The Thermooxidation and Resistance to Moulds Action of Some Polyethylene Sorts Used at Anticorrosive Insulation of the Underground Pipelines

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Polyethylene (PE) insulations have a wide applicability in the insulation of both underground pipelines and underground power cables. In this context, by coupled techniques of thermal analysis (TG/DTG+DTA) and microbiological determinations, have been studied thermooxidability and resistance to moulds action of some polyethylene sorts. Following the processing of the experimental data obtained by thermal analysis it was found that during the applied heat treatment (100 °C), in the first approx. 380 h, there is a growth of LDPE (low density polyethylene) polymerization degree by elongation of the aliphatic chains, after which the predominant process consists in the structure crosslinking. For MDPE (mean density polyethylene) samples, during the thermal treatment applied, it was found that the crosslinking degree of polyethylene (PE) increased without significant molecular weight change (with all the related consequences of increasing the weight of the tertiary and quaternary carbon atoms in the molecule). Microbiological determinations have highlighted that the resistance to filamentous fungal action of LPDE is higher than that of the investigated MDPE. It was found that after heat treatment applied (1000 h & 100 °C), both at LDPE and at MDPE, decreases the resistance to moulds action is decreased. It has also been found that moulds action resistance is substantially decreased when inoculated culture media and PE samples are exposed to an alternative electric field of 50 Hz – 6 $V_{rms/cm}$.

Keywords: PE insulation, underground pipelines, PE ageing, resistance to moulds

With a view to sustainable development, the issue of sustainability and safe operation of underground metallic pipelines, especially natural gas transport or oil products, is of paramount importance.

The durability and safety in operation of underground metallic pipelines are influenced by the aging of anticorrosive insulation due to chemico-physical and biological stress factors acting synergistically on polyethylene (PE) insulation applied to steel pipes [1-7].

As a result of technological developments, over the past two decades, at new investments, bituminous insulation of the steel pipes [1-3] has been replaced with PE- based performance insulation [4-7]. On the other hand, the PE is widely used in the manufacture of underground power cables - both in the basic insulation - metallic shielding [8-10] and the outer protective layer [11-15]. PE based insulations both to those on the steel pipes (hot foil [4, 7] or from granules by extrusion [5, 16]) and on the external protective layer of underground power cables (applied by extrusion) they are exposed to atmospheric weathering and solar radiation (UV and IR) during storage, and also, are exposed both to stress factors due to chemical and microbiological aggression of soil and electrical stress due to AC polarization during operation.

As a result of the continuous increase of the production and the consumption of electric energy, a new issue, namely induced AC voltage in the underground pipelines, which needs to be evaluated, has emerged in the practice for anticorrosion protection of the gas buses and/or oil products [17-21] and treated appropriately [22-25]. As a result of technological advances in recent decades, the share of non-linear consumers, generators of reactive powers and a broad spectrum of harmonics (such as LED laps, computers, etc., has substantially increased [26-30]) with major implications on disturbing signals induced in underground pipelines. Several recent studies have highlighted that the advanced state of degradation by corrosion of some underground power cables is largely due to the action of soil microorganisms on the outer PE protective layer [11-16, 31-33] - in particular of filamentous fungi like Penicillium funiculosum, Aspergillus niger, Scopulariopsis brevicaulis, Cladosporium sp, Trichoderma viridae, Aspergillus niger, Chaetomium globosum, Trichoderma viride ºi Chaetomium globosum. Most of these species have recently been identified [7] in the soil along the path of steel pipes insulated with heat applied PE foil. Advanced microbiological degradation found in the PE protective layer - but also in some painting materials [34] - is explained by the intensification of the metabolism processes of the mould when grow on polarized culture media in the AC [35-38]. Due to the microbiological degradation of EP protective coatings penetration of corrosive agents and soil microorganisms into the support metal under their synergistic action is facilitated [39-43]. Polymeric materials, due to their mass and high molecular weight, have good resistance to microorganisms action [44]. Biodeterioration and biodegradation of polymers occurs as a result of aging processes under atmospheric stress factors [45], UV radiation [46, 47] and / or mechanical stresses [48], when the polymer chain is fractionated and mass decreases and the molecular volume [49, 50], so the enzymatic activity of the microorganisms [51] makes it possible to metabolize the carbon in the polymer.

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Thus, experimental laboratory studies [34] and field investigations [52] report the biodegradation of polymers exposed to atmospheric stress factors [11,12,15,16,32] and those exposed to stress factors from polluted complex soil (Chemical and electromagnetic).

