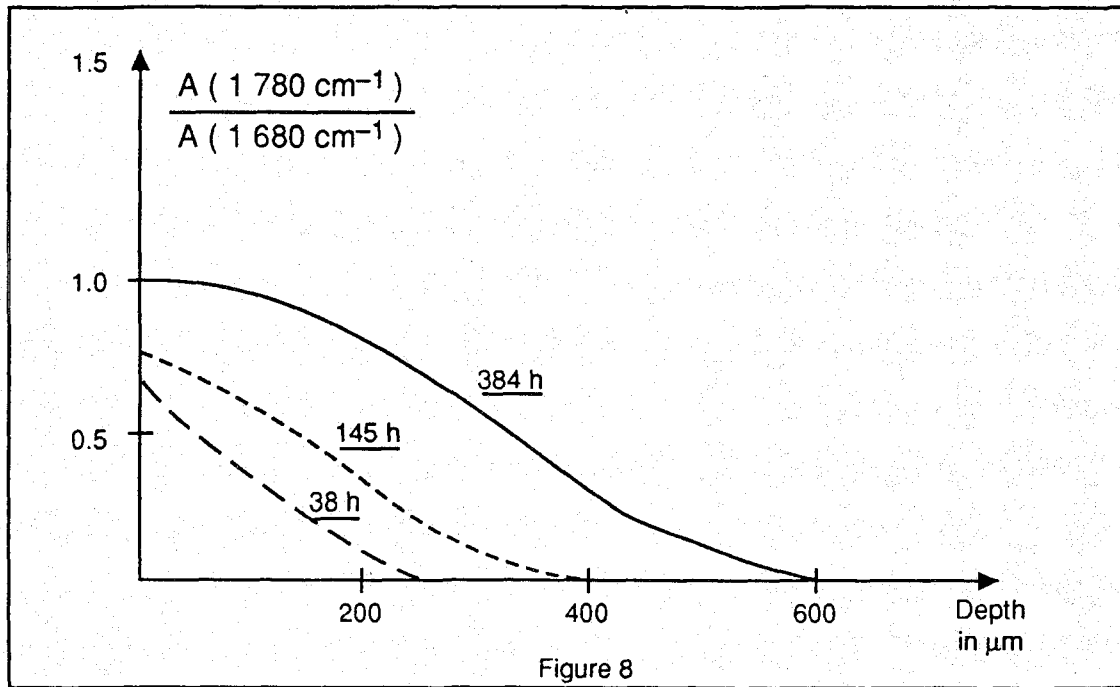
Figure 8

Thus we have as a function of thickness the following oxidation product concentrations:

Figure 9

The kinetics can also vary with time and follow a zero order reaction after a first order reaction as shown in the following figure:
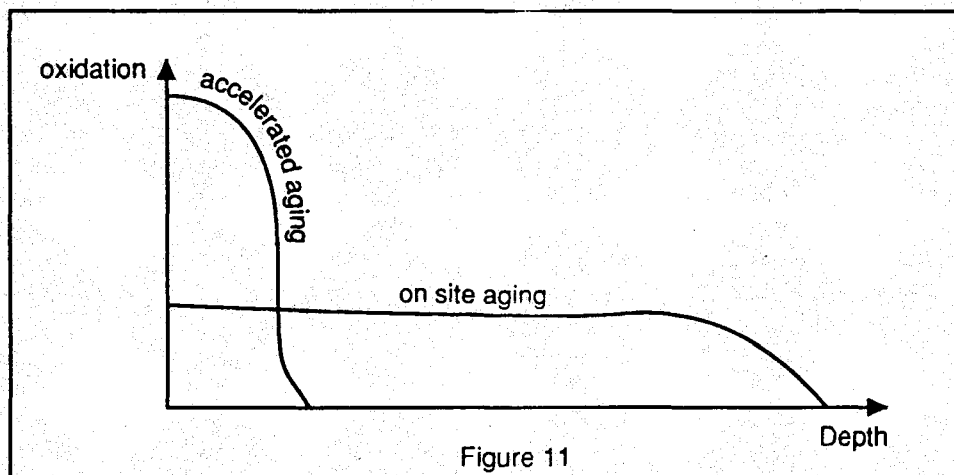

Figure 10
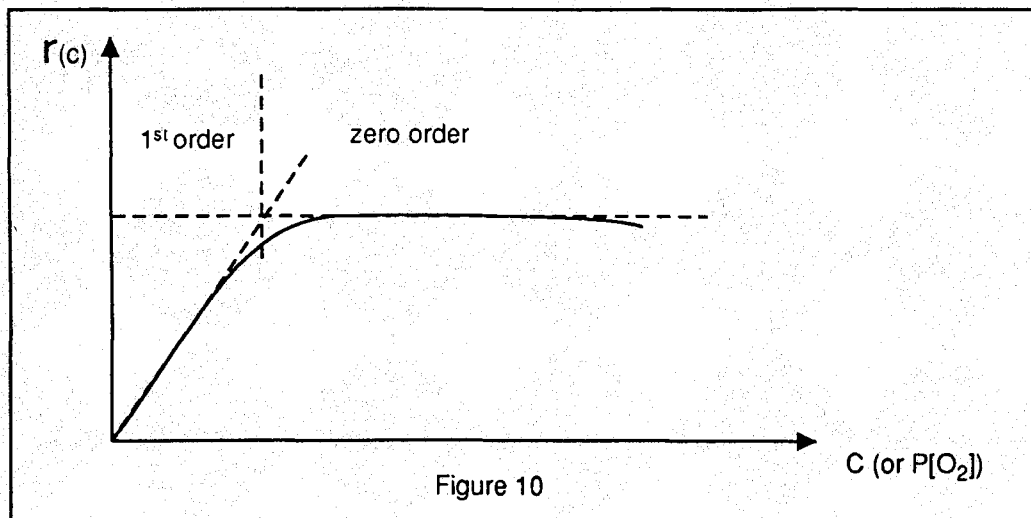
In this case

$r(C) = \alpha C / 1 + \beta C$

if $\beta C \ll 1$ 1st order $r(C) \simeq \alpha C$

if $\beta C \gg 1$ zero order $r(C) \simeq \alpha / \beta$

Mr VERDU questioned the validity of the results obtained by increasing temperature to induce acceleration inasmuch as the resultant change in oxidation rate led to a change in the thickness of the oxided layer (TOL) as shown below:

Figure 11

3.2.2 AGEING BY THE ELECTRIC FIELD

Communication by MM .LAURENT and .MAYOUX (cf Appendix 1)

Electric ageing of insulation: mechanisms and mode of deterioration

MM LAURENT and MAYOUX considered that it was necessary to discover the scenario governing electric ageing. They had been working on the subject for some time and their work was continuing. They explained their viewpoint.

Modelling of the electric ageing of energy transmission cables must perforce be based on sound knowledge of the various stages of the process and hence on observation. Once the successive phases had been identified, the task consisted in formulating assumptions on the physical, chemical and mechanical processes involved or A combination thereof controlling these phases. Performed on laboratory specimens, the identification of mechanisms led to microscopic models whose parameters could be quantified. It is only after reaching this stage that cable ageing modelling can be effected by taking account of the industrial configuration.

They proposed an electrical ageing scenario based on the existence of two types of defect:

- gas cavities,

- field concentration zones.

Both situations lead to breakdown due to the formation of electric treeing.

Long before the first electric discharge appears, they have shown that areas with a heavy concentration of carriers were the locus of energy dissipation phenomena of the order of a few elecron-volts (electroluminescence). Inasmuch as this process is powerfully non-linear in voltage, it can be considered to be a threshold phenomenon. Below this threshold the energy dissipated in the insulation cannot cause ageing.

The deterioration threshold can be determined on laboratory specimens.

Weibull statistics and the threshold concept to which they lead might well be the link between laboratory testing and the testing of actual cables.

Local structural modifications of the insulation occur during the ageing phase during which electroluminescence can be observed.

Both in the research conducted by SHIMIZU in Japan and by DENSLEY, BAMJI and BULINSKI in Canada and in their own work, experience had shown that the electroluminescence phenomenon was closely dependent on the gas impregnating the polymer. They emphasised the special role played by oxygen which, as in other circumstances, must be taken into account due to its possible mechanical effect but above all due to its chemical reactivity. This shows up more or less quickly dependent on the type of polymer. There was a distinct difference for example between a polyethylene and a polypropylene in which ageing had led to the creation of free radicals.

If account is taken of the activation energy levels required to create certain chemical entities of a peroxide type, one realises that they do not all have the same probability of being created.

Consideration of these functions alone or of the density of free radicals may not suffice to evidence ageing kinetics inasmuch as singlet and triplet states may in some circumstances exist upstream of the structural change process.

The foregoing was applicable to an ageing process within the volume of the polymer but also when discharges were involved, originating in cracks or in gas volumes created in the material.

These microcracks might originate in the local field which, due to its electromechanical effect, led to the destructuring of the polymer or, possibly, the release of molecules such as water, as has been shown by ZURKOV et alia.
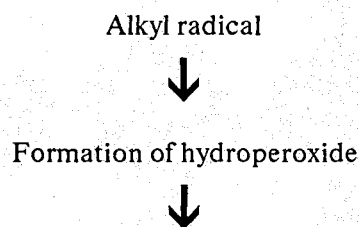
The overall process suggested is as follows:

Micro-fault

↓

Crack

↓

Microcavity

↓

Ionised treed medium

↓

Destructuring
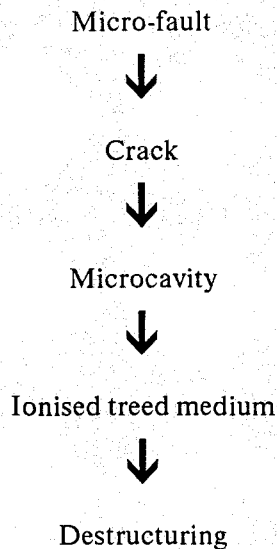
Comments were also made on the presence of oxygen and its effects.

Crack voltage was 50% lower than with H, N or A.

Oxidation could have the following form:

Alkyl radical

↓

Formation of hydroperoxide

↓

Phenomenon of decomposition with energy of the order of 3 eV and 1.8 eV

Combination of the two could lead to the emission of light already adverted to and the detection of singlet and triplet states.

Destructuring of the material

↓

Micro-cracking
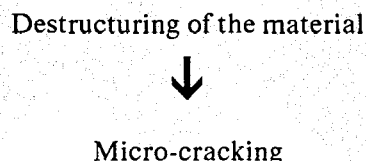
Small volumes had been found and it had also been observed that there was a possibility of bulk ionisation.

There was a gap between actual dimensions and those detected by the partial discharge method. In the case of a small volume around 10 μm diameter, it has been shown that there was a critical ratio between the inter-electric spaces. Plasma was formed and it was necessary to reason on the basis of the energy density developed in the material.

Communication by Mr LAMARRE (cf Appendix 1)

Electric ageing of insulation

Mr LAMARRE reported the work of MM CRINE and PARPAL. The latter were dissatisfied with the model they were using, service life being distorted.

They were currently proposing a new model for the ageing of dielectrics based on three points:

- use of the kinetic theory to investigate the phenomenon and the calculation of orders of magnitude,

- hypothesis of additional energy for the creation of microvacua in amorphous zones,

- hypothesis of local heating of the material due to an electromechanical effect.

The above reasoning was supported by experimental findings (breakdown test and SAXS measurements).

The time required to cross an energy barrier is defined by:

$t_b = (h/kT) \exp((\Delta G - e\lambda F)/kT)$ for high energy fields

with

λ being the mean free path of the electrons

F being the electric field applied

The term $e\lambda F$ corresponds to the lowering of the energy barrier due to the field applied

Parameters ΔG and λ can be deducted from the $\log(t_b)$ curve as a function of F

The deterioration process was as follows:

Below a critical field Fc, the energy acquired by an electron covering the distance λ is not sufficient to induce irreversible deterioration in the material.

On the contrary, for F > Fc exponential ageing is obtained as a function of the electric field applied. Parameter lamda is therefore constant and its order of magnitude is $\lambda_{max} = 100\text{Å}$. For these values of Fc and λ_{max}, there could be a deterioration process inasmuch as the order of magnitude of the energy acquired by the charge ($e\lambda_{max}Fc$) is equal to that of the cohesion energy (ΔH_{vap} - kT) of the polymer in its amorphous phase (Van Der Waals bonds).

λ_{max} corresponds to the size of the amorphous zones in the polymer (PE, XLPE). It is known that discharges are propagated preferentially between crystallites.

SAXS measurements revealed microcavities of the order of 100Å on specimens of aged PE.

The authors suggested that these microcavities were initially formed by local vaporisation of the material due to heating in the tangled zones of the polymer in its amorphous phase. The quantity of heat was thought to be produced by electromechanical effects. These effects were considered to be amplified by the presence of ionic impurities. These microcavities could reach a size equal to λ_{max} and an irreversible electric deterioration process would then ensue.

Fifty sets of data were processed and gave satisfactory results. They concerned various materials: XLPE, HDPE and PE exposed to water, air and to SF_6.

Previous findings had also been used and replotted. Here again coherent free energy values were obtained.

Ageing was conducted at 1 and at 60 kHz and cavities appeared between 10 and 20 kV/mm.

For example: at 12 kV   the material remained unchanged

                  at 20 kV   a distinct difference is observed.

This work confirmed that previously communicated by MM LAURENT and MAYOUX, particularly as regarded the existence of a threshold field value below which no irreversible deterioration of the polymer occurred.

Mr FAVRIE expressed his surprise that microcavities could be observed after applying an electric field of 10 to 20 kV/mm.

He explained that VHV 225 and 400 kV cables of his Company had been performing satisfactorily for many years at respective gradients of 10 and 15 kV/mm.

He specified that studies had been conducted at IREQ on moulded specimens.

Mr BERNSTEIN pointed out that microcavities of this size were connected to cooling of the material and were present in the majority of insulations.

3.2.3 EFFECT OF IMPURITIES

Communication by Mr LEUFKENS (cf Appendix 1)

Influence of pollutants on the deterioration of insulation electric properties

Mr LEUFKENS commented on an experiment performed at the University of Delft in 1987 and concerning the effects of different types of inclusions incorporated in the dielectrics of prototype electric cables with insulation 3.4 mm thick.

All the inclusions were more or less of the same size, their largest dimensions being between 0.5 and 1 mm.

Types of inclusion:

            - metal: copper
            - vegetable: wool, sisal
   - mineral: glass, salt.

Cable lengths of 10 metres were subjected to a voltage of 15 kV and later 28 kV, this latter voltage being maintained until breakdown.

Ten samples were tested for each type of inclusion and the results processed according to Weibull's law.

Generally speaking, the inclusions affected dielectric strength, smooth materials such as glass being the most harmful. The explanation was the absence of cohesion with the dielectric which generated treeing.

No partial discharges were detectable despite sensitivity as low as 0.05 to 0.1 pC.

Calculations showed that this was not an abnormal result inasmuch as discharges corresponding to the shape of the inclusion are at an extremely low level as shown below (Paschen's law).

| Discharges of 0,07 pC by 9,5 kV/mm | Discharges of 0,007 pC by 4,2 kV/mm |

Figure 12
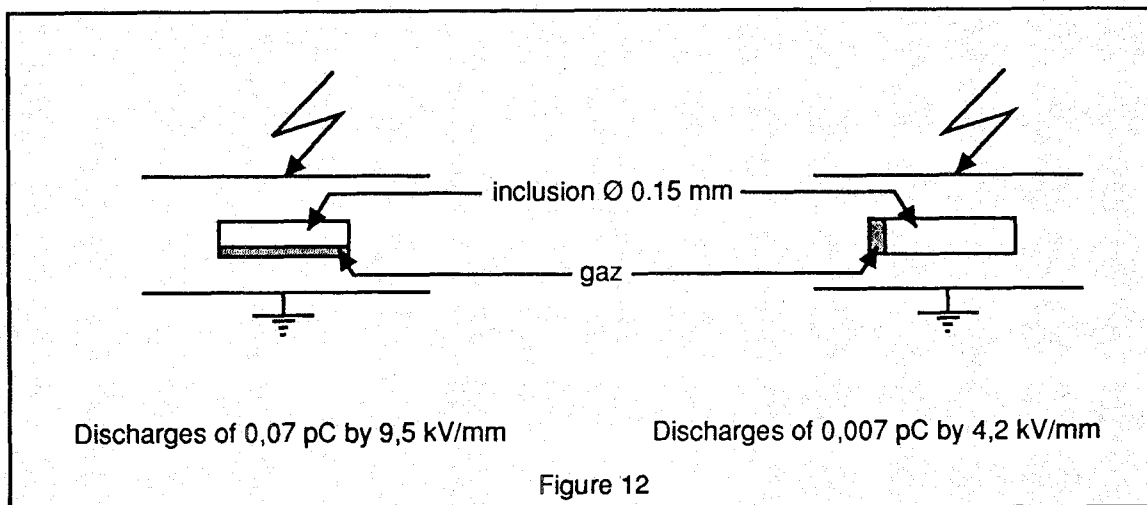
These values exceed the breakdown value.

Communication by MM BERNSTEIN and KATZ (cf Appendix 1)

Detection method for ionic metallic contaminants

Mr BERNSTEIN reported an experiment carried out in the Laboratories of the Cable Technology Laboratory and the University of Connecticut and sponsored by EPRI.

Cables rated at 15 kV and 35 kV underwent heating cycles raising their core temperature to 145°C and 175°C respectively for periods of 100 and of 322 days. Their insulation was then examined.

The slides presented showed clearly the presence of numerous brown patches which were investigated by various techniques to determine their origin:

- FTIR
- SEM
- DEA
- SEM/WDX,
- ....

The results showed a phenomenon of oxidation, the presence of chlorine, reduced crystallinity plus traces of cobalt, chromium, vanadium and copper.

Since the outer jacket of the cables was in PCV, the origin of the chlorine was attributed to PCV diffusion from the protective sheath during thermal deterioration due to the heat cycling.

It could be considered that the blackening was due to the effect of chlorine on trace metallic contaminants; this point had been checked by passing hydrochloric gas through the insulation, which had been cut up into thin spiral strips for this purpose, and the same blackening occurred after one hour at 175 °C.

This constituted a method for the detection of the presence of metallic contaminants which reacted with the chlorine ions, catalysing the insulation oxidation and inducing blackening.

The deteriorated parts were checked as follows:

- mechanical: properties down by 30%

- electric: the black patches had a dielectric strength of 48 kV/mm and breakdown did not occur on the patches but very close by. The weakening effect was therefore minor.

This led Mr BERNSTEIN to conclude that there was no correlation between the two types of approach: the physico-chemical approach and the electric approach.

It should be noted that the same cyclical test performed at 130°C, which is customary in the United States, did not result in black patches on the insulation.

3.3 DIAGNOSIS AND FEEDBACK FROM EXPERIENCE

Communication by Mr SCHÄDLICH (cf Appendix 1)

High gradient ageing of "model" cables with XLPE insulation

Mr SCHÄDLICH reported what he termed a simple experiment, the aim of which was to check whether high electric fields induced ageing or deterioration of the XLPE insulation.

Since full scale experiment of this type was difficult to conduct with HV or VHV cables, he had constructed models (cross-section 1.5 mm2 - insulation thickness 1.5 mm - triple extrusion SC - insulation SC) as is the practice for large diameter cables, vulcanisation being obtained by steam.

Using these models, the following tests were run on 5 times an active length of 2 metres:

Conditioning: 16 h at 90°C in an oven with application of air

Ageing: at 50 Hz, voltage 30kV, giving an average gradient of 20kV/mm and a maximum gradient of 30 kV/mm

Temperature: ambient

Duration: 1-2-4-8 etc weeks.

Evaluation of the ageing process is achieved by relating the breakdown voltage of the aged specimen with that of the new model.

Voltage was applied by steps of 3kV/5 min from 60 kV upwards and breakdown voltage was that calculated by Weibull with a probability of 63% and a confidence interval of 95%.

The entire results were not as yet known since the test was still ongoing. For other durations up to 8 weeks, no deviation in breakdown strength had been observed.

If the $-t.E^n$ = constant with n = 15 formula was applied, the result gave satisfactory performance of 5000 years at 15 kV/mm and it would appear possible to adopt a service gradient for XLPE cables of 15 kV/mm.

After ageing, cable insulation was examined and various tests performed:

- Differential enthalpic analysis

- Fourier transform infrared spectroscopy

- Microscope imagery analysis.

Only one extra peak, indicating conditioning temperature appeared with differential enthalpic analysis. Apart from this no difference was detectable even at vacuole level.

Communication by Mr DEJEAN

What resources are available to asses the condition of a cable in service?

Mr DEJEAN considered that major progress had been achieved in test methods but only at laboratory level.

Highly efficient resources were available for the selection of materials and for the dimensioning of cables dependent on the performance level desired.

Before delivery, routine electric tests were conducted on the reel to guarantee the quality of the product:

- Dielectric strength

- Shock resistance

- Partial discharges.

Once the cable was installed, it was still possible to ensure that the work was properly executed:

- DC testing of sheaths

- Oscillating wave test, possibly AC on insulation

- Echometry.

At the end of service life, after breakdown induced by analysis methods on samples, much information could be obtained:

- Effect of water

- Effect of oxygen

- Effect of electric field on imperfections.

However, during the entire service life of the cable we were incapable of doing anything. His conclusion from the Workshop was that there did exist methods of great potential interest:

- $\tan\delta$ at very low frequency

- Space charge measurements

- Measurement of partial discharges in situ.

And he expressed his impatience to have these methods available.

He then gave a list of routine checks which could be considered dependent on whether the environment was damp or dry.

Communication by Mr FAVRIE (cf Appendix 1)

Threshold gradients to be observed for LDPE insulated VHV cables

Mr FAVRIE stated that in his Company they had always been concerned with not exceeding in service the threshold gradient tolerated by the insulation.

He recalled how this had been improved in the past due to progress in materials quality and to fabrication conditions used by Manufacturers.

In 15 years, the maximum service gradient had risen from 5 to over 15 kV/mm while preserving the same level of reliability.

3800 km of LDPE cables in the 63 to 400 kV range and 1200 km of XLPE cables in the 63 to 138 kV range were currently in service and a single breakdown had been recorded, the origin of which was uncertain (apart from defects of mechanical origin and incidents connected with water treeing).

Confirming this in service experience on the grid, Mr FAVRIE reported that considerable test lengths had withstood far higher gradients without any apparent deterioration.

He quoted the case of a 400 kV cable which had withstood a long duration test lasting 145000 hours at 23 V/mm and 7700 hours at 27 kV/mm. A cable of the same type had passed the short duration tests at the level of 400 kV (10 impulses in each polarity at 1425 kV and 24 hours at 500 kV AC), the long duration test (7700 hours at 23 kV/mm followed by additional investigatory tests (10 impulses in each polarity at 1750 kV and 24 hours at 750 kV AC).

