

METHODOLOGY FOR EVALUATING THE DURABILITY OF HDPE OUTER SHEATHS OF UNDERGROUND ELECTRIC CABLES

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ABSTRACT

During their exploitation, hdPE outer sheaths of underground electric cables are submitted to the effects of various environmental factors such as: temperature, oxygen, water and electrical stresses. Such factors induce a series of PE structural changes at different (molar, macromolecular and macroscopic) scales. Among these changes, the formation of very polar oxidation products, in particular alcohols and carboxylic acids, leads to a significant increase in PE hydrophilicity favoring the water penetration into the sheath thickness, presumably up to the aluminum foil barrier. Then, the local corrosion and perforation of aluminum barrier would be responsible for the development of water treeing into the insulator. The present communication is devoted to the presentation of a general methodology for the evaluation of durability of hdPE outer sheaths. This methodology is based on a series of experiments aimed to elucidate the ageing mechanisms, but also to highlight the relevant kinetic parameters. These experiments are: thermal oxidation tests on stabilized and pure PE; determination of antioxidants chemical consumption and physical loss; determination of oxidation products build-up; water sorption tests on preliminary oxidized PE; and determination of oxidation products contribution to PE hydrophilicity.

INTRODUCTION

Underground cables for the distribution and transport of medium voltage electricity have undergone several major changes over the last 30 years. In the 1975s, electric cables with polymeric insulation were progressively introduced in the grid in replacement of paper impregnated cables. Synthetic cables were firstly sheathed with poly(vinyl chloride) (PVC) of which the main ageing mechanisms were the subject of many publications up to the end of the last century [1-3]. In the early 2000s, PVC was progressively replaced by high density polyethylene (hdPE), leading the French electricity supplier, EDF, to launch research works on PE durability.

The objective is now to elaborate a non-empirical kinetic model for lifetime prediction of hdPE outer sheaths in use conditions. This model is of key importance for EDF because it would allow to evaluate, at any time, the health of the underground electric network and to plan the replacement of damaged cables before their sudden failure. Moreover, it would give to EDF the opportunity to reduce significantly the cost of exploitation of the underground electric network.

To present a high heuristic value, such a model must be

derived from the ageing mechanisms taking place in use conditions. During their exploitation, hdPE outer sheaths are submitted to the effects of various environmental factors such as: temperature, oxygen, water and electrical stresses. From a rapid literature overview, it appears that the combined effects of temperature, oxygen and water would lead successively to:

a) Antioxidants depletion. Synergistic mixtures of antioxidants are incorporated into PE matrices in order to extend as much as possible the oxidation induction period. However, this stabilization effect is time limited. Indeed, antioxidants are not only consumed by the chemical reaction, but also are lost by physical processes, in particular by diffusion across the sheath thickness and evaporation at the polymer/air interface [4].

b) PE thermal oxidation. When antioxidants are vanishing, PE thermal oxidation accelerates sharply and reaches a steady-state [5]. That is the reason why the time for total antioxidant depletion corresponds to the end of induction period. From this moment, many oxidation products are formed and can be detected by common laboratory spectroscopic techniques. They are essentially hydroxyl and carbonyl species [6].

c) Water sorption. It is expected that the formation of very polar oxidation products, in particular alcohols and carboxylic acids, lead to a significant increase in PE hydrophilicity [7]. As a result, in a wet environment, the outer PE sheaths could absorb higher amounts of water.

d) Aluminum corrosion. If water reaches the aluminum foil barrier, aluminum could corrode and, at term, perforate. From this moment, water would penetrate into the insulator and induce its dielectric breakdown (see Figure 1).

On the contrary, effects of electrical stresses on polymer structure are badly known yet.

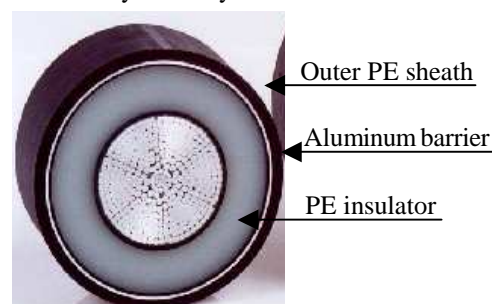


Figure 1: View of an hdPE sheathed cable.

Starting from these observations, a general methodology for evaluating the durability of hdPE outer sheaths can be tentatively defined. It is based on a series of experiments dedicated to the elucidation of the ageing mechanisms evidenced in the previous literature overview. The objective of the present communication is to check the validity of such a methodology.