Degradation capacity of natural and synthetic polymers of soil microorganisms can be substantially reduced by the addition of xenobiotic substances [53, 54]. It is noted that the ageing EP based anticorrosion insulation of steel pipes is the result of the thermooxidative and biodegradation processes that occur under the simultaneous and synergistic action of the stress factors acting on the pipes during transport, storage, burial and exploitation.

In this context, the paper aim consist in the experimental study of thermooxidative stability and resistance to moulds action on PE insulation in foil, thermal ageing and exposed to the 50 Hz electric field of the insulation.

Experimental part

Using coupled techniques of thermal analysis (TG/DTG + DTA), the thermooxidative behavior of some low density (LDPE) and mean density (MDPE) sorts of PE was evaluated.

Thermal analysis determinations were performed with a TG/DTG + DTA Analyzer equipment produced by Netzsch - Germany. The experiments were carried out in synthetic air atmosphere (99.999% purity), with a gas flow rate of 30 $cm^3\ min^{-1}$, under non-isothermal linear regime, at heating rate of 10 $K\ min^{-1}$. All measurements were made by heating the PE samples from the room temperature (RT) to 600 °C into Pt-Rh crucibles. The experimental results were processed using the dedicated Proteus Software, from Netzsch – Germany.

PE samples were taken from isolated steel pipes (applied hot foils [4, 7]) and exposed to thermal ageing at 100 ± 3 °C for 1000 h in a France Etuve XL 980.

For the comparative evaluation of mould resistance (exposed to thermal ageing, as well as control samples), according to [55-56], they samples were exposed on Czapek-Dox type saline gel culture medium with sucrose, being a readily assimilable carbon source.

The Czapek-Dox culture medium was prepared by dissolving in 1000 mL of deionised water of 2 g of sodium nitrate ($NaNO_3$); 0.7 g monopotassium phosphate (KH_2PO_4); 0.3 g dipotassium phosphate (K_2HPO_4); 0.5 g potassium chloride (KCl); 0.5g Magnesium sulphate heptahydrate ($MgSO_4\ 7H_2O$); 0.01 g iron (II) sulphate ($FeSO_4$); 30 g agar-agar and 30 g sucrose.

Culture media with PE samples were placed in Petri dishes at ϕ60 mm and inoculated by spraying with mixed inoculum of *Alternaria alternata, Aspergillus flavus, Aspergillus niger, Aspergillus ustus, Cladosporium herbarum, Paecilomyces varioti, Penicillium citrinum, Penicillium funiculosum, Stachybotris atra and Trichoderma viride*, having approx. 10^6 spores/ mL in saline solution.

The biological samples thus prepared were incubated for up to 28 days in a controlled atmosphere incubator (30 ± 20 °C, 90 ± 5 % RH).

In order to evaluate the influence of the electric field applied to the culture medium, some of the samples were exposed to a 50 *Hz* electric field (applied on the Petri dish between two parallel planar electrodes) with the intensity of 6 $V_{rms/cm}$ of biomass - controlled by the calculated voltage according to [57] .

Periodically, during incubation, the biological samples were analyzed and evaluated macroscopical (visual) and microscopical (stereomicroscopy).

Results and discussions

Thermal analysis

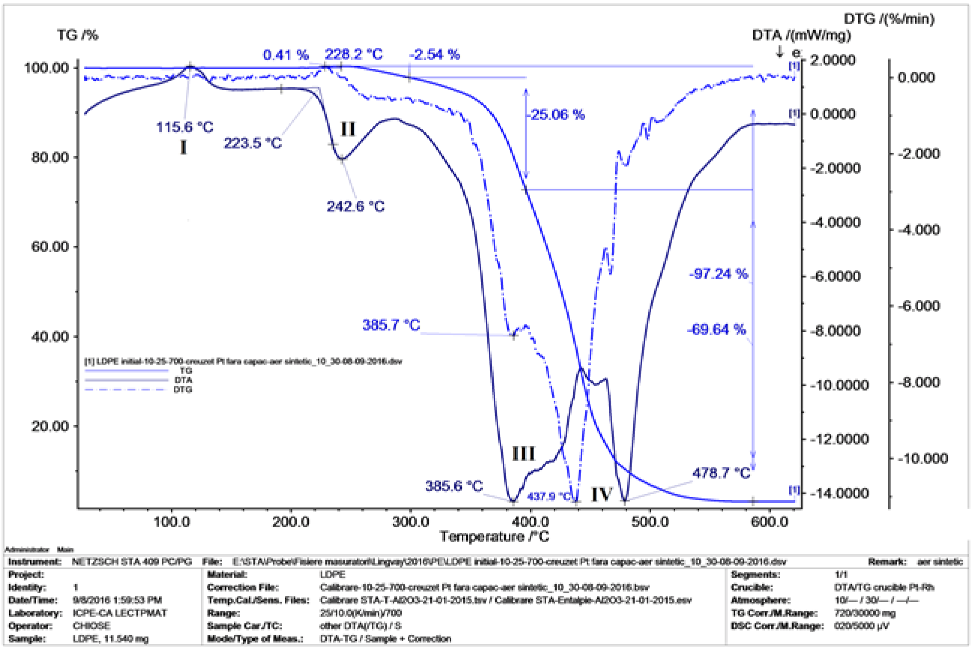
The thermogram recorded to the progressive heating of the LDPE sample before heat treatment (initially) is shown in figure 1.