He concluded that a routine test at 27 - 28 kV/mm was perfectly appropriate for cables having a operational gradient of around 15 kV/mm.

Communication by Ms LE PEURIAN (cf Appendix 1)

Impulse strength of aged cables

Ms LE PEURIAN presented the results of breakdown due to lightning impulse on new and aged cables, either on the EDF grid for 11 to 12 years or on the Renardières long-term test bench for 7000 to 10000 hours at 3 Uo and with thermal cycling.

No difference had been observed between new and aged cables.

Mr RIOT inquired if the cable for which the membrane voltage showed ageing due to ion permeability had been part of the series tested. Ms LE PEURIAN confirmed this.

Mr SRINIVAS pointed out that breakdown occurred at a specific localised point whereas ageing affected the condition of the material as a whole. It could be considered that we were not testing the same thing and that comparisons based on breakdown values might not be related to the evolution of ageing.

Communication by Mr JANAH (cf Appendix 1)

Characteristics of the insulation of a 225 kV cable after 7000 hours ageing with cycling

Mr JANAH explained the conditions of a 7000 test to which a 400 mm^2 cross-section copper cable insulated with 24 mm of XLPE had been exposed.

- Emax : 20 kV/mm - Emin : 7 kV/mm

- heating cycle 8h/16h raising conductor temperature to 90°C.

After testing, the characteristics of the insulation were measured and compared to those recorded in the new condition.

- Mechanical characteristics remained unchanged.

- There was little change in void distribution, slight resorption having been noted. Crosslinking had been performed in oil.

- Seven treeing incidents had been observed, their origin being contaminants. They were all located in the flux welding zone. It had not been possible to determine the origin of the contaminants, their dimensions being too small.

- The acetophenone level remained high after ageing. It was higher than the level recorded on crosslinked insulation on a catenary line with partial outgassing in the tube.

He concluded that no notable ageing had been revealed after the 7000 hour test.

4. <u>CONCLUSION</u>

To explain the ageing mechanisms and to know the state of the cables in service present much interest and justify the very important work completed for a few years and presented at the time of the workshop.

Analysis methods were presented. They call upon high technology equipments and require a pointed technicality but make it possible to detect microscopic charasteristics evolutions of insulating material.

The synthetic insulated cables in service do not present today faults ascribable to internal ageing causes and the following explanations can be advanced :

- the noted evolutions of characteristics materials involve only deteriorations not very significant of the cables functional characteristics. The operation stresses would be supported without any particular problem, at least with the in service feedback we know presently on these cables.

- the stresses which result from the operation conditions (electric field, temperature, oxidation,...) remain lower than a threshold where would be initiated the ageing mechanisms and which research-workers highlighted in laboratory.

To validate these assumptions, Chairman MASHIKIAN invites the scientists, the manufacturers and the operators to continue their work in collaboration in order to, in the long term, bring a supported answer.

May be they will then have more powerful tools to perfect the
dimensioning of the cable insulations with e view to the stresses
they will be able to support in total safety.

APPENDIX 1

CONTRIBUTIONS OF PARTICIPANTS

This Appendix contains the contributions of speakers during the Workshop.

To avoid any distortion in the intentions of speakers, their contributions are printed exactly as received by the Organisers.

A workshop is a place where running works can be discussed; so, the following contributions have not to be taken as reports because most of the time, exposed results will have to be validated further.

TOPIC: AGEING MECHANISMS

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PHENOMENES DE VIEILLISSEMENT CONTROLES

PAR LA DIFFUSION DES REACTIFS

1) <u>**Conditions pour un contrôle de la cinétique par la diffusion**</u>

Soit un processus de vieillissement impliquant la pénétration d'un réactif (oxygène, eau, ...) dans le matériau.

Soit P la perméabilité du matériau à ce réactif :

$$P = D.S \text{ (D : diffusivité, S : solubilité)}$$

Soit $l = 2e$ l'épaisseur de l'échantillon
(e est la demi-épaisseur)

Soit r_s la vitesse de consommation du réactif dans la couche superficielle (non perturbée par la diffusion)

A une température donnée T, il existe une constante α telle que :

si $r_s . e^{\alpha} < P$ le phénomène n'est pas contrôlé par la diffusion

si $r_s . e^{\alpha} > P$ le phénomène est contrôlé par la diffusion

En écrivant la loi de Fick modifiée par la consommation du réactif :

$$\partial C/\partial t = D\partial^2 C/\partial x^2 - r(C)$$

et en supposant qu'à l'état stationnaire $dC/dt = 0$, on peut déterminer la forme du profil de concentration $C(x)$ et la valeur de α. Généralement, on peut dire que $\alpha = 2$, soit :

si $r_s . e^{\alpha} < P$	pas de contrôle] par la
diffusion si $r_s . e^{\alpha} > P$	contrôle

2) <u>**Conséquences**</u>

2.1) <u>**Dans des conditions données de vieillissement (r_s et P sont fixes)**</u> :

on peut définir une épaisseur critique $l_c = 2 e_c$ telle que :

$$e_c = (P / r_s)^{\frac{1}{2}}$$

si $l < l_c$ le vieillissement est homogène dans l'épaisseur

si $l > l_c$ le vieillissement est hétérogène et la couche dégradée à une épaisseur de l'ordre de e_c

Si r_s varie au cours du vieillissement, l'épaisseur de la couche oxydée (TOL) va varier dans le sens opposé.

2.2) Vieillissement par rayonnement

Dans le cas du vieillissement photo ou radiochimique, une variable importante est l'intensité ou débit de dose I.

La cinétique de réaction nous donne la vitesse de consommation d'oxygène r_s en fonction de l'intensité :

$$r_s = \Phi \, I^\beta$$

Souvent $\beta = 1$ ou $1/2$

A température constante :

$$TOL = A \cdot I^{-\beta/2} \quad \text{où } A = \text{constante}$$

L'épaisseur de la couche oxydée est une fonction décroissante de l'intensité ou du débit de dose.

2.3) Vieillissement thermique

Soit $P = P_o \exp - Ep/R.T$ (Ep = énergie d'activation apparente de la perméation)

et $r_s = r_{so} \exp - E_R/R.T$ (E_R = énergie d'activation apparente de la réaction de consommation d'oxygène)

$$e_s = (P/r_s)^{1/2} = e_{so} \exp \left(1/2 \; \frac{E_R - Ep}{R.T}\right)$$

La variation de e_s, c'est-à-dire TOL, avec T dépend du signe de $E_R - Ep$. Généralement $E_R > Ep$ et TOL est une fonction décroissante de T.

3) Conclusions

Au-delà de certaines valeurs de la vitesse de vieillissement ou de l'épaisseur de l'échantillon, le vieillissement est gouverné par la diffusion du réactif. Dans ce cas, pour un échantillon épais, l'épaisseur de la couche oxydée est une fonction décroissante de l'intensité (vieillissement par irradiation), ou de la température (vieillissement thermooxydant). Dans ce cas-là, l'état vieilli, obtenu après vieillissement accéléré, n'est pas équivalent à l'état vieilli résultant du vieillissement naturel.

ELECTRICAL AGEING OF INSULATING MATERIALS : MECHANISMS AND DEGRADATION PROCESS

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INTRODUCTION

We consider that the modelling of the electrical ageing of polymer insulated power cables may be only based on a good knowledge of the different successive steps of the process. This implies the observation of the phenomenon. The different stages being cheked off, we have to formulate hypothesis on the processes : physical, chemical, mechanical or their conjunction, governing each of these hypothesis.

Mechanisms are identified on laboratory specimens which lead to macroscopic models, the parameters of which are measurable. Then and only after the previous stage, the cable outline may be taken into consideration to lead to the modelling of cable ageing. We envisage an ageing process based on the existence of two kinds of defects : gaseous cavities and high field concentration areas. These both situations lead to the breakdown through electrical treeing.

BULK EVOLUTION AND CRITICAL THRESHOLD

Long before the ignition of the first partial discharges, we have shown that light is emitted from the insulation around areas of local field concentration. This light is not related to partial discharges in the gas phase but comes from electroluminescence of the material when subjected to continuous space charge injection from local injecting sites. The injected carriers loose their energy in the dielectric and a small part of it is radiated off by luminescence. The occurrence of electroluminescence constitutes a warning since it is the indication that energy in the low electron-volts range is dumped into the material. Because the charge transfer process is very non linear with voltage, it can be characterized by a threshold. Below the threshold, the energy dissipated into the dielectric is too low for degradation to occur. The determination of this threshold on laboratory specimens is the aim of our actual research.

The effect of gas phase is very important on the tree initiation characteristic, at least on polyethylene and is likely the same in the breakdown process. Gas phase

can be present in the dielectric material under two different forms : (i) as an absorbed layer at the metal-polymer interface and (ii) as a dissolved phase mainly in the amorphous part of semi-cristalline polymer. Data relevant to a 50 % cristalline polyethylene demonstrate that the solubility of oxygen is 0.038 cm^3/cm^3.atm, and is as high as 0.225 cm^3/cm^3.atm in the case of CO_2. [Mic]

The effect of an adsorbed gas layer was investigated by T. Tanaka and coworkers [Tan] : they were using hypodermic like needle in order to introduce different gas at the interface between the needle and polyetylene. They report that electronegative gases (like O2 and SF6, in comparison with air and N2) enhance tree initiation voltage by modifying the interface electronic states by gas adsorption and by inducing chemical reactions at the metal surface.

Apparently contradictory results were obtained by S.S. Bamji et al [Bam], C. Laurent et al [Lau] and Shimizu et al [Shi] : they report a decreasing voltage to tree inception with electronegative gases (such as O2, SF6, CO2) and no effect for inert gases (such as N2). The difference in results are understandable in the following way : in the latter experiments, the polyethylene samples are first outgassed, and subsequently impregnated with various gases under a moderate overpressure. The experimental conditions are quite different in comparison with those used by T.Tanaka : in one case, the injected gases are mixing with the air naturally dissolved in the polymer, wether impregnation after outgassing leads to a more simple situation where only the impregnation gas is present in a significant proportion.

The effect of oxygen on the tree inception process is a very important result on a scientific and practical point of view. Outgassing increases the tree starting voltage in comparison with non-outgassed samples by a factor of 2 or more [Shi, Lau, Bam], which is much more important than any changes due to impregnation of gases reported so far. This behavior has been clearly attributed to the specific role of oxygen. The situation is twofold :

- oxygen can changed the characteristics of the interface, and modified the charge-exchange process. This is due to the electronegative character of oxygen which can act as an electron acceptor. This has been established considering that an outgassed sample containing a residual quantity of oxygen behave like a nitrogen impregnated sample.
- on the other hand, oxygen will favorize in a very efficient way the formation of free radicals and speed up the degradation process.

Under the effect of charge injection, local modifications of the polymer structure are taking place.

The ESR and FTIR techniques are efficient tools to propose a degradation process. For example an alkyl radical (- CH_2 - $\overset{\bullet}{C}H$ - CH_2) is detected during the initiation phase and a peroxy radical (- CH - O - O•) observed after a reaction with an oxygen molecule. During the following reactions formation and decomposition of hydroperoxides (- CH - O - OH) could be considered.

The different reactions insolve different energies, in the dissociation process for example ROO - H, R - OOH and RO - OH need 3.9 ev, 3 ev and 1.82 ev respectively. So we can say that during ageing, mechanisms are more probable than others and can justify the light emitted during electroluminescence and the structure changes observed by infrared spectroscopy.

We want to point out that it is difficult to generalize to all insulating materials initiation and propagation processes. Indeed in polymers exists the possibility of radical migration via a sequence of temperature dependent chemical reactions. Radical disappearance can be influenced by the local environment i.e the size of molecules as well as impregnating gas. So that near the glass transition temperature, Tg, or near the melting temperature, Tm, the free radical desappearance is related to the onset of mobility which is different in a cristalline phase than in an amorphous phase. This can explain the difference in the rate of decay of alkyl radicals in polyethylene and polypropylene.

On the other hand the chemical reactions may be accelerated by inclusion of a rapidly diffusing gas, such as oxygen or hydrogen which can react with polymer radicals leading to peroxy radicals and carbonyl function. This effect of gases was previously examined.

The only consideration of carbonyl functions as well as the rate of radicals to describe a kinetics of ageing are not sufficient since metastable states may be considered upstream from the structure changing process.

The previous arguments apply to the ageing of the bulk polymer or when discharges are responsible of this ageing because they grow inside cracks or microvoids created in to the insulating material.

However when discharges arise in the material, experimental results are at our disposal to explain the mechanism, but during the initiation process many parameters seem to play and more work is needed to make progress to prevent any breakdown. In other words it seems easier to explain the propagation process than the initiation one, since it was demonstrated when a microvoid exists the electrical breakdown occurs through an electrical treeing phenomenon.

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MODIFICATIONS OF THE MORPHOLOGY OF XLPE INDUCED BY HIGH ELECTRIC FIELDS

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OBJECTIVES AND SCOPE OF THE STUDY

Although there are several existing theories that attempt to describe the lifetime of XLPE subjected to high fields, there is yet no clear and undisputable physical explanation for the mechanism of loss of life. We have recently proposed that one major precursor step in XLPE aging is the formation of submicrocavities at fields higher than a given critical field (1). This does not mean that partial discharges (among other things) are not playing an important role in insulation aging; what we are saying is that microcavity formation is a precursor stage where the polymer morpholy has changed in a subtle but significant way.

In order to demonstrate the validity of our approach, we have measured morphological changes in electrically aged XLPE samples. The results obtained with 2 different techniques (small angle Xray scattering and neutron scattering) show that fields higher than 15-20 kV/mm induce morphology modifications. These results agree with those obtained years ago (2-3) in positron annihilation measurements which provide further evidence that our observations are not experimental artefacts. The results are discussed in the following sections. The limits of the experimental conditions used are also discussed in comparison with cable operation conditions.

EXPERIMENTAL

The samples were press molded plaques of commercially available XLPE cured under high pressure in nitrogen. They were electrically aged at 22° C in silicone oil (to avoid flash overs) for various time duration. The applied fields varied from 5 to 35 kV/mm. Before and after aging the morphology of the samples was analyzed by SAXS (and in a few cases by neutron scattering). Modifications in the spectra (after aging) were taken as evidence for morphological changes induced by field application. Below 5kV/mm, no significant difference in the spectra was noted (at least, for field application shorter than 30 days). The differences are usually assigned to defects (crystals being themselves considered as "defects"). The size of the induced defects can be grossly estimated by the method of Fankuchen (4). The values thus obtained (Table 1) should be considered only as first approximations but we are satisfied at the present time by an order of magnitude value. However, more precise values would be required for a more formal treatment of experimental data. It is obvious in Table 1 that above 15-20 kV/mm the average size of defects is approximately constant. Above this value, defect formation varies rapidly with time. In other words, defect size appears to have a maximum value but their number continues to increase with time of field application. The average size of defects appears to be equivalent to the thickness of the amorphous phase which suggest that defects are essentially located in the amorphous fraction of the polymer. Interestingly, defect formation is also frequency dependent (Table 1) which corresponds to the well known fact that cable lifetime is shorter at higher frequency.

Table 1

Sample	Size of defects (Å)	Size of amorphores phase (Å)
Unaged	0	89
Aged at 60Hz:		
12 kV/mm, 16h	0	70
20kV/mm, 20h	80	81
30kV/mm, 17h	83	91
Aged at 1kHz:		
24kV/mm, 1h	80	80
30kV/mm, 6h	97	82

In order to validate the above results with another technique, we have used neutron scattering to try to detect field-induced defects. Hydrogen atoms do not diffract neutrons but deuterons do. In fact, unaged XLPE samples soaked in heavy water show a strong signal (fig. 1) whereas the same unaged dry samples show no signal at all. The signal comes from heavy water occupying the free volume. Therefore, we speculated if there are additional morphology defects, they should be filled by heavy water, giving a stronger signal than in the unaged condition. This is exactly what was observed in the spectrum of a sample aged at 20 kV/mm (fig. 1). This confirms that high fields induce morphology changes in XLPE. The exact origin of these defects is not yet clear but their presence has been experimentally shown with 2 different techniques.

DISCUSSION AND CONCLUSIONS

A tentative explanation has been given for submicrocavity formation (1) which is supposed to occur above a critical field. From the results shown in Table 1 it seems that this critical field corresponds to the field value where the defect size reaches a constant value; thus, the critical field at 22° C would be around 15-20 kV/mm. This also corresponds to the limit of the exponential regime in the time dependence of XLPE life determined from accelerated aging tests (see fig. 2). This suggests that the rapidly decreasing breakdown strength of XLPE at high fields is due to submicrocavity formation. Below the critical field, life can be extremely long due to the absence of field-induced defects.

Note that the value of 15 kV/mm is also the field value where the kinetics of positron annihilation in polyethylene is significantly modified (2-3). Positrons are the antimatter of electrons and an excess of free electrons (as in cavity formation) will lead to more positron annihilation, as indeed observed. Therefore, the critical field value appears to be related with changes in many physical processes in PE. There are still many unknowns in the proposed model and the most important, especially from a practical point of view, is the role of thermal cycles. One expects that microcavities would collapse above 50-60° C and this may happens under real cable operation. Another parameter to be considered is the fact that press-molded samples are very different from extruded cables; the exact influence of localized polymer morphology is not well known. Nevertheless, the above experimental evidence of defect formation at high field suggests that more attention should be paid to the possible influence of submicrocavities on XLPE cable aging.

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FIGURE CAPTIONS

Fig.1 Neutron scattering spectra of unaged and aged XLPE sample soaked in heavy water .

Fig.2 Life curve of XLPE cable (see ref. 1 for details). Note the change slope at 15 kV/mm.
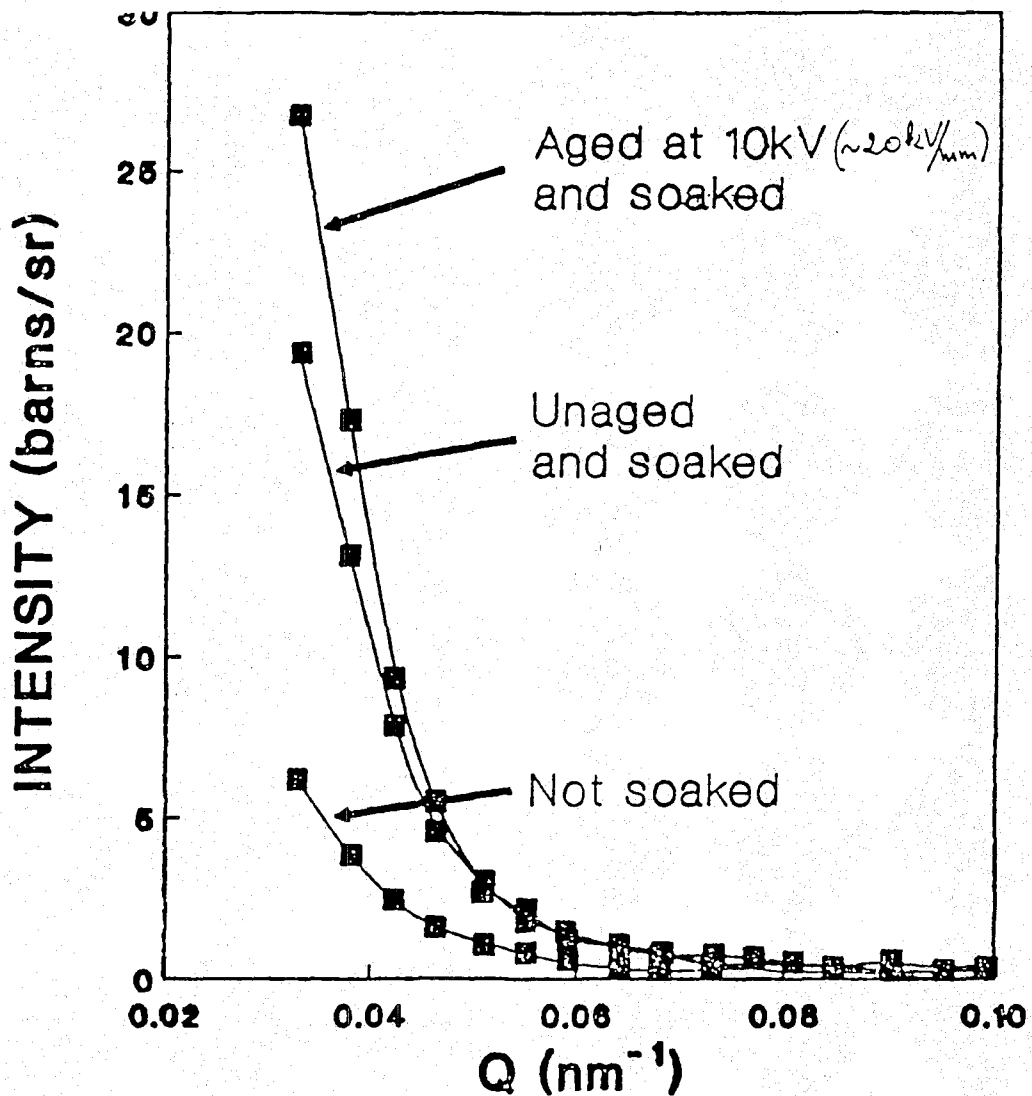
Fig. 1
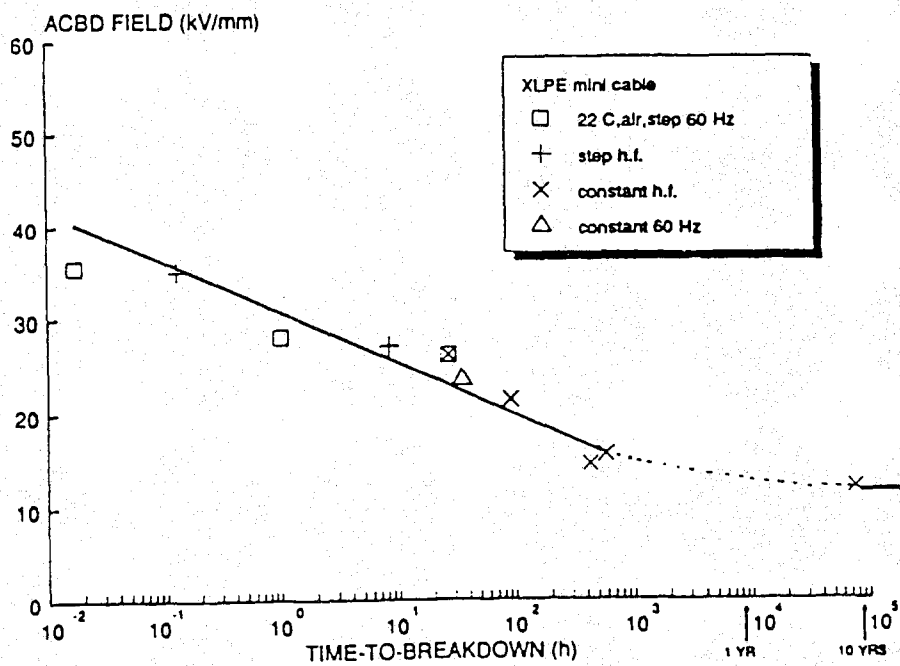
Fig. 2

Workshop on the ageing of power cables, Clamart 1991 June.

