

Jan Bursa, Jerzy Winkler

CHANGES OF THE PROPERTIES OF EPOXIDES UNDER
THE INFLUENCE OF OZONE

I. Changes of the dielectric properties

1. Introduction.

Fast development of industry requires the application of more and more developed network of electrical transmission lines, higher powers and voltages. The involved material requirements increase cannot be met by the traditional insulation materials. Hence, research has been made for last dozens of years to find novel and better plastics as electrical insulation materials, which could satisfy the needs of modern power engineering. Plastics in the form of elastomers for the insulation of cables, as well as moulding compounds, varnishes, and cast epoxides are applied in the insulating-constructive elements to a higher and higher degree. Especially the last group of the ones mentioned above, namely the group of cast epoxides, has wider and wider application.

Among many positive features which distinguish cast epoxides from materials used in HV insulating technique their main drawback is that their surface properties change in the period of exploitation. Due to the fact that insulation, especially HV overhead insulation, is not separated from outside environment and is affected by its conditions, it is important to obtain satisfactory resistance of the epoxides to various physical and chemical factors as: ionizing radiation, electric field, humidity, the influence of oxygen from the air and all the other polluting substances present in the air [1].

Eng. Jan Bursa - Technical University of Szczecin, Institute Electrical Engineering.

Prof. Dr. Jerzy Winkler - Electrotechnical Research Institute, Wrocław.

One of the factors which could influence destructively the properties of epoxide insulation is ozone - a very strong oxidizing agent which reacts with various organic and inorganic compounds [2], while gas which is met during a storm and the concentration of which is about $3 \cdot 10^{-6} \text{ g/dm}^3$ is refreshing, its concentration within the order of 10^{-5} g/dm^3 may cause death of man [3].

Ozone forms from oxygen in chemical reactions which occur under the influence of ultraviolet and cosmic radiation in the high spheres of the atmosphere (its max. concentration there is at the height of 80 km over the Earth). Ozone comes down to the Earth's surface due to the air currents [4]. Ozone forms also during electric discharges in the air oxygen atmosphere, as well as during partial discharges on the HV insulators when they work.

It can be concluded that ozone is a factor permanently present in the atmosphere of the air around the HV insulating-constructional elements. So, there is much probability that its activity can influence destructively the HV epoxy insulation.

In the article, there have been presented the results of investigations concerning the influence of persistently acting ozone on the surface properties of selected epoxides.

2. Methodology of the investigations

There has been applied a self-constructed ozonator in which two Po-100 ionizing tubes of the DO-10-6 type have been the generator. As the material under investigation there were flat test samples used, the material compositions of which are given in the table 1.

They were investigated in three various ageing cycles where the ozone concentrations were as follows: C_{O_3} I = $6 \cdot 10^{-6} \text{ g/dm}^3$, C_{O_3} II = $162 \cdot 10^{-6} \text{ g/dm}^3$, C_{O_3} III = $47 \cdot 10^{-6} \text{ g/dm}^3$. In the III cycle the relative humidity of the air in the chamber amounted 95%. In the I and II cycles there was low characteristic for given conditions humidity. There was the constant temperature in all the cycles. The ozone concentration was measured by means of iodometric method. The investigations were withdrawn continuously, at the times: P I = 600 h, P II = 1200 h, P III = 6900 h, respectively.

Table 1

The specification of material compositions of
test samples (p/w)

Symbols	Resin	Hardener	Accelerator	Filler
1	Ep 2 100	F 30	E ₂ 0,5	-
2	Ep 2 100	F 30	E ₂ 0,5	SiO ₂ 200
3	Ep 2 100	F 30	E ₂ 0,3	Al ₂ O ₃ ·3H ₂ O 200
4	CY 185 100	HHP 70	DX 065 6	-
5	CY 185 100	HHP 70	DX 065 6	SiO ₂ 320
6	CY 185 100	HHP 70	DX 065 6	Al ₂ O ₃ ·3H ₂ O 320

explanation: Ep 2 - dian epoxy resin Epidian 2, CY 185 - cycloaliphatic epoxy resin Araldit CY 185, F - phthalic anhydride, HHP - hexahydrophthalic anhydride (HT 907).

The test samples were taken out from the chamber at determined time intervals, and after the relaxation in the environmental conditions (circa 2 h). The following measurements were made in them: a) measurement of tracking resistance (according to ASTM D 2302 - 64 T), b) measurement of the electric surface resistance (ac. Polish standard) electric PN/E-04441), c) measurement of the surface resistivity (ac. PN/E-04405). In the process of ageing random photos were taken of fragments of test samples magnified under the optic microscope (the magnification x 1000).

