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ESTIMATION OF THE INFLUENCE OF PARTIAL DISCHARGES
ON AGEING OF POLYETHYLENE ON THE BASIS OF INFRARED
INVESTIGATIONS

1. Introduction

From among polymers, applied in electrical engineering as insulating materials, polyethylene is distinguished by a rather considerable resistance to ageing. However, the presence of oxygen causes oxidation and destruction of polymer chains. This process is considerably accelerated under the influence of light, elevated temperature etc. [1]. Partial discharges in the gaseous phase adjacent to polymer, and particularly in air, should also be numbered among factors accelerating ageing.

The influence of partial discharges on polyethylene has a complex character, i.e. that the surface of the investigated sample is subjected to the simultaneous action of a series of factors, connected with discharges, such as: ionic and electronic bombardment, ultraviolet radiation, local points of elevated temperature, ozone and nitric oxide medium etc. These factors may cause destruction of polymer, and also erosion of the surface, exposed to discharges [2,3,4].

Ageing of polyethylene is a composite process which changes the molecular structure of plastic. This appears in the change of its mechanical, and dielectric properties, of the molecular weight etc. In polyethylene, C = O carbonyl groups and C = C unsaturated bonds occur and disintegration as well as crosslinking of chains take place. As a result, solid and volatile products of destruction are formed [2,4,5], which can be identified among others by means of infrared investigations [2,5].

The increase in resistance to ageing, and thereby a considerable pro-

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longation of life time, can be obtained by modifying with the so-called stabilizers, added in a small quantity to polymer.

This paper presents the results of investigations on resistance of polyethylene to the influence of partial discharges in air. The results of investigations are compared with the results obtained for polyethylene by ultraviolet irradiation which is one of the factors of the damaging influence of discharges. The influence of two antioxidants, Ipognox-66 and Irganox-1010, on the increase in the resistance of polyethylene to discharges has been investigated. Introductory tests, to establish the relations between the rate of polymer ageing and the intensity of partial discharges, have also been carried out.

2. Materials and method of investigations

The following samples of polyethylene in the form of foil underwent investigations:

- polyethylene A without a stabilizer (A-0), 0,2 mm as well as 0,05 mm thick,
- polyethylene A + 0,3% Ipognox-66 (A-Ip), 0,4 mm thick,
- polyethylene A + 0,3% Irganox-1010 (A-Ir), 0,4 mm thick,
- cable polyethylene DFD-6603, 0,4 mm thick.

The foils were exposed to the action of partial discharges in a testing chamber with a plane-shaped air-gap, adjacent to one of the electrodes [6]. Ageing of foils was performed at 50 Hz alternating voltage. The width of the gap was changed in the range of 0,2 - 2,0 mm, and the value of applied voltage in the range of 2-7 kV; but most of the investigations were carried out for the 0,5 mm gap and the 3 kV voltage.

Ageing changes, occurring in polyethylene and the influence of partial discharges, were estimated on the basis of infrared absorption spectra, registered in the range of 650-4600 cm^{-1} . Before performing the measurements, the bloom, formed during the discharge activity, was removed from the IR samples by washing with alcohol.

The discharge current, calculated on the basis of the total charge measurements in one period of alternating voltage [7], was assumed as the measure of partial discharges intensity.

3. Results of investigations and discussion

It can be seen from the analysis of IR spectra, recorded for the polyethylene foils tested before and after their exposure to partial discharges in the air-gap, that significant changes occur only in the range from 1600 to 1800 cm^{-1} [6], irrespective of the discharge activity duration as well as of the presence and type of antioxidant in the sample (Figs 1 and 2). In this range, all functional groups, which contain carbonyl bonds $\text{C}=\text{O}$ (1685 - 1785 cm^{-1}) as well as any systems of unsaturated bonds $\text{C}=\text{C}$ (1580 - 1685 cm^{-1}), show absorption. One can see that the carbonyl band shows the greatest increase in absorption. That is why, it was assumed to consider ageing changes in the investigated foils mainly on the basis of the change in concentration of the $\text{C}=\text{O}$ groups.

The progressive ageing process of investigated foils is shown on the example of the A-O and A-Ir polyethylenes (Fig.3).