EXPERIMENTAL:

Material:

The commercial hdPE grade (Stenungsund SWPE) was supplied by Borealis. Its main characteristics are: melting temperature of $129.5 \pm 2^\circ\text{C}$, crystallinity ratio of $62 \pm 5\%$ and density of 0.944. It was received free of any adjuvants and stabilized by a common synergistic blend of two antioxidants, B225, supplied by Ciba Geigy. The blend B225 is constituted of an equimassic proportion of hindered phenol (Irganox 1010) and organic phosphite (Irgafos 168). The mass fraction of both antioxidants in PE was estimated around 0.13 %wt by UV and IR spectrometries. The mass fraction of Irgafos 168 was confirmed by elemental analysis (about 62 ppm of phosphorus). The main characteristics of both antioxidants are reported in Table 1.

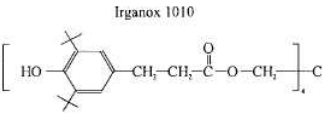
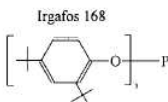
Chemical structure	Molar mass (g/mol)	Melting range ($^\circ\text{C}$)
 <p>Irganox 1010</p>	1178	110-125
 <p>Irgafos 168</p>	647	180-185

Table 1: Chemical structure and main properties of antioxidants under study [10]

Experiments were carried out on thin hdPE films of $140 \pm 30 \mu\text{m}$ thickness obtained by compression molding at 180°C under 3MPa pressure.

Methods:

Stabilized PE films were exposed in air-ventilated ovens at 120°C , 140°C , 150°C and 160°C during several thousands of hours. They were periodically removed from ovens to be analyzed by Fourier transform infrared (Brüker, IFS 28 spectrometer, 32 scans, 4 cm^{-1} resolution) and ultraviolet spectrometries (Perkin Elmer, Lambda 35, UV/visible spectrometer) in a transmission mode, in order to monitor the antioxidants depletion and their reaction products evolution. Attention was paid to absorption bands centered at 966 cm^{-1} (phosphates), 1211 and 1196 cm^{-1} (phosphites), 1740 cm^{-1} (esters) and 273 nm (phenols, phosphites and phosphates).

Pure PE films were exposed in air-ventilated ovens at 80°C , 100°C , 110°C and 120°C during several hundreds of hours. Most of the films were periodically removed from ovens in order to be analyzed by Fourier transform infrared spectrometry (Brüker, IFS 28 spectrometer, 32 scans, 4 cm^{-1} resolution) before and after gaseous treatments, in order to monitor oxidation products build-up. At first, ammonia (NH_3) was used to convert carboxylic acids into ammonium carboxylates [8]. Then, sulfur dioxide (SO_2) was used to convert hydroperoxides into a polymeric ester sulfuric acid [9]. By subtracting IR spectra obtained before and after each gaseous treatment, it was possible to deconvolute chemically the overlapped bands located in the carbonyl ($1830\text{-}1600 \text{ cm}^{-1}$) and hydroxyl regions ($3700\text{-}3200 \text{ cm}^{-1}$)

and thus, to identify all chemical species. Attention was paid to absorption bands centered at 1042 cm^{-1} (hydro-sulphates), 1557 cm^{-1} (carboxylates) 1700 cm^{-1} (unsaturated ketones), 1712 and 1721 cm^{-1} (carboxylic acids), 1718 cm^{-1} (saturated ketones), 1735 cm^{-1} (aldehydes), 1740 cm^{-1} (esters), 1785 cm^{-1} (γ -lactones), 3370 cm^{-1} (hydroperoxides and alcohols) and 3420 cm^{-1} (hydroperoxides and carboxylic acids).

Other PE films were removed from ovens in order to be immersed in distilled water at 25°C during several dozens of hours. Their equilibrium water concentration was determined by Karl-Fischer coulometry at 150°C under nitrogen gas with a drift of $15 \mu\text{g}/\text{min}$ during 15 minutes.

