

## THE ELECTRET EFFECT IN A MIXTURE OF POLYMETHACRYLATE AND BARIUM TITANATE

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It was found that a mixture of polymethyl methacrylate and ceramic  $\text{BaTiO}_3$  displays a permanent electret effect. By comparing the dielectric and electret parameters of mixtures of various compositions some conclusions are arrived at regarding the mechanism of the formation of the two types of charges. Analysis of these results confirms the previously propounded point of view, according to which in the mechanism of homocharge formation account should be taken of the ion component of the heterocharge which is incompletely recombined during electret discharging. By making an appropriate choice of the mixture composition it is possible induce an electret effect of pre-assumed time changes of the surface charge density.

From the voluminous literature treating the electret effect it is evident that the electret state is a result of a number of processes, the share of each of which depends on the material and conditions of sample polarization. According to the hypothesis of Gross [1] and Gemant [2] a heterocharge may appear due to the effect of a "freezing" of aligned dipoles, displacement of ions in an electric field and an accumulation of charges at macroscopic inhomogeneities of the dielectric. On the other hand, Gross assumes the homocharge to be due to local break-downs occurring in the layer of air between the dielectric and electrodes. In the papers [3, 4, 5] two of the authors put forth a different hypothesis regarding the formation of the homocharge. It states that the homocharge is primarily due to a displacement of ions, which in the first phase constituted a heterocharge, under the effect of an external field. It has been limited the part of the electric break-down as the only factor giving rise to the homocharge.

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Under suitably chosen polarization conditions it is possible to obtain a heterocharge slowly decreasing with time in polymethyl methacrylate [6, 7]. One view [8] is that this effect is caused by orientation polarization of the dipolar radicals  $O = COCH_3$  by the electric field. The mechanism by which the electret effect forms in the polycrystalline ceramic substance  $BaTiO_3$  is different. It is suggested in the papers [9, 10] that electronic processes are its source. By investigating mixtures of ceramic  $BaTiO_3$  and polymethyl methacrylate of various percentage compositions it is possible to establish the role played by orientation polarization and space charge polarization in the electret process.

### 1. Sample preparation and experimental technique

The  $BaTiO_3$  ceramics were obtained by the known method of triple sintering of  $BaCO_3$  and  $TiO_2$  in stoichiometric ratio. The final process was conducted at  $1350^\circ C$  for three hours, resulting in a ceramics of density  $5.57 \text{ g/cm}^3$ . This was pulverized and sifted through an appropriate sieve. The powder was mixed in various volume ratios with methyl methacrylate in which the polymerization process had been previously initiated. After the polymerization had been concluded at the higher temperature, samples were formed from the material obtained thus into disks 3 cm in diameter and 0.25 cm thick. Samples with 0 to 60 per cent volume content of  $BaTiO_3$  were successfully obtained without any considerable gradient of concentration. Further enrichment of the mixture with barium titanate led to a sharp rise in porosity. This is a known property of mixtures of solid dielectrics [11].

For investigating the dielectric properties plane electrodes were used, 2 cm in diameter and deposited on the sample surfaces from a colloidal solutions of silver. The capacitance measurements were made with a capacitance bridge at a frequency of 800 cps. In the temperature measurements use was made of a thermostat enabling temperature stabilization up to  $0.2^\circ C$ . Electrical conductivity was measured by a galvanometer with a current sensitivity of  $1 \times 10^{-10} \text{ amp/mm/m}$ , and by the method of discharging the capacitor. Since the surface charge was measured by the "moving electrode" technique, the samples were polarized with the use of nickel electrodes placed against accurately grounded surfaces of the samples.

### 2. Results

#### a) Dielectric properties of mixture

The dependence of the values of permittivity ( $\epsilon$ ) and conductivity ( $\gamma$ ) on the percentage content of  $BaTiO_3$  in the mixture is shown in Figs 1 and 2. The permittivity in the logarithmic scale is a linear function of mixture composition (curve *A* in Fig. 1). Its value varies from 3.6 for pure polymethacrylate to 34.9 for the mixture containing 55 per cent  $BaTiO_3$ . For the pure ceramics it amounted to 1280 at room temperature. With an increase in the percentage of  $BaTiO_3$  the experimental curve (*A*) deviates more from curve *B*, representing the Lichtenecker formula [12] for the permittivity of mixtures which, as is known, is found to hold for low admixture contents only.