> Contribution of: P.P.Leufkens
> Head of Technology Dep.
> NKF KABEL BV
> Delft - The Netherlands

> Contribution to par. 3.1 "Mechanisms of ageing":
> Which is the influence of the pollutants on the degradation
> of the dielectric properties of the insulation.

Dear Mr. Chairman,

In 1987 in Delft at the Techn. Univ. and at our company we have
performed some research on "The Effect of Different Types of
Inclusions on PE Cable Life" [1], which we abstracted as follow.

If the electrical stress in PE is increased, the limiting factor
for the reliability is the unavoidable presence of defects such
as protrusions and inclusions. Our present experiments on cable
samples have shown that conducting inclusions are not as harmful
as mineral particles, in particular glass.

The aim of the investigation is to make a classification of
different kinds of inclusions with respect to their effect on
cable life. To stay as close to a practical contaminated cable as
possible, real cable samples were made with foreign particles fed
into the extruder inlet. Three main groups were considered:

1. Industrial particles (copper)
2. Biological particles (wood, sisal)
3. Mineral particles (glass fiber, NaCl).

The size of the particles was kept as constant as possible (figu-
re 1) to compare the effects on cable life, based on the kind of
material only. The cable had 3.4 mm insulation wall thickness.
To get a classification of the effect of inclusions on cable
life, a combined AC 50 Hz step-up/endurance test was performed on
each 10 meter sample (more then 10 samples per inclusion cable
type). At first the voltage was raised in 15% steps up to 28
kV/mm. Then the stress was kept constant until all samples had
failed. The test circuit was made in order to keep the breakdown
energy low. The origin of BD's could be established in the cases
of a BD at lower voltage. Then particles were found to be the
cause.
No partial discharges have been found with detection with a
sensitivity of 0.05 up to 0.1 pC.

Figure 2 shows the results in Weibull diagrams.
We can clearly separate glass from all other inclusions because
of its extremely strong effect on cable life. In contrast to
expectations copper parts are not at all as detrimental.

The best explanation for the fenomena we could find is as fol-
lows:
Glass has an extremely smooth surface. Because of this the adhe-
sion between glass and PE is relatively low, and voids could be
generated at the surface of the glass particle.
Partial discharge then can start.
Trees were observed, starting at the edges of the copper and
glass particles.
One can imagine two situations:
1. Void at the end of a glass particle (fig. 3.a)
2. Void parallel to the surface of a glass particle (fig. 3.b)

The PD level can be calculated as well as the Ignition Voltage,
assuming values for void sizes, Paschen curve for atmospheric
air, and electrical stresses which are calculated by means of a
computer program. Figure 4 shows the stress differences between
glass and copper.

The calculations show an ignition voltage of 9.5 kV/mm and PD
level of 0.07 pC for the fig 3.a situation, and
4.2 kV/mm and 0.007 pC for fig 3.b
As in both cases the maximum voltage in the void exceeds the
breakdown value, PD will be present in the void. However, the
discharge magnitude is so small that it cannot be detected with a
sensitivity as high as 0.1 pC.

A final conclusion is that all polluted cables will show a high
failure percentage (>50%) at a type test for HV cables (23 kV/mm,
24 h).

REFERENCE
1. published: IEEE EI Vo. 23, dec. 1988 pp 1051-55
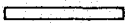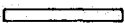
glass	▭	0.5–1.0 × ∅ 0.15
copper	▭	0.5–1.0 × ∅ 0.10
salt	⬠	0.5x0.5x0.5
wood	⟡	0.5x0.5x1
sisal	⟋	0.3x0.3x1
cork	⬡	0.5x0.5x0.5

Figure 1 – Dimensions of inclusions [mm]

I   fig 3.a   II   fig 3.b

fig 4a   glass $\varepsilon_r \sim 5$

fig 4b   Copper $\varepsilon_r \rightarrow \infty$
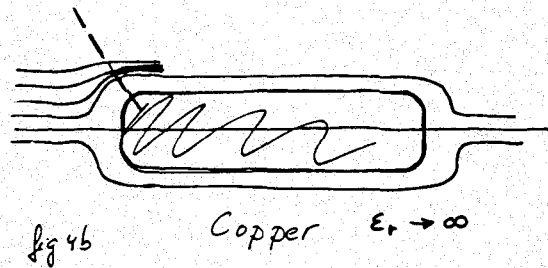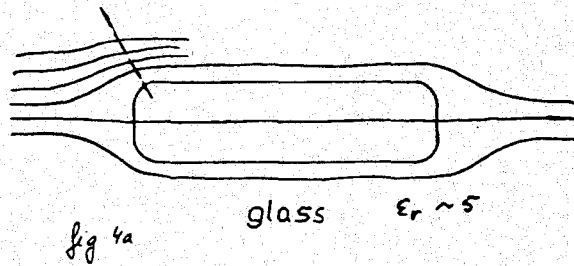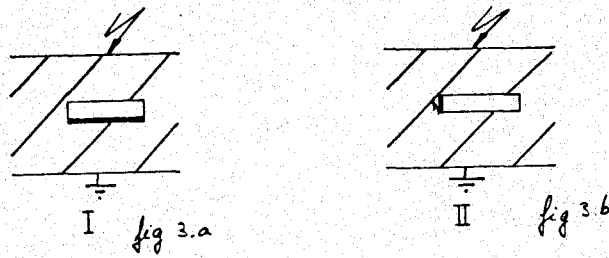
Figure 2 — Weibull curves (28 kV/mm)
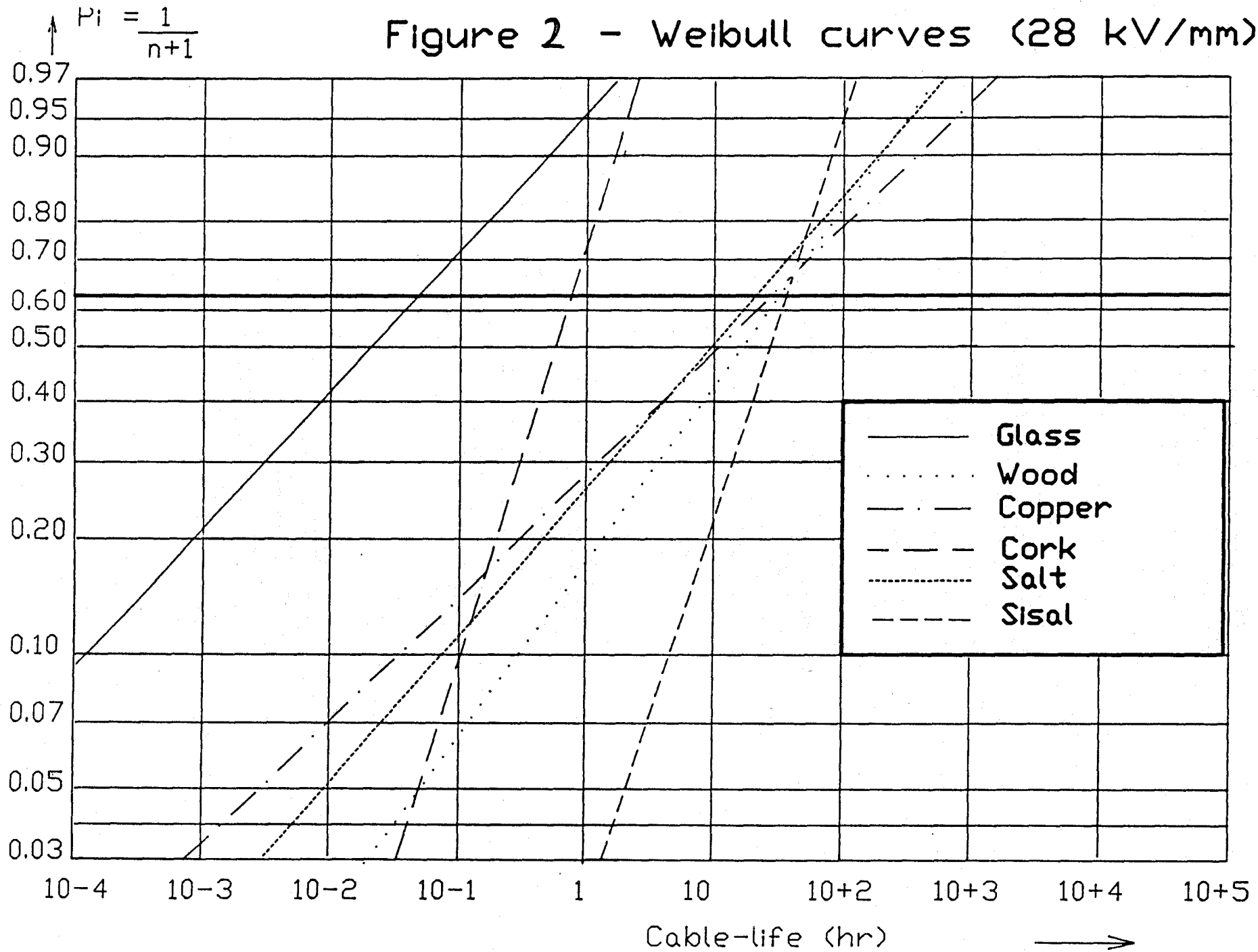
MECHANISM OF AGING

DETECTION OF METALLIC/IONIC CONTAMINANTS

BY

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USA   USA

This is with reference to the subject of aging <u>without</u> the accidental penetration of water. Some comments can be offered on the detection of inorganic ions/contaminants under accelerated aging conditions in the laboratory.

This summary is from (1) an EPRI-sponsored project on the thermal overload of cables, at Cable Technology Laboratories, RP 1516-01 (Final Report EL-5757, July 1988), (2) some diagnostics work performed by University of Connecticut (UCONN) as a Subcontractor on this project, and (3) additional diagnostics work that was performed at UCONN on Project RP 7897-01, "Evaluation of sensitive Diagnostic Techniques for Cable Characterization, (Final Report EL 7076, Volume I, December 1990).

This communication is concerned with 15 and 35 kV XLPE-insulated cable having 750 Kcmil (380 sq. mm) aluminum conductor, semiconducting coated

Nylon fabric binder internal to an ethylene copolymer conductor shield, 4.45 and 10.5 mm XLPE insulation, respectively, ethylene copolymer insulation shield, a copper wire metallic shield, Mylar separator, and a PVC jacket. The cables were steam-cured.

Cables were subjected to daily thermal cycles to 145°C or 175° C conductor temperature at rated voltage, while installed in a 2.75m long duct provided with two 0.75m radii bends; hence, the acceleration for these cables was primarily thermal, but operating voltage and mechanical stress were also applied.

It was observed that cables subjected to (100) daily load cycles exhibited dark brown spots within the insulation, mostly near the conductor shield. (The cable also experienced a general darkening, to yellow-tan, but that will not be focused upon in this discussion).

The dark spots were found to be a temperature related change in the insulation. The cables aged at 175°C had significantly darker spots than the cables aged only at 145°C. The spots also were darkest close to the conductors and decreased in intensity with an increase in the distance from the heat source, which in this case was at the conductor.

Microscopic examination of these spots revealed evidence that the spots had, a dark nucleus surrounded by a less dense (clear) area followed by a dark outer ring. To the naked eye these spots appeared as particles of degraded (oxidized) polyethylene. An analysis made at the University of Connecticut indicates that greater oxidation of the polymer had taken place at the location of these spots, and that they contained chlorine.

Since PVC jacket materials can degrade at these elevated temperatures (i.e., temperatures higher than anticipated may occasionally exist in normal service) to yield hydrogen chloride gas (HCl), it was concluded that such degradation was highly likely. The HCl gas would have diffused into the insulation, reacting there with some unidentified component. A higher concentration of dark spots, in the vicinity of the conductor shield, suggested that the hydrogen chloride reacted more extensively there than at any other region of the insulation.

Analytical tests performed at the location of the dark spot indicated the presence of chlorine, providing some evidence for the hypothesis. These results are shown in Table I. Other diagnostic tests were also performed. It was observed that there was a high degree of oxidation at these dark spot regions; this was ascertained by infrared spectroscopy and oxidation induction time. Reduced crystallinity was observed by Differential Scanning Calorimetry. Elongation was determined employing specimens containing dark spots and specimens cut near dark spot areas. The results indicated a 10 and 30 percent lower elongation for the insulation containing the dark spots after 100 cycles aging with maximum temperatures of 145°C, and 175°C, respectively. There was also a drop in tensile strength.

Attempts were made to determine if the dark spots were weak from a dielectric strength point of view. In spite of using small, rounded electrodes, located directly over the spots, in 0.5 mm thick slices of insulation, incorporating the spots. The voltage breakdown did not necessarily occur at the location of the dark spots. In many cases the breakdowns were immediately adjacent to the

location of the dark spots,in the clear insulation, indicating that even if the dielectric is weakened at this area, the degree of this effect on the dielectric strength is only minor. Results of 60 Hz voltage breakdown tests performed over the dark spots, in the radically sliced insulation, close to the conductor shield of a 15 kV, XLPE insulated cable, aged for 70 days at temperatures of 175°C provided a mean breakdown strength of 48 kV/mm.

Further analysis of these cables (and others) at the University of Connecticut (Dr. M. Ezrin) under EPRI contract, using SEM/WDX, demonstrated that certain metals (called transition metals) were present in trace amounts in various specimens; Cobalt, Chromium, Copper, Vanadium, Titanium, Zinc and Iron (all of which were largely absent in the non-spot areas). Different trace components were present in different samples. For this effort, a number of additional 15 kV XLPE-insulated cables with jackets were thermally aged 322 days at 145°C prior to examination.

From a diagnostics perspective, it became apparent that this interaction of HCl gas with the transition metals might be of value as a tool for determining the presence of the metals in the insulation wall. A method was developed using a glass tube that held insulation specimens (helically cut with a lathe) into 20 mil thick strips; the entire wall between the insulation and strand shield could be examined in this manner.

The tube (one end sealed) containing the specimens, was first flushed with nitrogen, and a mixture of air, water and HCl gas was entered into the tube. One hour at 175°C was adequate to induce dark spot formations. It is concluded that when the metallic contaminant is present, it reacts with the chloride ion

(forming the metallic chloride), which in turn results from water ionizing the gas. Since transition metal ions are known catalysts for oxidation, this would explain the increased localized oxidation observed in this cable study.

This method is a potential diagnostic tool for determining presence of specific metallic contaminants, in locations where this may be suspected.

TABLE I

CHLORINE CONTENT IN THE INSULATION OF 15 KV CABLES AFTER 101 THERMAL CYCLES

Max. Cyclic Aging Temperature At Conductor (° C)	Observation	% Chlorine in XLPE
145	Dark Spot	.09
175	Dark Spot	.26
175	Near Insulation Shield	.02
175	Near Conductor Shield	.01

(a) For detailed information, see EPRI Final Report EL-5757

TOPIC: DIAGNOSIS AND FEEDBACK FROM EXPERIENCE

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▼
ALCATEL
KABELMETAL

21.06.1991

High stress ageing of XLPE insulated model cables

Some international cable experts have reported about indications of a threshold value of about 30 kV/mm for the electrical stress in XLPE cables. The question is how to define such a threshold (parameters, changes).

We consider the short term AC strength as most important criterion for the evaluation of extruded cable insulations. A decrease in AC breakdown strength indicates a deterioration of the insulation e.g. by water or electrical treeing. An increase may be interpreted by stressgrading due to migration of polar groups or the formation of small bow tie trees.

Many ageing tests of high voltage cables with high stresses were already carried out. The problem is that usually a comparison of the AC strength before and after ageing is not possible due to practical reasons (terminations!). The general information that no breakdown occured is unsatisfactory.

We reported at the CIGRÉ conferences 1986 (1) and 1990 (2) about AC ageing tests with HV cables where a destructive impulse test was carried out as an indicator test for deterioration of the insulation. One result was that high AC prestressing increases the impulse strength.

Test details: 75 m cable 300 mm² with 18 mm insulation
                   AC stress 50 kV/mm ($\triangleq$ 530 kV) over 240 h
                   impulse stress > 180 kV/mm at 20 °C
                   bow tie trees < 5 µm

Another high stress test was carried out with model cables. This makes it possible to measure the AC short term strength as a function of the ageing time.

Design of the model cable:

solid copper conductor: 1.5 mm²
crosslinked conductor screen: 0.7 mm
crosslinked insulation: 1.5 mm
crosslinked insulation screen: 0.2 mm

The three layers are extruded in one step with laboratory equipment. Crosslinking is carried out with steam in a second step. This model cable is used for evaluating the influence of water (3).

Testing procedure

Specimens: 5x 2 m active length

Conditioning: 16 h at 90 °C in an oven with
circulating air

Ageing: U = 30 kV, 50 Hz
E_{mean} = 20 kV/mm
E_{max} = 30 kV/mm
room temperature
1; 2; 4; 8 weeks, test continues

Evaluation: Determination of the residual AC breakdown
strength with step rising voltage (3 kV,
5 min). Start at 60 kV.
Calculation of the characteristic breakdown
strength (Weibull 63 %) and the 95 % confidence interval.

The results (figure 1) show no change in the AC strength.

By FTIR (Fourier Transform Infrared Spectroscopy) we could not see any differences between unaged and aged samples.

The microscopic investigations of stained wafers revealed no treeing.

So we conclude that no electrical ageing (decrease of breakdown strength) took place.

Using the life time formula $t \cdot E^n$ = const. with n = 15 the test results (8 weeks/30 kV/mm) mean a life time of 5000 years at 15 kV/mm. This consideration supports the opinion that from the electrical ageing point of view service stresses of 15 kV/mm in XLPE cables are possible.

(1) Proceedings of the 1986 Session p. 15
(2) Report 21-106 of the 1990 Session
(3) Paper A 7.5 Jicable 1991

Emax in kV/mm

Ageing stress at room temperature

Ageing time in weeks
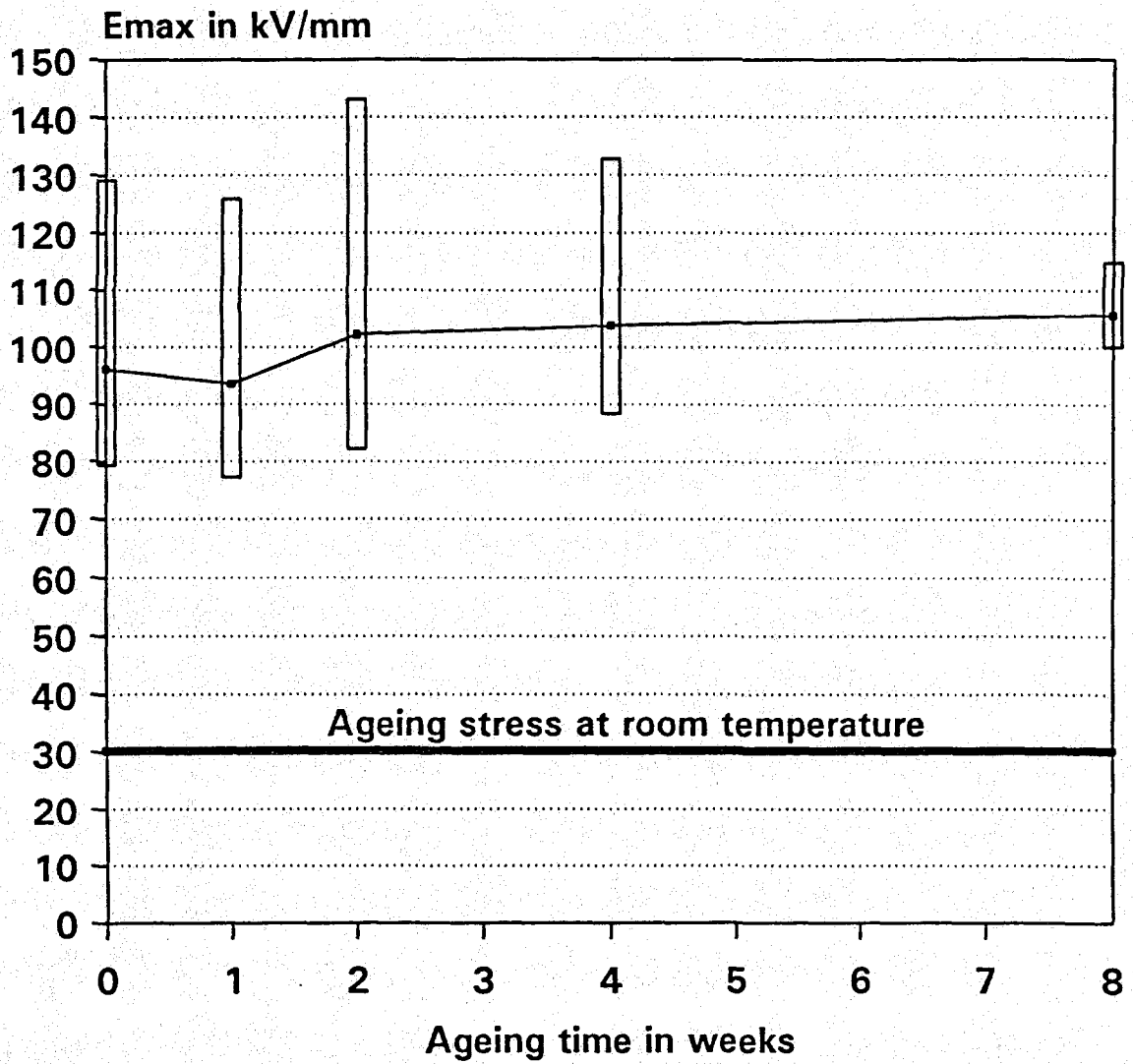
☐ 95 % Conf. Interval   ─●─ 63 % (Weibull)

kabelmetal electro/20.06.91

SILEC

ATELIER "VIEILLISSEMENT"

RETOUR D'EXPERIENCE DIAGNOSTIC

INTERVENTION DE M. FAVRIE

La notion de gradient de seuil est prise en considération depuis de nombreuses années et notre expérience en service des câbles à isolation polyéthylène basse densité en particulier, en confirme la validité.

