

Ryszard Dobroszewski, Jadwiga Olsztyńska, Marek Sudoł

FORMATION OF THE SUPERFICIAL BLOOM AND ITS PART IN THE PROCESS
OF OXIDATION OF POLYETHYLENE UNDER THE INFLUENCE OF PARTIAL
DISCHARGES

1. Introduction

During the investigations on the resistances of thermoplastic dielectrics to the action of partial discharges, it was found that on the surface of samples a mat bloom occurs. This bloom is a product of polymer destruction [1,2,3,4], and therefore it also occurs in practical insulating systems as a result of discharges in gas-filled microgaps or cavities. The bloom is composed of droplets and crystalline forms. Adhesion forces bind it to the surface of the sample.

However, the presence of the bloom changes the character of the sample surface; this can influence the dynamics of partial discharges in the gas gap and this in turn can influence the rate of polymer oxidation.

This paper shows results of microscopic investigations as well as the results of investigations on bloom chemical composition occurring on the surface of polyethylene due to the action of partial discharges in the model system with an open air-gap. The influence of bloom periodic removal from the surface of the sample on the current of partial discharges and on the rate of polymer oxidation is also shown.

2. Influence of the superficial bloom on the intensity of partial discharges and on oxidation of polyethylene

When estimating the resistance of polyethylene to prolonged action of partial discharges, differences were stated between the values of absorp-

Dr. Ryszard Dobroszewski, Eng. Jadwiga Olsztyńska - Technical University of Poznań, Electrical Power Institute.
Eng. Marek Sudoł - Pedagogical High School, Institute of Chemistry, Opole

tion increments of the C = O carbonyl band, determined for samples of the same foil lot and for the same aging times, as it is shown in Figure 1.

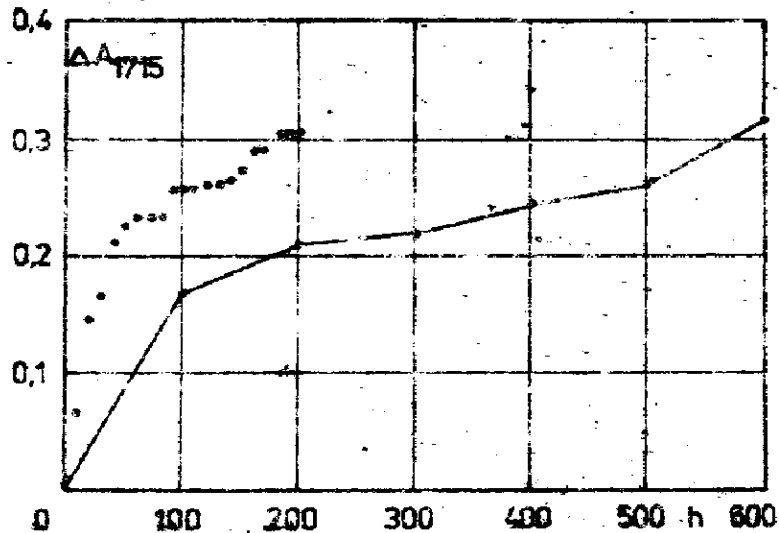


Fig. 1. Dependence of the oxidation rate of polyethylene, exposed to partial discharges, on the frequency of superficial bloom removal

As it can be seen, a more rapid increase in absorption characterizes samples aged only 200 hours, where the measurements, connected with the removal of the forming bloom, were performed every 10 hours, i.e. 20 times. For samples aged during a considerably longer time, when the measurements were performed every 100 hours, the same values of absorption as previously, has been reached not before 600 hours of partial discharge activity. It results from this that the frequency of bloom removal has an influence on the rate of oxidation of the investigated foils. This can be explained by the presence of a thicker film of superficial bloom which protects polymer from access of oxygen, or else that it causes a decrease in intensity of partial discharges.

In order to confirm the second thesis, 6-hour ageing of samples was carried out without interruptions and at an interval of five minutes every hour - not removing and removing the bloom; at the same time measurements of the total charge of discharges in one period of alternating voltage, were performed. The results of these measurements served as a calu-

late the values of the current of partial discharges. The investigations were carried out on the A-0 polyethylene foil (without the antioxidant), 0,2 mm thick, applying a 0,5 mm gap and the voltage of 3 kV, and each series of measurements was repeated three times. Figure 2 shows typical changes in the current of discharges during the ageing of samples.