The electrical conductivity of the mixtures measured at room temperature varies between  $2.7 \times 10^{-15} \text{ ohm}^{-1}\text{cm}^{-1}$  for pure polymethacrylate and  $1.6 \times 10^{-13} \text{ ohm}^{-1}\text{cm}^{-1}$  for a mixture containing 57.5 per cent of  $\text{BaTiO}_3$ , the measuring field being 15 kV/cm. For the pure  $\text{BaTiO}_3$  ceramics the conductivity is  $4 \times 10^{-12} \text{ ohm}^{-1}\text{cm}^{-1}$ . Hence, the electrical con-

TABLE I

Percentage composition	Activation energy ( $W$ ) [eV]
Polymethacrylate	1.75
Polymethacrylate+15% $\text{BaTiO}_3$	1.58
Polymethacrylate+26% $\text{BaTiO}_3$	1.45
Polymethacrylate+32% $\text{BaTiO}_3$	1.30
Polymethacrylate+45% $\text{BaTiO}_3$	1.03
Barium titanate	0.87

ductivity of polymethyl methacrylate at room temperature is three orders lower than that of barium titanate, but its rise with temperature is more impetuous. For both the pure components and their mixtures  $\ln \gamma$  is a linear function of  $1/T$  (Fig. 3), which is evidence of the activation character of the conduction. The activation energies obtained from the relevant graphs vary in dependence on the mixture composition, as is shown in Tabel I. As is seen,

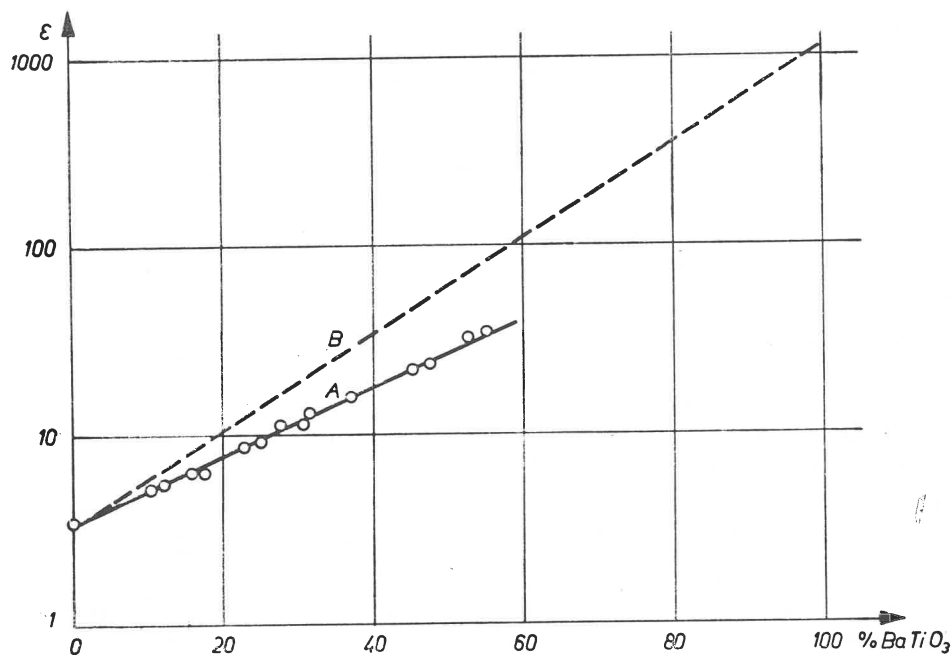


Fig. 1. Permittivity versus percentage of  $\text{BaTiO}_3$  in polymethyl methacrylate. *A* — experimental curve, *B* — curve plotted according to Lichtenecker's formula

polymethyl methacrylate has much lower values of permittivity and conductivity than barium titanate, whereas its activation energy is larger. By mixing these materials in different proportions it is possible within certain limits to obtain materials of different values of  $\epsilon$ ,  $\gamma$  and  $W$ , and to examine the effect of these quantities on the electret properties.

