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Corrosion phenomena on evaporated metal layers under electric stress

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The metallization of insulating materials has gained great importance during the last few years. Vaporization in a high vacuum is increasingly employed. Today, glass, ceramic materials, and also organic insulating materials can be coated with a metal layer. While the coating of inorganic insulating materials is comparatively simple, the coating of organic materials causes difficulties. However, organic insulating materials with a metal layer offer a great variety of interesting new technical applications, e.g. in foil-type capacitors which require very thin foils. Nevertheless, during operation several problems can arise.

1. Introduction

In the field of electrical engineering it is often useful or even necessary to coat insulating materials with a metal layer. In connection with plastic foils, for example, the dimensions of electrical capacitors have been considerably reduced. This is of particular advantage when the high breakdown strength of very thin films is utilized. In use these capacitors can be stressed with high d.c. voltage without problems. On the other hand, for a.c. voltage stress above 300 V, difficulties occur due to corrosion of the metal layers.

2. Metallized film capacitors and their operating characteristics

Corrosion phenomena are known in roll-type capacitors which are built up of two rolled one-sided metallized plastic tapes, contacted electrically on both sides of the roll (Fig. 1). The metal layer consists of aluminium or zinc with a width ranging from 50 to 70 mm and a theoretical thickness of 50 nm, while the substrate is frequently made out of polypropylene with a thickness of 12 μm. From the economical and technical point of view it is also desirable to employ these capacitors at higher voltages in a dry mode without an impregnating medium, thus utilizing the high breakdown strength of the thin insulating materials. Under an a.c. voltage stress of more than 300 V (or 25 kV mm^{-1}, respectively) the metal layer is usually destroyed over a long period of time. This results in a loss of capacitance. Indeed, this voltage establishes an upper limit for the practical application of these capacitors.*

The relevant physical processes are of both practical and theoretical interest, so this problem was subjected to a detailed investigation. First, rolls of normal size according to Fig. 1 with a capacitance of about 5 μF were studied. The decay of the capacitance was measured as a function of the time of operation. Specimens with complete breakdowns due to thermal overload or production failure leading to short circuits were excluded from the evaluations.

3. Corrosion phenomena

Corrosion occurs neither for a d.c. voltage nor a chopped d.c. voltage, but only for a.c. voltages with amplitudes above 300 V. With rising voltage amplitudes the corrosion increases. The loss in capacitance can reach several per cent after one month. Corrosion is stronger in the outer layers of the roll than in the inner ones (so far as capacitors with a winding mandrel are concerned). Finally, the boundary zones of the tapes are more heavily destroyed than the centres. This is true for both aluminium and zinc evaporation.

There is no uniform optical appearance of the corrosion phenomena, but two fundamentally different processes can be distinguished. Fig. 2 shows a few examples. Irregular shapes can be observed (Fig. 2a) growing from the edges. A reason for this may be the increased field strength at the edges, and also the fact that air can penetrate into the roll from these edges. Such corrosion phenomena are characterized by self-healed breakdowns with the well-known circular insulating areas [1, 2] on the twin metal layers. In this way, parts of the layers situated one upon the other are also damaged, so that the optical appearance of superposed layers is often rather similar. In between the irregularly corroded zones, small discharge paths are often formed (Fig. 2a) which means that this corrosion path is caused by creepage currents. Less frequent are transparent circular corrosion sites with diameters of up to 10 mm (Fig. 2b). These zones can grow together or lead to a retreat of the edges of metal layers (marked by arrows in Fig. 1). It is remarkable that the substrate shows no damage at these spots, and thus there is no mark on the layer of the adjacent film. However, it was a disadvantage for a detailed investigation that some of the corroded

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*It is noteworthy that capacitors of this kind are manufactured and employed successfully in considerable numbers not only for d.c. voltages but also for low a.c. voltages.

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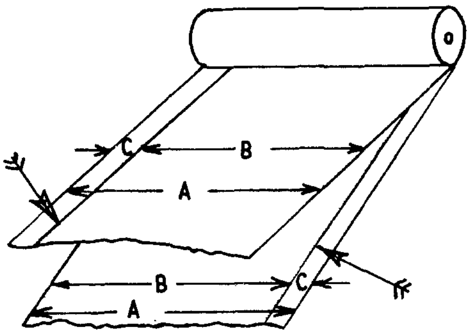


Figure 1 Structure of a capacitor consisting of two one-sided metallized plastic tapes wound upon each other: (A) plastic tapes, (B) metal layers, (C) non-metallized zones.

metallic particles stuck to the opposite foil when the roll was opened, and thus the total picture was disturbed.

4. Influence of air

As shown in the previous section, the self-healed kind of corrosion intrudes from the boundary zones into the roll and diminishes towards the axis (and thus with higher values of pressure inside the roll). Furthermore, corrosion can be significantly suppressed when the rolls are subjected to a drying process under vacuum and when the front areas are sealed afterwards. These observations indicate that air plays an important part. However, air does not have to be present between metal layer and substrate. Corrosion also occurs when both sides of the foils are metal-coated, as well as in the areal type of corrosion which is of a completely different kind.

5. Design of specimens

These considerations led to a design of specimen according to Fig. 3, with metallization on both sides. The metal layer with a theoretical thickness of 50 nm was evaporated in a high vacuum of 10^{-4} mbar (10^{-2} Pa) with the help of a template. The thickness was checked by an instrument using the displacement of the resonance frequency of a small quartz plate. A uniform metallization was reached by letting the templates spin at constant speed together with the foils during the metallization process.

6. Combination of materials

The study of corrosion phenomena was extended to other metals and substrates. As well as the metals aluminium and zinc, also nickel, silver and gold were investigated at high grades of purity (Table I). For several reasons it was not possible to manufacture these coatings with exactly the same thickness. However, the thickness was checked by measurements of the electrical resistance of the metal layers between two cutting edges forming a square area. As expected, these values of layers obtained under growing conditions by vaporization are higher than the values for the solid material. Also an influence of the substrate can be recognized. Moreover interaction between the atoms of the layer and the structure of the substrate is possible. The structure of the substrate may cause epitaxy (i.e. a crystallographically oriented growth). For this it is assumed that energetically the adsorption of a certain geometric arrangement is favoured, especially for mica. This concerns questions involving the theory of nucleus formation. No definite statement can therefore be made on the microstructure of the coating.

The investigations concerned foils of cellulose acetate (CA), cellulose acetobutyrate (CAB), polypropylene (PP), polystyrene (PS), polyethyleneterephthalate (PETP), polycarbonate (PC) and polyimide (PI) (Table II). The foils had a thickness of 12 μm (occasionally 20 μm) resulting in capacitances of 6 to 10 nF. For reasons of comparison, mica (clear muscovite of the best quality) with a thickness of 15 to 19 μm was also included.