By analyzing figure 1, it is observed that, at the progressive heating in synthetic air medium, the investigated material undergoes several PE characteristic processes.

Thus, at Tm = 115.6°C, the material melts through an endothermic process (I).

The first exothermic process of thermooxidation (II) with formation of solid peroxides (increase of sample weight with Ä*m* = 0.41 %) has the characteristic temperature T_{Max2} = 242.6°C followed by two protruding processes (exotherm) of thermooxidation with formation of volatile products (III and IV) having the characteristic temperatures T_{Max3} = 385.6°C and T_{Max4} = 487.7°C, when the mass losses are significant (25.06 and 69.64 % respectively).

At 600 °C the material degradation is complete, the total mass loss being 97.24 %.



Administrator Main

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Project:
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Date/Time: 9/8/2016 1:59:53 PM
Laboratory: ICPE-CA LECTPMAT
Operator: CHIOSE
Sample: LDPE, 11.540 mg

Material: LDPE
Correction File: Calibrare-10-25-700-creuzet Pt fara capac-aer sintetic_10_30-08-09-2016.bsv
Temp.Cal./Sens. Files: Calibrare STA-T-Al2O3-21-01-2015.tsv / Calibrare STA-Entalpie-Al2O3-21-01-2015.esv
Range: 25/10.0(K/min)/700
Sample Car./TC: other DTA(/TG) / S
Mode/Type of Meas.: DTA-TG / Sample + Correction

Segments: 1/1
Crucible: DTA/TG crucible Pt-Rh
Atmosphere: 10/— / 30/— / —/—
TG Corr./M.Range: 720/30000 mg
DSC Corr./M.Range: 020/5000 µV

Fig. 1. The thermogram recorded on the initial LDPE sample

Table 1
EVOLUTION OF SPECIFIC LDPE PARAMETERS DURING THERMAL AGEING

Sample	Process I		Process II			Process III			Process IV			Δm total & 600 °C [%]
	T_m [°C]	ΔH	T_{Max2} [°C]	ΔH	Δm_2 [%]	T_{Max3} [°C]	ΔH	Δm_3 [%]	T_{Max4} [°C]	ΔH	Δm_4 [%]	
Initial	115.6	endo	242.6	exo	0.41	385.6	exo	–25.06	478.7	exo	–69.64	–97.24
Aged 384 hours &100 °C	120.9	endo	252.1	exo	0.05	396.4	exo	–6.42	449.3	exo	–93.04	–99.46
Aged 717 hours &100 °C	123.5	endo	252.8	exo	0.69	384.6	exo	–38.3	436.8	exo	–59.8	–99.36
Aged 1000 hours &100 °C	123.8	endo	251.7	exo	1.02	381.4	exo	–21.2	422.7	exo	–77.19	–98.39

Table 2
EVOLUTION OF MDPE SPECIFIC PARAMETERS DURING THE THERMAL AGEING

Sample	Process I		Process II			Process III			Process IV			Δm total & 600 °C [%]
	T_m [°C]	ΔH	T_{Max2} [°C]	ΔH	Δm_2 [%]	T_{Max3} [°C]	ΔH	Δm_3 [%]	T_{Max4} [°C]	ΔH	Δm_4 [%]	
Initial	129.9	endo	263.4	exo	0.27	338.8	exo	–7.64	395.6	exo	–83.13	–98.30
Aged 384 hours & 100 °C	130.9	endo	259.0	exo	0.39	336.6	exo	–7.83	401.0	exo	–83.83	–98.81
Aged 717 hours & 100 °C	130.1	endo	261.0	exo	0.56	335.3	exo	–7.44	399.6	exo	–83.66	–98.30
Aged1000 hours & 100 °C	129.8	endo	259.8	exo	0.74	333.7	exo	–9.17	391.7	exo	–80.68	–98.10

This thermal behavior is characteristic for PE, as reported in [5, 8, 58, 59].