#### b) Electret properties of mixture

In order to investigate the electret parameters of the mixture in dependence on its percentage composition, the conditions of polarization, storage and measurements were kept identical for all the samples. Every sample was polarized in a field of strength  $E_p =$

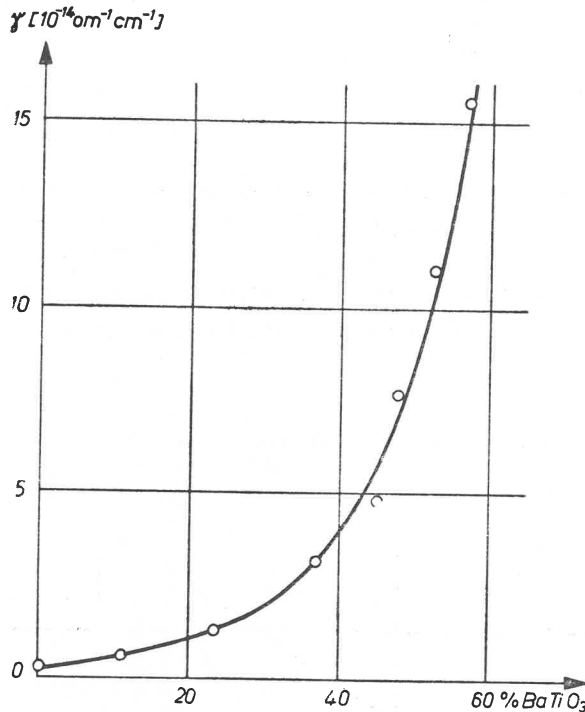


Fig. 2. Electrical conductivity versus percentage of BaTiO<sub>3</sub> in polymethyl methacrylate

$= 8 \text{ kV/cm}$  at a temperature  $T_p = 155^\circ\text{C}$  and for a time  $t_p = (1.5+0.5)$  hours. The time of 1.5 hr concerns the isothermal process ( $T_p = 155^\circ\text{C}$ ), and the time 0.5 hr to the cooling process. Immediately after polarization the samples were short-circuited for ten minutes in order to be rid of unstable surface effects. For as had been found in an earlier work this procedure substantially affects the course of variations in the surface charge density with time [3]. By using the technique already mentioned, a number of electrets of the same diameter (3 cm) and thickness (0.25 cm) were prepared from the materials of the different compositions. They were stored in the free state (*i.e.* unscreened and not short-circuited) under identical conditions of humidity, pressure and temperature.

Time characteristics of the surface charge density,  $\sigma = f(t)$ , for the electrets in mention are depicted in Fig. 4. The curves *A*, *B*, *C*, *D* and *E* relate to the samples with 0, 10, 28.5, 47.6 and 56.4 per cent of BaTiO<sub>3</sub> in polymethyl methacrylate, respectively. In all of the examined electrets there is observed immediately after polarization a heterocharge which after a time  $\tau_1$  (time of polarity reversal) converts into a homocharge. After a time  $\tau_2$  lapses