3. Results

The measurements of tracking resistance are presented on the fig.1. To discuss them one may state as follows:

- the values of the Wt indicator were lowest for the plastics without fillers and highest for the plastics with an aluminum filler,

- the values of the Wt indicator for the cycloaliphatic composites (4), (5) and (6) were higher than their dian counterparts,

- in all I and II cycles the runs of the curves $Wt = f(T)$ are similar. All the curves were slightly lowering and after circa 250 h of ageing they gained flat, stable runs.

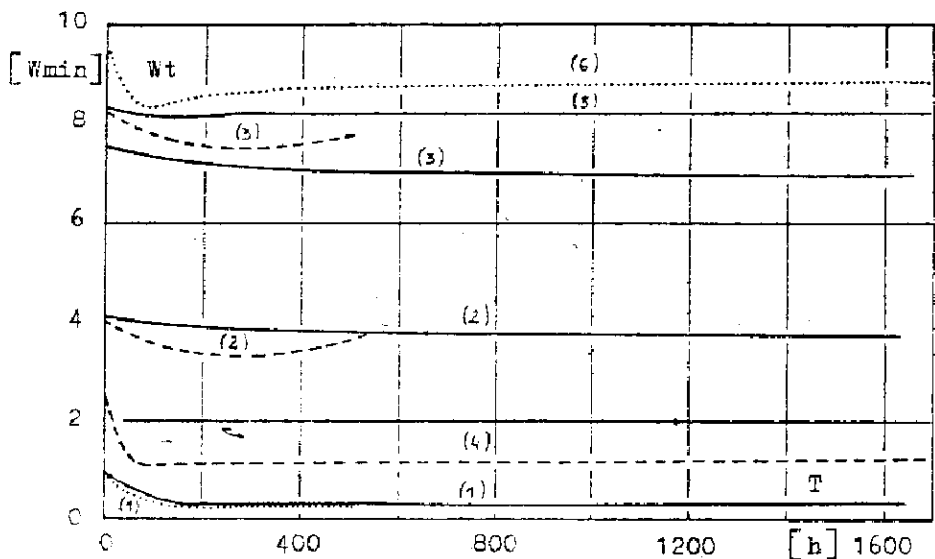


Fig.1. Changes of tracking resistance as the function of time of ageing by ozone for dian composites (1), (2), (3) and cycloaliphatic composites (4), (5) and (6)

The measurements of the resistance to the electric arc are given in the table 2. It can be observed that the lowest initial resistance to the electric arc has been defined for plastics without fillers (1) and (4), among which Araldit CY 185 (4) has the higher resistance. Among the composites with fillers, SiO_2 produces slightly higher resistance. After very long processes of ageing (circa 7000 h) slight drop of resistance for all the plastics can be observed and it is more visible for the dian ones. In case of plastics (3), (4) and (6) the result of testing was not the conductive path but erosion. After the time of ageing amounting to circa 7000 h a conductive path in case of (3) was observed instead of erosive losses characteristic for shorter times of ageing.

The measurements of surface resistivity are presented in the fig.2 and 3. On the given background it can be stated that:

- dian and cycloaliphatic composites have nearly identical surface resistivity in the order of $10^{16} \Omega$, when not aged,
- in the process of ageing by ozone in the first cycle of investigations the highest stability in the group of dian composites is characteristic of the composite (2) and the lowest one is characteristic of the composite (1),

Table 2

Change of resistance to the electric arc of the composites under investigation in the time of ageing by ozone

Ageing time	Composites					
	1	2	3	4	5	6
h	a					
0	46/35	194/192	187/182	134/131	200/200	201/195
cycle II						
144	45/37	196/191	189/185	-	-	-
336	45/32	192/185	190/182	-	-	-
480	44/37	195/190	188/180	-	-	-
1700	46/37	196/191	189/182	-	-	-
cycle III						
672	-	202/200	205/200	131/128	203/202	199/188
1392	25/20	205/200	193/190	-	-	-
3411	-	185/182	210/210	131/127	199/196	-
3819	36/25	-	-	-	-	198/195
cycle I (+500 h) + cycle II (+800 h) + cycle III						
6915	-	-	184/183	-	183/185	189/185
7323	29/12	186/183	-	-	-	-

explanation : mean value/smallest value

- in the second cycle of investigations the surface resistivity lowered by about three orders for the dian composites and by more than two orders for the cycloaliphatic composites. After about 400 - 500 h the minimal values could be observed. Within the interval of 500 to 900 h of ageing for the dian composites and 500 to 700 h for the cycloaliphatic ones there rose resistivity, which then established for further times of ageing at the level two orders lower than the initial one for the dian composites and from one order (5) to two orders (4) lower

for the cycloaliphatic composites. The minimum value is practically the same in all cases and amounts to circa $10^{15} \Omega$.