Thermograms recorded on the LDPE samples exposed to heat treatment at 100°C have the same pattern as the thermogram in figure 1 - the registered differences being at the characteristic parameters, respectively T_m, T_{Max2}, T_{Max3}, and T_{Max4} as well as the mass losses Δm.

The evolution of these parameters is summarized in table 1.

By analyzing the data presented in table 1, it was found that after the first 384 h of thermal treatment on LDPE investigated, the melting point T_m increased by 5.3°C indicating an increase in the polymerization degree. Also, significant changes are noted in process II when T_{Max2} increases by 9.5 °C and Δm_2 decreases from 0.41 to 0.05 %, indicating that during the first 384 h of heat treatment decreased the thermooxidation with the formation of solid products, explained by reducing the number of tertiary carbon atoms in the polymer structure [5, 8, 59].

These findings suggest that LDPE investigated during the first 384 h of heat treatment decreases the crosslinking degree and increases the polymerization degree by increasing the length of the polymer chains.

These structural changes have a major influence on the processes III and IV of thermooxidation with formation of volatile products, respectively III increases T_{Max3} and decreases Δ_{m3} and at IV decreases T_{Max4} and increases Δm_4.

It is also noted that to the continued heat treatment (717, respectively 1000 h) the melting point has a slight tendency to increase, T_{Max2} changes are relatively small (below 1°C), Δ_{m2} has a pronounced growth trend (from 0.05 to 0.69 %, respectively 1.02 %) and T_{Max3} and T_{Max4} continuously decrease suggesting that the crosslinking rate increased and, implicitly, the thermooxidation with formation of volatile products of the polymeric.

It is noted that these structural changes during heat treatment cause changes in the mechanical characteristics of the polymer [60] and that by analyzing the evolution of the parameters T_m, T_{Max2}, T_{Max3}, Δm_2 and Δm_3 the lifetime of the polymer can be estimated [61].

The thermograms recorded on the MDPE samples both the initial and the heat treatment at 100°C are identical to the thermogram in figure 1 - the registered differences being at the characteristic parameters, respectively T_m, T_{Max2}, T_{Max3}, *and* T_{Max4} as well as at mass losses Δm.

From the comparative analysis of the data in table 1 with those in table 2, it is found that major differences in the thermal behavior of investigated LDPE and MDPE are recorded in the first 384 h of treatment at 100°C, when unlike LDPE at MDPE increases the crosslinking degree without aliphatic chain extension.

It is also noted that T_{Max2} at MDPE is slightly higher than that of LDPE, indicating a lower thermooxidation with peroxide products formation, whereas T_{Max3} is substantially (by about 40°C) less MDPE than LDPE, indicating a tendency to degradation by forming volatile products more pronounced at MDPE.

Results of microbiological determinations

Figures 2- 6 show representative images captured on microbiological samples after 672 h incubation.

The results of the observations of the mold growth on the investigated PE samples are summarized in table 3 (no field exposure during incubation) and in table 4 (microbiological samples exposed to an electric field of 6 V_{rms}/cm biomass).

By comparative analysis of figures 2, 3, 4, 5 and 6 and of the observations in table 2 and table 3 it is found that LDPE both initial samples and thermally ageing samples exhibit higher mould action resistance than MDPE samples. This behavior can be explained by the fact that mould enzymes act [51] primarily on carbon atoms with high activity.

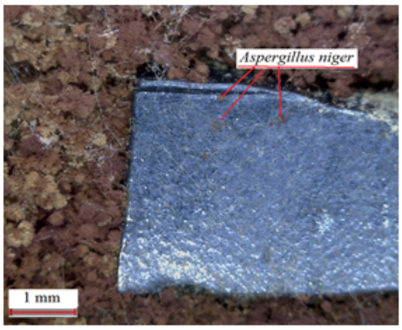

Fig.2. Image of the initial MDPE sample (no electric field exposure)

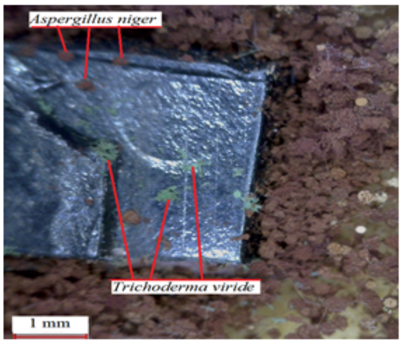

Fig. 3. Image of the thermal aged (1000 h & 100°C) LDPE sample (no electric field exposure).