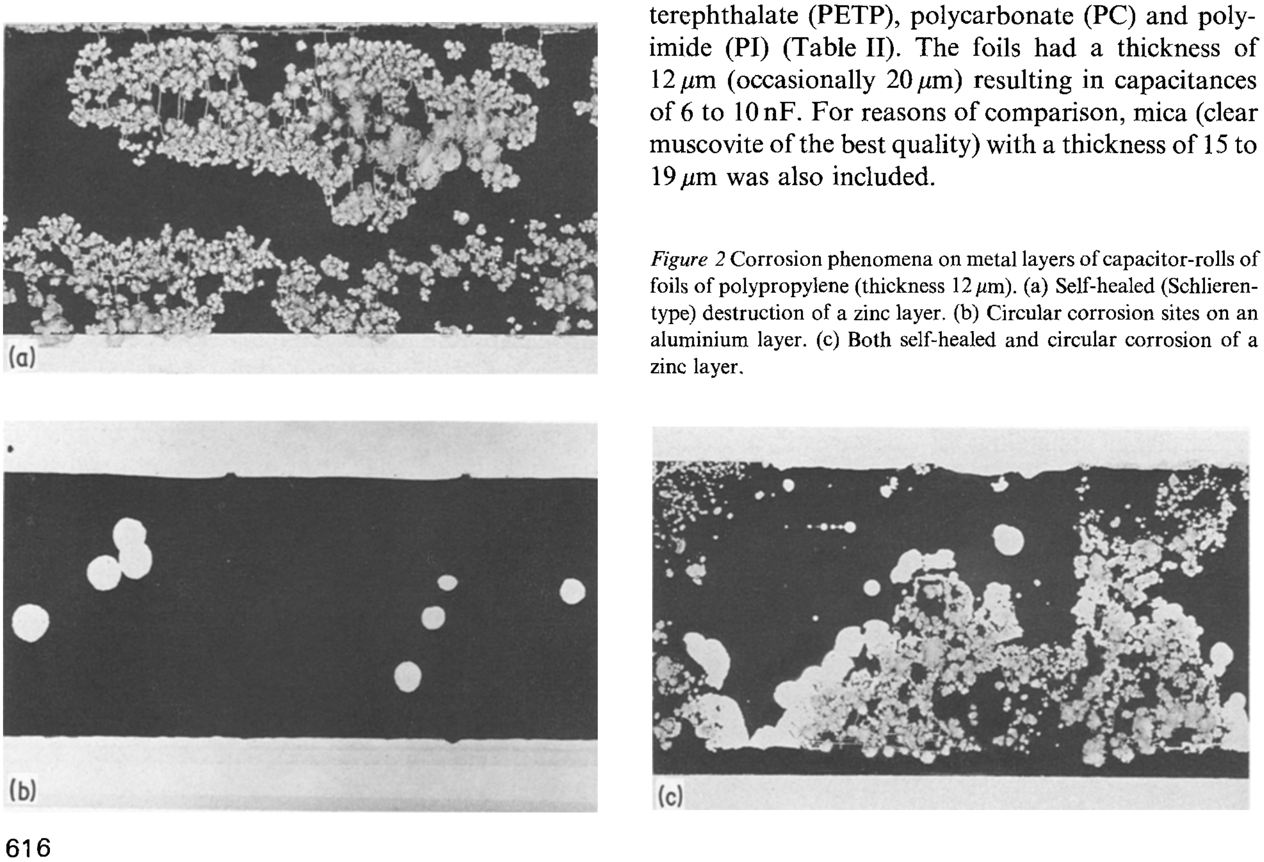


Figure 2 Corrosion phenomena on metal layers of capacitor-rolls of foils of polypropylene (thickness 12 μm). (a) Self-healed (Schlieren-type) destruction of a zinc layer. (b) Circular corrosion sites on an aluminium layer. (c) Both self-healed and circular corrosion of a zinc layer.

TABLE I Properties of the investigated metal layers

Metal	Density at 20° C ($g\,cm^{-3}$)	Weight of electrode (mg)	Normal potential with regard to hydrogen (V)	Resistivity at 20° C ($10^{-6}\,\Omega\,cm$)	Resistance $R_{\square}$ (calculated) (Ω)
Al	2.7	0.52	−1.66	2.65	0.53
Zn	7.1	1.37	−0.76	5.7	1.14
Ni	8.9	1.71	−0.23	6.9	1.38
Ag	10.5	2.02	+0.80	1.49	0.30
Au	19.3	3.71	+1.7	2.06	0.41

TABLE II Properties of the investigated foils

Substrate	Manufacturing technique	Thickness (μm)	Long-term thermal stability (° C)	Dielectric number	Calculated value of capacitance (nF)
CA	One-sided mat-cast foil without plasticizer	20	60	3.8	6.47
CAB	One-sided mat-cast foil without plasticizer	20	70	3.6	6.13
PP	Foil stretched longitudinally and transversely	12	75	2.3	6.53
PS	Foil stretched longitudinally and transversely	12	75	2.5	7.09
PETP	Isotropic foil of high purity	12	100	3.4	9.65
PC	One-sided mat-cast foil without plasticizer; somewhat crystallized and longitudinally stretched	12	120	2.9	8.23
PI	One-sided mat-cast foil (not stretched)	12	230	3.4	9.65

7. Test arrangements

The specimens were operated as small capacitors in two different arrangements, with an a.c. voltage of normally 400 V at room temperature. For this purpose the two connecting ends had to be carefully contacted. This was done with help of a graphitic conducting varnish. One of the two devices (shown in Fig. 4) can be characterized by the fact that the specimens were covered and pressurized at 10 to 150 mN mm^{-2}.

In the second case the specimens were freely suspended and surrounded by air on each side. This second arrangement had the advantage that the surfaces could be observed at any time. Furthermore, corrosion was accelerated and the duration of the experiment reduced.

To avoid electrical damage the electrical circuit of a medium voltage tranformer and the specimen

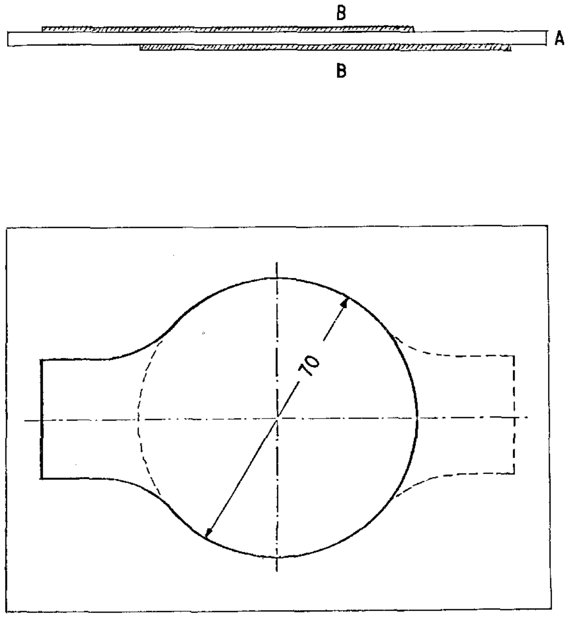


Figure 3 Metallized foil of insulating material: (A) substrate of plastic or mica, (B) Evaporated metal layers. Measurement given in mm.