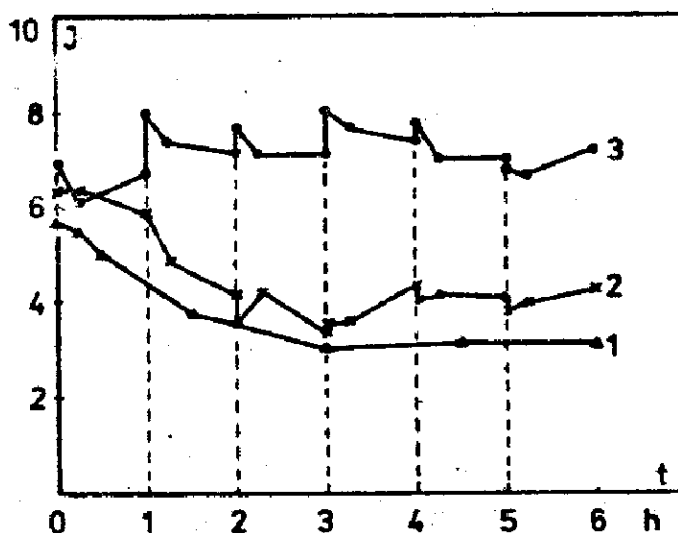


Fig.2. Typical changes in the discharge current during the ageing of polyethylene: 1-continuous stressing, 2-intermittent stressing, 3-intermittent stressing, the bloom layer removed

It is visible in the figure that as well at continuous stressing as when short interruptions are made without removing the bloom, the current of discharges is subjected to similar changes, viz. during the first 2 hours it decreases by a half, and then during 6 hours it maintains almost the same level. When interruptions are made and the bloom is removed, it can be assumed that the current of discharges is practically constant. A slight increase in the current is characteristic at the beginning of each hour cycle, when the bloom has only just begun to occur on the aged sample.

On the basis of the presented results, it can be inferred that the formation of the bloom on the surface of the aged polymer is the cause of the decrease in the current of discharges. The decrease in the current of

discharges in the air-gap may contribute in consequence to the reduction in the rate of polyethylene oxidation. It can be expected that the longer the period of ageing between subsequent IR measurements will be, the thicker the film of bloom will be and thereby slower oxidation of the aged sample. It also results from this that the maintenance of identical conditions of ageing is influenced not only by the constant width of the air-gap and constant value of the applied voltage, but also by the frequency of interruptions connected with the removal of the superficial bloom.

3. Microscopic observations

The surface of thermoplastic-polymer samples, exposed to partial discharges, undergoes erosion and is coated with bloom which is visible even with unaided eyes. On the basis of microscopic investigations, Reyn- ders stated the occurrence of the bloom in the form of droplets as well as in the crystalline forms on the surface of the air-filled cavity, con- tained between the foils of polyethylene [2,3].

The microscopic observations, carried out by the authors proved that droplets and crystals are constituents of the bloom deposited on the polyethylene exposed to partial discharges in an open air-gap [1,5]. It was noticed that the shape of crystals depended on the width of the gap and on the value of the applied voltage; figure 3 shows examples of diffe- rent geometrical forms of the bloom on the surface of foil A-0. At rela- tively low voltages (to about $2 U_1$), forms approximated to cuboids occur, but at higher voltages the forms of rhomboidal parallelepiped or more composite polyhedral forms.

Similar, more or less regular geometrical forms of the bloom were ob- served on the surface of polyethylene foils containing antioxidants (Fig. 4), and also on the surface of other thermoplastic polymers [1].

It was found that apart from crystalline forms, droplets always occur they are distinctly seen in Figures 5 and 3 (in other photographs the droplets are less visible on account of the small depth of focus of the microscope).

It should be pointed out that, in Reyn- ders investigation, droplets

occurred only in the case of discharges of great intensity and after opening the cavity, they disappeared during several minutes. The results of our investigations show that these droplets are much more durable and disappear only after at least some tens of hours whereas crystalline forms undergo partial disintegration, probably because of loss of water. Microscopic observations allowed also to establish that after the evaporation of the droplets, minute crystals remain in their place (Fig.6).