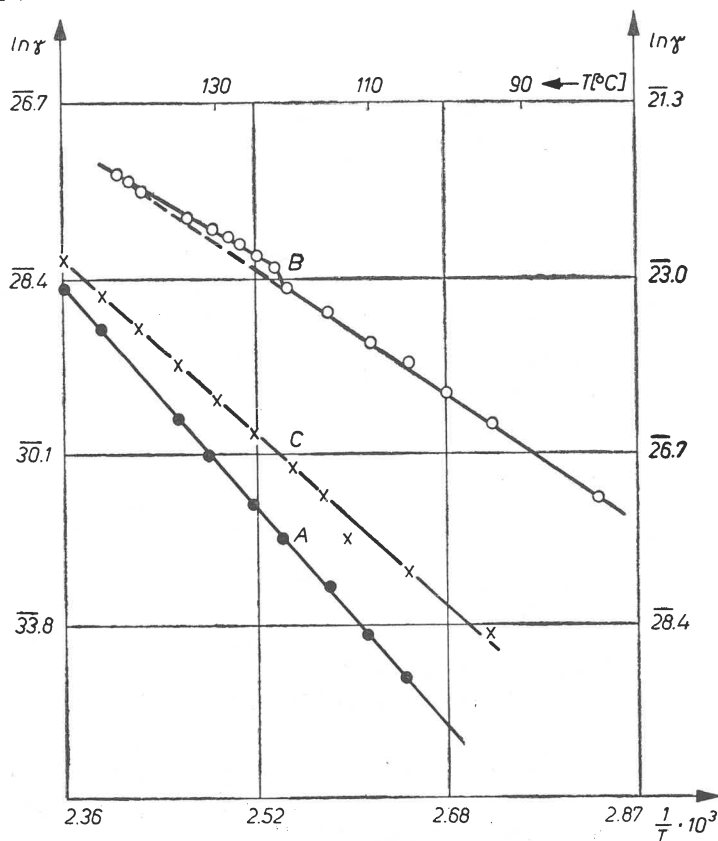


Fig. 3. Temperature dependence of electrical conductivity. Curve *A* — pure polymethyl methacrylate (left axis). Curve *B* — BaTiO<sub>3</sub> ceramics (right axis). Curve *C* — mixture containing 32% BaTiO<sub>3</sub> (left axis)

the homocharge reaches maximum value ( $\sigma_{\max}^{\text{homo}}$ ) and then slowly decreases. The dependence of the initial value of the heterocharge surface density ( $\sigma_0^{\text{het}}$ ) and the maximum value of the homocharge on the percentage of BaTiO<sub>3</sub> is shown in Fig. 5. The character of their shape is like that of the conductivity *versus* mixture composition curves. The dependence of the polarity reversal time on mixture composition (Fig. 6, curve *A*) deserves special attention. For pure polymethyl methacrylate  $\tau_1$  is of the order of 10<sup>3</sup> hrs, whereas for the material containing 56.4 per cent BaTiO<sub>3</sub> it is shorter by three orders of magnitude. The resistivity of the samples behaves similarly (Fig. 6, curve *B*).

The electret parameters do not depend on the material used alone. Among other things, the strength of the polarizing field pronouncedly affects their values. To look into this

matter more closely, the sample containing 47.5 per cent  $\text{BaTiO}_3$  was polarized in fields of strengths from 0.4 kV/cm to 30 kV/cm. The  $\sigma_0(E_p)$  curves for the anode (A) and cathode (K) sides are shown in Fig. 7. In the 0.4 to 2 kV/cm range there is, with a rise in polarizing field, an increase in the initial value of heterocharge from  $1.5 \times 10^{-9}$  coul/cm<sup>2</sup> to  $6 \times 10^{-9}$  coul/cm<sup>2</sup>.