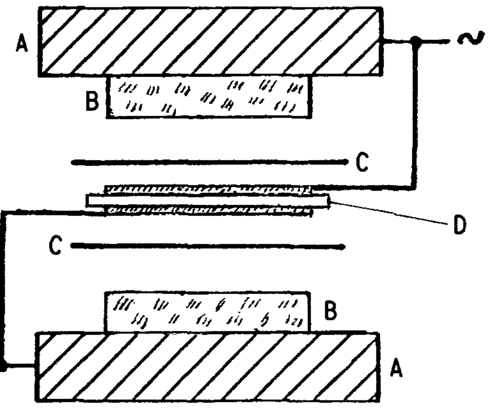


Figure 4 Test arrangement: (A) iron plates (weight: 4 kg; occasionally with a window); (B) plates of acrylic resin; (C) covering foils (same material as substrate); (D) metallized sample.

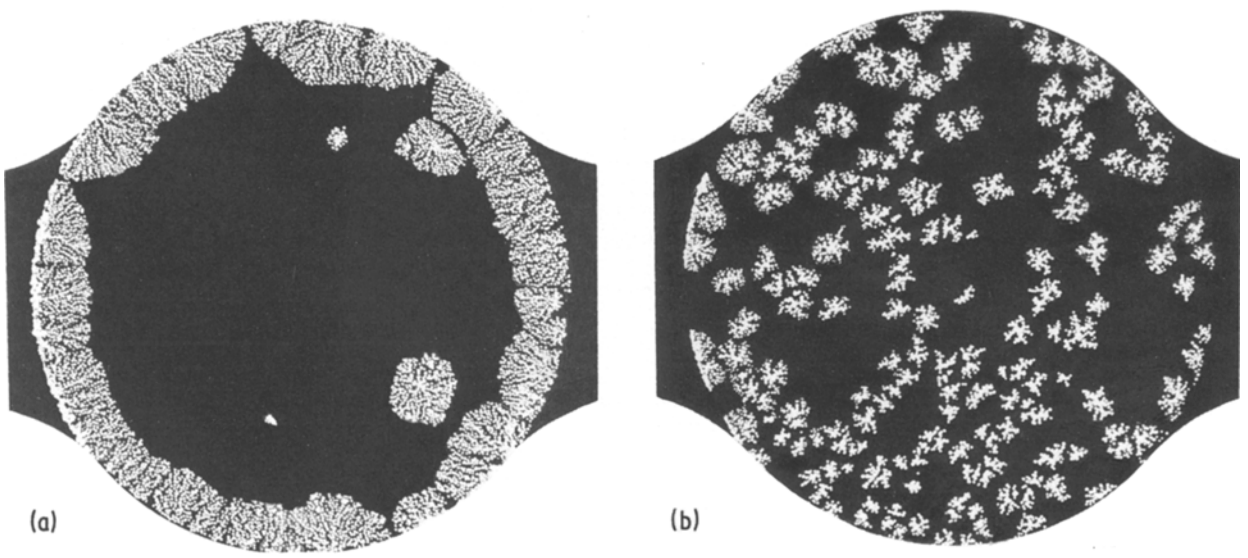


Figure 5 Corrosion on foils of polycarbonate coated with aluminium and stressed under pressure. $d = 12\,\mu m$, $U = 500\,V$; $t =$ (a) 380 h (b) 600 h.

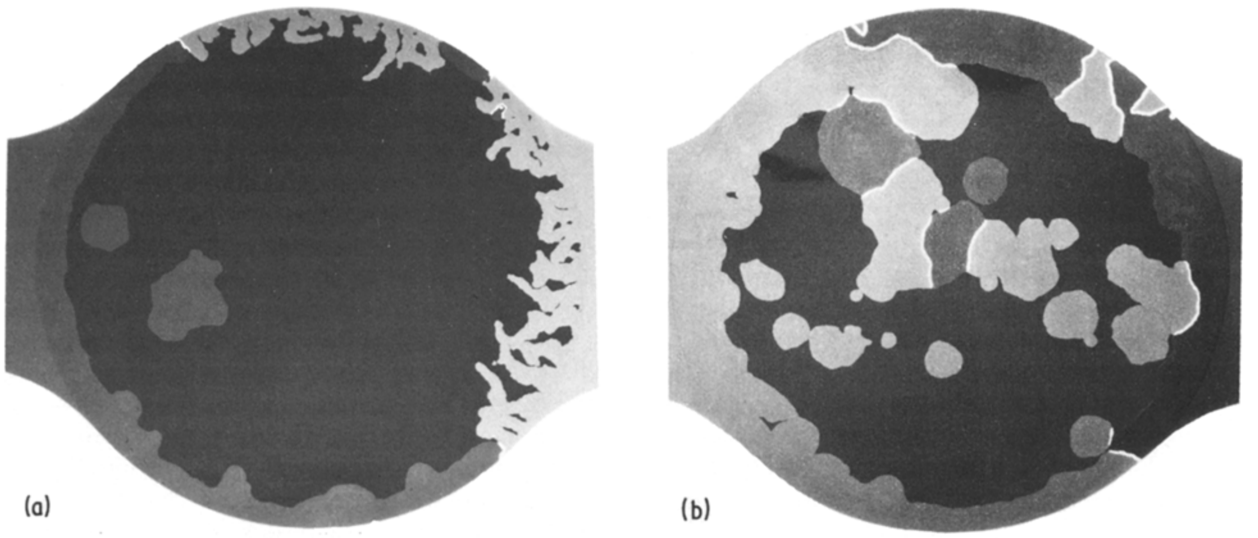


Figure 6 Corrosion phenomena of freely suspended foils with aluminium layer. (a) CAB foil ($d = 20\,\mu m$, $U = 450\,V$, $t = 240\,h$). (b) PI foil ($d = 12\,\mu m$, $U = 500\,V$, $t = 25\,h$).

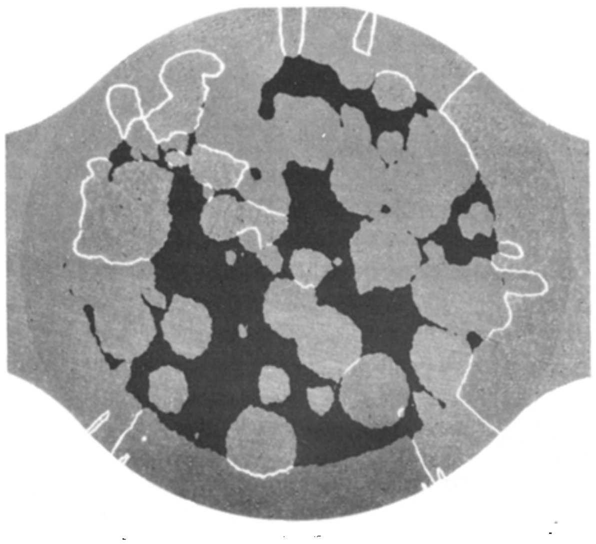


Figure 7 Corrosion of an aluminium layer on mica for freely suspended arrangement. $d = 15\,\mu m$, $U = 500\,V$, $t = 25\,h$.