RESULTS:

Antioxidants depletion:

Examples of kinetic curves of antioxidants depletion in ambient air at 150°C are presented in Figures 2 and 3. These results call for the following comments:

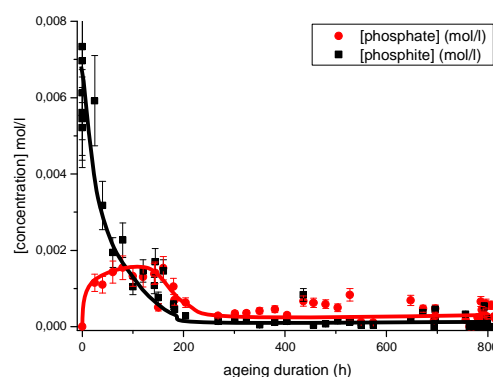
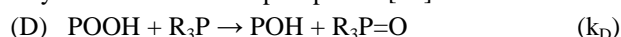


Figure 2: Phosphites depletion and phosphates evolution in ambient air at 150°C .

- Phosphite antioxidants (e.g. Irgafos 168) are efficient at high temperature. That is the reason why they are currently used to prevent oxidation during melt processing. They decompose hydroperoxide groups (POOH) by a non-radical way and transform into phosphates [10]:



where R_3P and $\text{R}_3\text{P}=\text{O}$ designate respectively phosphites and phosphates, and k_D is a rate constant.

Thus, their consumption rate writes:

$$v_D = -k_D [\text{POOH}] [\text{R}_3\text{P}] \quad (\text{Equ. 1})$$

Between 120 and 150°C , the initial value of v_D is very high, presumably because rate constant k_D is very fast (typically $k_D \gg 1 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$), but also because PE contains a low, but non negligible, initial POOH concentration. Since v_D is proportional to POOH concentration, it decreases rapidly in the early periods of exposure and vanishes approximately when the phosphate concentration becomes maximum. From this moment, phosphites and phosphates are mainly lost by evaporation. Their evaporation rates write:

$$v_{E1} = -\beta_{\text{R}_3\text{P}} [\text{R}_3\text{P}] \quad (\text{Equ. 2})$$

$$v_{E2} = -\beta_{\text{R}_3\text{PO}} [\text{R}_3\text{PO}] \quad (\text{Equ. 3})$$

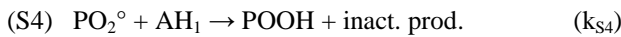
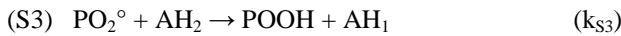
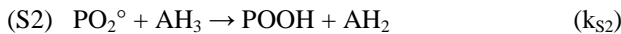
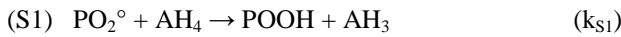
where $\beta_{\text{R}_3\text{P}}$ and $\beta_{\text{R}_3\text{PO}}$ are the coefficients of crossing of PE-air interface by phosphites and phosphates respectively.

Since both molecules present relatively close molar masses (647 and 665 g.mol⁻¹ respectively), it is expected that:

$$\beta_{R3P} \approx \beta_{R3PO} \quad (\text{Equ. 4})$$

Kinetic modeling of phosphites and phosphates evaporation in ambient air at 150°C by Eqs 2 and 3 has led to values of $\beta_{R3P} \approx 3.10^{-6} \text{ s}^{-1}$ and $\beta_{R3PO} \approx 1.10^{-6} \text{ s}^{-1}$, we can consider that $\beta_{R3P} \approx \beta_{R3PO} \approx 10^{-6} \text{ s}^{-1}$ confirming the above assumption.

- On the contrary, phenolic antioxidants are efficient at low temperature. They are thus used to prevent oxidation in use conditions at long term. The phenol group O-H is characterized by a very low dissociation energy $E_D \approx 335-355 \text{ kJ.mol}^{-1}$ [11-13] against $E_D \geq 380 \text{ kJ.mol}^{-1}$ for methylene and methyne C-H bonds in polyolefins. Thus, Irganox 1010 contains four very labile hydrogen atoms allowing to scavenge efficiently peroxy radicals (PO_2°) [10]. In a first approach, its stabilization mechanism can be oversimplified as follows:



where $AH_{4...1}$ designate respectively Irganox 1010 and its reaction products and $k_{S4...1}$ are rate constants.