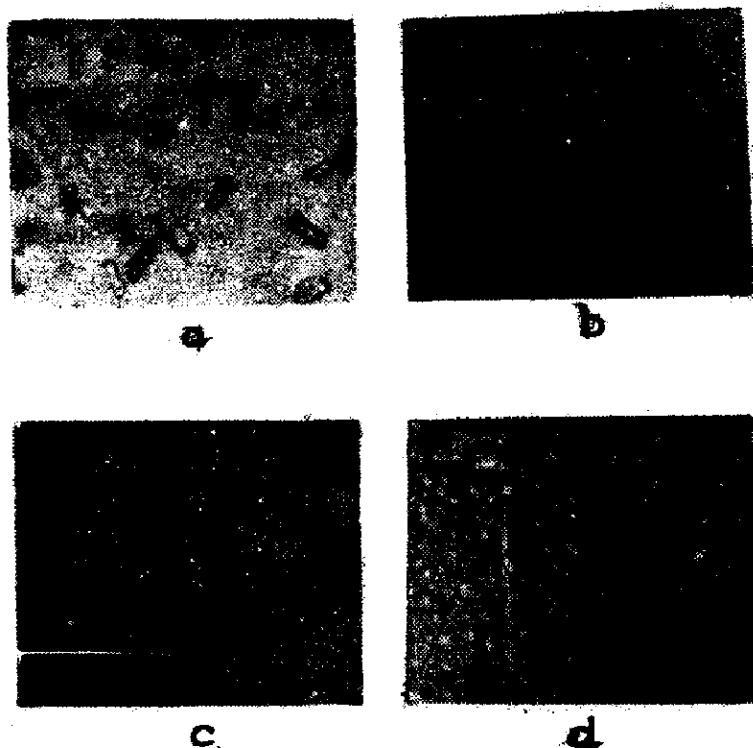


Fig.3. Micrographs of different forms of the bloom depositing on the surface of polyethylene A-0 exposed to partial discharges (magnification 320 x):

- a) air gap of 0,2 mm, voltage 3 kV
- b) air gap of 0,2 mm, voltage 5 kV,
- c) air gap of 0,2 mm, voltage 7 kV,
- d) air gap of 1 mm, voltage 7 kV.

After removing the bloom by washing the sample with alcohol, minute cracks were observed on its surface, as Figure 7a shows. Mayoux observed similar cracks in the case of electron beam influence on polyethylene [6]. The surface of polyethylene undergoes also cracking as a result of the UV radiation activity; in this case, however, the cracks are much larger (7b).

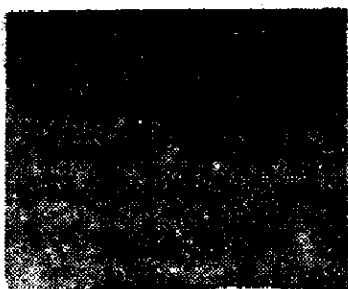


Fig.4. Micrograph of the bloom on the polyethylene samples containing antioxidant Irganox-66 (magnification 320x)

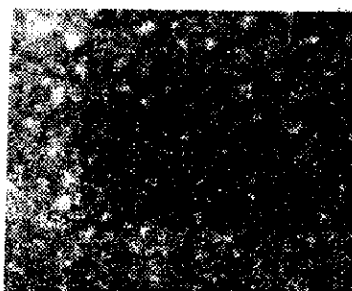


Fig.5. Micrograph of the bloom in the shape of droplets, forming a liquid film on the polyethylene sample (magnification 480 x)

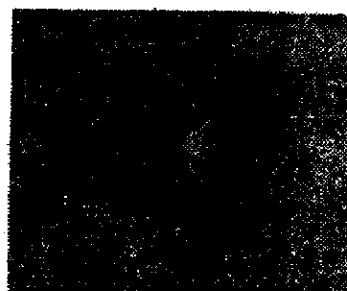
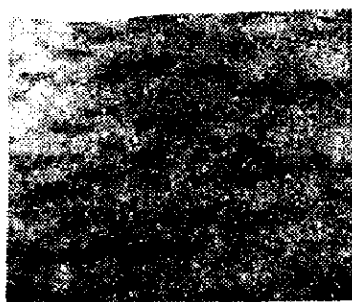
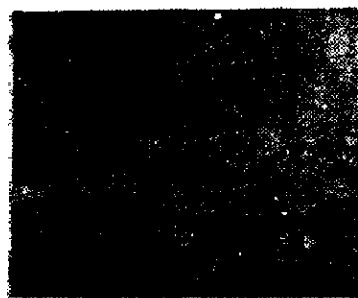