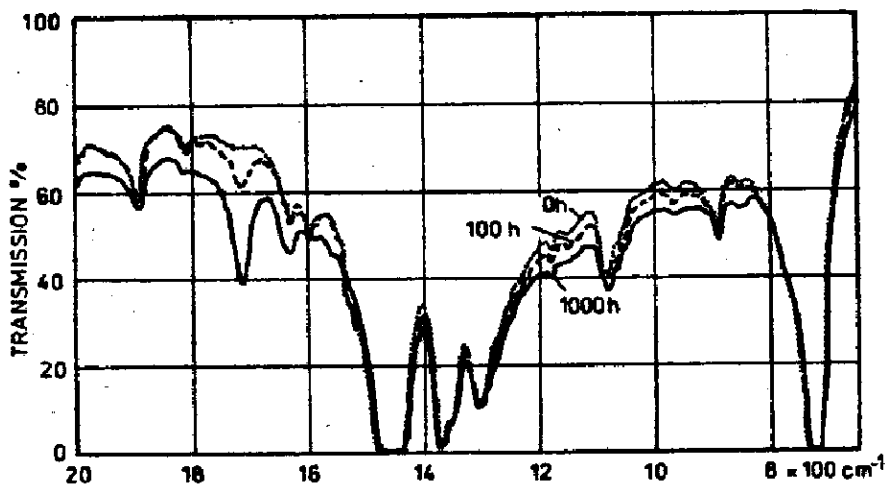


Fig.1. IR spectra of polyethylene A-Ip exposed to partial discharges for different periods (width of the gap $f=0,5$ mm, voltage $U=3$ kV)

Changes in the intensity of absorption bands show that together with the passage of ageing time, the contents both of the carbonyl groups $\text{C}=\text{O}$ and of unsaturated bonds $\text{C}=\text{C}$ increase progressively in the investigated samples. The maximum of the carbonyl band absorption, at wave number 1715cm^{-1} , suggests that ketones are principally formed, containing the $\text{C}=\text{O}$ group inside the chain ($\text{R}-\text{CO}-\text{R}'$).

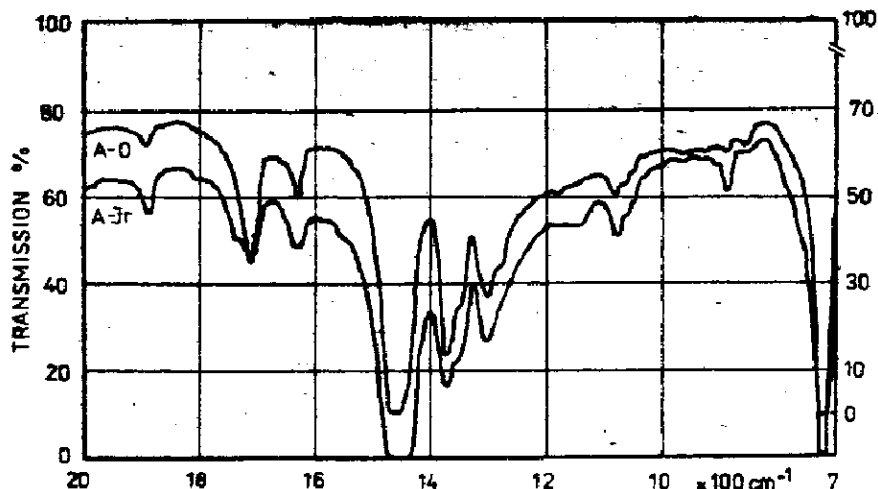


Fig.2. Influence of the antioxidant Irganox-1010 on ageing of polyethylene, exposed to partial discharges during 400 h ($d = 0,5 \text{ mm}$; $U = 3 \text{ kV}$)