There is no reason to assume that Irganox 1010 (AH_4) and its reaction products ($AH_{3...1}$) behave differently with respect to peroxy radicals. In a first approach, it can be thus written:

$$k_{S4} = k_{S3} = k_{S2} = k_{S1} \quad (\text{Equ. 5})$$

Thus, the consumption rate of phenol groups writes:

$$v_s = -4k_{S1}[PO_2^\circ][AH_4] - 3k_{S1}[PO_2^\circ][AH_3] - 2k_{S1}[PO_2^\circ][AH_2] - k_{S1}[PO_2^\circ][AH] \quad (\text{Equ. 6})$$

$$\Rightarrow v_s = -k_{S1}[PO_2^\circ](4[AH_4] + 3[AH_3] + 2[AH_2] + [AH])$$

$$\Rightarrow v_s = -k_{S1}[PO_2^\circ][OH] \quad (\text{Equ. 7})$$

About 70 % mole of phenol groups are consumed by the chemical reaction at 150°C in ambient air (Figure 3). On the contrary, ester groups and other phenol groups are lost by evaporation. Their evaporation rate writes:

$$v_{E3} = -4\beta_{AH4}[AH_4] - 3\beta_{AH3}[AH_3] - 2\beta_{AH2}[AH_2] - \beta_{AH}[AH] \quad (\text{Equ. 8})$$

where $\beta_{AH4...1}$ are the coefficients of crossing of PE-air interface by Irganox 1010 and its reaction products respectively.

Since all these molecules present very close molar masses (1178, 1177, 1176 and 1175 g.mol⁻¹ respectively), it can be written:

$$\beta_{AH4} = \beta_{AH3} = \beta_{AH2} = \beta_{AH} \quad (\text{Equ. 9})$$

Equ. 8 can be thus rewritten:

$$v_{E3} = -\beta_{AH}(4[AH_4] + 3[AH_3] + 2[AH_2] + [AH]) \Rightarrow v_{E3} = -\beta_{AH}[OH] \quad (\text{Equ. 10})$$

Kinetic modeling of esters evaporation in ambient air at 150°C by Equ. 10 has led to a value of $\beta_{AH} \approx 5.10^{-7} \text{ s}^{-1}$.

- When the phenol groups concentration becomes very low

(typically $10^{-3} \text{ mol.l}^{-1}$), thermal oxidation accelerates sharply and consumes suddenly all remaining phenol groups. From this moment, high concentrations of oxidation products can be detected by IRTF spectrometry (Figure 3).

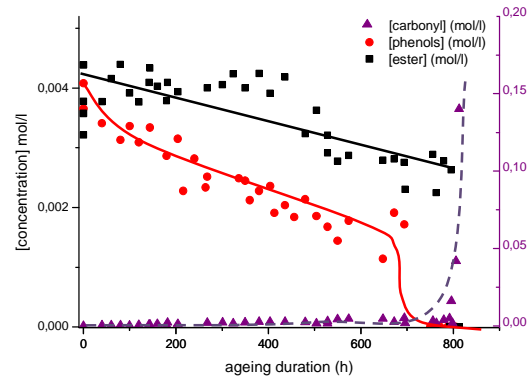


Figure 3: Phenols and esters depletion and carbonyls build-up in ambient air at 150°C.

PE thermal oxidation

Examples of kinetic curves of oxidation products build-up in ambient air at 100°C are presented in Figures 4 and 5. These results call for the following comments:

- Carbonyl species are essentially composed of ketones, aldehydes and carboxylic acids (Table 2). Esters and γ -lactones are practically undetectable.

Carbonyl species	Mole fraction (%)
Ketones	47 ± 4
Carboxylic acids	20 ± 5
Aldehydes	33 ± 5

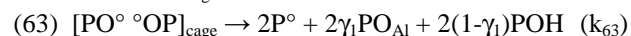
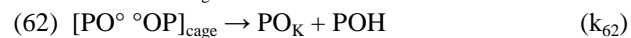
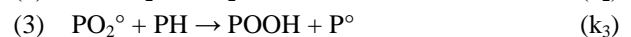
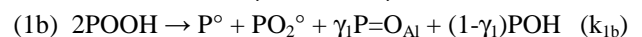
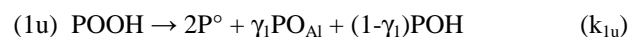
Table 2: Composition of carbonyl species in ambient air at 100°C.

- Hydroxyl species are essentially composed of :

Hydroxyl species	Mole fraction (%)
Hydroperoxides	54 ± 9
Alcohols	34 ± 9
Carboxylic acids	12 ± 4

Table 3: Composition of hydroxyl species in ambient air at 100°C.