Fig.6. Micrograph of small crystals remaining after evaporation of droplets (magnification 480 x)



a



b

Fig.7. Micro-cracks of the polyethylene surface:
 a) exposed to partial discharges (magnification 480 x),
 b) exposed to u.v. radiation (magnification 40 x)

The erosion of the surface of the polyethylene foil exposed to partial discharges, can be well seen under the scanning microscope (after removing the bloom), particularly when using a device to obtain profilograms; this is presented in Figure 8.

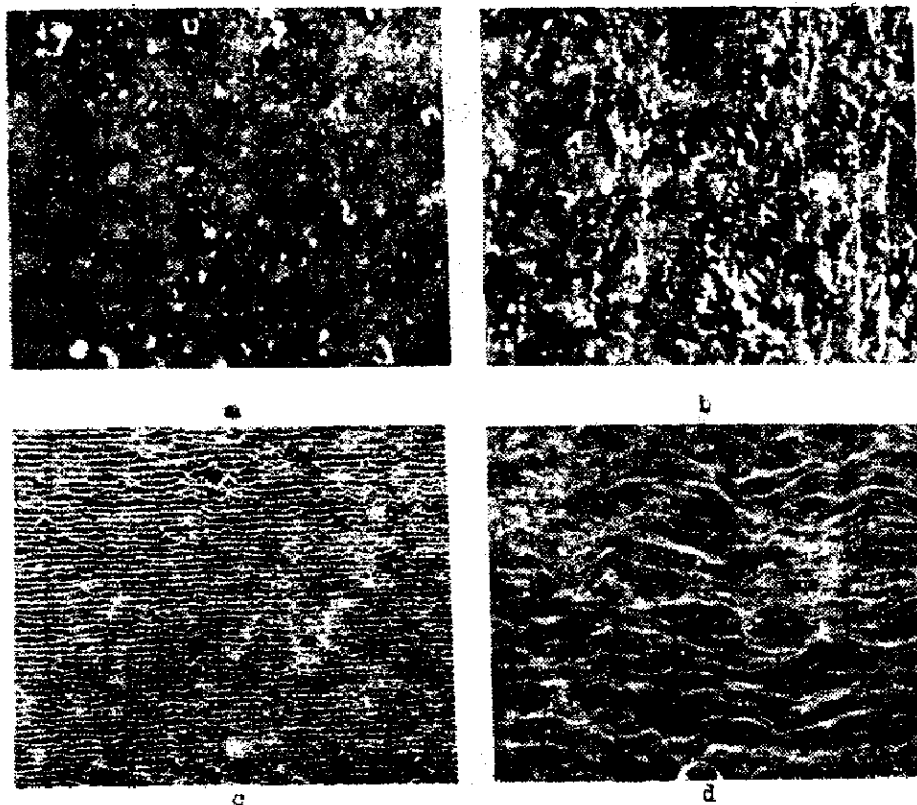


Fig.8. SEM micrographs (a), (b) and profilograms (c), (d) of the polyethylene surface (magnification 300 x):

(a), (c) - virgin sample,
 (b), (d) - eroded sample due to partial discharges

4. Determination of the chemical composition of the bloom

The bloom is deposited on the surface of polyethylene during the partial discharges activity. Therefore, it is one of the products of discharges in the system air-gap-polymer, as ozone or nitric oxides, or new bonds and functional groups formed in aged polymer.

The presence of the bloom on the aged foil of polyethylene during the infrared investigations has no influence on the enrichment of the spectrum; this is shown in figure 9. The IR spectra, recorded for a sample

with bloom, and ~~then after its removal~~, do not show any qualitative differences. This testifies that both the bloom and the investigated polyethylene show absorption in the same ranges of the spectrum. It can be a confirmation of the statement that the bloom is a product of destruction of aged polyethylene long-chains. That is why, the chemical composition of the bloom cannot be determined precisely on the basis of the presented spectra. It should be also pointed out that the quantity of the bloom is not great, in relation to the total mass of the investigated sample, and amounts merely e.g. to about 0,05% for the foil aged 100 hours. Therefore, identification of the bloom should be performed after separating it from the polymer.