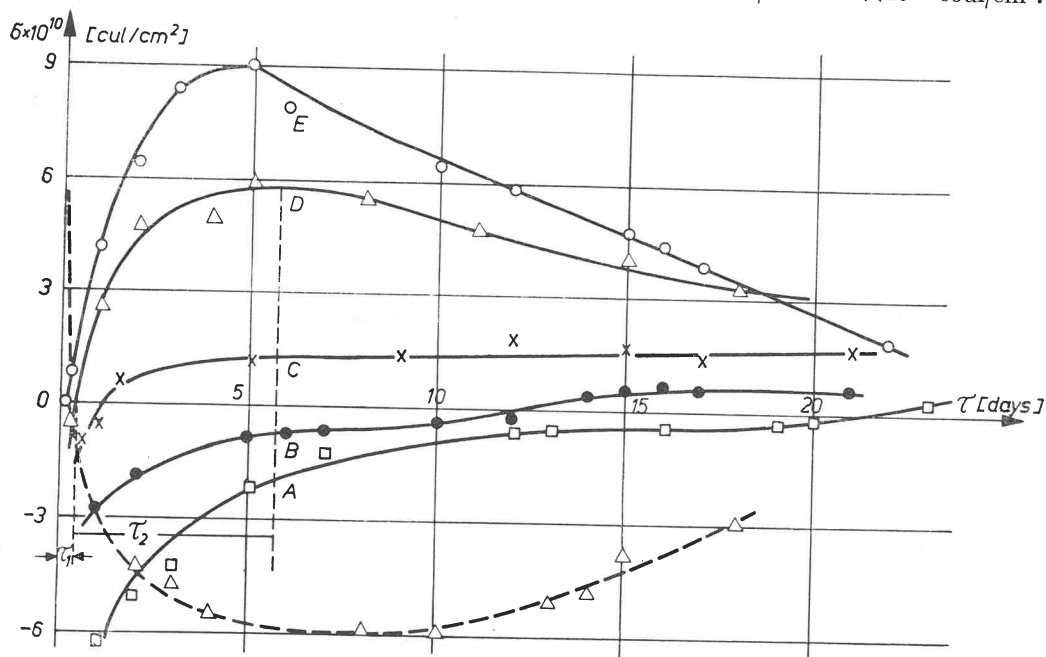


Fig. 4. Time dependence of surface charge density for samples of different mixture compositions. The continuous line is the curve for the anode sides of the electret and the broken line the cathode side of the electret of the mixture containing 47.5%  $\text{BaTiO}_3$ .

With a rise in field strength from 3 to 16 kV/cm for the anode side and from 3 to 18 kV/cm for the cathode side, the heterocharge drops to nil. A further rise in field brings about an increase in homocharge to a value of  $4 \times 10^{-9}$  coul/cm<sup>2</sup> for the anode side and to  $3 \times 10^{-9}$  coul/cm<sup>2</sup> for the cathode side.

### 3. Discussion of results

The relatively high electrical conductivity of the polycrystalline barium titanate ceramics is linked with its complex structure. Such ceramics contains two phases — crystalline and gaseous. The former consists of microscopic single crystals of dimensions of the order of tens of microns. The gaseous phase is due to the porosity of the samples, which cannot be avoided even by the most careful preparation of the ceramics. Besides the crystalline and gaseous phases there is yet a certain percentage of amorphous phase [13]. Owing to these facts, in considering the electrical conductivity of this type of material account should be taken of the processes conditioning the penetration conduction and unstable processes associated with the accumulation of charge at the boundary of phase separation. The latter

lead to the occurrence of space polarization. The penetration polarization does not vary with time and consists in the motion of charges through the bulk of the dielectric and its exchange between the dielectric and electrodes [14]. The true conduction, also known as polarization conduction [15], should be distinguished clearly from penetration conduction. The additional

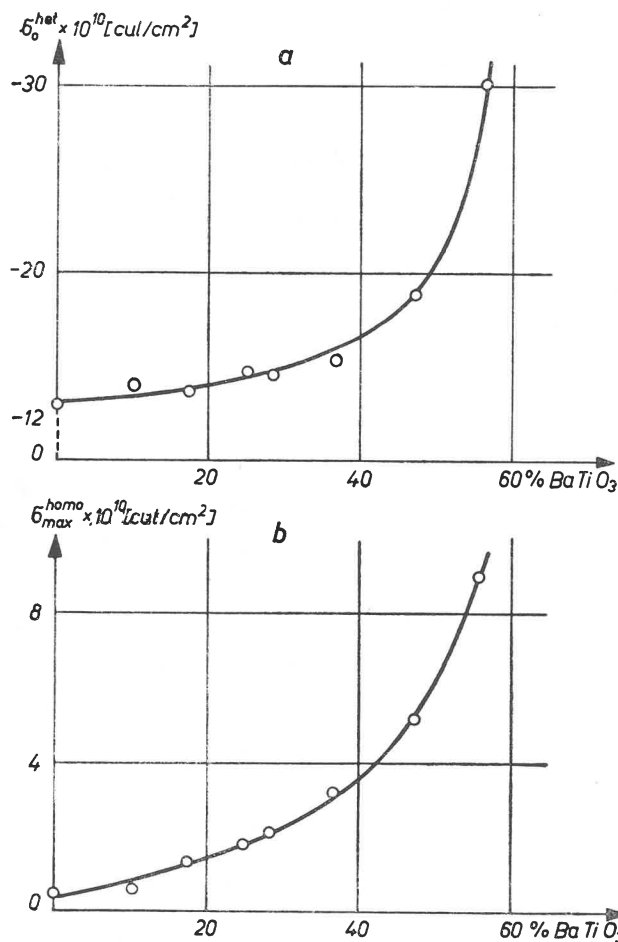


Fig. 5. The dependence of a) the initial values of heterocharge surface density and b) the maximum values of homocharge density on the percentage of BaTiO<sub>3</sub> in polymethyl methacrylate, for the anode sides of the electret

currents due to the mentioned absorption processes become added to the current of penetration conduction, causing the current appearing after applying the voltage to have a larger value than that of the penetration conduction observed after the state of polarization of the dielectric becomes settled. The time variations of the polarizing current ( $I_p$ ) are proof that there is an absorption current. This is illustrated by Table II, which concerns the sample containing 45 per cent BaTiO<sub>3</sub> polarized at 120°C by a field of strength 8 kV/cm. As is seen, within half an hour the polarizing current decreases by over three times.