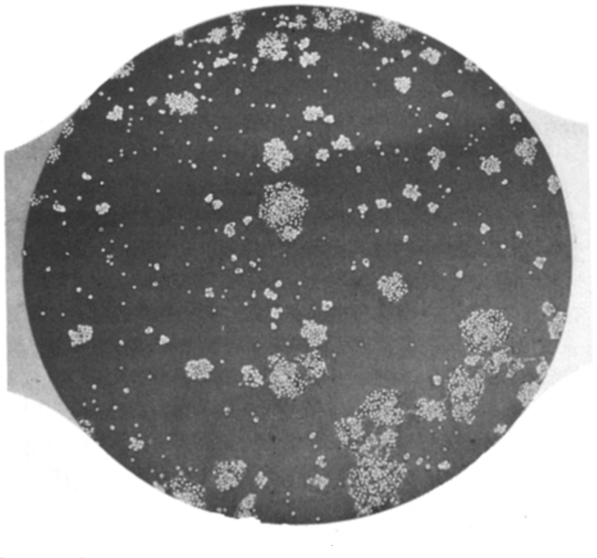


Figure 8 Corrosion of a silver layer on polyimide for freely suspended arrangement. $d = 12\,\mu m$, $U = 400\,V$, $t = 170\,h$.

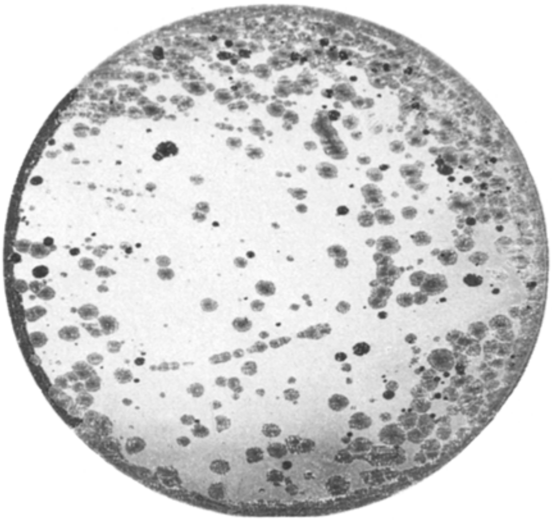


Figure 9 Corrosion of a silver layer on mica for freely suspended arrangement. $d = 19\,\mu m$, $U = 600\,V$, $t = 850\,h$.

included a microfuse of 80 mA which turned off the voltage in case of a complete breakdown.

8. Basic observations and visual evaluation

There is a fundamental difference between self-healing corrosion and the areal type of corrosion, as shown in Section 3. The first kind (Fig. 2a) is caused by a self-healing effect in which the metal layer is evaporated so much that around the breakdown district a circular metal-free area is formed, which then once more electrically insulates the layers [1, 2]. This process is dependent on the breakdown strength of the dielectric, which is influenced by factors such as the ambient atmosphere. For the rolls studied the a.c. voltage had to reach a value of at least 300 V. Below this level there was no damage.

For specimens which are stressed under pressure (Fig. 4) corrosion also grows from the borders in the form of brushes towards the centre, and has the same appearance on both sides. Such radiating corrosion patterns occur more rarely in the centre of the surface. They also consist of self-healed breakdowns which happen one after the other, and can be detected by blue flashes and short sounds. Such a breakdown damages the dielectric in its neighbourhood, so that further breakdowns occur in radial directions starting from the centre and increasing in number, which leads to a star-like picture. Pictures of this kind are shown in Fig. 5 for two polycarbonate films coated with aluminium. The damage increases with time in more than a proportional manner, so that the decrease in capacitance can reach up to 30% after a month. With an increase of the mechanical pressure (up to e.g.

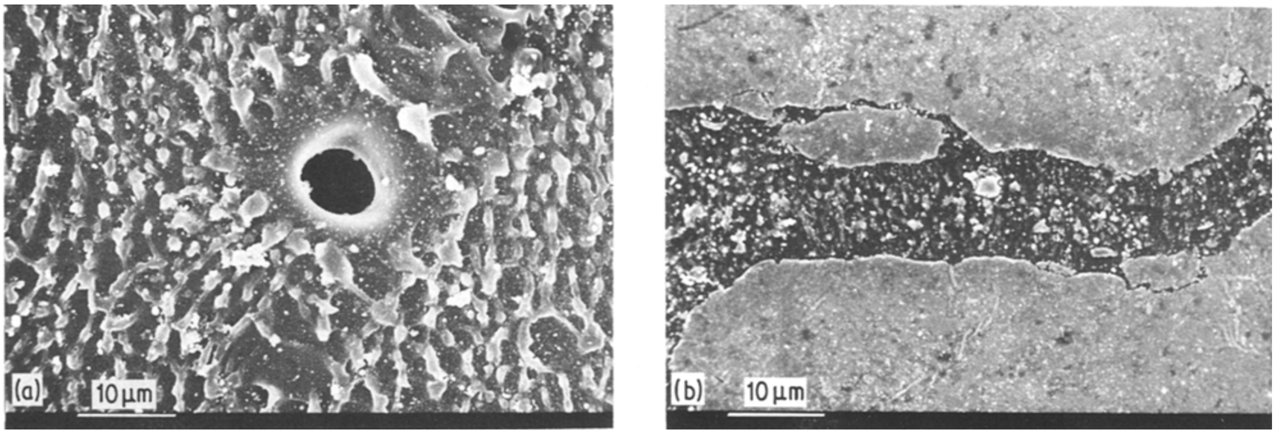


Figure 10 SEM photographs of self-healed breakdowns on polypropylene rolls. (a) With aluminium evaporation ($d = 8\,\mu m$). (b) With zinc evaporation (filament discharge path from Fig. 2a).

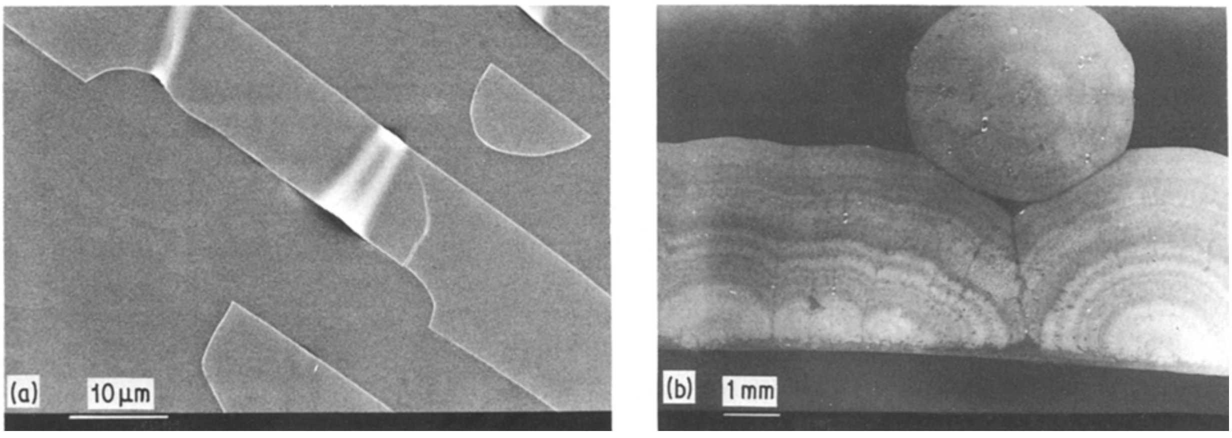


Figure 11 SEM photographs of transparent sites of corrosion on polypropylene rolls. (a) With aluminium evaporation (as Fig. 2b). (b) With zinc evaporation (as Fig. 2c).