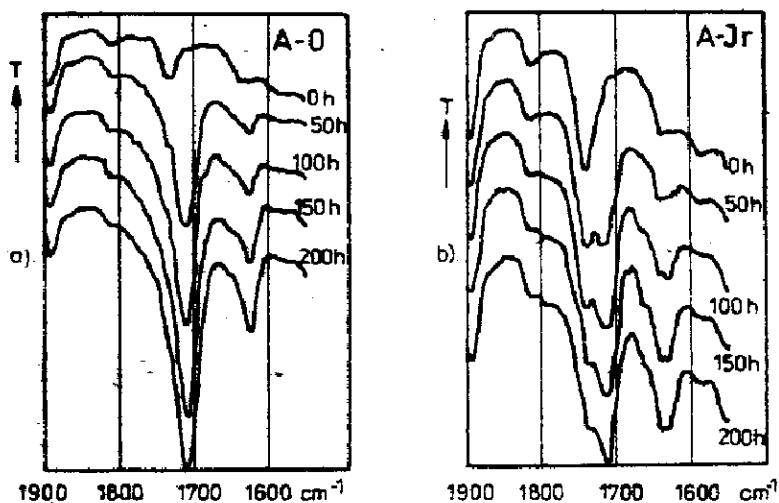


Fig.3. Increase in concentration of the $\text{C}=\text{O}$ groups and of the number of $\text{C}=\text{C}$ bonds of polyethylene foils, aged under the influence of partial discharges

Maximum 1740 cm^{-1} , marked weaklier or more distinctly, testifies also the presence of the $\text{R}-\text{CO}-\text{OR}'$ ester groups (the A-Ir virgin sample contains ester groups, coming from the introduced antioxidant). At the same

time, the presence of other functional groups, containing C=O bonds, cannot be also excluded, because the considered bands are broad and comprise in its reach a whole range of absorption of carbonyl groups, from unsaturated ketones (1685 cm^{-1}) to peracids (1785 cm^{-1}); besides these groups may occur in small concentration or be characterized by low coefficients of absorption.

In spite of a sufficient quantity of oxygen in the open ageing system, in the investigated foils, the content of unsaturated C=C bonds increases (in modified samples, the C=C bonds come in part from aromatic components of antioxidants). Aged samples give a composite C=C band with maximum at 1630 cm^{-1} , e.g. for the A-Ir sample (Fig.3b), three successive bands at wave numbers 1630 cm^{-1} , 1640 cm^{-1} and 1660 cm^{-1} can be distinguished. The occurrence of several bands of absorption can result as well from the type of the formed C=C bond (cumulated, conjugated, insulated), as from its position in relation to other functional groups, found in the chain.

Many authors inform [2,4,5,8,9], that in polyethylene, exposed to the action of partial discharges, in the atmosphere of air or oxygen, apart from the C=O groups and C=C bonds, hydroxyl OH (about 3400 cm^{-1}), ester R-CO-OR' ($1180-1280\text{ cm}^{-1}$), and also vinyl RCH=CH₂ (910 and 990 cm^{-1}), trans-vinylene RCH=CHR' (965 cm^{-1}) as well as vinylidene R₂C=CH₂ (868 cm^{-1}) groups are formed. According to Toriyama [9], apart from the above mentioned groups, alkyl ozonides $\begin{array}{c} \text{C}-\text{O}-\text{O}-\text{C} \\ | \\ \text{O} \end{array}$ (1054 cm^{-1} and 1107 cm^{-1}) as well as alkyl esters of nitric acid RO-NO₂ (853 cm^{-1} , 1280 cm^{-1} and 1635 cm^{-1}) are also created. On attributing the 1280 cm^{-1} and 1635 cm^{-1} bands to esters of nitric acid, he questions the presence of the C-O-C and C=C bonds in aged samples. However, ozonides and esters of nitric acid should show absorption in ranges attributed to other functional groups occurring in polyethylene and to identify them, nothing but infrared investigations are insufficient.

Most of the above mentioned functional groups show absorption in the range of wave numbers $800 - 1300\text{ cm}^{-1}$. The use of this range of spectrum, to estimate ageing changes in polyethylene, presents however great difficulties. In this interval, due to absorption caused by complex valency vibrations of chain fragments of different -CH₂ groups content, displacements and superposition of absorption bands take place [10], and in consequence they lead to a considerable decrease in the transmission level and

even decay of some peaks. This is illustrated best by the spectra of foils A-0, aged by the action of partial discharges in an air-gap, recorded successively: with reference to air as well as with reference to a virgin sample (Fig.4).