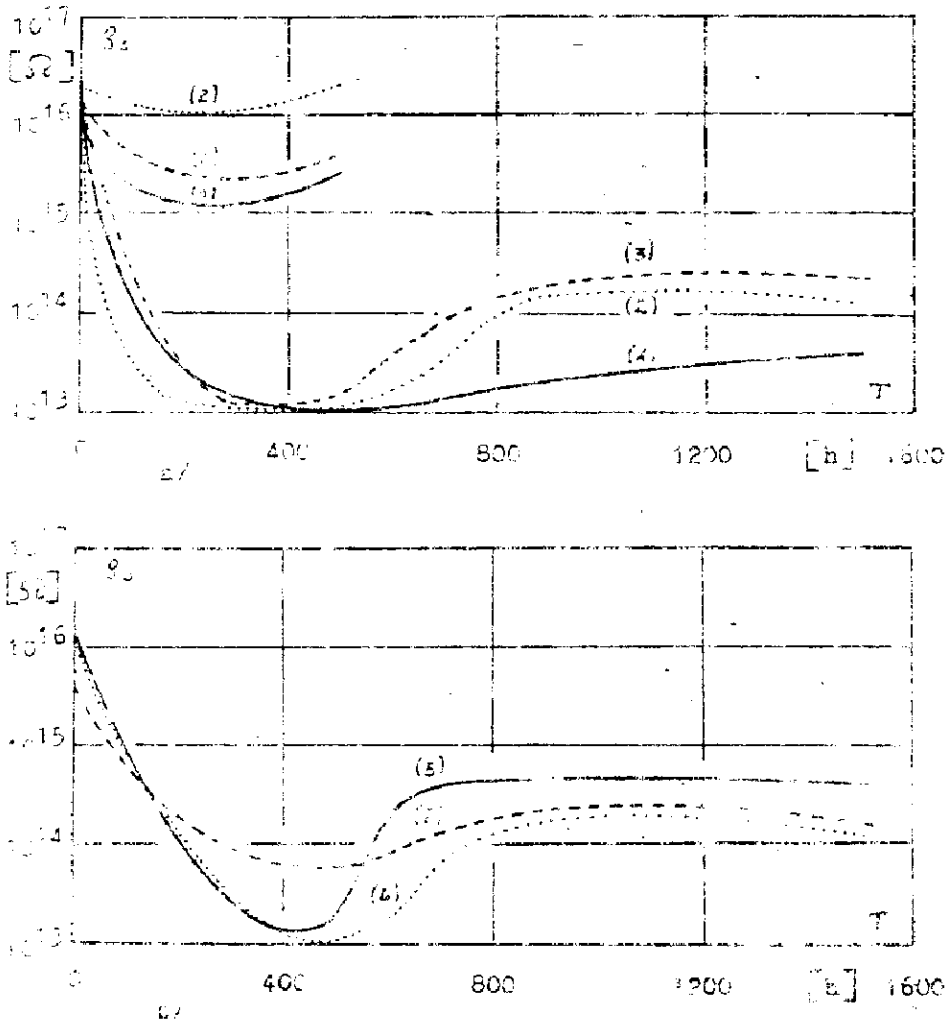


Fig. 8. Changes of the surface resistivity as the function of the ageing by ozone for dian composites in the II cycle (a) and for cycloaliphatic composites in the II cycle (b).

the runs of the surface resistivity curves in the ageing cycle as the time function for the third cycle of investigations are shown in Fig. 9. The interval of $t = 1500$ h and they resemble the results achieved in the first cycle of the investigations. The minimal values, however, are reached in this case - after the period of about 1000 h. For the dian composites within the range of 1000 - 2000 h, there is rise of R_s to $10^{15} Ω$.