TABLE II

$t_p$ [min]	1	2	3	4	5	6	7	8	9	10	11	15	20	25	30
$I_p$ [ $10^{-9}$ A]	6.3	5.4	4.8	4.35	4.1	3.75	3.45	3.4	3.3	3.3	2.8	2.8	2.35	2.1	1.9

The conductivity of polymethacrylate is lower than that of  $\text{BaTiO}_3$  by three orders of magnitude. This is undoubtedly linked with the different number of free charge carriers in the two materials and with the possibility, as regards  $\text{BaTiO}_3$ , of an exchange of charge with the electrodes because of inhomogeneities of the field in the gap between the electrodes and the dielectric. As may have been expected, the conductivity of the mixture displays values intermediate between those of the components.

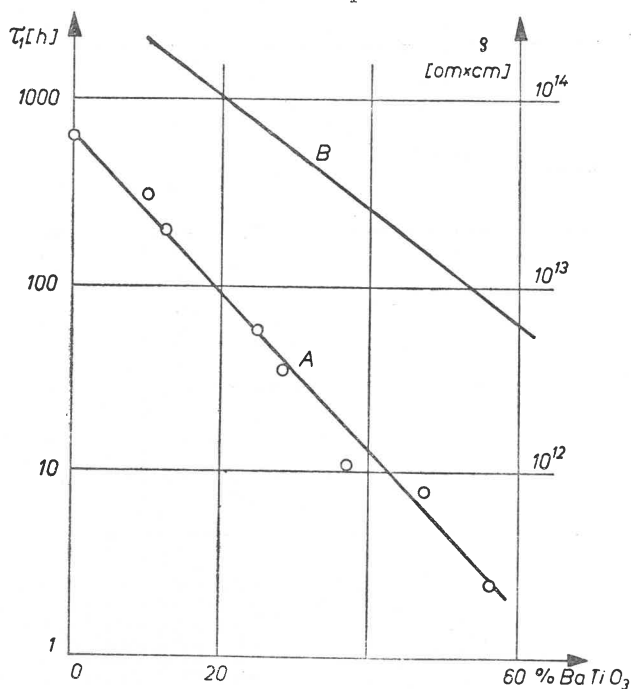


Fig. 6. Dependence of polarity reversal time (curve *A*) and resistivity (curve *B*) on content of  $\text{BaTiO}_3$  in the mixture

The number of free charges has been found to affect the electret properties. As far as in the case of  $\text{BaTiO}_3$ , independently of the polarization conditions, a homocharge is always observed, in the case of polymethyl methacrylate there appears as a rule a heterocharge at the beginning. In the case of a mixture of these two materials there also initially appears a heterocharge, and the time of the hetero- to homocharge conversion depends on the composition of the mixture. It follows from a comparison of the curves *A* and *B* in Fig. 6 that with an increase in the number of free charges in the material the time required for polarity reversal decreases. On the other hand, by comparing the dependences of the initial



value of heterocharge and the maximum values of homocharge on the percentage composition of the mixture (Fig. 5) with the same dependence of the electrical conductivity (Fig. 2) it is seen that an increase in free charge carriers brings about a rise in the initial value of heterocharge and also in the maximum value of homocharge. It may thus be concluded that in all of these cases there is a reversal of polarity, but in  $\text{BaTiO}_3$  the time of this reversal is probably so short that it is unobservable with the measurement techniques now in use.