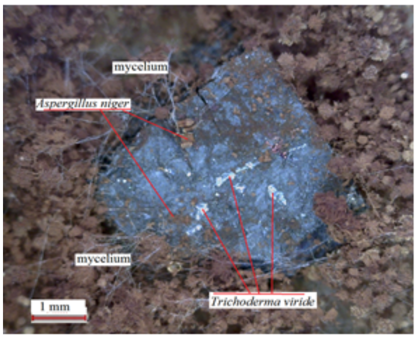

Fig. 4. Image of the thermal aged (1000 h & 100 °C) MDPE sample (no electric field exposure).

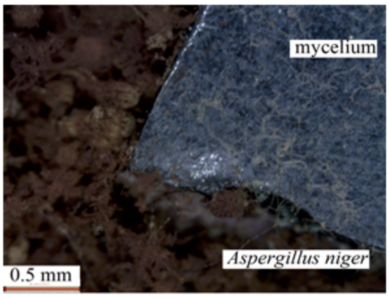

Fig. 5. Image of the initial LDPE sample exposed to electric field 6 V_{rms}/cm -50 Hz.

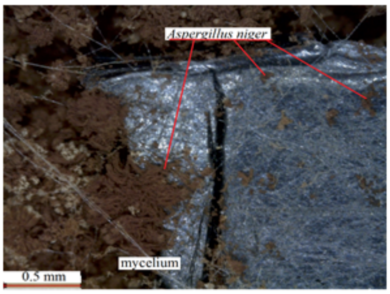

Fig. 6. Image of the initial MDPE sample exposed to electric field 6 V_{rms}/cm -50 Hz

In case of MDPE with a higher crosslinking degree, the number of tertiary and quaternary carbon atoms (with higher activity [5, 8, 58, 59]) from molecule is higher than for LPDE. It is also noted that at the exposure during incubation of the microbiological samples in an electric field of 6 $V_{rms/cm}$ and 50 *Hz* the increases of *Aspergillus niger* are much stimulated on both the culture medium and the investigated PE samples.

The decrease in the resistance of the investigated PE sorts - both in the initial and the thermally ageing state - to the action of *Aspergillus niger* filamentous mould can be explained both by stimulation of growth and multiplication [37, 38] and by changes in enzyme activity [51] and / or the mould metabolism [35, 36] exposed to the 50 *Hz* electric field.

It is interesting to note that increases in Trichoderma viride were observed only in PE samples (both in initial samples and thermally ageing samples) not exposed to the electric field, which is probably due to the fact that the increase in *Aspergillus niger* have as result, complete inhibition of *Trichoderma viride*.

The evaluation results, of the coverage degree of PE samples with mould growths and the qualifiers according to [56] after 672 h of incubation are summarized in table 5.

By analyzing the data presented in table 5, it is found that mold resistance to the investigated LPDE type is excellent for initial and good samples in the case of thermally ageing samples 1000 h at 100 °C - even at 50 *Hz* electric field exposure.

It is also found that the investigated MDPE has a limited resistance - even low, at exposed in electric field of 50 *Hz* - at moulds action.

By correlating these results with the fact that, in the case of insulation PE by extrusions applied, mould action resistance is lower than that with hot foil PE insulation [16], it is found that, in order to ensure operating safety and high durability, even to underground pipes with high-performance PE insulation is required proper treatment of induced voltage from undergound pipelines [2, 25].