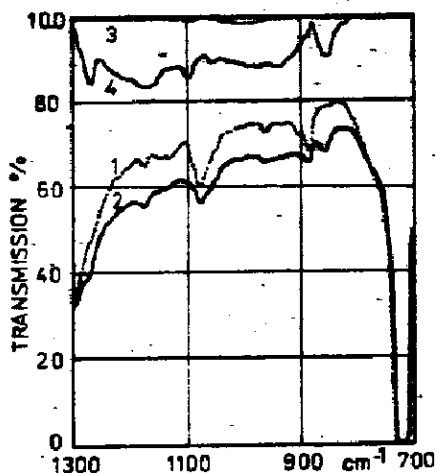


Fig.4. Decrease in the level of transmission for the A-0 polyethylene foil after 200 h. of ageing ($d = 0,5$ mm, $U = 3$ kV)
 1 - virgin sample to air, 2 - aged sample to air, 3 - virgin sample to another virgin sample, 4 - aged sample to a virgin one

Progressive ageing changes in polyethylene can be defined best by performing a half-quantitative evaluation of the increase in concentration of the $C=O$ carbonyl groups, by determining the increments of absorption value and by plotting kinetic curves [6,11]. Figure 5 shows such curves for the band of groups $C=O$ (1715 cm^{-1}), and in addition in Figure 6 for the band $C=O$ (1630 cm^{-1}), as well. The values of absorption are calculated in relation to the band 4270 cm^{-1} , assumed as internal standard.

The shape of the above presented kinetic curves indicates that the degree of ageing of the investigated foils is different. As it could be expected, the A-0 polyethylene is the most susceptible to the ageing due to discharges. The application of antioxidants influences clearly the increase in resistance of investigated foils to partial discharges [12]. Ipnognox-66 proved to be more useful between the two applied antioxidants. The sample containing Ipnognox-66 is just as resistant to oxidation as the

known insulating polyethylene DFD, and at the same time its tendency to form double bonds $C = C$ is less.

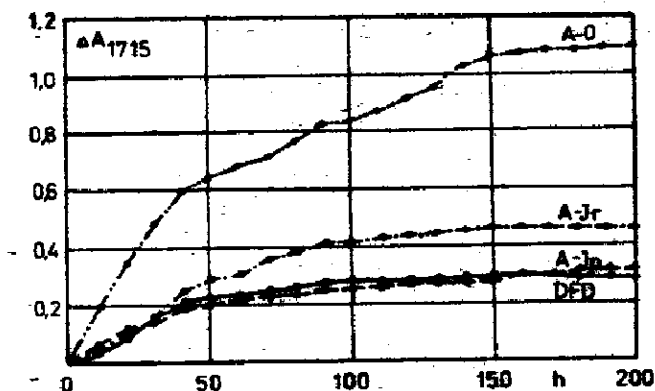


Fig.5. Kinetic curves of the $C = O$ carbonyl band of polyethylene foils, aged as a result of the exposure to partial discharges for 200 h. ($d = 0,5$ mm, $U = 3$ kV)

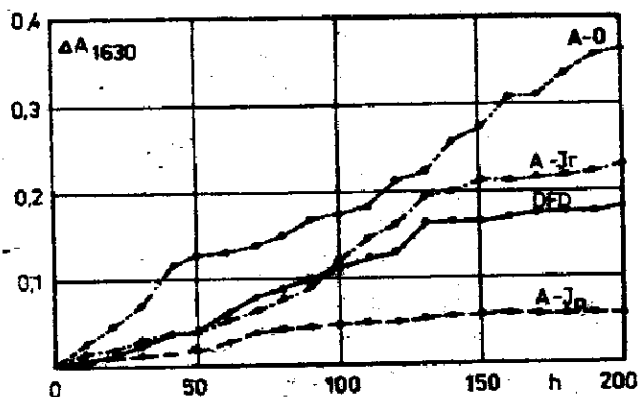


Fig.6. Kinetic curves of the band of the $C = C$ double bonds of polyethylene foils, aged as a result of the exposure to partial discharges for 200 h. ($d = 0,5$ mm, $U = 3$ kV)