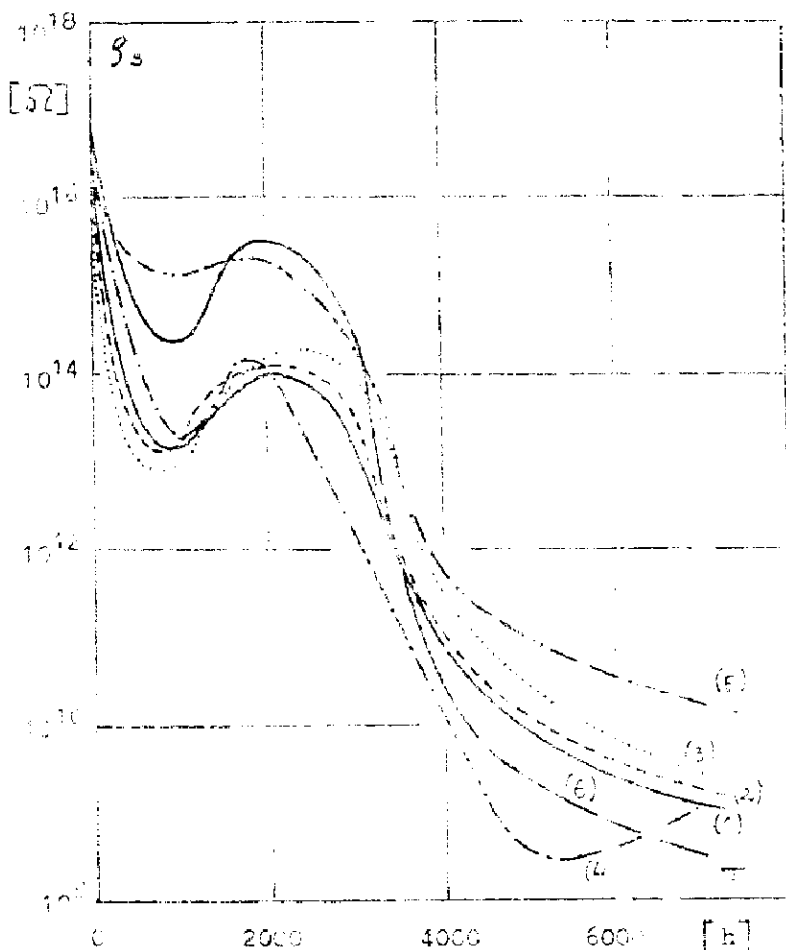


Fig.3. Changes of the surface resistivity as the function of time of ageing by ozone for diam composites (1), (2), (3) and cycloaliphatic composites (4), (5), (6) at the III cycle

In the range of 2000 - 3000 h there can be noticed stability (plain minima) and in the range of 3000 - 7000 h there is a slower than at the beginning lowering the curves to the value of circa $10^9 \Omega$. The minimal values for (1), (2) and (3) are practically similar and amount to about $10^9 \Omega$. In case of the composites (4), (5) and (6) the minimal values ρ_s are from $0,1 \cdot 10^9$ for (4) to $1 \cdot 10^{10} \Omega$ for (5). In case of the glassion the rise of resistivity is being observed within the range of 1000 - 1500 h, the stability of the value ρ_s in the range of 1500 - 2200 h and further initially faster (to about 4500 h), then slower lowering of the

resistivity till the end, that is till the value of about $10^9 \Omega$ for (4) and (6) and about $10^{10} \Omega$ for (5).

Fig. 4 shows the photos of the surfaces of plastics which were not aged and the photos of those which were aged by ozone, the concentration of which was $87 \cdot 10^{-6} \text{ g/dm}^3$ within the time period of 4620 hours.