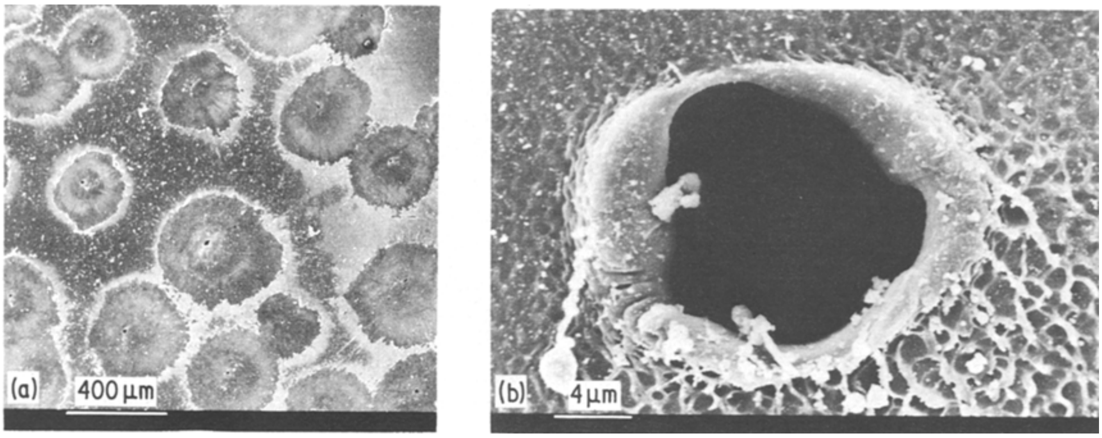


Figure 12 (a) SEM photographs of corrosion on a polycarbonate foil metallized with aluminium and stressed under mechanical pressure (as Fig. 5a). (b) Higher-magnification view of one of the spots of breakdown.

150 mN mm^{-2}) this can largely be avoided. This is also in agreement with results from roll-type capacitors, for which corrosion decreases towards the centre of the roll. These self-healing processes also occur in the freely suspended arrangement, and they are observed in various degrees for CA, CAB, PP, PETP and PC, seldom for PI, and very seldom for PS [1].

In the second case (areal-type corrosion) the metal layer is converted to an insulating layer without breakdown (Fig. 2b). This is true for the roll and to a greater degree for freely suspended specimens, for which corrosion occurs over the whole area. A planimetric measurement of the corroded spots shows that their share is equivalent to the measured decrease in capacitance. Thus, the decrease in capacitance is a measure of the amount of metal layer destroyed; in other words, when the layer loses its metallic character the body loses capacitance by the same amount. This is of particular interest.

The freely suspended specimens usually show on both sides these alternatively corroded zones, which in the case of aluminium and zinc are transparent and non-conductive. This is shown in Figs. 6 and 7. In the black zones the metal layer remained undamaged on both sides. Depending on the intensity of the grey tone it can be recognized on which side the damage occurred (e.g. Fig. 6b). When there is no metal on either side very slender transparent lines appear (see Figs. 6b and 7). Here, corroded zones on the two sides meet and corrosion must necessarily come to a stop, since no opposite layer under voltage is present. Thus, it can occasionally lead to an isolation of undamaged metallic zones which then have no electrical contact with the electrode and can no longer contribute to the capacitance. Such wide zones of corrosion of the areal type are typical for CA, CAB, PP, PS, PETP, PC and PI. A similarity with the transparent zones in Figs. 2b and c is clear. Furthermore, the dielectric losses vary over a wide range. Depending on the substrate and on its specific state (ambient climate), respectively, even with equal composition of material half of the original area can be lost after 300 h. PI suffers little destruction, while for PP and PETP relatively strong corrosion occurs.

The assumptions so far made are true for aluminium and zinc. There are difficulties concerning the evaporation of metals with high boiling points, since the substrates often cannot withstand the conditions of evaporation. However, self-healing processes can also be observed for nickel, silver and gold, but on a smaller scale. These effects are depicted in Fig. 8 for a layer of silver on a substrate of polyimide. Due to the high electrochemical potential (Table I) in this case, no large zones of areal-type corrosions can be seen.

Under the conditions described above no breakdown (and also no self-healing breakdown) occurs with mica sheets. Both for aluminium layers (Fig. 7) and for nickel layers, corrosion on mica is of the areal type and very strong. In the case of silver there are intermittent zones of corrosion (Fig. 9). For aluminium coated sheets corrosion can be complete after only one day, while the process lasts one month for nickel and silver. Gold layers on mica substrates remain undamaged after several months, even under aggravated conditions. This clearly indicates that besides the metal layer, the substrate influences corrosion significantly.

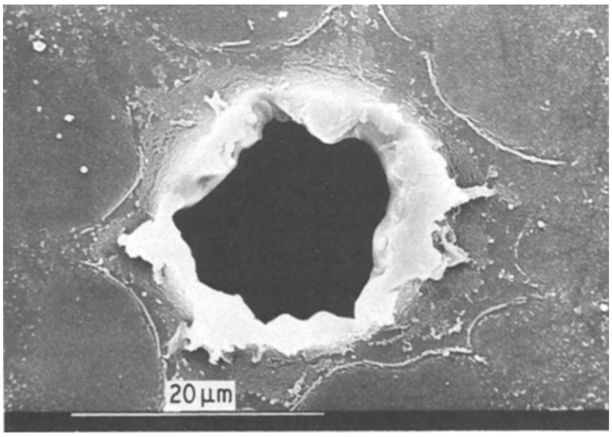


Figure 13 SEM photograph of a self-healed breakdown of a polyimide foil metallized with aluminium for freely suspended arrangement. $d = 12\,\mu\text{m}$, $U = 400\,\text{V}$, $t = 4300\,\text{h}$.