Différents facteurs ont conduit à une augmentation des gradients de fonctionnement du matériel ; on peut citer entre autres :

- l'amélioration de la qualité des matières premières, en particulier au niveau des impuretés dans les matériaux isolants,

- la maîtrise des procédés de fabrication,

- l'interprétation des essais de longue durée.

SILEC
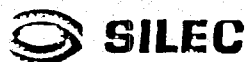
Nous sommes ainsi passé en moins de 30 ans d'un gradient maximal de service de 4 - 5 kV/mm à plus de 15 kV/mm.

Notre expérience en service est importante et correspond à plus de 3800 km de câbles isolés au PEBD de 63 kV à 400 kV et à plus de 1200 km de câbles isolés au PRC de 63 kV à 138 kV.

Si l'on exclut les défauts d'origine mécanique et les incidents liés au water treeing, il n'y a eu qu'un seul claquage câble, en 225 kV, après quelques mois de service et son origine est incertaine.

Il est intéressant de voir que des câbles 400 kV ayant subi des essais de longue durée à des gradients élevés de l'ordre de 27 kV/mm, aient conservé leurs qualités pour passer avec succès les essais de type de courte durée du matériel 500 kV. Ces essais de courte durée ont été effectués sur 2 échantillons de câbles 400 kV, l'un de section 1 x 630 mm^2 Aluminium et l'autre de section 1 x 1200 mm^2 Cuivre.

On trouvera dans les 2 tableaux ci-joints l'ensemble de ces résultats.

L'expérience acquise en service et l'interprétation des essais de longue durée, nous ont permis d'adopter des gradients de fonctionnement jusqu'à plus de 15 kV/mm pour les câbles THT ; le gradient maximal pendant l'essai de routine peut atteindre des valeurs de l'ordre de 27 - 28 kV/mm, valeurs que nous considérons comme raisonnable de ne pas dépasser pour l'instant.

Essais éffectués sur un câble 1 x 1200 mm^2 Cu - Tsp 230/400 kV

SPECIFICATION DU CABLE : 1 x 1200 mm^2 Cu-Epaisseur d'isolant PEBD : 27 mm

Longueur de câble (m)	Accessoires	Nature de l'essai séquence des essais	Tension (kV) conducteur/écran	Durée	Température (°C) sur le conducteur
25	2 extrémités extérieures	**1.Essais de courte durée :**			
		- Ondes de choc*	1425	1,2/50µs	75
		- Tension alternative	500	24 h	
		(50 Hz)			
		2.Essai de longue durée :			
		- Tension alternative	460	7700 h	80 et 85**
		(50 Hz)			
		3.Essais de courte durée :			
		- Ondes de choc	1425	1,2/50µs*	75
			1700	1,2/50µs***	
		- Tension alternative	500	24 h	
		(50 Hz)	700	4 h	

* 10 chocs de polarité + et 10 chocs de polarité -

** 167 cycles thermiques 20/80 °C suivis par au moins 83 cycles 20/85 °C

durée d'un cycle : 8 h de chauffage

16 h de refroidissement

*** 5 chocs de polarité + et 5 chocs de polarité -

Essais éffectués sur un câble 1 x 630 mm² Alu - Tsp 230/400 kV

SPECIFICATION DU CABLE : 1 x 630 mm² Alu-Epaisseur d'isolant PEBD : 30 mm

Longueur de câble (m)	Accessoires	Nature de l'essai	Tension (kV) conducteur/ écran	Durée	Température (°C) sur le conducteur
200	2 extrémités en caisson blindé 2 jonctions	Essai de longue durée : - Tension alternative (50 Hz)	400 460	14500 h 7700 h	80 et 85** 80 et 85**
25 m prélevés sur la longueur de 200 m	2 extrémités extérieures	Essais de courte durée : - Ondes de choc* - Tension alternative (50 Hz)	1425 1550 500 650	1,2/50 µs 1,2/50 µs 24 h 24 h	75 75

* 10 chocs de polarité + et 10 chocs de polarité -

** 167 cycles thermiques 20/80 °C suivis par au moins 83 cycles 20/85 °C

    durée d'un cycle : 8 h de chauffage

                 16 h de refroidissement

ASSESSMENT OF THE BREAKDOWN VOLTAGE
UNDER IMPULSE CONDITIONS
OF NEW AND AGED CABLES

par Mme S LE PEURIAN
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Various High Voltage cables samples, news and aged either after long duration tests or in service, have been subjected to impulse tests (1,2 / 50 μs) by increasing the voltage up to breakdown according to IEC 230 Publication.

Cables have been first heated with a current flowing into the conductor up to a temperature of 95°C.

No significant difference was observed between breakdown voltages of new and aged cables.

ALCATEL CABLE

Power department

Calais plant

Calais, 1991/05/20

**A 225 kV CABLE INSULATION CHARACTERISATION
AFTER 7000 HOURS AGEING WITH LOAD CYCLES**

INTRODUCTION :

A 50 meters length of 225 kV cable made by MDCV process has been aged 7000 hours with load cycles.

One meter sample has been cut off in the middle of the length to make a first investigation program on insulation properties after ageing and compare them with the unaged ones.

This paper reports first results obtained until now.

1/ DIMENSIONNEL ET CONDITIONS DE VIEILLISSEMENT

1/ DIMENSIONAL CHARACTERISTICS AND AGEING CONDITIONS

1.1/ Dimensionnel

1.1/ Dimensional characteristics

Composition	Epaisseur Thickness (mm)	Diametre Diameter (mm)
Conducteur Conductor		23.2
Ruban semi-conducteur Semi-conductive tape	0.4	24.0
Semi-conducteur interne Inner semi-conductive layer	1.4	26.8
Isolant Insulation	23.9	74.6
Semi-conducteur externe Outer semi-conductive layer	1.3	77.2

Table 1 : Dimensionnel du câble 1 x 400 mm² Cuivre XLPE 225 kV

1.2/ Conditions de vieillissement

L'échantillon calorifugé a subi 292 cycles de chauffage sous une tension de 270 kV.

.cycle de chauffage : 8h/16h
.gradient à l'âme : 20 kV/mm
.gradient externe : 7 kV/mm
.température visée au conducteur : 90°C

2/ ANALYSES COMPARATIVES

Ce paragraphe présente les premiers résultats obtenus

1.2/ Ageing parameters

The length was lagged. Number of load cycles : 292. Applied voltage : 270 kV

.load cycle : 8h loading/16h cooling
.conductor field : 20 kV/mm
.external field : 7 kV/mm
.expected conductor temperature : 90°C

2/ COMPARATIVE ANALYSIS

This section reports first results obtained.

2.1/ Evolution des caractéristiques méca-
niques

Les propriétés mécaniques ont été analysées
dans le sens longitudinal du câble sur toute
l'épaisseur de l'isolation. Les résultats sont
regroupés dans le tableau 2.

2.1/ Mechanical characteristics evolution

Mechanical properties have been analysed
along the longitudinal axis, on the total in-
sulation thickness. Results are summarized
in table 2.

	New state Etat neuf		After 7000 h ageing Etat vieilli	
	T (MPa)	A (%)	T (MPa)	A (%)
SC interne inner SC	25.2	517	24.5	518
	25.6	537	26.2	541
	26.7	525	25.0	547
	25.4	533	25.6	546
	25.3	520	26.3	536
	25.9	530	25.3	536
	24.8	529	25.8	532
	24.2	527	24.8	541
SC externe outer SC	24.9	529	25.3	542

Tableau 2 : Evolution des propriétés mécaniques
Table 2 : Mechanical properties evolution

On observe aucune différence entre l'état
neuf et l'état vieilli. Le câble a gardé ses
propriétés mécaniques tout au moins dans
le sens longitudinal (sens perpendiculaire
au champ électrique). Il serait intéressant
de comparer les propriétés mécaniques
dans le sens radial, c'est à dire dans le sens
du champ électrique. Cette étude pourra se
faire sur des micro-éprouvettes.

No change appears between the new state
and aged state. Cable kept his mechanical
properties in longitudinal axis (perpendi-
cular to the electrical field). It should be
interesting to compare mechanical cha-
racteristic along radial axis which is paral-
lel to electrical field. This study can be
made using smallest test piece

2.2/ Distribution radiale des vacuoles

Les figures 1 et 2 montrent la répartition
des vacuoles respectivement à l'état neuf et
vieilli.

2.2/ Radial micro-voids distribution

Figures 1 and 2 show the microvoids distri-
bution respectively at the new state and
aged state.
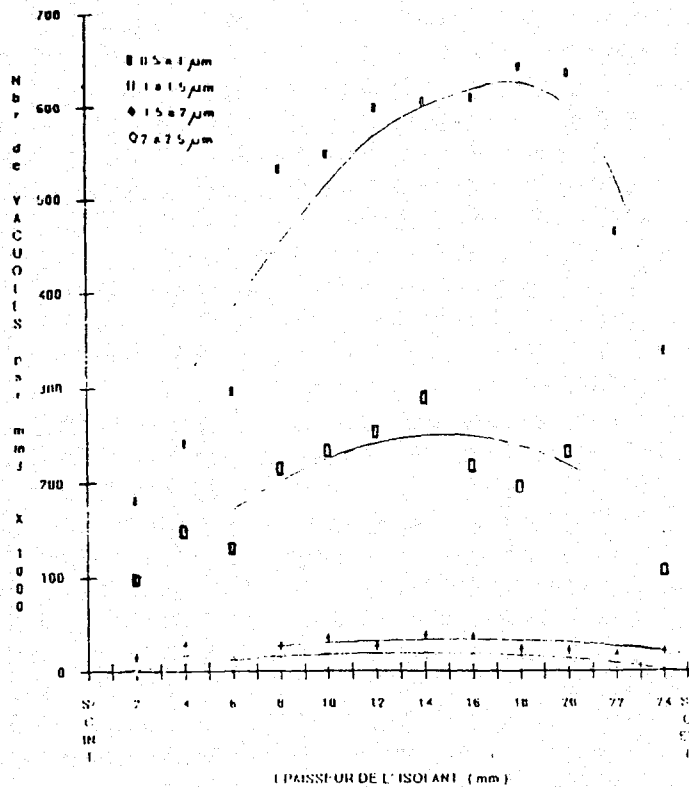
Figure 1 : Répartition des vacuoles à l'état neuf
Microvoids distribution at new state

Figure 2 : Répartition des vacuoles après 7000 h d'essai
Microvoids distribution after 7000 h testing

La résorption des vacuoles, que nous attribuons à la diffusion des bas poids moléculaires du polyéthylène, n'est pas aussi importante que celle que nous avons pu constater sur des câbles fabriqués sur ligne chaînette.

Microvoids reduction, due to self-diffusion of low molecular weight of polyethylene, is not so important in this case than those we have yet seen on catenary line cable.

Comme nous le verrons plus loin, cette résorption moindre peut être attribuée au process de fabrication lui même. En effet, la quantité de sous produits de réticulation est beaucoup plus importante dans les câbles fabriqués par procédé MDCV que ceux fabriqués sur ligne chaînette.

As we will see after in this report, this smalest reduction can be attributed to the process. Effectively, curing by-products amount is more important for cables made by long die process than those made by catenary line process.

2.3/ Recherche des arborescences

Un nombre très faible d'arborescences naissantes (7 arborescences) ont pu être observées sur les échantillons microtomés, l'analyse ayant porté sur plusieurs cm³ d'isolant. Ces débuts d'arborescences ont été décelés systématiquement dans la zone de raccordement des flux de matière prenant naissance sur des contaminants (taille 5 à 10 μm) comme le montrent les photos 1 et 2. La nature des contaminants donnant naissance à ces arborescences n'a pas pu être déterminée étant donné la difficulté d'amener l'inclusion en surface.

2.3/ Trees investigation :

This kind of analysis have been carried out on several cubic centimeters of insulation. However, only few new born tree have been detected (really 7) on microtomed samples. A singular remark to be made is that these newborn trees were systematically located in the flow line jointing area. They started always from very small contaminants (5 to 10 μm size) as shown in photos 1 and 2. The nature of contaminants has not been determined due to the difficulty to get them in surface.

Un autre examen sur ce câble après quelques milliers d'heures de vieillissement supplémentaire nous permettra soit de confirmer les observations actuelles, soit de suivre la croissance de ces arborescences.

An other examination after some supplementary thousands hours ageing will permit us to confirm this very good result or to follow trees growth
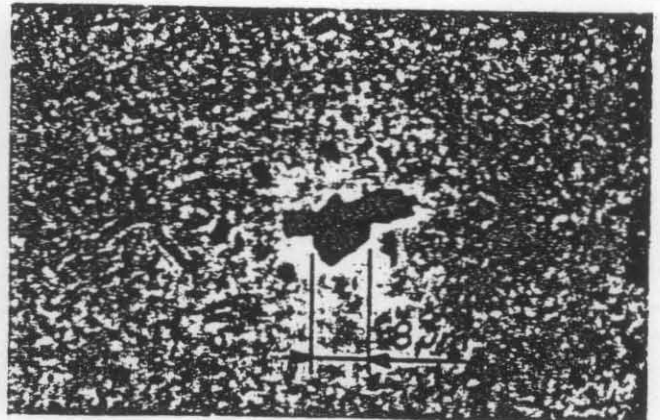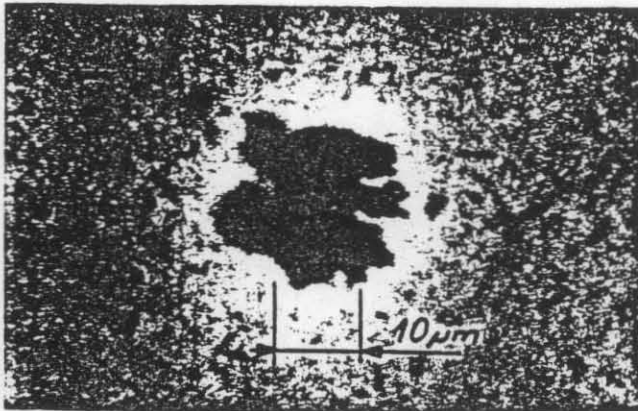
Photo 1 et 2 :
Début d'arborescences à partir d'inclusions dans le plan de joint
Newborn trees from contaminants in flow lines jointing area

2.4/ Analyses infra-rouge

L'analyse infra-rouge permet de suivre l'évolution de différents composants de l'isolation suivant un axe radial à partir de films obtenus par déroulage au tour. Parmi les paramètres que l'on peut suivre, on peut citer :

.la diffusion aux interfaces semi-conducteur/isolant
.l'oxydation
.le taux de cristallinité
.les sous-produits de réticulation

Dans un premier temps, nous nous sommes attachés à suivre l'évolution du taux d'acétophénone bien connu pour être un inhibiteur d'arborescence. La figure 3 montre la répartition du taux d'acétophénone du câble 225 kV fabriqué sur la ligne MDCV avant et après vieillissement.

2.4/ Infra-red analysis

Infra-red analyse permits to characterize several insulation components along the radial axis on tapes peeled from the cable by cutting on a lathe. Among parameters we can follow, most interesting are :

.diffusion phenomenon at semi-conductive layers/insulation interfaces
.oxidation
.cristallinity ratio
.curing by-products

In a first step, we begun to follow acetophenone amount changes (well know to be tree inhibitor) between the new state and after 7000 hours ageing. Figure 3 shows radial distribution of acetophenone for this 225 kV cable made on MDCV line before and after ageing.
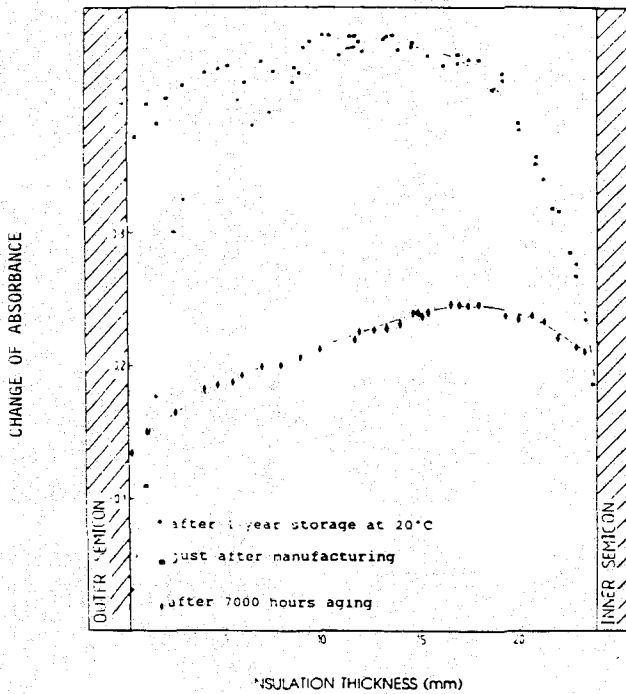
Figure 3 : distribution radiale de l'acétophénone
radial distribution of acetophenone

Figure 4 : Distribution radiale de l'acétophénone
Radial distribution of acetophenone

Pour avoir un élément de référence, nous avons effectué une étude comparative de la distribution radiale d'acétophénone entre deux câbles MT de spécifications quasi-identiques. l'un fait sur ligne MDCV, l'autre sur ligne chaînette. Les résultats sont regroupés sur la figure 4.

On constate une différence importante entre les deux procédés de fabrication. La teneur moindre en acétophénone pour le câble fait sur ligne chaînette est à relier au dégazage partiel dans le tube lors de la fabrication.

L'acétophénone qui reste piégé dans l'isolant du câble 225 kV fait sur ligne MDCV confirme l'absence d'arborescence après 7000 heures de vieillissement.

3/ CONCLUSION :

Les analyses effectuées à ce jour ne montrent pas de vieillissement notable de l'isolation. Une autre série d'analyse sera menée après une année supplémentaire de vieillissement sous haut gradient électrique pour suivre l'évolution des propriétés physiques et chimiques de l'isolation.

To have a reference, a comparative study has been carried out. The radial distribution of acetophenone has been determined for two cables having quite the same specification but elaborated with two different processes : one was made with MDCV line, the other with a catenary line. Results are shown in figure 4.

One can see an important difference between the two processes. For the catenary made cables lower acetophenone amount can be attributed to partial degassing occuring during processing.

Acetophenone trapped in the insulation of the 225 kV MDCV made cable confirms absence of trees after high stressing 7000 hours ageing.

3/ CONCLUSION :

Analysis made until now do not show changes of insulation properties. An other serie of analysis will be carried out after one more year ageing to follow possible physical and chemical changes of insulation under high electrical stress

TOPIC: EXPERIMENTAL TECHNIQUES

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MESURE DE CHARGES D'ESPACE

DANS DES CABLES VIEILLIS ET NEUFS

par A. TOUREILLE et A. SABIR

I- INTERETS DES MESURES DE CHARGES D'ESPACE

Dans les isolants solides soumis à des contraintes électriques élevées un certain nombre de mécanismes encore mal connus conduisent très souvent à l'installation d'une charge d'espace qui rompt la neutralité électrique de certaines régions de l'isolant. Cette non-neutralité persiste même si on supprime la contrainte électrique extérieure qui lui a donné naissance.

Cette charge d'espace, qui s'accumule dans certaines régions de l'isolant, a pour effet d'augmenter le champ électrique local, ce qui réduit la tenue en tension, donc la rigidité diélectrique et la durée de vie des dispositifs travaillant sous tension élevée comme les câbles .

Il ressort des derniers Congres Jicable , la nécessité de faire des études sur la mise en évidence de charges d'espace et leur influence dans les matériaux destinés à être utilisés dans les cables Haute Tension .En effet, les phénomènes tels que la fiabilité et le vieillissement semblent être corrélés avec l'apparition et le développement de la charge d'espace.

II LA METHODE DE L'ONDE THERMIQUE.

Nous avons mis au point au cours de ces dernières années au lABORATOIRE D'ELECTROTECHNIQUE DE MONTPELLIER une méthode de mesures des charges d'espace valable pour les structures épaisses tels que les cables . Cette technique-récemment validée- est basée sur le principe d'une onde thermique qui "remue" les charges électriques pour les mettre en évidence . La non destructibilité de la mesure permet de voir l'évolution de ces charges dans le temps. Les derniers développements de cette méthode montrent des possibilites réelles pour son application "in situ" sur un cable en service. La précision de la méthode peut atteindre quelques ppm: il s'agit donc d'un nouveau moyen d'analyse. Nous fondons beaucoup d'espoir sur les applications futures de ce nouvel outil : origine , nature et cinétique de la charge d'espace, explication cas par cas du claquage.

III- RESULTATS OBTENUS PAR L'ONDE THERMIQUE SUR DES CABLES H.T.

En utilisant la méthode nouvelle de l'onde thermique,qui permet de travailler sur des épaisseurs de plusieurs millimètres, nous avons déterminé le champ électrique local et la densité volumique de charge d'espace dans différents CABLES au PRC en faisant varier les paramètres de formation tels que le gradient appliqué, le temps d'application, la température,le vieillissement .

Nous appelons V_f, t_f, T_f, t_{cc} respectivement les tensions, temps, température de formation et le temps de conservation en court-circuit.

CABLE NEUF

L'échantillon neuf (cable D) de 11 mm d'isolation a été polarisé sous les conditions suivantes:

V_f = +70 kV continus sur le conducteur central

t_f = 89 h

T_f = 70 °C

Après deux jours de mise en court-circuit on a réalisé la mesure du courant dont le traitement a donné la distribution du champ électrique dans l'isolant indiquée par la figure 1. La densité de charge correspondante est donnnée par la courbe a de la figure 2.

On note que le maximum du champ électrique est du même ordre de grandeur que le champ moyen appliqué. La distribution de la charge d'espace montre une densité de charge négative de faible amplitude au centre de l'échantillon. De part et d'autre de cette charge négative, il y a une densité de charge positive qui présente un maximum de 80 mc/m^3.

Après 10 jours de court-circuit la densité de charge d'espace est donnée par la figure 2 b .

On note la disparition des charges négatives au centre de l'échantillon qui ont probablement diffusé vers les électrodes et ont été recombinées.

Devant l'intéret évident de ces résultats , nous avons testé la méthode sur l'influence du vieillissement dans des câbles PRC à forte épaisseur d'isolant (16 mm) en comparant les distributions de charges résiduelles de 2 échantillons de câbles ayant subi des traitements différents (câbles A et B).

CABLE A

Le câble A a subi une série de tests sévères (plusieurs milliers d'heures sous deux fois la tension normale à une température dépassant 100 °C). L'échantillon a été polarisé sous les conditions suivantes:

V_f = + 65 KV continu sur le conducteur central (anode)

t_f = 89 h

T_f = 70 °C

Le champ électrique et la charge d'espace sont représentées sur les figures 3 et 4 (mesure faite après 2 jours de court-circuit)..

La première constatation réside dans l'apparition d'alternance de régions positives et négatives conduisant à des domaines à fort champ électrique.