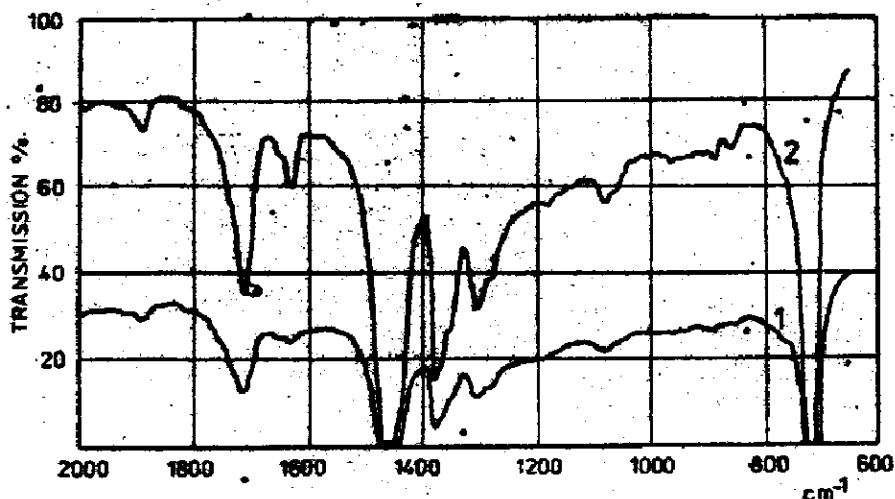


Fig.9. Influence of the superficial bloom on the IR spectrum of polyethylene A-0 exposed to partial discharges:
 1 - sample with the bloom layer,
 2 - sample after removing the bloom.

As it can be seen, the superficial bloom diffuses the beam of radiation, the stronger the longer the time of its ageing is. As ageing time elapses, the IR spectra become more and more flattened, and particular bands of absorption undergo blurring and even disappear this makes correct interpretation of results impossible. It appears therefrom that the bloom, which is a product of aged polyethylene destruction, does not bring anything cognitive into the infrared investigations but only hinders them. That is why it ought to be removed from the surface of the sample before performing the IR measurement.

It was found that bloom dissolves in water and alcohol, but does not in benzene. In alcoholic solution of the bloom, placed between two thin foils of polyethylene, the presence of carbonyl groups $C=O$ ($1700-1800\text{ cm}^{-1}$) was stated and also of hydroxyl groups OH ($1600-1700\text{ cm}^{-1}$ and $3200-3600\text{ cm}^{-1}$), originating in part from water (Fig.10).

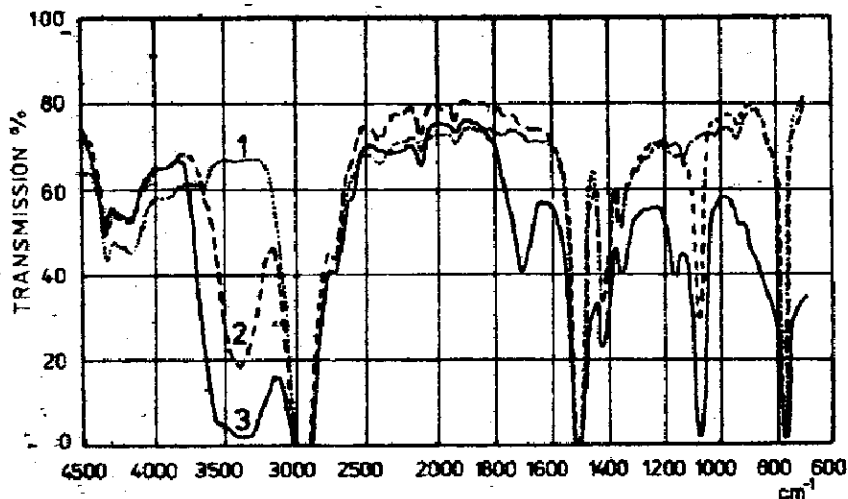


Fig.10. IR spectrum if the bloom dissolved in methyl alcohol:
 1 - polyethylene A-O,
 2 - polyethylene A-O with methanol,
 3 - polyethylene A-O with methanol and bloom.