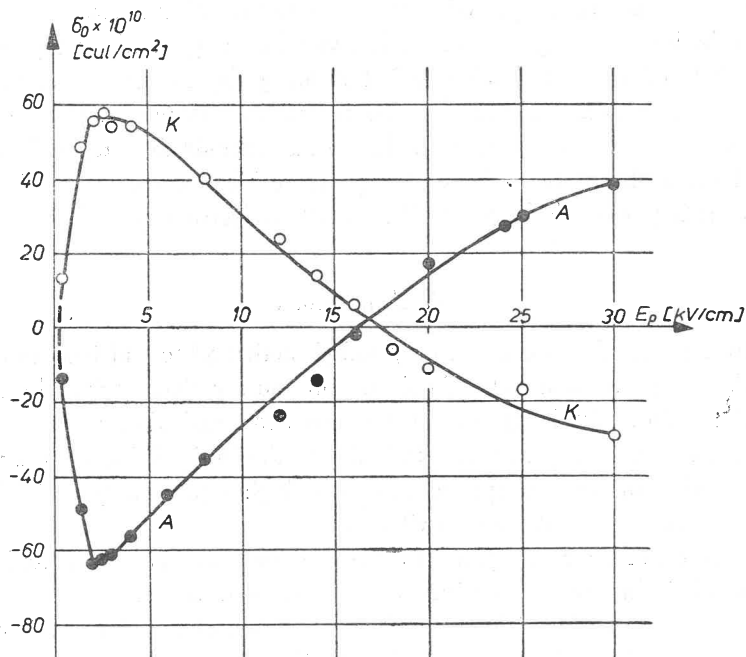


Fig. 7. Initial values of surface charge density versus polarizing field for the electret made from the mixture containing 47.5%  $\text{BaTiO}_3$ . Curve A — anode side of electret, curve B — cathode side

The described dependences may be utilized for determining the mechanism of the formation of the two kinds of charges. If polar molecules alone participated in the electret effect, then with an increase in polarizing field strength one should expect the occurrence of some sort of "saturated state" of the initial value of heterocharge. As is seen in Fig. 7, an increase in field strength does not induce such a state, but only shortens the time of polarity reversal and after the polarity is changed causes an increase in the value of homocharge. This fact confirms the hypothesis propounded in Ref. [5] that in the formation of the homocharge there is participation of that part of the heterocharge which, when being displaced by the internal field of the electret, does not become recombined.

It may be concluded from the character of the curve  $\sigma_0 = f(E_p)$  that the process of space charge polarization begins to dominate the orientation processes in the examined material (45%  $\text{BaTiO}_3$ ) when the field strength reaches a value of approximately 2 kV/cm. If it is assumed that the mean distance between adjacent grains is of the order of their dimensions ( $\bar{x} = 50$  microns), then the transition of an electron between the boundary separating the phases requires the work  $W = E_p \cdot e$  of approximately one electron-volt.

The fact that the value of the activation energy for this mixture (Table I) is equal to one electron-volt rather points to the important role of electrons in the migration of charge.

Polymethyl methacrylate has polar groups [8] which under the effect of a polarizing field become aligned and form the observed slowly time-variable heterocharge. This fact can be explained by the insignificant number of free charges in this material which, according to Ref. [5], are primarily responsible for the formation of the homocharge. That only a homocharge is observed in BaTiO<sub>3</sub> may also be made to conform with the results of the cited paper and explained by both the large number of free volume charges and the high value of electrical conductivity of this material. These factors bring about a reversal of polarity within a time shorter than that which elapses from the instant the polarization process is concluded and the instant measurements are started. One cannot exclude that in the formation of the homocharge there is also participation of charges (especially electrons) transferred from the electrodes or arising from discharges at the dielectric-electrode gaps [1].

#### 4. Conclusions

1) Electrets made of a mixture of polymethyl methacrylate and barium titanate ceramics demonstrate a permanent state of polarization and are characterized by the following properties: *a*) the time of polarity reversal becomes shortened when there is more BaTiO<sub>3</sub> in the mixture; the resistivity behaves similarly, *b*) the initial value of heterocharge and the maximum value of homocharge increase with higher percentages of BaTiO<sub>3</sub> in the mixture, as does the electrical conductivity.

2) In the process of heterocharge formation the dipolar component and ionic component participate, which is in agreement with the hypothesis of Gross.

3) In the homocharge formation there is participation of the dielectric's volume charges, being in the first phase of the electret's lifetime the ionic component of the heterocharge (this is in conformity with the results of Ref. [5]), and charges transferred from the polarizing electrodes [1].

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