It can be seen in Figure 5 that the curves of increase in concentration of carbonyl groups have a saturated character, i.e. they approach the boundary value. The shape of curves results from the quantity of absorption increments in particular measuring periods [7]. These increments diminish as ageing time elapses (Fig.7). Such a behaviour of investigated samples can be explained by the addition of oxygen to polymer, limited only to superficial layers and the groups, containing oxygen formed du-

ring the first period of oxidation in consequence of steric interaction, make the addition of further oxygen atoms difficult, in spite of the presence of a strongly oxidizing environment i.e. of ozone and nitric oxides.

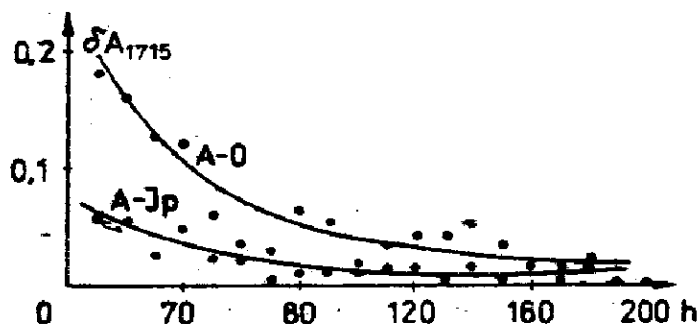


Fig 7. Absorption increments of the carbonyl band for the polyethylene foils in successive time intervals of ageing ($d = 0,5$ mm, $U = 3$ kV)

Therefore, when applying an asymmetrical air-gap, only the surface of the sample adjacent to the gap, in which discharges take place, should undergo destruction. This is confirmed by the increase in intensity of carbonyl band absorption during the action of discharges for 40 hours on one side of the investigated foil and then, after turning it over, on the other side for the same time (Fig.8a). The kinetic curve 1 shows a distinct jump of increase in absorption (ΔA_{1715}), corresponding to the ageing start of the other side of the foil. Curves, plotted for partial absorption increments (δA_{1715}), after each 10 hours of ageing of samples (Fig.8b), confirm still more distinctly the superficial oxidation of polyethylene.

The distribution of absorption increments shows that faster saturation of the superficial layer with the formed $C = O$ groups follows after turning the foil over. However, the total increase in absorption is much less than for the primary side (Fig.8a). This can be explained by partial oxidation of this surface of the foil, due to discharges of low intensity in the residual air-gap between the investigated foil and the electrode, even before turning the sample over. The existence of this unintended air-gap results from the inaccurate adhesion of the sample to

the electrode. In this case, sticking the sample by means of generally used insulating oils or lubricants is inadvisable because of changes caused in the IR spectra of investigated samples.

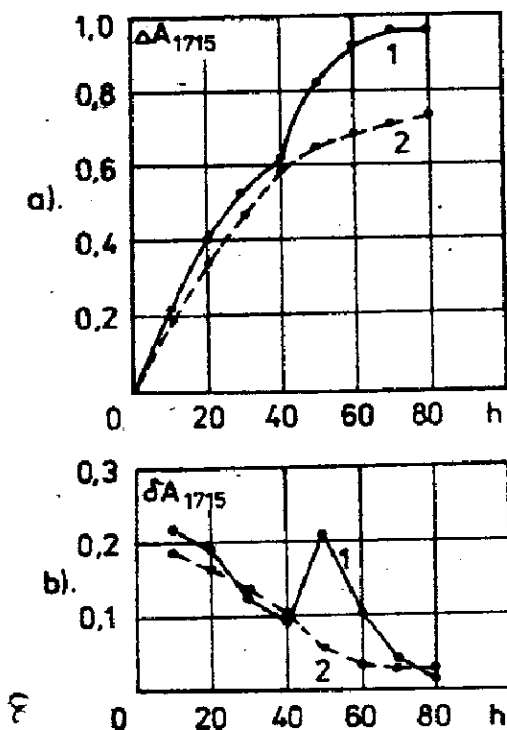


Fig.8. Changes in absorption of the carbonyl band of the A-O ($d = 0,5$ mm, $U = 3$ kV) polyethylene foil
 a - kinetic curves; b - absorption increments in time intervals of ageing; 1 - sample aged bilaterally, 2 - sample aged unilaterally