En effet du côté de la cathode le maximum du champ électrique est de 9 KV/mm alors que le champ moyen appliqué n'est que de 4.1 KV/mm.

On note un maximum de densité de charge d'espace positive du côté de la cathode qui est de 123 mc/m^3 alors que du côté de l'anode ce maximum ne dépasse pas -20 mc/m^3.

CABLE B

Le câble B est un câble du même type que le câble A sauf qu'il n a pas subi de traitements aussi sévères : son utilisation a été faite sous des conditions normales.

Dans le but de comparer ces deux câbles et de voir l'effet du vieillissement, on a formé l'échantillon B sous les mêmes conditions que l'échantillon A. Le traitement numérique du signal donné par l'onde thermique conduit à la distribution du champ électrique représentée par la figure 5 et la densité de charge d'espace correspondante est portée sur la figure 6.

Pour ce câble on note aussi la présence de zones d'alternance positives et négatives de plus faible amplitude mais s'étalant sur toute l'épaisseur de l'échantillon. Le maximum du champ électrique est de 3.7 kV/mm et le maximum de la densité de charge est de 50 mc/m^3.

En comparant les courbes des figures 4 et 6 on observe un comportement différent des deux câbles. En effet, du côté de la cathode, l'amplitude de la densité de charges positives dans le câble vieilli est plus de deux fois plus grande que celle du câble B, alors que du côté de l'anode la densité de charge est faible.

EVOLUTION EN FONCTION DU TEMPS DE COURT-CIRCUIT

Il est communément établi et reconnu que la charge d'espace évolue en fonction du temps. Cette évolution est occasionnée par plusieurs phénomènes, par exemple la recombinaison par conduction et par diffusion. Notre méthode permet effectivement de faire l'étude de cette évolution. Nous avons donc effectué sur les échantillons A et B une série de mesure des charges d'espace en fonction du temps de court-circuit dont nous allons présenter deux résultats pour montrer l'évolution de la charge d'espace.

Les courbes a et b de la figure 7 correspondent respectivement aux densités de charge mesurées dans le câble A après 2 jours et 20 jours de court-circuit.

On note la disparition de la charge négative qui était au centre de l'échantillon qui a probablement diffusée vers les électrodes et, de ce fait, occasionné la diminution des charges positives situées de part et d'autre de cette charge négative. De plus ces charges positives sont diminuées aussi par les charges négatives près des électrodes.

Sur la figure 8 on donne les distributions des charges d'espace mesurées dans l'échantillon B après 2 et 20 jours de court-circuit, courbes a et b. Ces courbes montrent une évolution presque identique à celle observée dans le câble A et confirment bien la disparition des charges négatives au centre de l'échantillon.

IV CONCLUSION

Ainsi la mesure des charges d'espace par l'onde thermique est un nouveau moyen de caractériser et de diagnostiquer les câbles H.T. Les résultats qui devraient en sortir vont permettre de comprendre de nombreux phénomènes électriques tels que l'origine, la nature et la cinétique des charges , la conductibilité et la rigidité à long termes .

Alors un nouveau type de recherche sur l'optimisation des matériaux pourra etre entrepris : il devrait conduire à une amélioration des durées de vie, et à une plus grande fiabilité.
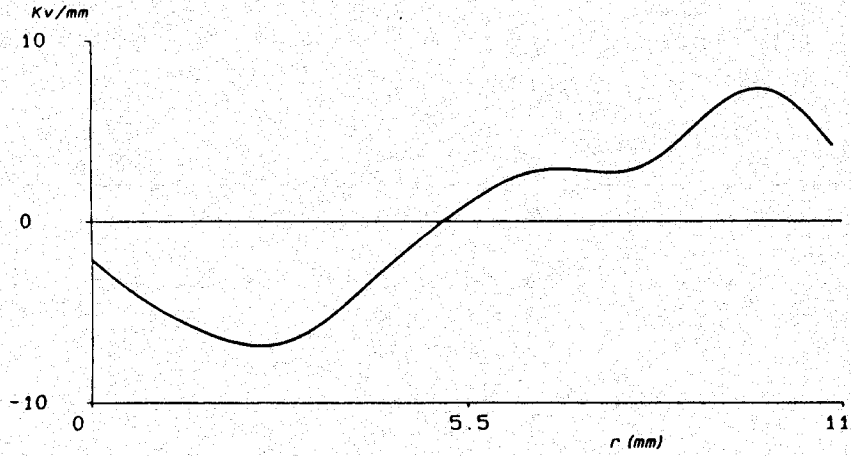
Fig. 1 : Distribution du champ électrique dans le câble D
tcc=2 jours

Fig. 2 : Evolution de la densité de charge d'espace dans le câble D
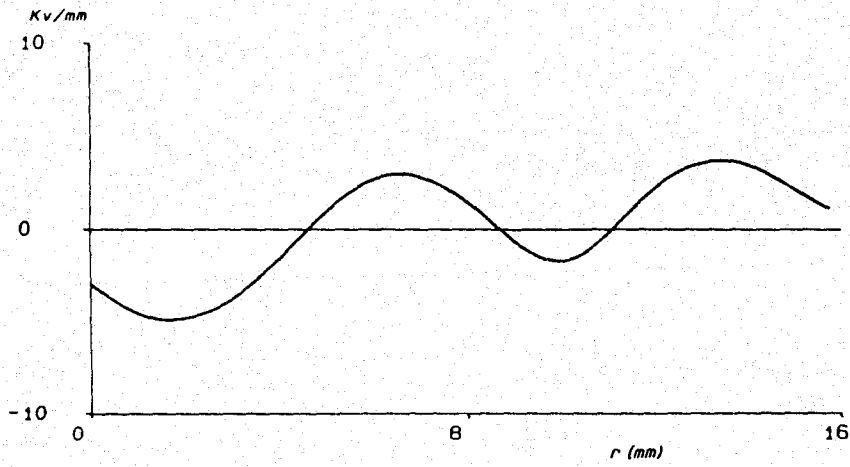a) tcc=2 jours
b) tcc=10 jours
a ————
b --------

Fig. 3 : Distribution du champ électrique dans le câble A
tcc=2 jours
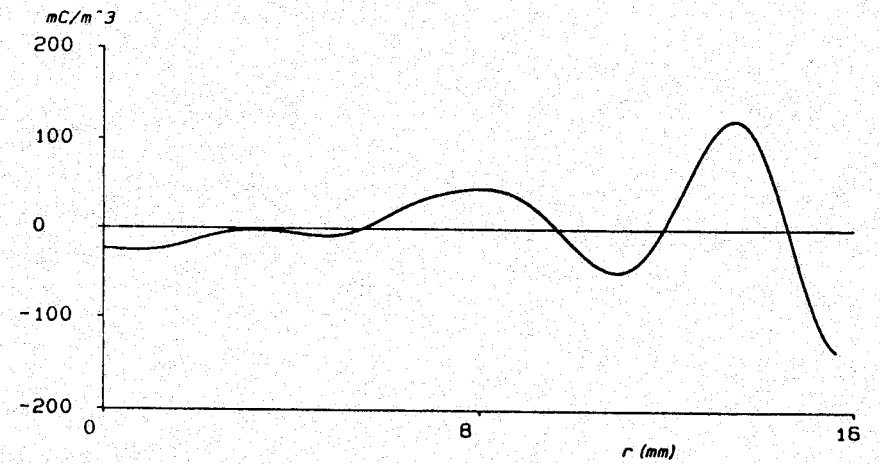
Fig. 4 : Densité de charge d'espace dans le câble A
tcc=2 jours

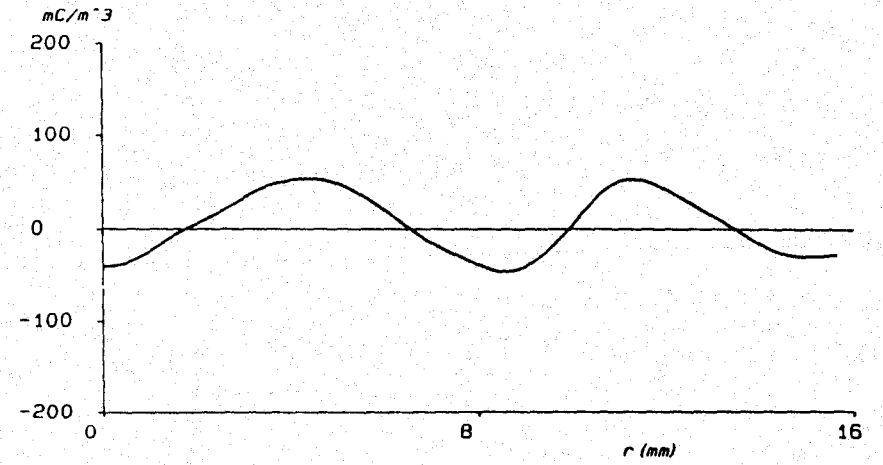Fig. 5 : Distribution du champ électrique dans le câble B
tcc=2 jours

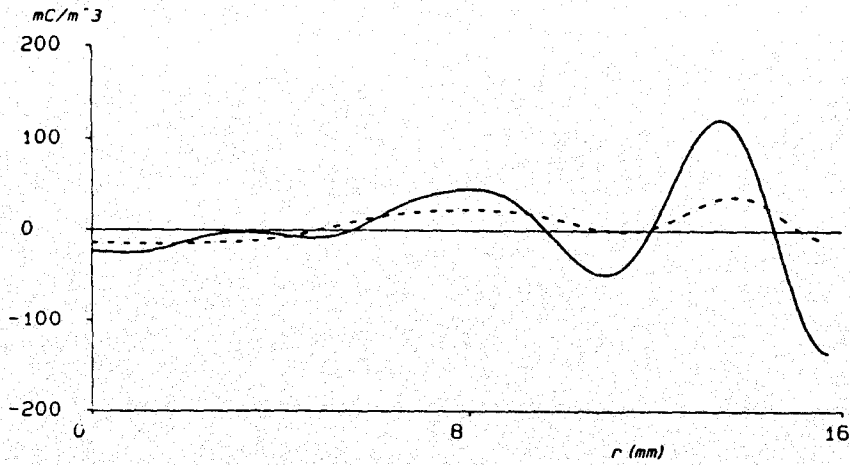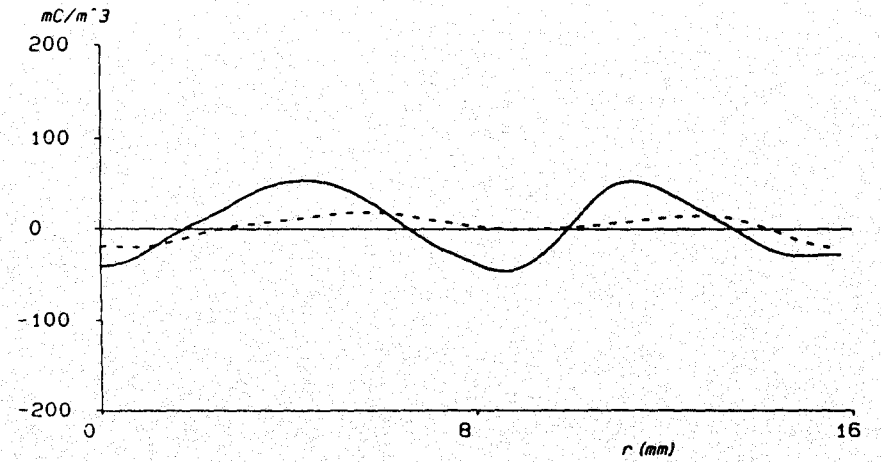Fig. 6 : Densité de charge d'espace dans le câble B
tcc=2 jours

Fig. 7 : Evolution de la densité de charge d'espace dans le câble A
a) tcc=2 jours
b) tcc=20 jours
a ————
b ----------

Fig. 8 : Evolution de la densité de charge d'espace dans le câble B
a) tcc=2 jours
c) tcc=20 jours
a ————
n ----------

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$$\boxed{\text{ATELIER VIEILLISSEMENT / JCABLE 91}}$$

I . INTRODUCTION

La tenue diélectrique des isolants solides présentes des difficultés d'interprétation encore non résolues sur le plan fondamental et constitue, dans la pratique,un des problèmes clés du bon fonctionnement des câbles.

La performance à long terme des isolants électriques est présentée comme dépendant de deux aspects: la nature des isolations utilisées et les contraintes auxquelles elles sont exposées.

L'évolution à long terme des propriétés électriques des matériaux isolants utilisés en haute et très haute tension est un des principaux facteurs limitatifs de la fiabilité des câbles, on constate en effet, dans certains cas, une dérive de leurs propriétés en fonction du temps pouvant conduire à la détérioration de l'isolation par rupture diélectrique.

Le concepte de vieillissement se rapporte à la capacité du matériaux ou du câble ("produit") d'assurer un certain nombre de fonctions. Par conséquent, il ne s'agit pas d'une propriété réellement intrinsèque puisqu'elle se rapporte non seulement à la nature du câble lui même, mais également à ce qu'il est sensé assurer.

Lorsque nous évaluons un vieillissement nous cherchons à mettre en évidence le changement de valeur de certaines propriétés. L' évaluation peut être faite de différentes manières. Nous pouvons sélectionner la caractéristique à suivre en fonction de son importance vis-à-vis du fonctionnement du matériel. Mais nous pouvons également suivre l'évolution d'une caractéristique qui n'est pas vitale pour le fonctionnement à condition que celle-ci soit facilement mesurable et que sa valeur soit sensible à l'évolution des propriétés du câble, ceci bien évidemment afin d'établir une corrélation avec ses performances en service.

II. INFLUENCES DES CHARGES D'ESPACE DANS LES PHENOM ENES DE VIEILLISSEMENT

L'apparition et l'accumulation des charges d'espace dans l'isolant, les distorsions du champ électrique appliqué qui en résulte, la quantité et la nature des charges d'espace en présence, jouent un rôle déterminant dans l'evolution de certaines propriétés comme la rigidité diélectrique et par conséquent sur la durée de vie des matériaux (et câbles) soumis à des champs électriques élévés.

En effet, un champ électrique appliqué à un isolant placé entre deux électrodes, peut faire apparaitre plusieurs phénomènes: orientation des dipôles ou transfert d'ions ou électrons aux interfaces isolant/semi-conducteur.
Cela produit une nouvelle distridution des charges et des dipôles qui modifie le champ interne.
Cette distridution de charges peut alors affecter considérablement le comportement à long terme et les performances du matériau d'isolation dans le cas d'un renforcement du champ appliqué. Cette situation pourrait être la cause d'un certain nombre de claquages d'isolants.

III. RESULTATS

III.1 Vieillissement sur câbles

Des résultats présentés à JCABLE 91 (1) ont montrés dans le cas d'un câbles vieilli une plus grande quantité de charges d'espace stockées dans certaines parties de l'isolation. Le champ résiduel maximum observé dans ce câble est 2 à 3 fois supérieur au champ appliqué.

III.2 Mesure précédant un claquage imminent

Des mesures de répartition de charges d'espace ont été réalisées sur un échantillon plan de polyéthylène réticulé soumis à des conditions de formation (tf,Vf,Tf,tcc) ayant aboutis à un claquage quelques jours après la mesure.

On observe juste avant le calquage une augmentation considérable des homocharges injectées et des champs internes résiduels proche de 100 kV/mm. Ces champ vennant renforcer le champ appliqué, le claquage se produira 3 jours plus tard dans les même conditions de formation.

IV. CONCLUSION

Il faut remarquer que quelques jours avant le claquage de l'échantillon la valeur mesurée du champ maximum du aux charges d'espace est légèrement inférieure aux valeurs de rupture diélectrique observées sur ce type de matériau.

(1) Conférence JCABLE 91 Réf: B.8.2.

CONDITIONS DE FORMATION ET DE MESURE

ECHANTILLON

- Isolant PRP : plaque de 1.8 mm d'épaisseur
- Semi-conducteur : interface irrégulière
  : nombreuses impuretés

FORMATION (1)

Fig. 1 et Fig. 2 : Densité de charge et champs électriques

Tf : 50°C
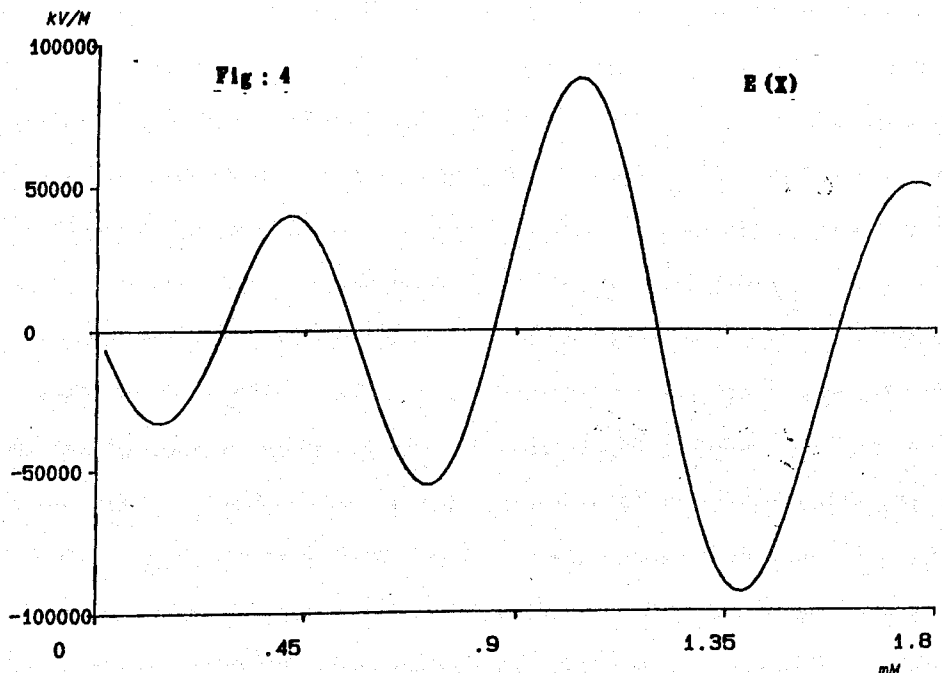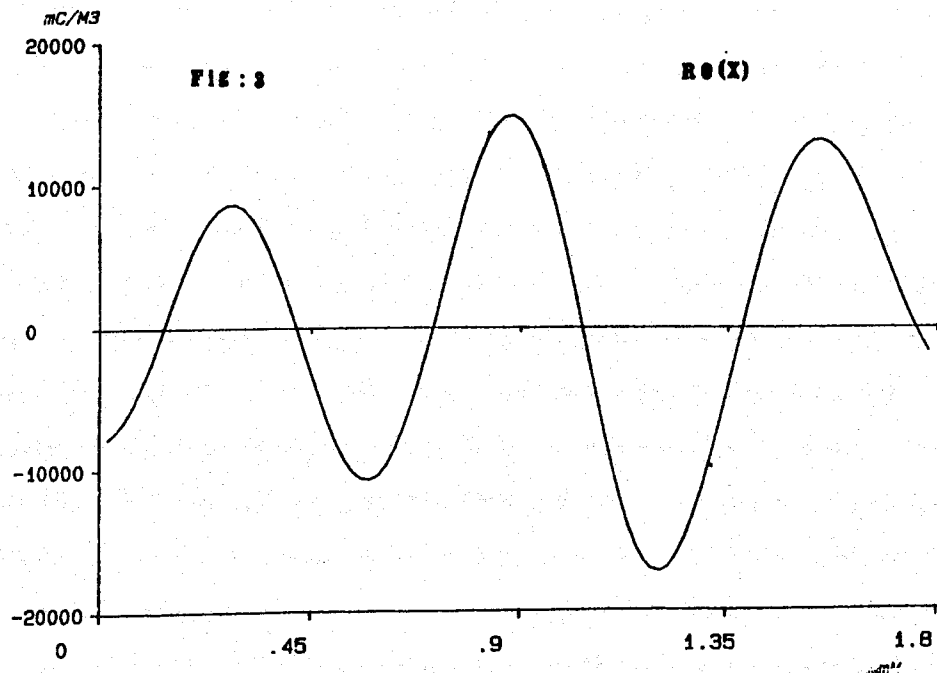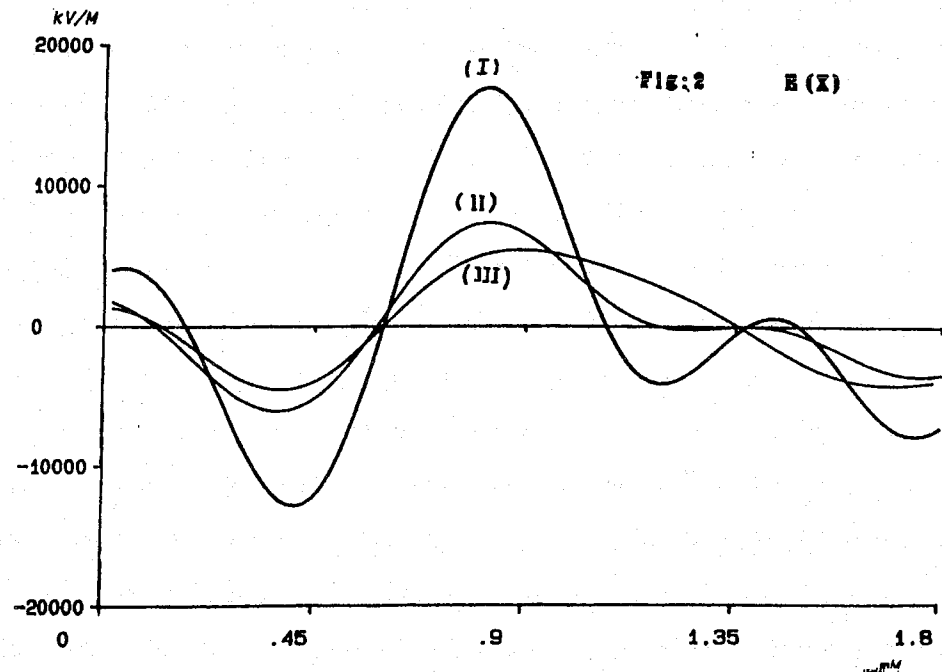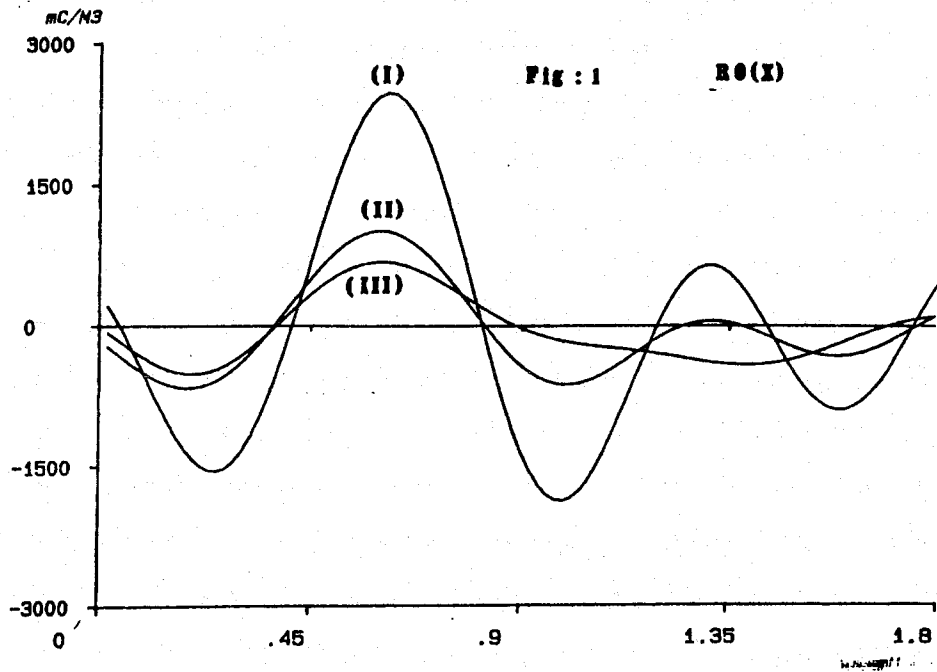Vf : 10 kV/mm
tf : 3 jours
tcc : 3 h (I), 3 j (II), 5 j (III)

FORMATION (2)

Fig. 3 et Fig 4 : Densité de charges et champs électriques

Tf : 70°C
Vf : 20 kV/mm
tf : 3 jours
tcc : 3 h

CLAQUAGE (3)

Formation 2 avec tf = 6 jours

mC/M3

3000

1500

0

-1500

-3000

0   .45   .9   1.35   1.8

(I)   Fig : 1   RO(X)

(II)

(III)

kV/M

20000

10000

0

-10000

-20000

0   .45   .9   1.35   1.8

(I)   Fig:2   E(X)

(II)

(III)

mC/M3

20000

10000

0

-10000

-20000

0   .45   .9   1.35   1.8

Fig : 3   RO(X)

kV/M

100000

50000

0

-50000

-100000

0   .45   .9   1.35   1.8

Fig : 4   E(X)

J I - C A B L E 91

LA MICROSCOPIE INFRAROUGE APPLIQUEE AU CONTROLE DES CABLES ELECTRIQUES
ATOCHEM
A. GASCOIN - Ph. MONTAGNE

1 - PRINCIPE

Certaines absorptions IR permettent d'approcher plusieurs composants du Polyethylene, notamment :

paramètres quantifiables	bande IR (cm-1)
proportion de phase cristalline	1897
proportion de phase amorphe	1302 et 1353
branchement court (Me, Et, Bu)	1378
insaturation vinylidène	888
insaturation vinyl 1-2	910
insaturation trans vinylène 1-4	965
oxydation - anti-oxydant	3640 pour l'IRGANOX 1076

Le principe de la microscopie IR consiste à focaliser un rayon IR sur une partie bien ciblée d'un échantillon de polyéthylène et d'en mesurer son absorption relatif à l'un des paramètres ci-desssus .