- The formation of this wide variety of oxidation products can be partly explained by the classical “closed-loop” mechanistic scheme [14]. In its simplest form (in oxygen excess), it writes:



where PO_{Al} , PO_K and POH designate aldehydes, ketones and alcohols respectively.

However, this mechanistic scheme totally ignored the

formation of carboxylic acids. They presumably come from the thermal oxidation of some oxidation products (e.g. aldehydes, alcohols and hydroperoxides), of which the corresponding C–H bond presents also a very low dissociation energy ($E_D \approx 368 \text{ kJ.mol}^{-1}$). The integration of these reactions into the previous mechanistic scheme is in progress at the laboratory.

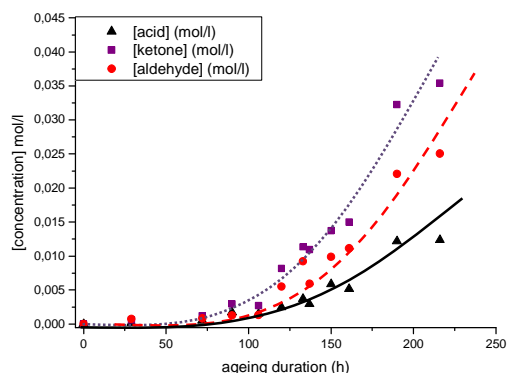


Figure 4: Carboxylic acids, aldehydes and ketones build-up in ambient air at 100°C.

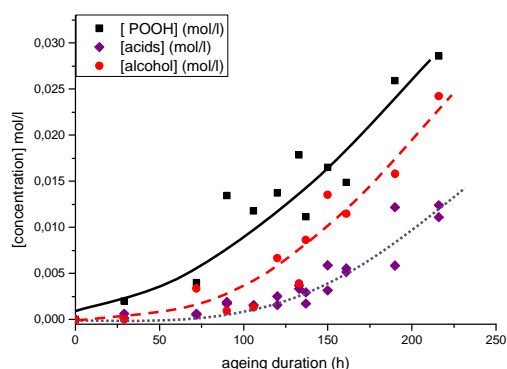


Figure 5: Hydroperoxides, acids and alcohols build-up in ambient air at 100°C.

Water sorption:

The molar water uptakes by some important structural groups are reported in Table 4 [7]. As expected, the main contributors to hydrophilicity are very polar oxidation products, i.e. alcohols and carboxylic acids. These values are under checking at the laboratory on a series of virgin ethylene copolymers containing only one type of oxidation product in their monomer unit.

Knowing the alcohols and carboxylic acids concentration after PE thermal ageing, it becomes thus possible to predict the increase in water concentration in 100% RH at 25°C:

$$\Delta[\text{H}_2\text{O}] \approx x_{\text{POH}}[\text{POH}] + x_{\text{POAc}}[\text{POAc}] \quad (\text{Equ. 11})$$

where POAc designates carboxylic acids and x_{POH} and x_{POAc} are the respective molar water uptakes per alcohol and carboxylic acid group (Table 4).

Let's consider a PE film preliminary oxidized during 225 hours in ambient air at 100°C. Application of Equ. 11 gives a value of $[\text{H}_2\text{O}] \approx 7.10^{-2} \text{ mol.l}^{-1}$ i.e. $\approx 1330 \text{ ppm}$. This theoretical value remains now to be confronted to the experimental one to check the validity of our approach.

Structural groups	Literature
Methylene	5.10^{-5}
Carboxylic acid	1.3
Aldehyde	0.3
Ketone	0.3
Hydroperoxide	-
Alcohol	2

Table 4: Molar water uptakes per structural group in 100 % RH at 25°C reported in the literature [7].

CONCLUSION AND PROSPECTS

A general methodology for evaluating the durability of hdPE outer sheaths has been presented. It is based on a series of experiments which have allowed us to elucidate the ageing mechanisms, but also to highlight the pertinent kinetic parameters. It has been clearly shown that PE thermal oxidation accelerates sharply when the antioxidants are vanishing and thus, leads to a significant increase in PE hydrophilicity. The resulting increase in water concentration can be predicted from relatively a simple relationship, knowing the oxidation products concentration in PE.

Now, the next step will consist in building a general kinetic model for lifetime prediction of hdPE outer sheaths in use conditions. This model will be derived from the different ageing mechanisms, but also will integrate the structure property/relationships established in the present article.

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