The presence of water in bloom was stated as well, when IR spectra of samples, covered with drops making practically a uniform liquid film (Figs 5 and 11), were recorded. The exuded water may originate in part from the decomposition of polyethylene, and partly from the condensation of steam in the atmospheric air. It has been noticed that the formation of the liquid film on the surface of the foils is enhanced by a great air relative humidity and by temperature lower than the room one. When heating the aged sample during several hours at the temperature of 100°C , the bloom decays. It was stated that at this temperature bloom undergoes sublimation.

Therefore, in order to omit the influence of solvents, the bloom destined to further identifying investigations was isolated from aged foils by sublimation. The bloom was subjected to an elementary microanalysis to

define the chemical composition, and the obtained results are presented in table 1.

Table 1
Results of the blood elementary microanalysis (%)

C	H	N	O
19,2	4,7	0,0	75 - 76

Attention is drawn to the great content of oxygen in relation to the content of carbon. This indicates that blood is intensely oxidized. The presence of nitrogen in the blood was not found.

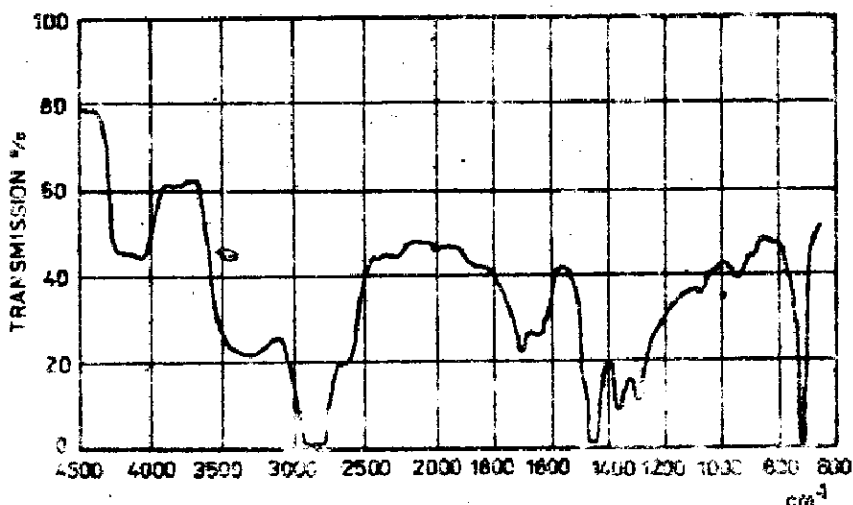


Fig. 11. IR spectrum of the polyethylene A-0 covered with a layer of drops, as in Fig. 5.

In order to determine functional groups and to establish the structure of compounds constituting the bloom, it was investigated by the following methods: of nuclear magnetic resonance (NMR), of mass spectrometry, as well as of the infrared and ultraviolet spectroscopies. The presence of methylene $-\text{CH}_2-$, carboxyl $-\text{COOH}$ as well as of hydroxyl $-\text{OH}$ group was stated.

It was established that the compounds containing 3, 5 and 7 atoms of carbon in a molecule enter into the composition of the bloom. The presence of malonic acid $\text{CH}_2(\text{COOH})_2$, tartaronic acid $(\text{OH})\text{CH}(\text{COOH})_2$ and also some

pounds of definite molecular mass, but not yet determined exactly structure:

- general formula $\text{HOOC-C}_3\text{H}_2\text{O}_8\text{-CH}_2\text{OH}$, MW 242,
- general formula $\text{HOOC-C}_4\text{H}_6\text{O}_7\text{-CH}_2\text{OH}$, MW 256,
- general formula $\text{C}_6\text{H}_{14}\text{O}_{11}$, MW 262,

was stated. The last compound contains also the $\text{-CH}_2\text{OH}$ group, but it does not contain the -COOH and $\text{C}=\text{O}$ groups. It should be pointed out that all these compounds are hydrated very greatly.

5. Summary and discussion

The presented results of investigations show that the presence of the bloom on the surface of aged samples changes the conditions occurring in the air-gap and causes changes in the mechanism of partial discharges [7, 8, 9, 10]. This leads to the decrease in the current of discharges, and consequently to the reduction in the rate of polyethylene oxidation.