2 - PREPARATION DE L'ECHANTILLON
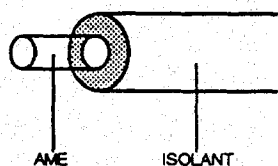
1- morceau de cable à examiner
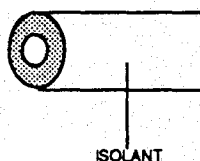
2- retrait de l'âme conductrice

3- découpe de rondelles au microtome (e≈200µ)

3 - MONTAGE EXPERIMENTAL

SPECTRE IR

LUNETTE BINOCULAIRE (x 10)

M5

M6

A   DIAPHRAGME

M4

M2

OP

RONDELLE DE POLYETHYLENE

M1

IR TRANSMIS
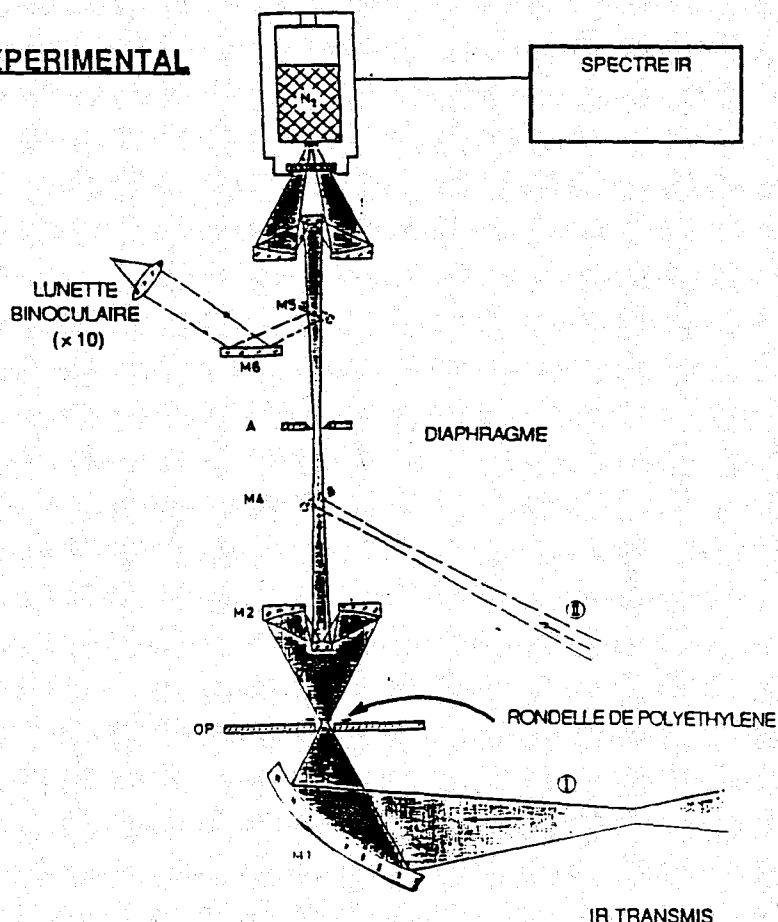
4 - EXEMPLE DE RESULTATS OBTENUS
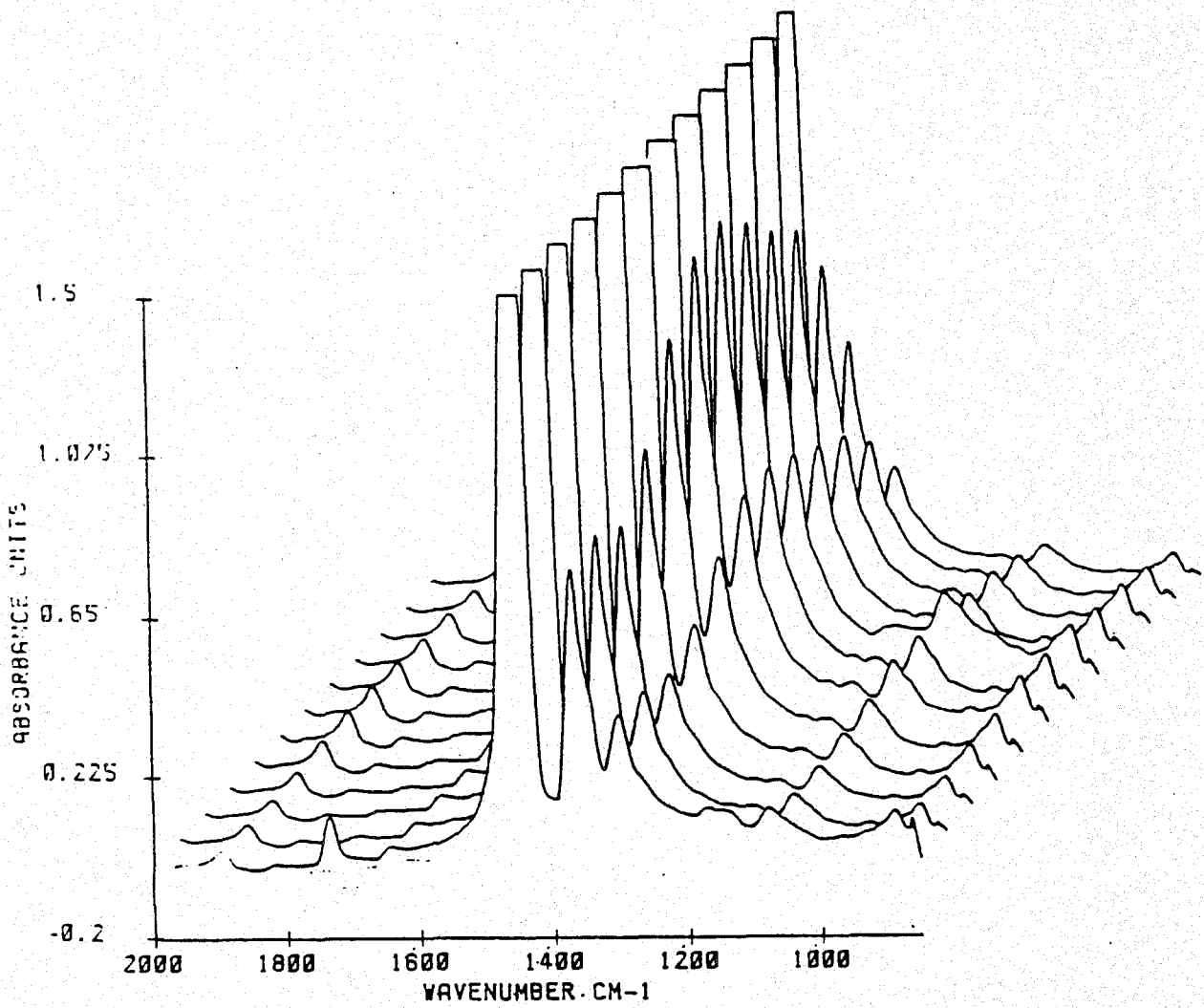
12 PAS DE 1000 MICRONS
SPOT D'UN DIAMETRE DE 50 MICRONS $\quad \sigma = 4 cm^{-1} \; \Delta$

CABLE EDF
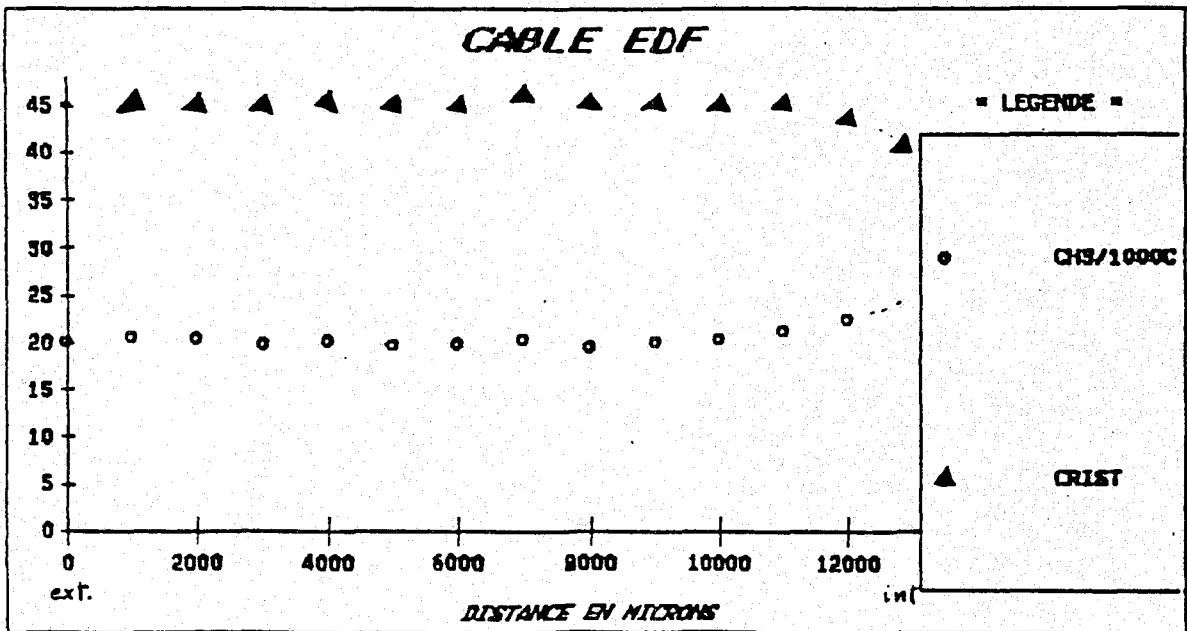
ANALYSE PAR CARTOGRAPHIE I.R.T.F. DU VIEILLISSEMENT SOUS CHAMP ELECTRIQUE DE FILMS DE POLYPROPYLENE

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38042   GRENOBLE -Cédex

Le vieillissement de films de polypropylène imprégnés (145 V_{eff} /μm et 80°C) sous atmosphère d'oxygène a été analysé par la mesure de la tension de claquage du film et par cartographie I.R.T.F.

Dans une couronne périphérique,située sous l'électrode,les tensions de claquage sont trouvés jusqu'à 30% plus faible.
Par spectroscopie I.R.T.F. on détecte la formation de groupements carboxyles ($1708 cm^{-1}$) et une bande d'absorbtion, située à $1018 cm^{-1}$, attribuée à la dismutation radicalaire du polypropylène.La cartographie I.R.T.F. permet de localiser ces dégradations:la fonction carboxyle apparait dans la couronne là ou l'abaissement de la tension de claquage est importante;la bande à $1018 cm^{-1}$ se situe dans le polypropylène dégradé au centre de l'électrode.
Ces observations nous permettent de proposer deux mécanismes de dégradations controlés par la diffusion de l'oxygène dans le milieu.
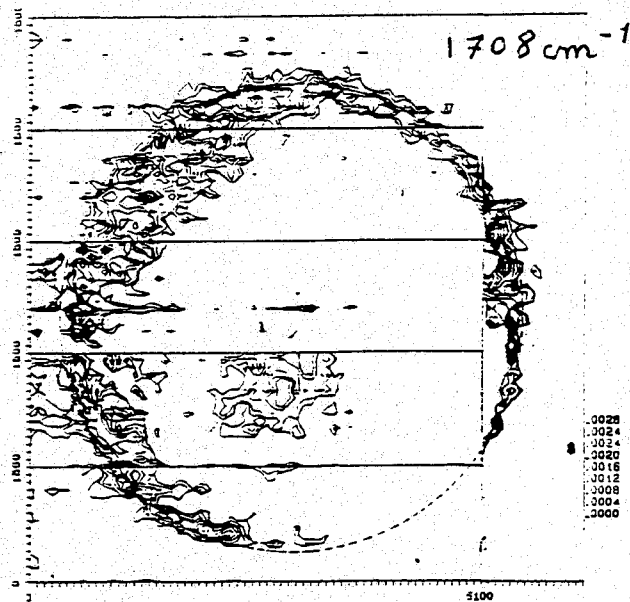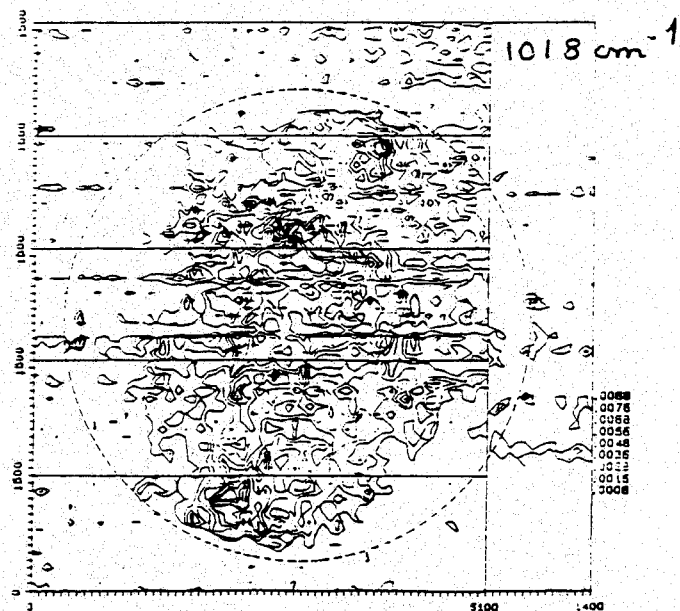
Workshop "Ageing 91"

Membrane potential technique applied to the study of cable insulation modification

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ENSCP , 11 rue P. et M. Curie 75231 Paris Cedex 05

It is well known that the semi-conductors loaded with furnace carbon black are a source of contamination since they contain many metallic and organic impurities [1]. Systematic studies have shown that metallic impurities migrate into the insulation [2][3] and initiate water or electrical trees [4][5].

In order to study more precisely the migration of impurities we performed membrane potential measurements. This technique consists in measuring the evolution with the concentration of the potential difference between two compartments separated by a membrane (in our case a 40 μm thick sample) and containing two salt solutions at different concentrations. The experimental set up used is shown in figure 1.
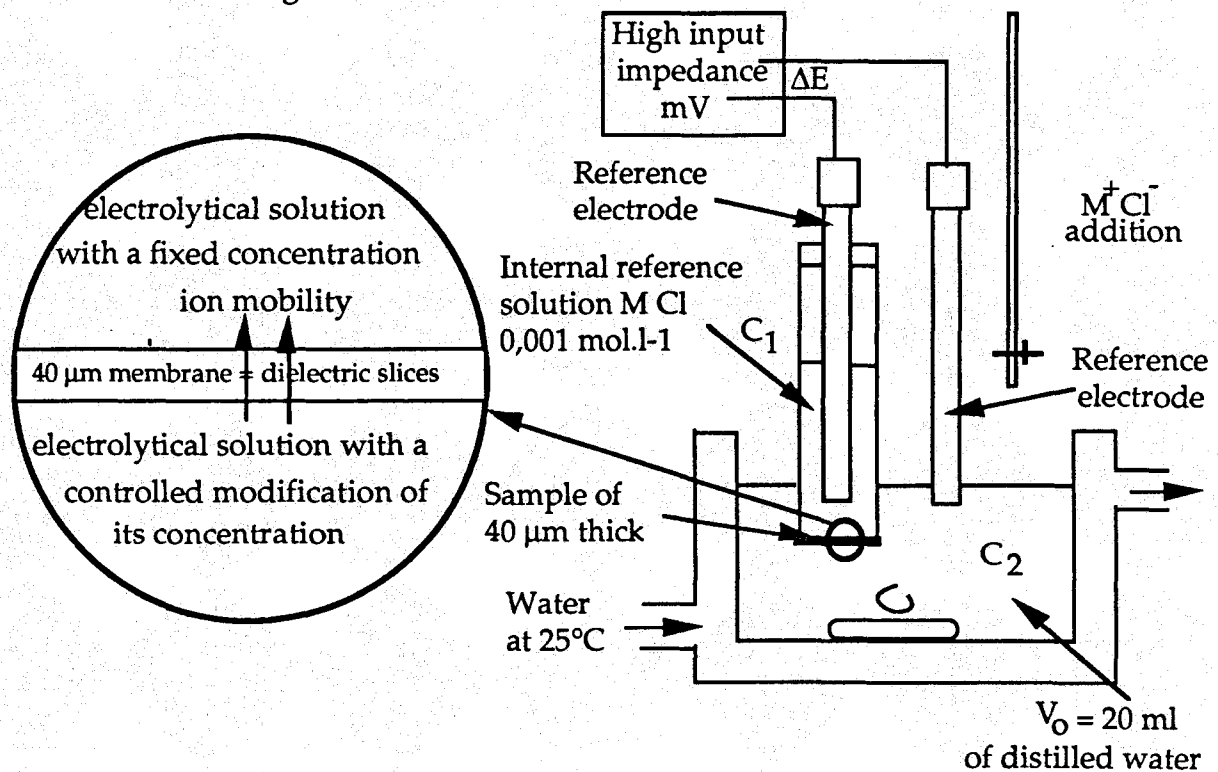
figure 1

Experimental set-up used for membrane potential measurements

With a perfectly insulating membrane no measurement is possible. On the contrary, the existence of a potential difference ΔE point out an ionic conduction and involve the presence of ionic carriers . If this potential difference is compare to a diffusion potential, then ΔE can be written in the form :

$\Delta E = k + (2t^+ - 1) RT/F \log C_1/C_2$

with : k : constante including Nernst's parameters

t$^+$: cation transport number

C$_1$: and C$_2$ concentrations (mol.l-1) of salts in each compartment

Assuming :

J$_i$: Flux density

X$_i$: Force

c$_i$: concentration of i

ω_i : Mobility of i

t$_i$: Transport number of i

F : Faraday number

E : Electric potential

M$^+$X$^-$: Electrolyte

$J_i = \omega_i.c_i.X_i$ with $X_i = -1/T \, grad\mu_i$

$J_M = \omega_M.c_M \, [-1/T(d\mu_M/dx + FdE/dx)]$ (1)

$J_X = \omega_X.c_X \, [-1/T(d\mu_X/dx - FdE/dx)]$ (2)

Electroneutrality => J$_M$ = J$_X$

then $\omega_M d\mu_M - \omega_X d\mu_X = -F(\omega_M + \omega_X)dE$ (3)

$(\omega_M - \omega_X /\omega_M + \omega_X) \, RTlnC_2/C_1 = -F\Delta E$ (4)

$t_M = \omega_M / \omega_M + \omega_X$ and $t_X = \omega_X / \omega_M + \omega_X$ with $t_M + t_X = 1$

then $\Delta E = (1-2t_M) \, RT/F \, ln \, C_2/C_1$ (5)

By this way it is possible to determine whether or not there is an ionic transport of cations such as H$^+$, K$^+$ and Na$^+$ through the polymer film. Samples cut out of a new cable (N) appear perfectly insulating. The junction potential is very instable and no measurements is possible. In the case of field aged cable (FA) the junction potential is stable and the accuracy of measurements is +/- 0,5 mV. The results obtained with HCl, KCl and NaCl (figure 2) point out transport properties.
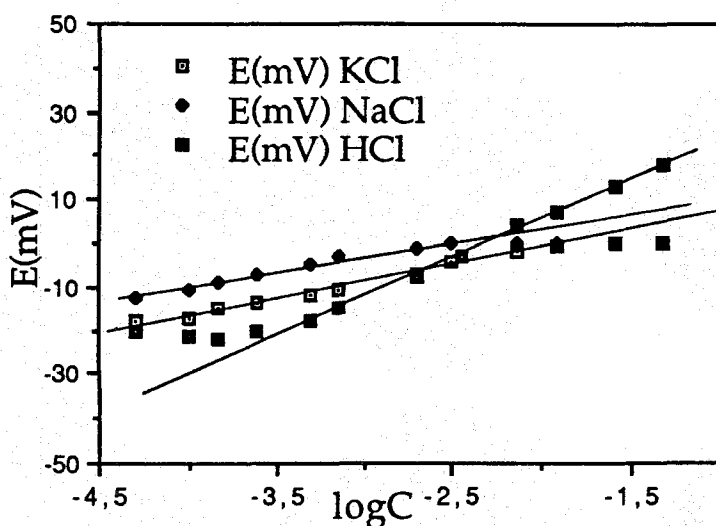

figure 2

Membrane potential results for field aged 40 μm thick polyethylene dielectric samples

The curves E(mV) versus logC are characteristic of cationic carriers presence (t$^+$>0,5) in the membrane. The slopes values indicate that t$^+$H+>>t$^+$K+>t$^+$Na+, then the selectivity of the material is higher for H$^+$ than for K$^+$ and Na$^+$. The

transport numbers for H^+, K^+ and Na^+ are about : $t^+_{H^+}=0,65$; $t^+_{K^+}=0,57$ (E=8mV/log unit) ; $t^+_{Na^+}=0,56$ (E=7mV/log unit) .Thus, in the case of field aged cables (FA) , there is appearence of ionic conductibility which could be associated to the presence of ionic carriers. These carriers could stimulate the mineral impurities diffusion under electrical and temperature stresses.