In order to investigate the greatness of the influence of discharges in the residual air-gap on polyethylene oxidation, an additional experiment was carried out by ageing four foil layers simultaneously, each of them 0,05 mm thick, so that the total thickness would be the same as previously. Figure 9 shows the kinetic curves of the C = O carbonyl band for particular layers. It is noticeable that mainly the first layer, which is attacked by discharges in the model gap, undergoes oxidation. The degree of oxidation of the remaining layers is practically equal, but several times lower than of the first layer. The oxidation of these layers

indicates that microdischarges take place not only between the foil and the adjacent electrode, but also between particular layers of the foil. It results from the above mentioned, that under the applied conditions of ageing, both surfaces of the investigated foil undergo oxidation, although not in an equal degree, because the intensity of discharges in both gaps, i.e. in the model and residual ones, is diversified, and probably also on account of the difficult access of oxygen to the microgaps.

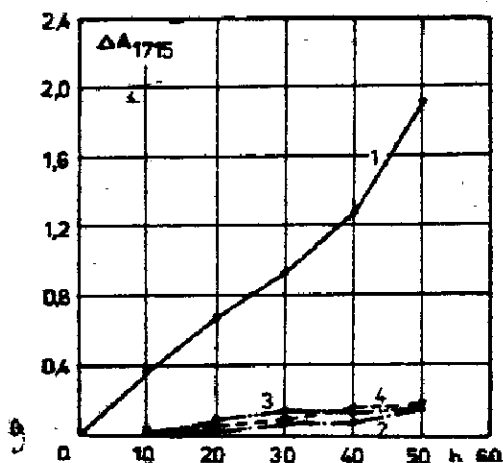


Fig.9. Kinetic curves of the carbonyl band, obtained during the exposure to discharges on a 4-layer system of the A-O foil
1 - layer adjacent to the air-gap, 2 and 3 - central layers, 4 - layer adjacent to the electrode.

Superficial oxidation is probably one of the reasons that even long-lasting influence of partial discharges does not cause such a considerable destruction of polyethylene, as ageing under other conditions, e.g. during exposure to ultraviolet radiation [13]. This is shown in Figure 10. It is visible that ultraviolet radiation causes the increase in or the formation of new absorption bands almost in all the range of the IR spectrum. Ester bonds $C=O$ (1177 cm^{-1}), vinyl $RCH=CH_2$ (910 cm^{-1} and 990 cm^{-1}) and trans-vinyl $RCH=CHR'$ (965 cm^{-1}) bonds are formed. The carbonyl band is considerably more intensive, with the marked second maximum at 1785 cm^{-1} , corresponding to the presence of the $C=O$ groups in the system of peracids $R-CO-(O)OH$, whereas the band of the $C=C$ bonds is sharp with maximum at 1640 cm^{-1} . This is a proof that the process of pro-

gressive destruction of polyethylene occurs according to different mechanisms in both cases. The above statement may also be confirmed by the different shape of kinetic curves of the C = O carbonyl band, shown in Figure 11.