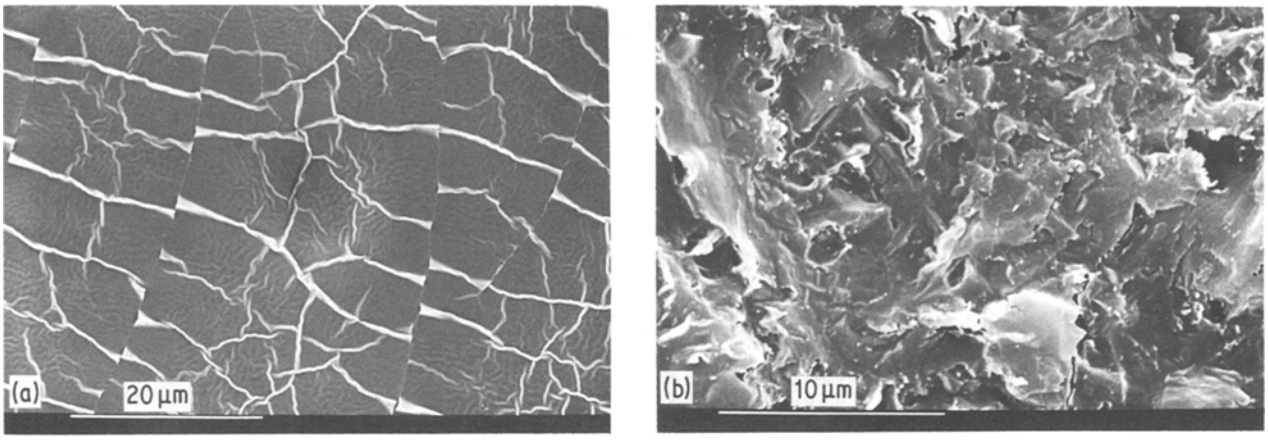


Figure 14 SEM photographs of areal corrosion on a cellulose acetobutyrate foil metallized with aluminium (as Fig. 6a). (a) Smooth side. (b) Mat side.

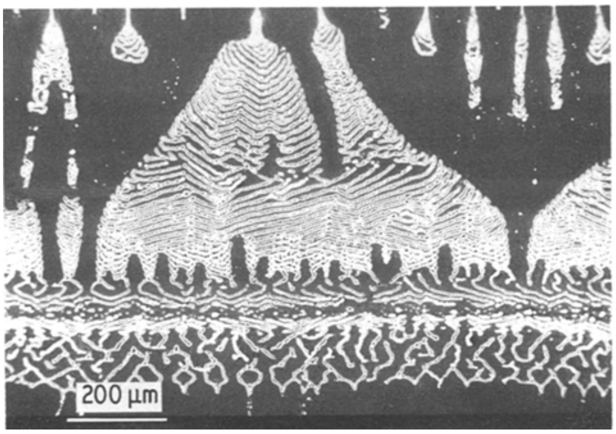


Figure 15 SEM photograph of areal corrosion on a polypropylene foil metallized with aluminium for freely suspended arrangement. $d = 25\,\mu\text{m}$, $U = 600\,\text{V}$, $t = 1100\,\text{h}$.

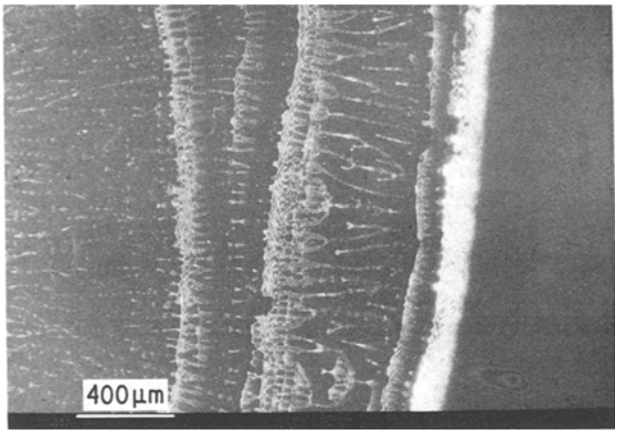


Figure 17 SEM photograph of areal corrosion on a polyimide foil metallized with aluminium for freely suspended arrangement. $d = 12\,\mu\text{m}$, $U = 500\,\text{V}$, $t = 390\,\text{h}$.

9. Investigations with a scanning electron microscope

9.1. Rolled samples

If the corroded specimens are investigated with the help of a scanning electron microscope (SEM), holes of self-healed breakdowns can be identified with diameters of $8\,\mu\text{m}$ in the case of Fig. 10a. Around these spots there is a clear zone which is succeeded by more corroded metal. This is a self-healed process [1, 2] in which the breakdown is interrupted by evaporation of the thin aluminium layer. All this leads to an increased amount of corrosion. Fig. 10b shows a discharge path (creepage current path) from Fig. 2a, for a zinc layer without breakdown in a zone of self-healed discharges.

Obviously, the transparent zones of the aluminium layer (Fig. 2b) consist of brittle aluminium oxide

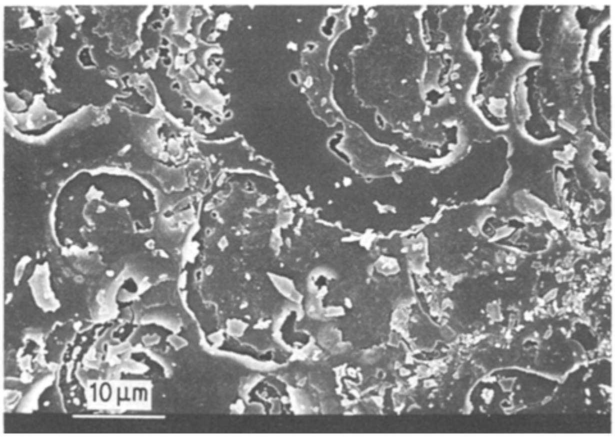


Figure 16 SEM photograph of areal corrosion on a polyethylene terephthalate foil metallized with aluminium for freely suspended arrangement. $d = 12\,\mu\text{m}$, $U = 500\,\text{V}$, $t = 300\,\text{h}$.

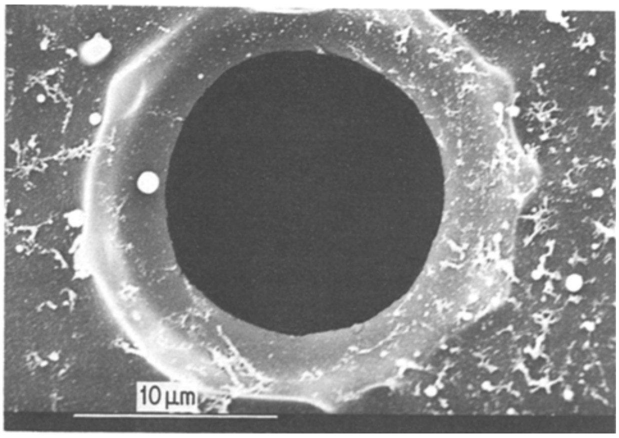


Figure 18 SEM photograph of a self-healed breakdown of a polyethylene terephthalate foil metallized with nickel for freely suspended arrangement. $d = 12\,\mu\text{m}$, $U = 400\,\text{V}$, $t = 6400\,\text{h}$.