By this new technique we pointed out the modification of the insulating material of the cable with ageing and in particularly the modification of its ionic transport properties. Furthermore, we attempted to identify the physico-chemical changes in aged materials.

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[3] M.S. Mashikian , J.H. Groeger , S. Dale ; E. Ildstad - IEEE , Boston , June 1988 , pp 314-320

[4] J.P. Crine , S. Hridoss , P. Hinrischen , A. Houdayer , G. Kajrys - Conf. Insu. Dielec. Phenom. , 1988 , p 94.

[5] J.P. Crine , S. Pelissou , Y. Mc Nicoll , H. Saint-Onge - 2nd Int. Conf. Prop. Appl. Dielec. Mat. , Beijing , september 1988

Breakdown Statistics on Thin Polyethylene Cables Slices

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A statistical analysis of breakdown voltages of polyethylene insulated power cable slices is performed on populations containing a large number of data (80 samples, 40x40 millimeter size and 200 micrometer thick).

Each sample is placed between two electrodes and submerged under dielectric silicon oil at room temperature. The tension is increased from zero until the breakdown voltage of the polyethylene slice, with a speed of 4 kV/s. The sample thickness is then measured on 4 points around the breackdown (the medium value is retained). For each sample, the parameters thickness and breakdown voltage are noted.

A rigorous statistical approach including confidence intervals computation demonstrates that the correct description is a three-parameter Weibull distribution, i.e. with a non-zero location parameter. It can be shown that a data set described by a two-parameter Weibull function contains additionnal statistical dispersion factors which may or may not yield informations on the insulation itself. In other word, a zero location parameter always results from non-homogeneities of the sampling. This can be due to uncontrolled experimental parameters or to defects of various origins, but ageing is also a source of scattering. The discrimination between these two possibilities can be done by comparative testing. When obtained under carefully controlled experimental conditions, the location parameter value (threshold field) must be considered as a quality factor to the system under test. The statistical analysis, when performed on large number of data, provides a very sensitive tool to investigate small changes in electrical insulation.

The method of determination of breakdown voltages and the equipment are described in the referring procedure (annex 4).

STUDY OF AGEING IN INSULATING POLYMERIC MATERIALS BY THERMALLY STIMULATED CREEP SPECTROSCOPY.

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Université Paul Sabatier.

INTRODUCTION

Insulating polymeric materials (polyethylene, polypropylene...) are generally semicristallines. They are constituted by an intimate mixture of ordered crystals -lamellar crystallites and/or spherulites- and a metastable randomly structured amorphous regions. Because the two phases, there is an interphase : paracrystalline domains and/or rigid amorphous domains stressed by crystallites.
Upon metastability, the properties of polymeric materials change with time. This spontaneous ageing is characterized by an endothermic phenomenon in Differential Scanning Calorimetry (1).
This physical ageing must be distinguished from the stimulated ageing caused by modifications of physical and/or chemical bonds caused for instance by electrical stress or environmental conditions (water, ions...).
These modifications affecte fundamentally the molecular mobility of the disordered phases (paracrystalline domains, rigid amorphous domains and the true amorphous phase).
The process by which the molecules rearrange is characteristic of the structure and morphology of the polymers and the quantitative study of its kinetic can be used to quantify the ageing procedure. In fact, this kinetic is particularly complexe: it corresponds to a distribution of retardation times. The Thermally Stimulated Creep (TSCr) spectroscopy is well suited to the investigation of the kinetic of return to equilibrium of a polymeric material.

METHODS

Thermally Stimulated Creep Principle.

The TSCr principle and the torsion pendulum used for this work have been extensively described elsewhere (2,3). However, the general outlines are mentioned below.

The TSCr principle is shown in figure 1. A static shear stress σ is applied to the sample at a temperature T_σ for a time t_σ ($\sim$2 min.) allowing molecular orientation. The viscoelastic strain is frozen by a rapid quench to a temperature To much smaller than T_σ where any molecular motion is hindered; then the stress is removed. The sample is subsequently warmed up at a controlled rate (7°C/min.). The mobile units can reorient.
The recovery γ, its time derivative $\dot{\gamma}$ and the temperature T are recorded versus time t. The plot of the normalized magnitude $|\dot{\gamma}/\sigma|$ versus temperature represents the complex TSCr spectrum.
A comparative study of such complex TSCr spectra gives a qualitative information on a ageing procedure.

Experimental resolution of the complex TSCr spectra.

By applying the technique of fractional stresses in TSCr experiments, the complex spectra can be resolved experimentally into elementary spectra characterized by only one relaxation time:

$$\tau_i = \tau_{oi} \exp(\Delta H_i/kT)$$

Then each elementary spectrum is characterized by an activation enthalpy ΔH_i and an activation entropy associated with τ_{oi}. Then, the compensation diagram (ln τ_{oi} as a function of ΔH_i) can be constructed.
The existence of compensation lines will be indicative of cooperative movements and the corresponding molecular entities will be identified.

AGEING IN LOW DENSITY POLYETHYLENE (LDPE)

Reference LDPE

The TSCr spectroscopy has been applied to low density polyethylene (LDPE) in the temperature range -180°C , 80°C.
Figure 2 shows the complex TSCr spectra of reference LDPE. The peaks situated at -125°C and 51°C have been associated with the γ and α modes observed in the litterature, in the same temperature range (4,5).
These complex spectra have been resolved by using fractional stresses procedure. The corresponding elementary spectra are reported on figure 3. It is interesting to note that an additional peak situated around -20°C can be distinguished: it has been designated by β .
Each elementary peak is characterised by an activation enthalpy (ΔH_i) and an activation entropy associated with τ_{oi}. Those values have been plotted on a compensation diagram (figure 4).

The compensation lines correspond to the   and   modes in the order of increasing activation enthalpies.

The experimental points corresponding to the highest values of activation enthalpies correspond to the α mode. Contrarily to the γ and β modes, they do not follow any compensation law. This result is in agreement with the assignement of this mode to molecular mobility in the paracristalline phase.

AGEING UPON ELECTRIC FIELD

All the experimental parameters have been kept constant. All the ageing process have been performed at 75°C under a static electric field of 10 KV/mm.

Ageing in deionized water.

Data reported in figure 5 corresponds to an ageing time of 1000 hours. The key difference with reference LDPE diagram is the existence of three compensation lines instead of two. A decrease of activation enthalpies has been observed as a result of water absorption: it is the so-called plasticization process. The experimental points constituting the additional compensation line corresponds to the enthalpy range of the α mode. The hypothesis of a transformation of paracrystalline domains into amorphous regions has been proposed for interpretating these observations.

Ageing in CuSO4 solution.

Reference LDPE has been soaked under electric field in a CuSO4 solution for 1000 hours. Figure 6 shows the corresponding compensation diagram. This ageing process induces a destructuration of LDPE. Ionic interactions might play the role of tie points and inhibit cooperative movements. It is important to note that this mechanism take place after the plasticization process, for a soaking time higher than 300 hours.

Ageing in KMnO4 solution.

Reference LDPE has been soaked under electric field, in a KMnO4 solution for 1700 hours. Figure 7 shows the corresponding compensation diagram. Despite the long soaking, it is important to note that the compensation diagram is only slightly modified regarding reference LDPE. The comparative study of figures 5 and 7 shows that KMnO4 ions have an inhibiting, effect of the plasticization process, especially in paracrystalline domains.

CONCLUSION

The comparative study of LDPE samples aged in ionic solutions under electric field shows the existence of two step process in the modification of amorphous phases:

-a plasticization effect due to water molecules;
-a destructuration of the amorphous phases due to the modification of the Van der Waals interactions by ionic species.

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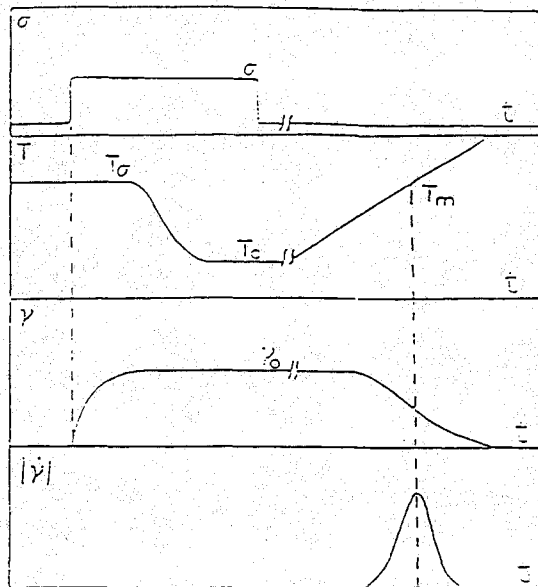
FIG. 1.- Principle of Thermally Stimulated Creep.
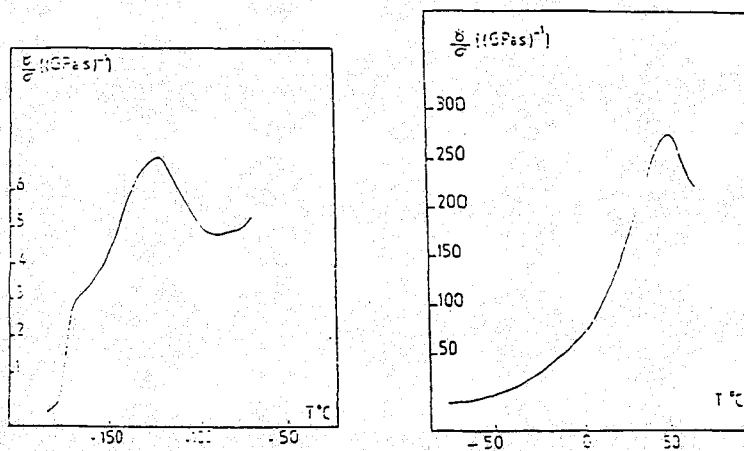
FIG. 2.- TSCr complex spectra of reference LDPE.
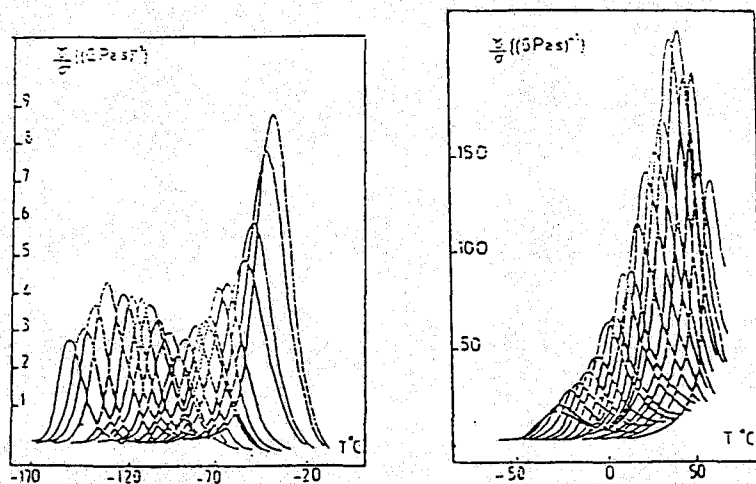
FIG. 3.- TSCr complex spectra resolved in elementary spectra.
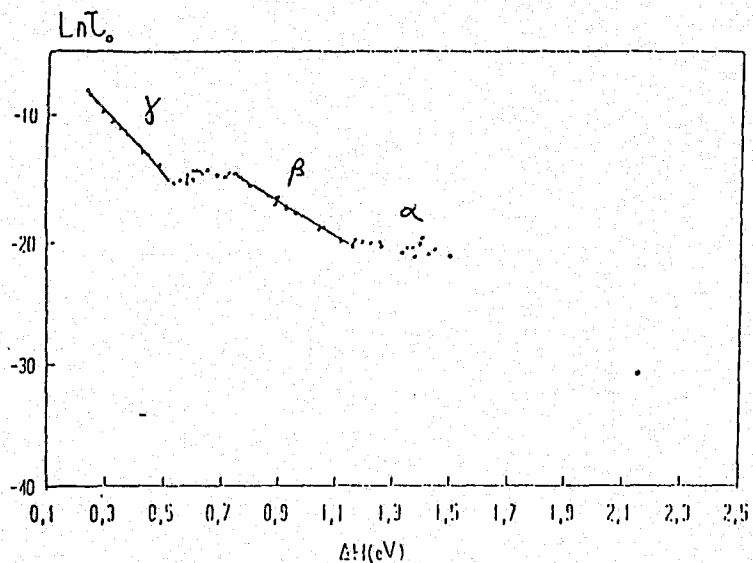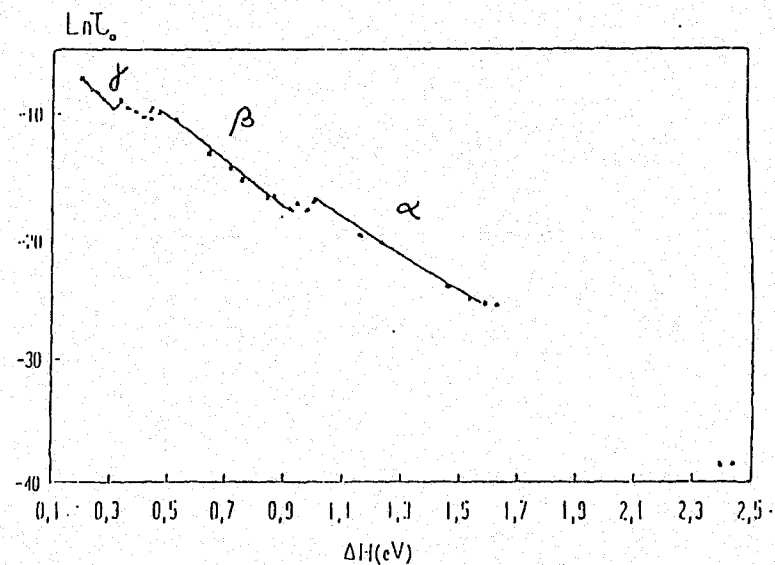
FIG. 4.– Compensation diagram of reference LDPE.
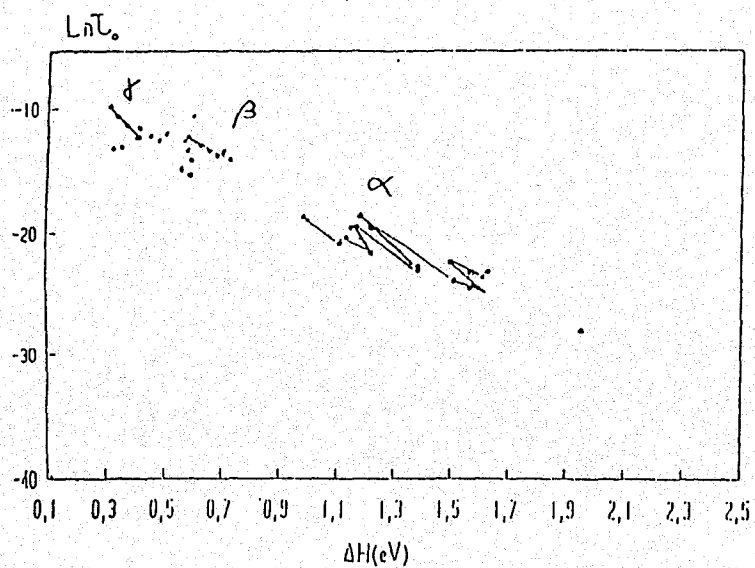

FIG. 5.– Ageing in deionized water.

FIG. 6.– Ageing in $CuSO_4$ solution.

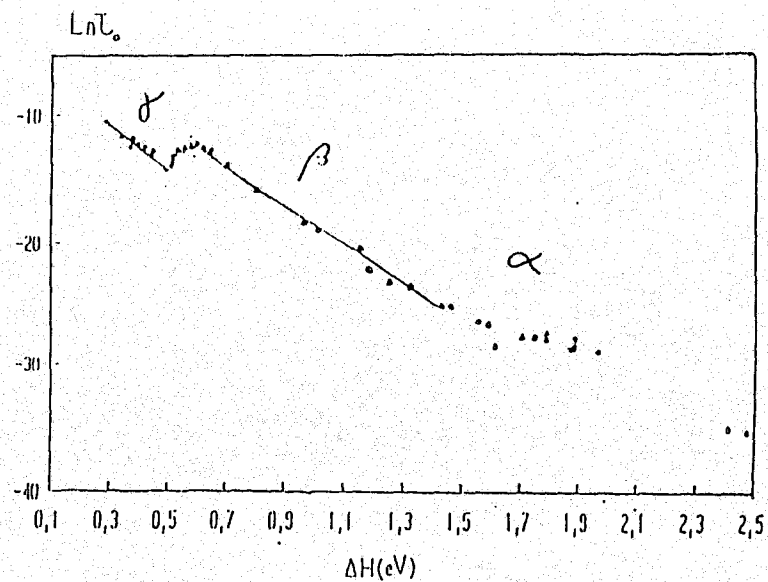FIG. 7 – Ageing in $KMnO_4$ solution.

METHODES RAPIDES DE DETERMINATION DE L'ENDURANCE

THERMIQUE DES MATERIAUX ISOLANTS

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Deux tendances antagonistes gouvernent tous les progrès obtenus sur les matériels électrotechniques au cours des années écoulées :

- la première voudrait sans cesse réduire le volume des équipements. Elle impose l'augmentation continue de la densité de courant dans les conducteurs, du champ électrique dans les isolants et de l'induction dans les matériaux magnétiques lorsqu'il y en a (cas des transformateurs et des machines tournantes par exemple). Ces augmentations ont pour conséquence inévitable une augmentation de la température de service,

- la seconde vise à obtenir une durée de vie des matériels accrue et dans tous les cas, à une meilleure connaissance de "l'espérance de vie".

Or il est clair que ce sont les matériaux isolants qui sont le plus sensibles à la dégradation de leurs propriétés sous l'action de la chaleur.

L'aptitude des matériaux isolants solides à supporter, pendant la durée du service, des températures élevées est donc un paramètre dimensionnant majeur pour la plupart des matériels électrotechniques.

C'est la raison pour laquelle les scientifiques et les ingénieurs se sont préoccupés très tôt de déterminer cette propriété des matériaux que l'on appelle l'ENDURANCE THERMIQUE.

Depuis la loi empirique de Montsinger, qui établissait que la durée de vie d'un matériau était divisée par deux pour une augmentation de température de 10°C, bien des progrès ont été réalisés. Malheureusement, ces progrès ne se traduisent pas par une simplification de ce sujet difficile. Il n'est donc peut être pas inutile de faire l'état de la recherche et de la normalisation dans ce domaine.

La méthode conventionnelle de détermination des propriétés d'endurance thermique des matériaux isolants électriques est décrite dans le guide CEI 216 dont la quatrième édition a été publiée en 1990.

Signalons également que le document ISO 2578 traite de cette même méthode en se limitant au cas des matières plastiques.

Nous ne détaillerons pas ici les principes de cette méthode, nous contentant de rappeler les points principaux suivants

a) *lors de la détermination de l'IT (Indice de Température), la plus basse température d'exposition doit être choisie pour que la valeur moyenne (ou médiane) du temps jusqu'au point limite (fin de vie) soit supérieure à 5000 h,*

b) *l'extrapolation nécessaire à la détermination de l'IT ne doit pas excéder 25 K,*

c) *la plus haute température d'exposition doit être telle que la valeur médiane du temps jusqu'au point limite ne soit pas inférieure à 100 h.*

Le point a) ci-dessus constitue le handicap majeur de la méthode conventionnelle décrite dans la publication 216. En effet, compte tenu des essais préliminaires et des éventuelles reprises d'essai, la détermination de l'indice de température d'un matériau inconnu nécessite entre 12 et 18 mois.

C'est pour cette raison qu'a été préparé le rapport technique CEI 1026 actuellement en cours d'impression et qui traite de l'application des méthodes d'essai analytiques sur l'endurance thermique des matériaux isolants électriques.

Ces méthodes reposent sur le principe suivant :

Le vieillissement thermique des matériaux isolants se compose principalement de réactions chimiques qui entraînent des modifications progressives des propriétés physiques des matériaux et finissent par altérer leur fonctionnalité. La composition chimique (résultat de la détérioration due aux réactions de vieillissement thermique) et la valeur de n'importe quelle propriété physique des matériaux sont par conséquent étroitement liées.

Il est donc possible d'estimer la performance à long terme des matériaux grâce à une mesure appropriée des VITESSES DE REACTION de vieillissement (qui décrivent la vitesse de dégradation) combinée à des essais de vieillissement de type conventionnel.

Les principes retenus dans le document CEI 1026 sont les suivants :

1) Les méthodes analytiques utilisées doivent être assez sensibles pour permettre les mesures de vitesse de réaction jusqu'aux températures d'utilisation des matériaux.

2) De nombreuses méthodes analytiques se sont révélées acceptables pour la mesure des vitesses de réaction et ont fourni des renseignements sur ces vitesses de réaction.

   Le LCIE a principalement travaillé sur l'utilisation de la chromatographie en phase gazeuse.

3) La mesure des vitesses de réaction de vieillissement permet de déterminer la vitesse du processus de vieillissement (ou d'autres réactions), produisant ainsi des renseignements sur la pente de la courbe d'endurance thermique, par exemple.

4) Les valeurs de vitesse de réaction ne permettent pas, à elles seules, de décrire entièrement l'endurance thermique des matériaux. Elles doivent être combinées à des essais de vieillissement de type conventionnel pour produire des valeurs d'endurance thermique réelles comme celles figurant dans la Publication 216 de la CEI.