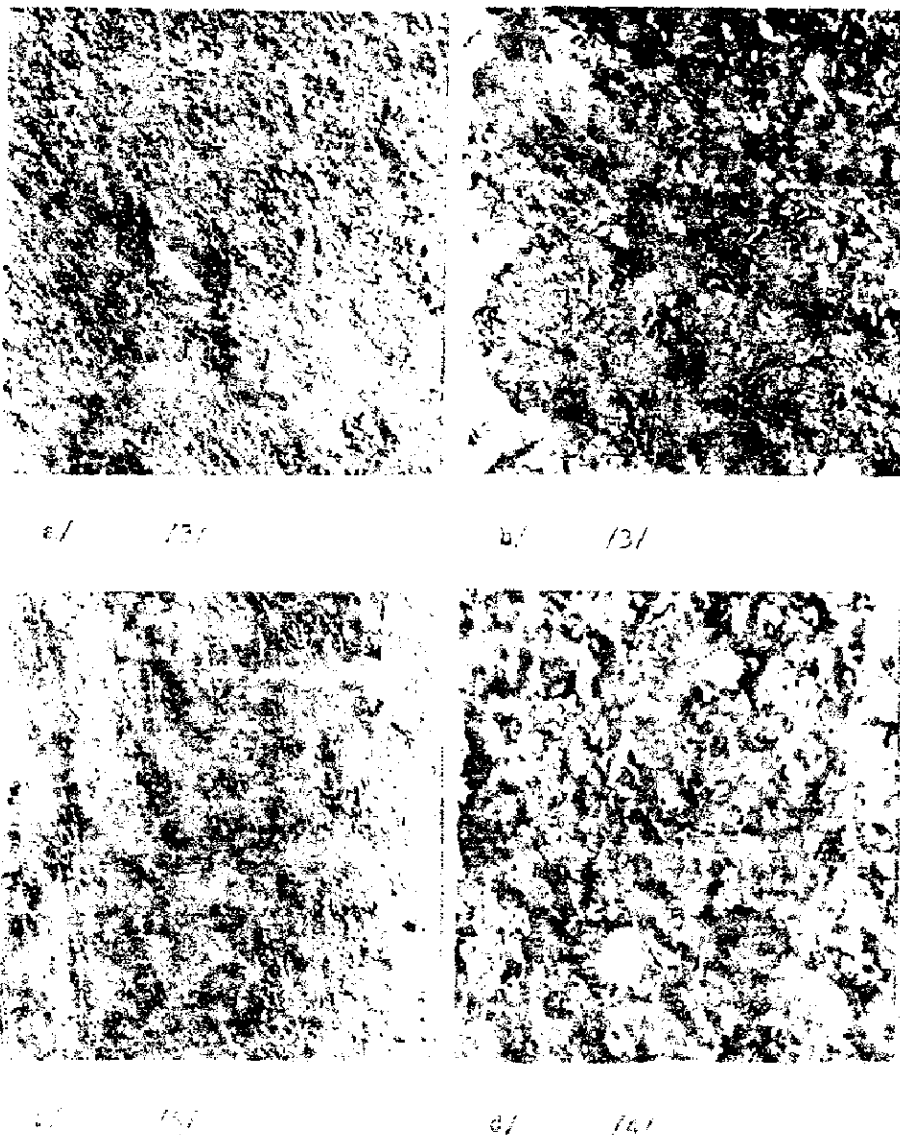


Fig. 4. Microscopic photos of the surfaces of the samples of PVC (4) and (6) which have not been aged. (b) and (d) aged by ozone for 4620 h.

4. Results discussion

a) Positive is the influence of fillers which extend the resistance of the materials for electrical insulation against exposing to ozone.

b) If the drop of ρ_s caused by the presence of the better conducting oxidation products on the plates is comprehensible, it is more difficult to explain its rise after it goes over its minimum value. It is probably caused by the impeding activity of the protection layer which forms on the surface of the plastic and hinders the diffusion of ozone into the non-oxidized plastic and volatile products from the non-oxidized plastic.

c) After the time of ageing by ozone within the order of 7000 h, resistivity drops to values by eight orders lower than the initial one. Plastics lose in fact their positive insulating properties.

d) The investigations of tracking resistance are not very applicable because they are not sensitive enough to trace out changes which take place in the thin surface layer. Besides, as the ammonium chloride is being applied, its solution may change the protection layer forming on the surface.

e) The investigations to the electric arc may also be little applicable in case of tracing changes which occur in the very thin surface layer of the aged plastics.

f) The quantity of ozone concentration has a visible influence on the surface resistivity of investigated composites.

5. Conclusions

1. On the basis of the resistivity measurements and observations of the microscope photos a conclusion may be proposed that ozone and quantity of its concentration have a visible influence onto the epoxides.

2. Treatment with ozone caused the loss of insulating properties of plastics, which is reflected by the drop of surface resistivity even by eight orders of magnitude.

3. Tracking resistance and resistance to the electric arc dropped only slightly in the process of ageing. The methods of measuring the trac-

king resistance and the resistance to the electric arc should be admitted as not very applicable to identify the changes taking place on the aged surfaces of epoxides.

4. After the time of ageing overage 7000 h (III cycle) the hydrated aluminum oxide in the oxidized dian composite (3) lost its extinguishing qualities.

R e f e r e n c e s

1. Subocz L.: Trwałość izolatorów epoksydowych. PN IBI PS nr 91, Szczecin 1978.
2. Razumowski S.D., Zajkow G.E.: Ozon i jego reakcje s organicznieskimi sojedineniami, Nauka 1974.
3. Report prepared in General Chemistry Institute of Technical University of Łódź.
4. Kychtera M., Bartkova B.: Tropikalizacja urządzeń elektrycznych. WNT 1966.