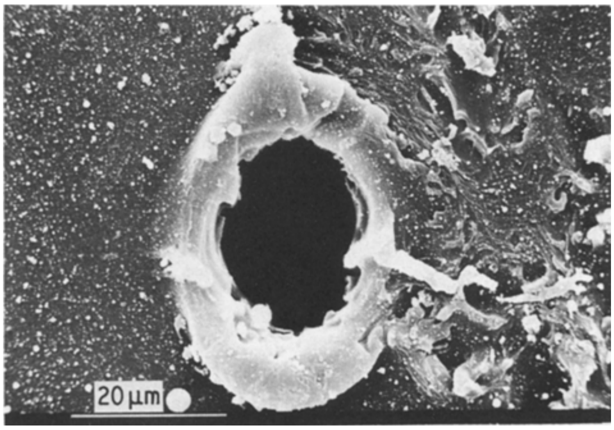


Figure 19 SEM photograph of a self-healed breakdown of a polystyrene foil metallized with silver for freely suspended arrangement. $d = 12\,\mu\text{m}$, $U = 400\,\text{V}$, $t = 1990\,\text{h}$.

(sapphire). During unwinding of the roll this layer ruptures slightly along the edges of the hexagonal crystal and is partly lifted from the substrate. Fig. 11a shows a photograph taken with an SEM of the remaining uniformly aligned parts of the crystal. The transverse stripes are folds which are caused by crystal growth. In the case of zinc layers (Fig. 11b) a completely different structure but also transparency can be recognized.

9.2. Specimens corroded under pressure

Fig. 12a shows an SEM photograph of the polycarbonate specimen previously depicted in Fig. 5a at lower resolution. Around the points of breakdown, circular insulating zones with diameters ranging from 300 to $500\,\mu\text{m}$ can be recognized. As shown in Fig. 12b the spots of breakdown have diameters of approximately $15\,\mu\text{m}$ with distinct border warpings, for substrates with thicknesses of $12\,\mu\text{m}$.

9.3. Freely suspended specimens

The freely suspended specimens coated with aluminium exhibit also self-healed breakdowns (Fig. 13). More significant, however, are the areal-type corrosion processes. On one side of the specimen (e.g. Fig. 14 for a foil of cellulose acetobutyrate), a similarity with the corrosion phenomena of the polypropylene roll of Fig. 11a is often found. On the other side, however, irregular flakes (variably oriented crystallites) can be observed which obviously is connected with crystal formation. Possible reasons are forces of attraction or repulsion between electrostatically charged crystallites, which cause considerable mechanical tensions in the layer and can lead to the strange structure. Further SEM photographs (Figs. 15, 16 and 17) show similar phenomena. Often the large transparent corrosion sites are not structured at all, which may be caused by a monocrystal.

Different effects can be expected for nickel and silver. These metals oxidize much slower than aluminium or zinc, so that in the case of a plastic dielectric, corrosion is only determined by an accumulation of self-healing processes. Examples of this kind are shown in Figs. 18 to 21. Sometimes an elongated shape of breakdown hole is noticeable; this is caused by the previous stretching of the foil during the fabrication. There are no areal-type oxidation processes for plastic substrates like in those of Figs. 6 and 7. For gold, corrosion can only occur at weak points of the plastic substrate in the form of self-healing breakdowns (Fig. 22).

The corrosion of an aluminium coating on a mica sheet is areal, occurs very fast and only rarely shows zones with any structure. For nickel, corrosion is also areal and displays hardly any structure in the SEM. For silver, corrosion on mica occurs in discrete areas (Fig. 23). Naturally, the picture differs from one side of the specimen to the other.

Unfortunately, the small quantities of corrosion products (of the order of $13\,\mu\text{g}\,\text{cm}^{-2}$ for aluminium and $36\,\mu\text{g}\,\text{cm}^{-2}$ for zinc) do not allow a reliable analysis. It is likely that the corrosion product of the aluminium film is monocrystalline aluminium oxide (Al_2O_3) [3]. It is also probable that the electrochemical conversion of the zinc layer is zinc oxide. Gold obviously grows epitaxially on the mica crystal and, as mentioned before, no corrosion whatever is observed.

10. Measurements in a dry environment

The unpredictable variations of the amount of corrosion and the influence of air led to the

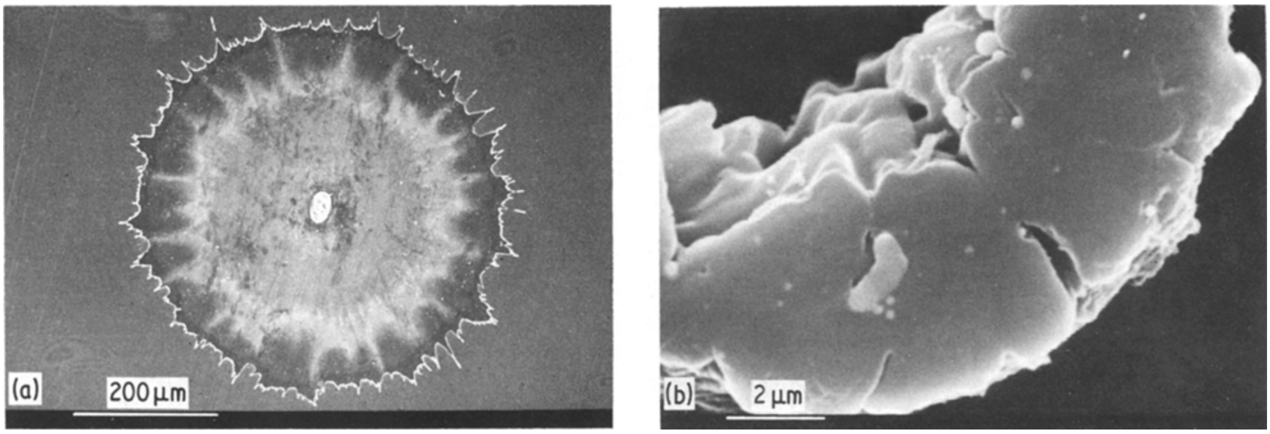


Figure 20 SEM photographs of a self-healed breakdown of a polycarbonate foil metallized with silver for freely suspended arrangement. $d = 12\,\mu\text{m}$, $U = 450\,\text{V}$, $t = 45\,\text{h}$. (a) Low and (b) high magnification.

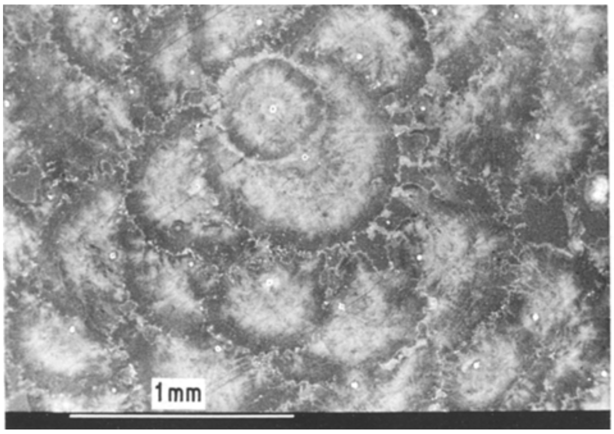


Figure 21 SEM photograph of corrosion on a polyimide foil metallized with silver (as Fig. 8).