5) La mesure analytique des vitesses de réaction a pour but d'assurer le même mécanisme physique ou chimique de vieillissement lors d'essais de vieillissement conventionnels qu'aux températures d'utilisation, mais à une vitesse beaucoup plus élevée.

La comparaison entre les méthodes d'essais décrites dans ce rapport et les méthodes d'essais d'endurance thermique conventionnelles, énoncées dans la Publication 216 de la CEI, fait apparaître les différences suivantes :

- les méthodes d'essais de ce rapport produisent des données expérimentales jusqu'aux températures d'utilisation des matériaux, éliminant ainsi toute nécessité d'extrapolation ;

- le temps d'essai total sera plus court, car les essais de vieillissement conventionnels sont moins nombreux et moins longs, et les méthodes analalytiques exigent elles-mêmes peu de temps : une réduction des temps dans un rapport 10 est possible ;

- les conditions de service réelles peuvent être simulées avec précision, surtout en ce qui concerne le vieillissement dû à l'humidité atmosphérique et à l'oxydation.

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APPLICATION OF TIME-DOMAIN SPECTROSCOPY (TDS) TO THE ASSESSMENT OF CABLE AGING

by
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Background and Description

During the past two years, we have been conducting exploratory research on behalf of Consolidated Edison Company of New York to determine the merits of time-domain dielectric spectroscopy (TDS) as a diagnostic tool for the assessment of cable insulation aging. Although the main objective of this work is to study the aging of non-shielded low voltage power plant cables, the exploratory work included, in addition to this type of cable, some high voltage shielded cables with extruded insulation. In view of the limited time allocated to this presentation, the results obtained on only two types of cable materials and constructions will be presented.

TDS consists in determining the tanδ versus frequency spectrum of cables through one single application of a step voltage. Figure 1 provides a block diagram illustrating the method. The charging current resulting from the application of a step voltage (± 100V) is integrated, amplified, digitized and, then, analyzed by Fast-Fourier transformation to provide the complex capacitive value of the test sample. This, in turn, leads to the calculation of the complex permittivity ($\epsilon = \epsilon' + j\,\epsilon''$, where $j = \sqrt{-1}$) and tanδ, as a function of frequency.

Summary of Selected Results

The cable samples were aged in the laboratory under the following conditions:
- At temperatures of 60, 90 and 120°C, dry.
- At temperatures of 60 and 90°C, wet (in contact with water).
- At temperatures of 60 and 90°C in contact with mineral oil.

The two cable samples for which results are provided in this brief report were:

- <u>Sample A</u>: two 2.1 mm^2 copper conductors insulated with flame retardant ethylene-propylene-diene monomer (EPDM), surrounded with a fabric assembly wrap and jacketed with chlorosulfonated polyethylene (CSPE).

- <u>Sample B</u>: two 1.3 mm^2 copper conductors insulated with flame retardant ethylene-propylene rubber (EPR), surrounded with a glass-reinforced silicone rubber assembly wrap and jacketed with chlorinated polyethylene (CPE).

The TDS measurements were obtained by connecting the two central conductors together and applying the test voltage between these and an outer electrode installed over the jacket. The results shown in this report are, therefore, the tanδ of the composite cable covering.

The following results are shown:
    Sample A aged dry (90 and 120°C)
    Sample A aged wet at 90°C for
    Sample A aged in contact with oil
    Sample B aged dry at 120°C,
    Sample B aged wet at 90°C
Each set of results is given for different aging test durations.

<u>Conclusions</u>

Aging appears to affect the tanδ spectrum, mostly in the lower range of frequencies. The characteristic peaks of the unaged samples may be due to interfacial polarization. The changes of the spectra are different depending on the types of cable coverings and on the aging conditions. The TDS method has merits as a diagnostic tool for cable aging and deserves to be further and systematically explored.
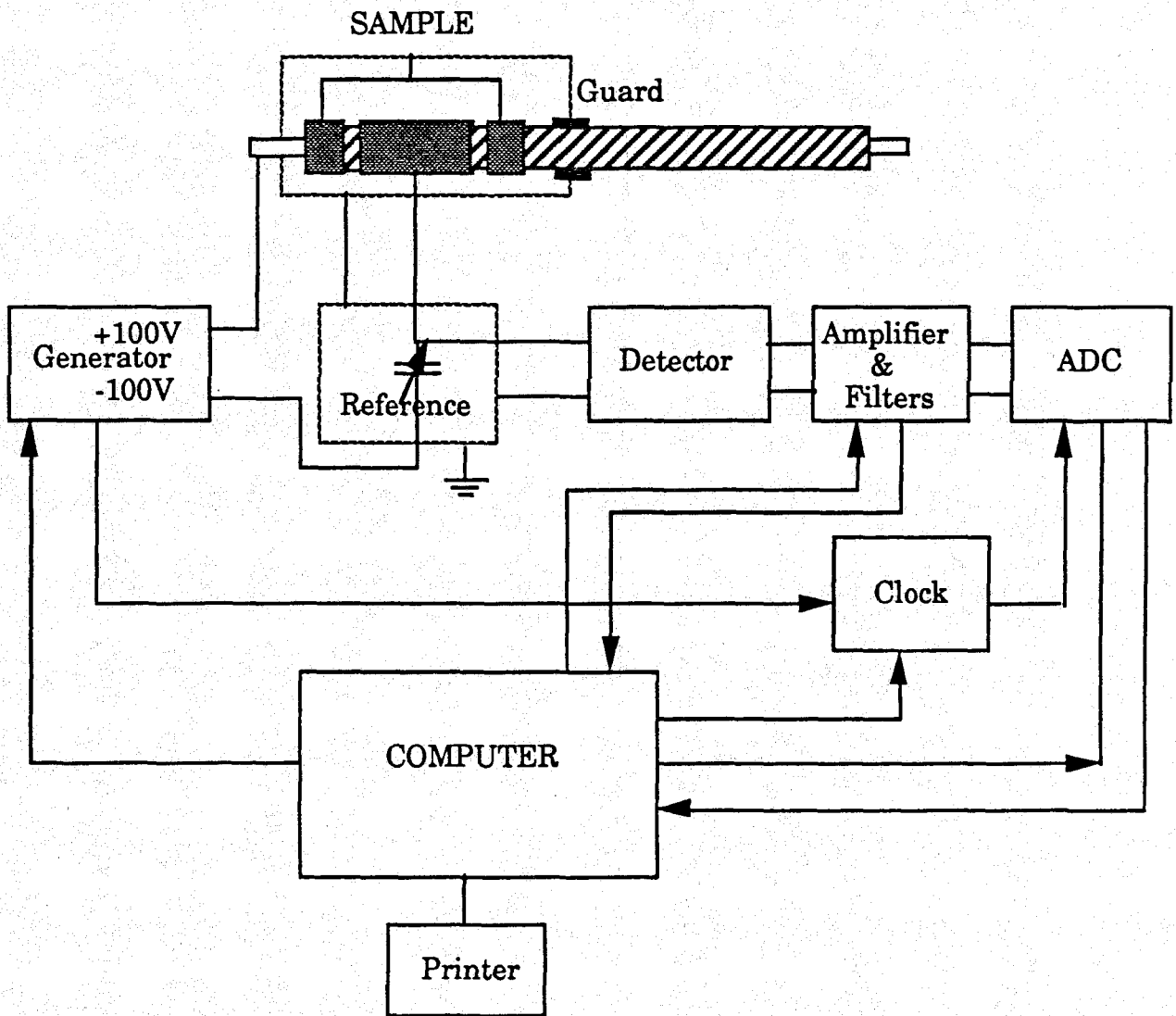
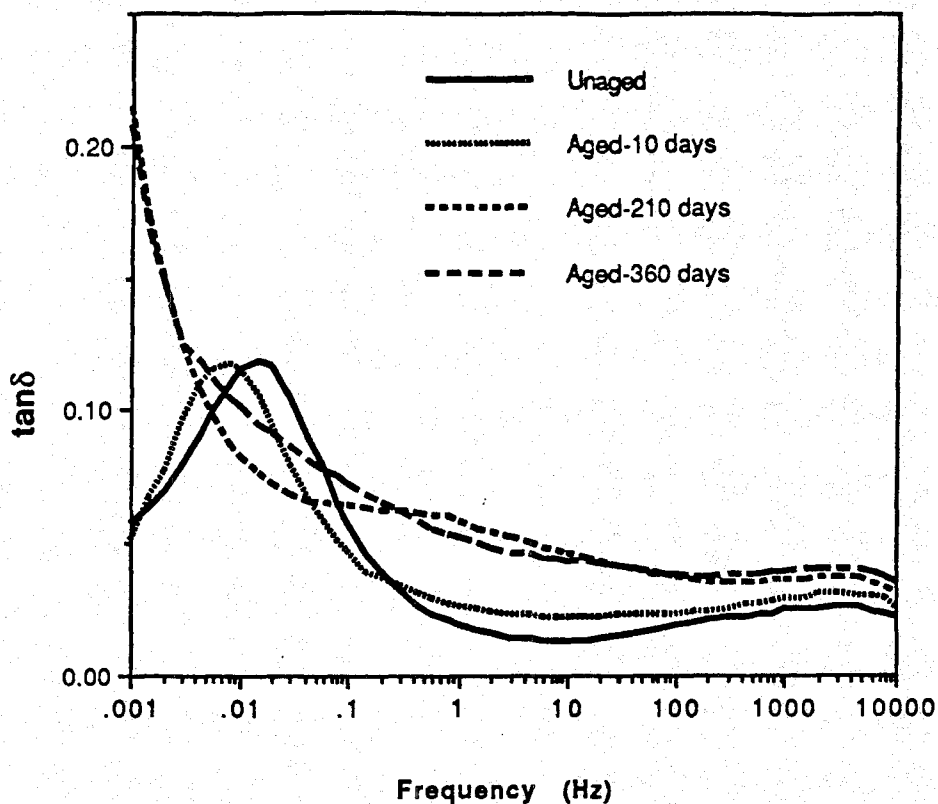Figure 1. Block diagram illustrating the principle of TDS.

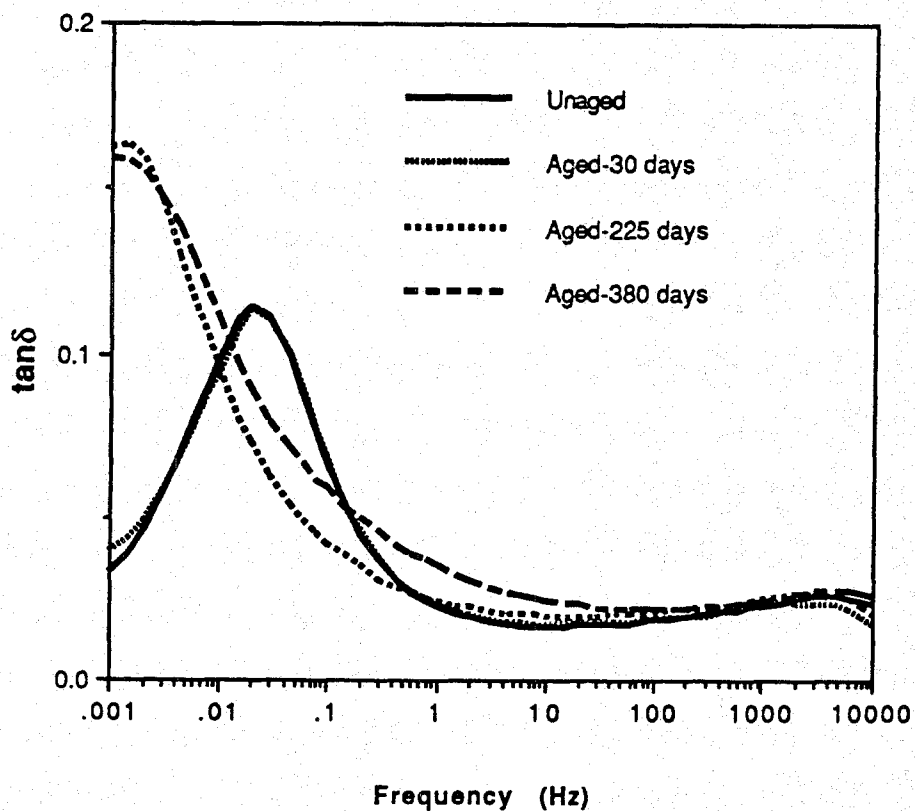Figure 2. TDS spectrum for Sample A aged dry at 120°C.

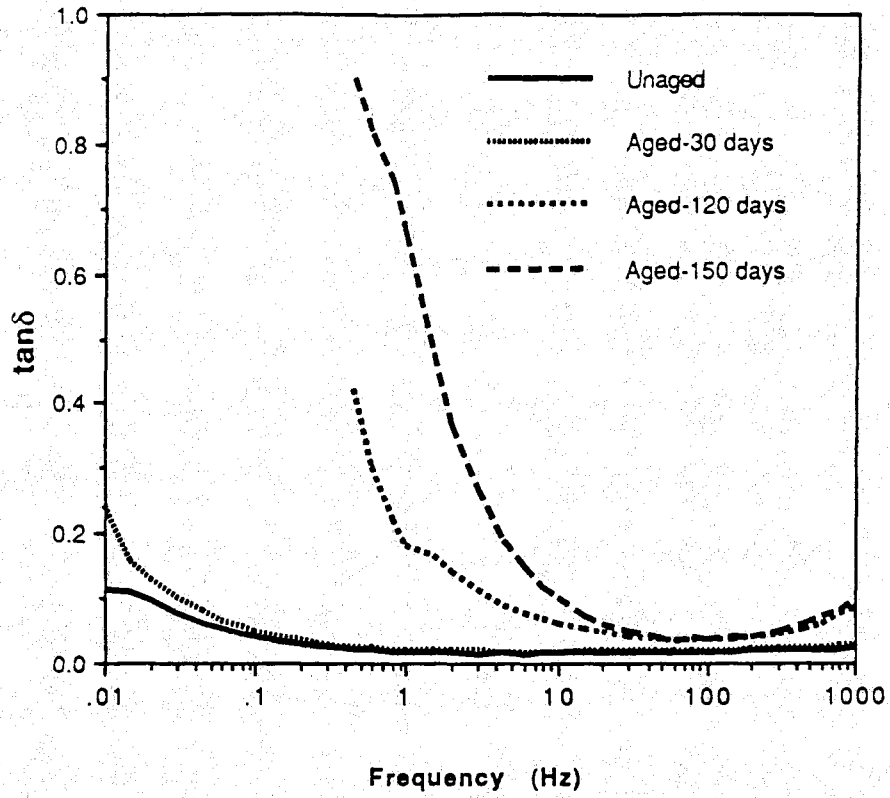Figure 3. TDS spectrum for Sample A aged dry at 90°C

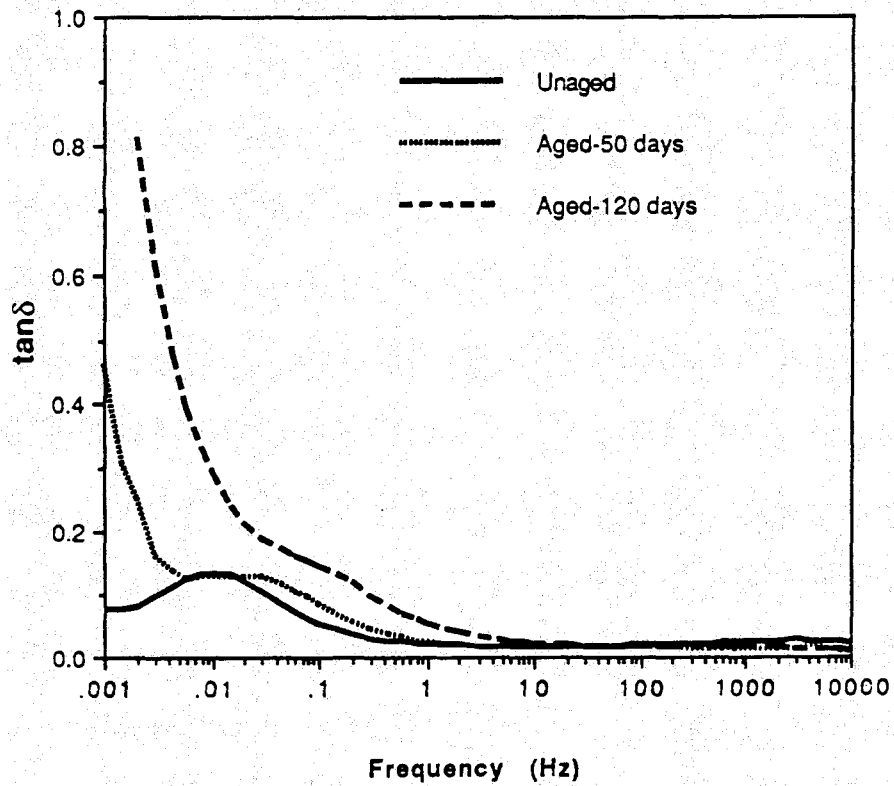Figure 4. TDS spectrum for Sample A aged wet at 90°C.

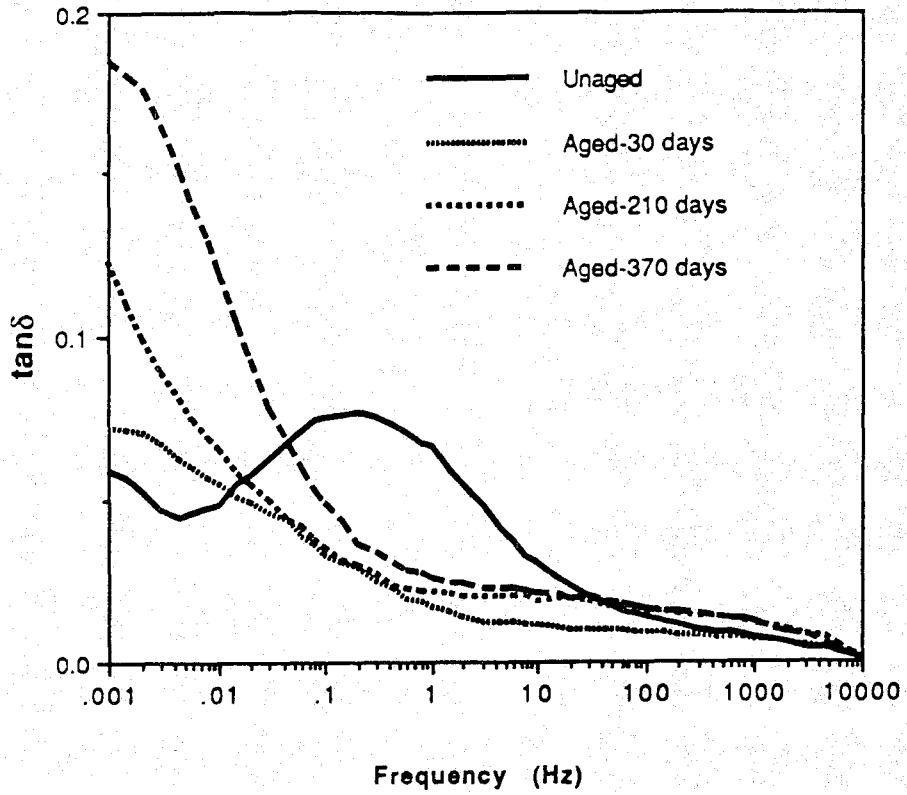Figure 5. TDS spectrum for Sample C aged in oil at 90°C.

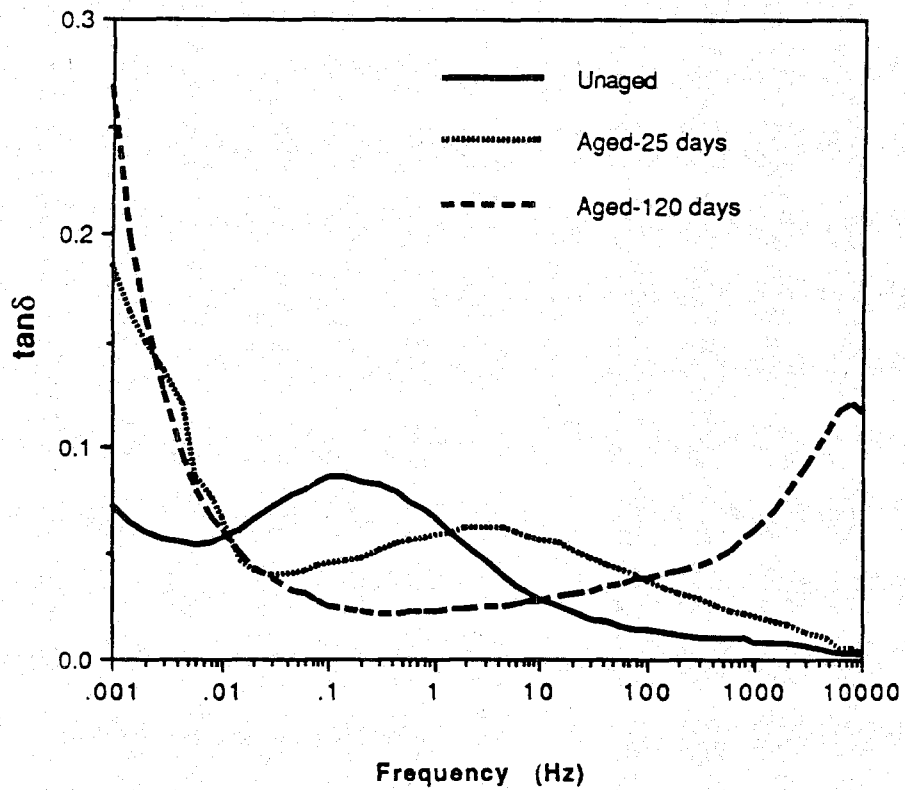Figure 6. TDS spectrum for Sample B aged dry at 120°C.

Figure 7. TDS spectrum for Sample B aged wet at 90°C.

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APPENDIX 3

<u>LIST OF ABBREVIATIONS AND SYMBOLS USED</u>

DEA	Differential Enthalpic Analysis
CEA	Canadian Electrical Association
GC	Gas Chromatography
ddp	difference of potential
EDF	Electricité de France
EPRI	Electric Power Research Institute
eV	Electronvolt
HV	High Voltage
IR	Infrared
IREQ	Hydro-Quebec Research Institute
FTIR	Fourier transform infrared
SEM	Scanning electron microscope
MV	Medium voltage
PE	Polyethylene
LDPE	Low Density Polyethylene
XLPE	Cross-linked Polyethylene
ppm	parts per million
SAXS	Small angle X-ray spectroscopy
SEE	French Society of Electrical and Electronics Engineers
REA	Rural Electricity Association
VHV	Very High Voltage
TSC	Thermally stimulated currents