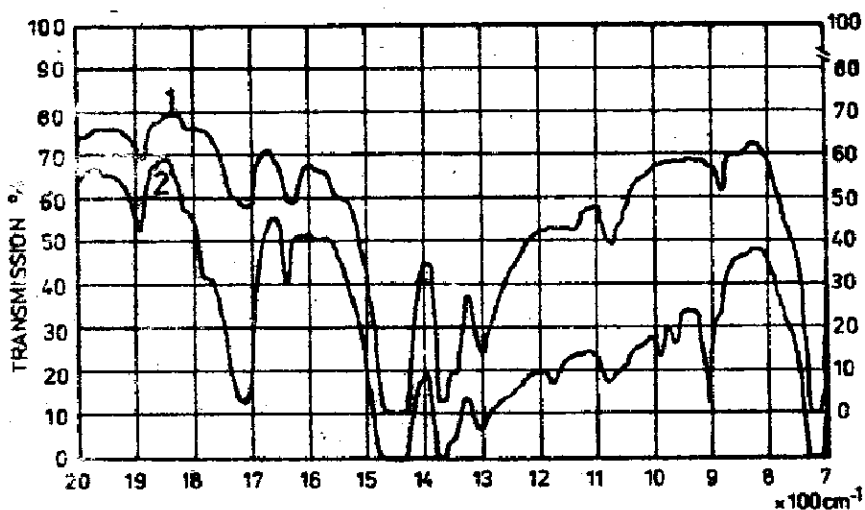


Fig. 10. Comparison of IR absorption spectra of the A-Ir foils, exposed to:

- 1 - partial discharges ($d = 0,5$ mm, $U = 3$ kV, time 1000 h.),
- 2 - ultraviolet radiation (time 100 h.)

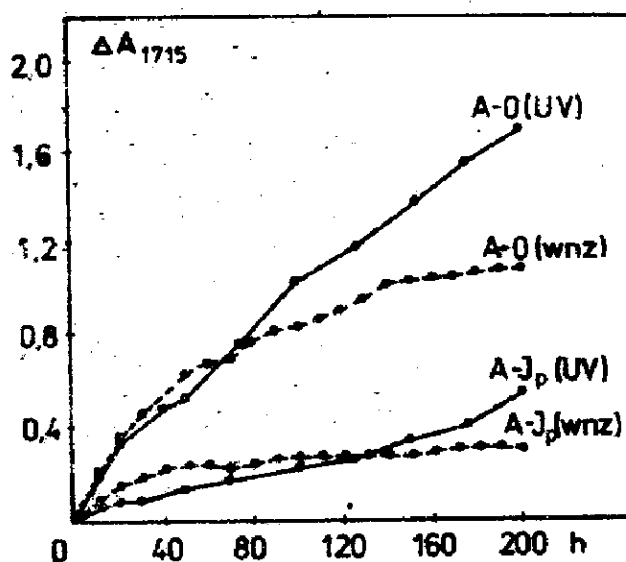


Fig. 11. Comparison of kinetic curves of the C = O band of foils A-0 and A-Ip, aged as a result of the exposure to partial discharges ($d = 0,5$ mm, $U = 3$ kV) and the uv radiation

The above presented investigations of polyethylene ageing, under the influence of partial discharges, were carried out on maintaining constant width of the air-gap and constant value of voltage. Thus, it was endeavoured to maintain identical conditions of discharges development, in order to make a comparative evaluation of different materials possible, e.g. of polyethylene containing different antioxidants.

It is known that the change in the value of voltage or in the width of a gap causes a change in the intensity of partial discharges. As a result the rate of the polymer ageing process should also undergo a change. In order to control this thesis, a successive cycle of investigations was carried out. Discharges in the gaps of different width, at different values of voltage, acting on identical samples of polyethylene during 6 hours, caused various degrees of their oxidation, as figure 12 shows. Therefore, the dependence of the rate of polymer ageing on the intensity of partial discharges was proved in an indirect way.

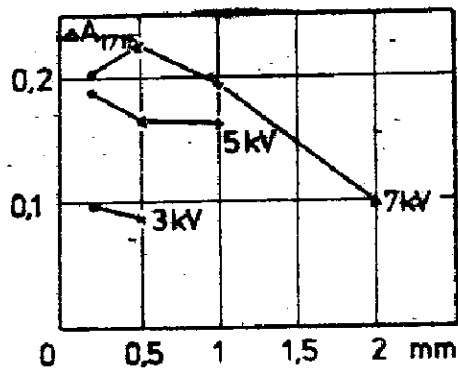


Fig.12. Changes in absorption of the carbonyl band of foil A-0, according to the voltage and width of the gap

So far, however, there are no consistent opinions, which of the physical quantities determining the discharge intensity is responsible for the rate of insulating material ageing. But there are grounded reasons that the current of partial discharges can be this quantity [7]. A preliminary attempt has been made, to show that such an assumption is right, by carrying out measurements of the current partial discharges in gaps of various width, at various voltage values, and the obtained results are presented in Figure 13. A clear similarity of Figure 12 and 13 diagrams can be ob-

served, although the measurements of the carbonyl band absorption were performed after 6 hours, and those of the discharge current after 10 minutes, from the moment of switching on the voltage.