Table 3
OBSERVATIONS ON MICRO-BIOLOGICAL SAMPLES UNEXPOSED AT THE ELECTRICAL FIELD DURING INCUBATION

Samples		Observations and incubation times						
		24 h	48 h	72 h	336 h		672 h	
LDPE	Initial	On poorly developed primary mycelium culture medium	Rare young fructifications *Aspergillus niger*. No increase on PE	Young and mature fructifications *Aspergillus niger*. No increase on PE	The medium completely covered with *A. niger*, *Trichoderma viride*, traces of *A. flavus*	No increase on PE	The medium completely covered with *Aspergillus niger* and *Trichoderma viride*	No increase on PE
	Aged 1000 hours& 100 °C					*Trichoderma viride*, rare young fructifications *Aspergillus niger*, traces of *Aspergillus flavus*		*Trichoderma viride*, rare young and mature fructifications *Aspergillus niger*.
MDPE	Initial					*Trichoderma viride*, rare young fructifications *Aspergillus niger*		*Trichoderma viride*, rare young and mature fructifications *Aspergillus niger*
	Aged 1000 hours& 100 °C					*Trichoderma viride*, rare young and mature fructifications *Aspergillus niger*		*Trichoderma viride*, rare young and mature fructifications *Aspergillus niger*

Table 4

OBSERVATIONS ON MICROBIOLOGICAL SAMPLES EXPOSED DURING INCUBATION AT ELECTRIC FIELD 6 V_{rms}/cm – 50 Hz

Samples		Observations and incubation times						
		24 h	48 h	72 h	336 h		672 h	
LDPE	Initial	Well-developed primary mycelium No increases on PE samples	Young and mature *Aspergillus.niger* fructifications. No increases on PE samples	The medium covered by *A. niger*. No increases on PE samples	The medium completely covered with *Aspergillus. niger*	Primary mycelium traces	The medium completely covered with *Aspergillus niger*	Well-developed primary mycelium
	Aged 1000 hours& 100 °C					*Rare young and mature fructifications Aspergillus niger*		Mature and young fructifications *Aspergillus niger*
MDPE	Initial					Mature and young fructifications *Aspergillus niger*		Mature fructifications *Aspergillus niger*
	Aged 1000 hours& 100 °C					Mature fructifications *Aspergillus niger*		Massive increases *Aspergillus niger*

Table 5

THE COVERAGE DEGREE OF THE PE SAMPLES WITH MOULD AFTER 672 h OF INCUBATION

Degree of coverage [%] and Q* [56]					
PE sample		Without electrical field		Exposed to 6 V_{rms}/cm 50 *Hz*	
		[%]	Q*	[%]	Q*
LDPE	initial	-	0	-	1
	ageed	5	2	10	2
MDPE	initial	5	2	30	3
	ageed	20	2	60	4

Q - Qualifying in accordance with [56]:* ***0* *= without microbiological colonies;* ***1*** *= colonies*

On the other hand, it is considered that the high resistance to cellular enzymatic activity of the LDPE investigated sort with low crosslinking degree makes this material suitable for use in special applications where it is not exposed to thermal stress, e.g. biocompatible medical devices [62].

By correlating the results regarding the behavior at thermal stress with the resistance to the action at microorganisms of the PE sorts investigated, it is observed that at the PE use in the realization of natural gas transmission and distribution networks, in order to increase the safety of the networks, it is necessary to take into account changes in the physico-chemical [63-66] and microbiological behavior of the polymeric material following thermal treatments (such as welding [67] and applied mechanical stresses).

Conclusions

By using coupled techniques of thermal analysis (TG/DTG + DTA) and specific microbiological determinations (both in the absence and in the presence of an alternative electric field of 50 *Hz* - 6 $V_{rms/cm}$), it was study the thermooxidation and resistance to the moulds action, of some sorts of polyethylene (PE) used at anticorrosion insulation of underground pipes have been studied.

Following experimental data processing, it was found that:

- major differences in the thermal behavior of LDPE and MDPE sorts investigated are recorded in the first 384 hours of treatment at 100 °C, when polymerization process of LDPE sort takes place by elongation of the aliphatic chains as opposed to MDPE at which, the crosslinking degree increases occurs, without changing the melting temperature;

- in culture medium inoculated with spores from 10 mould species on both the LPDE and MDPE samples, in the absence of the overlapping electric field, only *Aspergillus niger* and *Trichoderma viride* were grown, the increases being higher on MDPE (resistance to moulds action is less) than at LPDE;

- after applied heat treatment (1000 h & 100°C), both LDPE and MDPE resistance to mould action decreases;

- the presence of the disturbing electric field of 50 *Hz* - 6 $V_{rms/cm}$ intensifies the microbiological activity, especially of *Aspergillus niger* (which inhibits the development of other species - including *Trichoderma viride*) and therefore substantial decreases the resistance to moulds action of the investigated PE sorts.

In view of these findings, in order to prevent the biodegradation of modern PE insulation applied to underground pipelines, it is necessary to AC tray currents, to be suitably treated (values limited to less than 0.15 V_{rms}) [19, 21, 25].

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