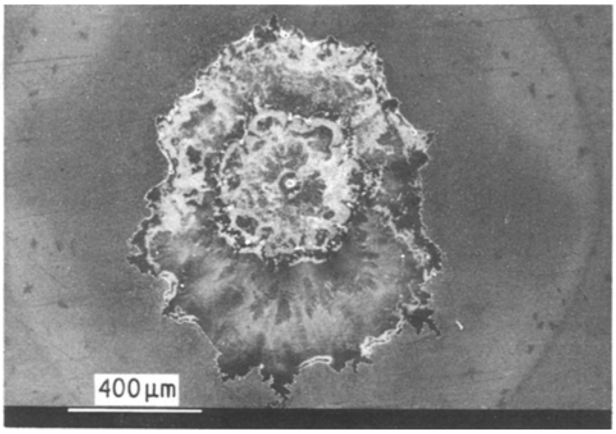
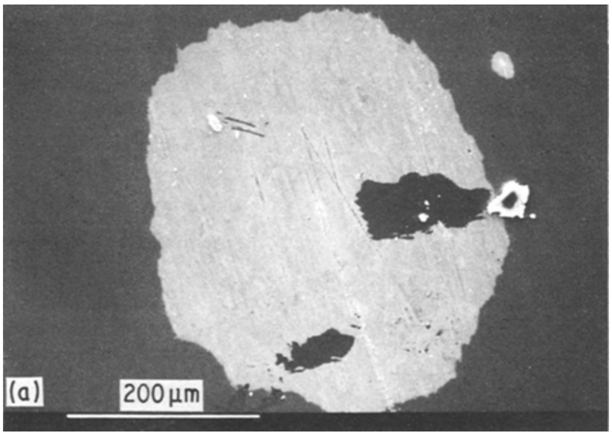


Figure 22 SEM photograph of a self-healed breakdown of a polyimide foil metallized with gold for freely suspended arrangement. $d = 12\,\mu\text{m}$, $U = 400\,\text{V}$, $t = 1100\,\text{h}$.

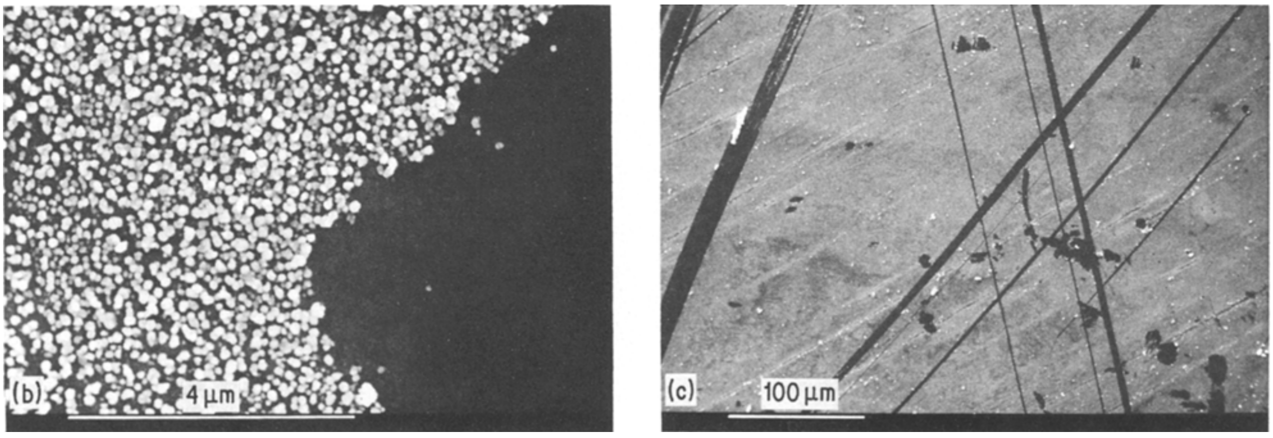
assumption that the air humidity, which varied both in the laboratory and during operation, was responsible for the destruction. Measurements in a dry environment were therefore performed. A gel of granular silicon dioxide (silica gel) was used for drying the experimental vessel. An indicator was added to check the air humidity. Measurements were started 14 days after the insertion of the specimens. The results were surprising. Even after several month no destruction was observed for each investigated combination of materials including mica. In the absence of water (air humidity), neither the self-healing processes nor the areal type of destruction occurred, except for breakdown caused by overstressing.



Consequently in the first type of corrosion (self-healing process) the breakdown strength is reduced by the absorption of air humidity. The second type (areal corrosion) is caused by an electrochemical process due to electrolysis of the water that is present in and on the substrate, and which naturally depends on the air humidity. For these mechanisms the ambient temperature is of influence too. An important role is played by the substrate itself and the state of its surface. The water molecules are not only located on the surface of the foil. Depending on the material, the foil also contains a certain amount of water inside it. In the case of mica H_2O groups adsorbed on the surface are responsible for the unexpected corrosion of the metal film.

In this context another result is of importance. For plastic foils breakdown can occur due to overstressing (e.g. 150 days at $40\,\text{kV}\,\text{mm}^{-1}$) in a dry environment. In this case the molecules at the point of breakdown are split. In the case of a substrate containing oxygen atoms the released oxygen may lead to a spontaneous oxidation of the metal layer. This behaviour was observed, for example, for the substrates polyethyleneterephthalate (with silver) and polyimide (with aluminium).

Figure 23 SEM photographs of corrosion on mica metallized with a silver layer (as Fig. 9). (a, b) first side; (c) second side).



11. Conclusion

The corrosion of thin metal layers stressed with an a.c. voltage is a very complex phenomenon. As shown by the investigations reported here there are on the one hand the known self-healing breakdowns, and on the other hand there is an areal corrosion of the metal layer. For the latter case the insulating material is not destroyed, in contrast with the case of self-healing processes. The corroded areal-type zones in the cases of aluminium and zinc are transparent and electrically non-conductive. If certain preconditions are fulfilled, self-healed breakdowns are also observed for nickel, silver and gold. Due to the high electrochemical potential there is no areal-type corrosion of these metals. In a perfectly dry system there are no corrosion phenomena at all, which is regarded as an important result of the present study. In the first case (self-healing process) there is a breakdown phenomenon in the dielectric with previous absorption of water, and in the second case (areal-type corrosion) there is an electrochemical process, namely the effect of oxygen ions which are generated from the dissociation of water (from air humidity) located on the surface of the metallized dielectric. During the positive half-cycle OH^- ions are deposited on the metal, from which hydrogen is released during the next half-cycle. This necessarily leads to an oxidation. These processes are of particular importance for the aluminium and zinc layers used in film capacitors. In the case of mica substrates the water molecules adsorbed on the surface cause corrosion of the metal layer in a very short time even under normal atmospheric conditions, particularly for aluminium (and zinc). Corrosion occurs for aluminium, zinc and nickel over large sites, while it is island-shaped in the case of silver. The corroded zones are transparent in the case of aluminium and zinc, in contrast with nickel and silver. The corroded site is always electrically non-conductive. Due to the small available quantities of corroded material a detailed analysis is extremely difficult. As the study showed there is also no corrosion of the metal layer on mica as a substrate under a dry atmosphere. In all cases, gold on mica remains undamaged, even after a stress of several months.

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