It can be seen in the microscopic observations that bloom does not cover the surface of polyethylene with a uniform film. Single drops and crystals are spaced thus that a part of the surface remains vacant. Solid products of polyethylene destruction constitute the crystalline phase of the bloom, whereas water, and virtually the solution of nitric acid constitute the liquid phase (in case of discharges in the air-gap). The same compounds which occur in the crystalline phase are also dissolved in the drops and at least in some of them.

The investigations have shown that malonic and tartaric acids enter into the composition of the crystalline phase as well as compounds of not yet established exactly structure, containing 5 or 6 carbon atoms in a molecule. However, according to the authors of some papers, oxalic and succinic acids [1] compose crystals. All the above mentioned acids are dicarboxylic acids, differing in content of carbon atoms. Various lengths of carbon chains of identical compounds can be perhaps explained by the application of different conditions of ageing and by the differences in the spacial structure of the investigated polyethylenes.

It ought to be pointed out that the generating of the bloom under the influence of partial discharges is the result of destruction and superfi-

cial erosion of polyethylene, testified by microscopic observations, and particularly by profilograms of the surface. The destruction of polyethylene takes place under the influence of complex energetic activity of electrons and gas ions as well as of UV radiation [6,7]. The mechanism of destruction is composite and not well known.

On the basis of presented results, it is difficult to infer the mechanism of polyethylene decomposition under the influence of partial discharges. It cannot be defined if destruction of polyethylene follows e.g. under the influence of electronic bombardment or the chemical action, or if disruption of the normal chain takes place or if they are detached side-branchings. It is known that the energy of electrons, under the conditions of discharges in the gas gap, can reach the value exceeding 10 eV [7], higher than the energy of particular interatomic bonds of macromolecule (of the order of several eV) and is sufficient to disrupt them. Nitric acid, or a mixture of O_3 and O_2 , cause also degradation and decomposition of macromolecules into dicarboxylic, hydro carboxylic and even multi-carboxylic acids. The statement of the presence of dicarboxylic acids in the bloom may, therefore, confirm that under the influence of partial discharges in the air-gap, where ozone, oxygen as well as nitric oxides and water are present, chemical destruction of polyethylene may occur. Other authors put forward similar conclusions [12]. It ought to be supposed that identical compounds are products of secondary reactions and can differ very much in length from primarily detached fragments of the chain.

In conclusion it should be stated that test results showed the influence of deposited superficial bloom on the partial discharge current and on the oxidation rate of polyethylene. Although limited range of investigations does not allow to determine the mechanism of bloom formation, nevertheless the obtained results can contribute to better knowledge of the destruction process of polyethylene exposed to partial discharges.

R e f e r e n c e s

1. Dobroszewski R., Olsztyńska J., Sudoł M.: X Symp. Electr. Discharges in Gases, Politechnika Warszawska, 1985.

2. Reynders J.P.: IEE Conf. Diel. Mater. Meas. and Appl., Cambridge 1975.
3. Reynders J.P.: IEE Conf. Diel. Mater. Meas. and Appl., Birmingham, 1979.
4. Wolter K.D., Johnson J.F., Tanaka J.: IEEE Trans. Electr. Insul., vol EI-13, No 4, 1978.
5. Dobroszewski R., Grzybowski S., Olsztyńska J., Kuffel E.: Conf. Electr. Insul. and Dielectr. Phenom., Nat. Acad. of Sci., Philadelphia, 1984.
6. Mayoux C.: IEEE Trans. Electr. Insul., vol. EI-11, No 4, 1976.
7. Mason J.H.: IEEE Trans. Electr. Insul., vol. EI-13, No 4, 1978.
8. Dobroszewski R., Grzybowski S., Olsztyńska J.: IX Symp. on Electrical Discharges in Gases, Politechnika Warszawska, Kazimierz Dolny 1985.
9. Dobroszewski R., Gałczyński K., Siódka K.: IX Symp. "Problemy wyładowań niezupełnych w układach elektroizolacyjnych" PTETIS-AGH, Zakopane 1983.
10. Goliński J.: Prace Instytutu Elektrotechniki, Zeszyt 111, Warszawa 1979.
11. Bojarski J., Lindeman J.: Polietylen. WNT. Warszawa 1963.
12. Toriyama Y., Okamoto H., Kazanashi M., Horii K.: IEEE Trans. Electr. Insul. vol. EI-2, No 2, 1967.