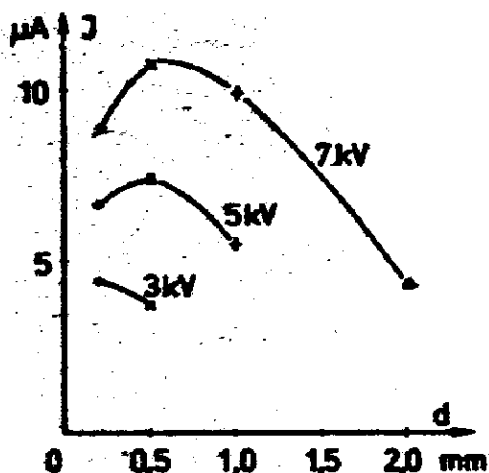


Fig.13. Results of partial discharge current measurements as a function of voltage and gap width

The dependence of the rate of the polyethylene ageing process on the discharge current is even better visible in Figure 14, which suggests the linear relationship.

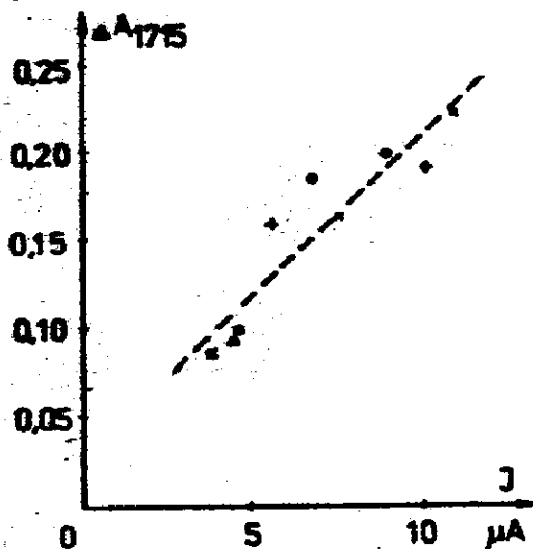


Fig.14. Dependence of the carbonyl band absorption on the current of partial discharges
 o - $d=0,2$ mm, x - $d=0,5$ mm, + - $d=1,0$ mm, Δ - $d=2,0$ mm

Nevertheless, these observations ought to be treated very cautiously, because the intensity of partial discharges changes during ageing of the sample [14, 15, 16]. This problem will be the subject of further investigations.

4. Summary and conclusions

It has been shown that by means of infrared investigations, the qualitative and half-quantitative estimation of chemical changes, occurring in polyethylene during the process of its ageing, due to the influence of partial discharges, can be conveniently performed.

It results from the carried out investigations that during ageing the C = O groups and the unsaturated C = C bonds are mainly formed. It is known that the presence of the C = O groups is the cause of the increase in the loss factor and dielectric permeability, whereas the unsaturated C = C systems by stiffening the bonds can cause fragility of polyethylene.

In the case of the half-quantitative estimation, the absorption band of the C = O carbonyl groups is particularly useful. The carbonyl groups are characterized by a high absorption coefficient [17] and their occurrence is often the first symptom of polyethylene ageing. It should be noticed that the infrared investigations allow an earlier detection of ageing changes in polyethylene than the measurements of dielectric properties.

Making use of absorption bands from the range of wave numbers 800 - 1300 cm^{-1} , for a more complete characteristic of the polyethylene ageing process, ought to be treated very cautiously. Changes in this range of spectrum are not great, there are no sharp absorption bands and it cannot be exactly established if they result from the increase in concentration of the absorption group or they are caused by skeleton vibrations of the chain.

The results of investigations suggest that the rate of the polyethylene ageing process depends on the current of partial discharges. However, this observation should be treated with great reserve. Its confirmation requires the performance of accurate investigations, taking into account variability of discharge intensity during ageing of polymer.

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