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INFLUENCE OF FILM THICKNESS, TEMPERATURE AND INORGANIC FILLERS ON THE VOLUME ELECTRIC RESISTIVITY OF HEAT-CURING EPOXY VARNISH

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ABSTRACT

The dependence of the volume electric resistivity of heat-curing epoxy varnish on the film thickness, temperature and nature of inorganic fillers for films obtained by spraying on steel supports cured for 30 minutes at 160 ºC was determined. Film thicknesses ranged between 5 and 56 μm, temperature between 24 ºC and 140 ºC and the fillers were rutile type titanium dioxide, micronized mica, colloidal aluminium oxide and aluminium silicate. The experimental data, treated statistically by the linear regression method shows a linear dependence of the volume electric resistivity on the film thickness and a hyperbolic one on temperature. The highest volume electric reisitivity was obtained for films containing titanium dioxide and the lowest one for those with aluminium silicate. The volume electric resistivity depends on film thickness for films deposited from solution and can not be considered a material constant.

RESUMO

A dependência da resistividade elétrica do volume de vernizes epoxi tratadas com calor da espessura dos filmes, temperatura e natureza das cargas inorgânicas para filmes obtidos através de pulverização sobre suportes de aço tratados por 30 minutos a 160 ºC foi determinada. A espessura dos filmes variou entre 5 e 56 μm, a temperatura de 24 ºC a 140 ºC e as cargas usadas foram dioxido de titânio do tipo rutila, mica micronizado, óxido de alumínio coloidal e silicato de alumínio. Os resultados experimentais, tratados estatisticamente com o método de regressão linear, mostram uma dependência linear da resistividade elétrica do volume com a espessura do filme ou película e uma dependência hiperbólica com a temperatura. Os valores mais altos da resistividade elétrica do volume foram obtidos para películas contendo dioxido de titânio e os valores mais baixos com películas contendo silicato de alumínio. A resistividade elétrica do volume depende da espessura dos filmes depositados da solução e não pode ser considerada uma constante.

KEYWORDS: Insulator, Volume Electric Resistivity, Epoxy Resin, Varnish, Heat-Curing Resin, Inorganic Fillers for Insulators.

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INTRODUCTION

The use of a composite material of the paint type as an electric insulator implies a detailed analysis of its behaviour under various circumstances. Thus, besides the electric behaviour, some other properties such as resistance to chemical agents, solvents, humidity, temperature, mechanical impact, thermal shock, electromagnetic fields, etc., must be known, such properties limiting their uses.

The volume electric resistivity results from Ohm's Law and it is a material constant.

In the case of polymers, the volume electric resistivity depends on the presence of free ions in their composition[1]. Potential sources of free ions are low molecular weight impurities such as solvents, monomers, water, catalysts and condensation products. Polymer chemical structure contributes only indirectly to the ion mobility by its chain flexibility.

The volume electric resistivity of polymers is of the order of 10^{13} to 10^{19} Ω x cm and it decreases with increasing temperature according to an Arrhenius type law:

$$\rho_v = \rho_0 \exp (\Delta E/RT) \qquad (1)$$

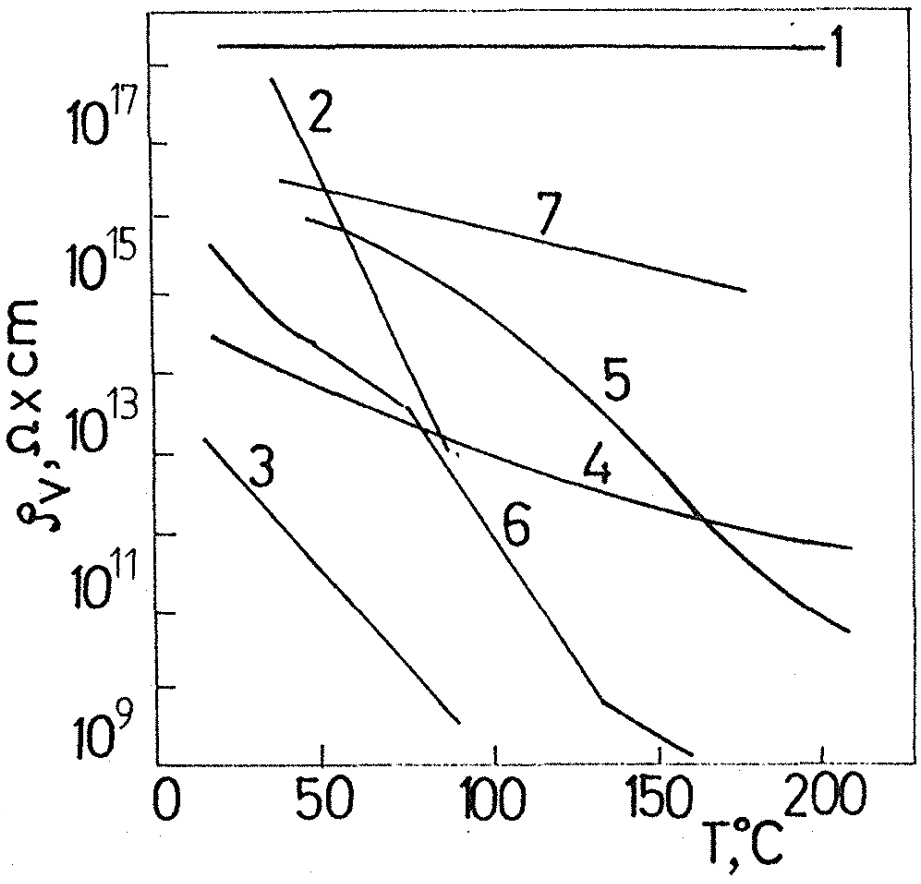
where ρ_v is the volume electric resistivity, ρ_0 is a constant practically independent of the temperature T, ΔE is the activation energy (the difference of energy between the activated and the ground state of the ions), and R is the gas constant. At temperatures higher than the glass transition, the mobility of the chain segments increases with temperature and consequently the mobility of ions present as impurities also increases, thus increasing the volume electric resistivity. The temperature dependence of ρ_v for some polymers is shown in Figure 1.[2]

The filler particles diminish the mobility of macromolecular segments by their adsorption on surfaces[3]. For the particular case of films, the volume properties are affected by the contribution of superficial properties, that can prevail for very thin films (small volume to surface ratios). The film volume properties are comparable with those of the corresponding bulk compound only for thick films. In such a situation the following questions arise:

- Is the volume resistivity a material constant, that is independent of the film thickness?
- Does its temperatures dependence obey Equation (1) ?
- How does the nature of the filler influence the value of the volume electric resistivity?

The above questions are especially valid for films deposited from solution, that besides other impurities, inevitably contain varying quantity of solvents, even if they are applied in very thin layers and drying is carefully done.

In order to answer the above mentioned questions, the present paper studies the dependence of the volume resistivity of a heat-curing epoxy varnish on the film thickness, temperature and type of inorganic fillers.



1 - TEFLON
2 - POLYETHYLENE
3 - POLYVINYL CHLORIDE
4 - SILICONE
5 - SILICONE RUBBER
6 - SEMIRIGID EPOXY
7 - *p*-POLYXYLYLENE

FIGURE 1. DEPENDENCE OF THE VOLUME ELECTRIC RESISTIVITY ON TEMPERATURE FOR VARIOUS POLYMERS.[2]

MATERIALS AND METHODS

A Danish 6138/000 CEAST type Teraohmeter coupled with two cylindrical electrodes having a standardized diameter of 5 cm and and area of 9.6349 cm^2, equipped with a guard electrode was used to measure the electric volume resistivity. The two electrodes were thermostated at temperatures ranging between 24 ºC and 140 ºC.

The film thickness was measured using a Polish type electromagnetic Ultrameter with an accuracy of $\pm$ 1 μ .

The inorganic fillers were dispersed in a 1 liter German mill with ceramic balls for about 80 hours to obtain a convenient degree of dispersion. The degree of grinding of fillers into the resin was measured with a Romanian Grindometer. The viscosity was checked by means of a viscosimetric cup with a 4 mm nozzle diameter at a temperature of 25 ºC.

The following materials were used to obtain electroinsulating samples: (a) epoxy resin based on bisphenol A and epichlorhydrin having the following characteristics: epoxy equivalent - 0.02 to 0.05/100 g of resin, concentration - 39%±1, solvent - monobutyl-diethyleneglycol, viscosity at 25 ºC - 3800 to 7000 mPa x s; (b) inorganic fillers: rutile type titanium dioxide with an oil index of 18 g/ 100 g; micronized mica with a maximum humidity of 1%; aluminium silicate having a maximum humidity of 4%, an oil index of maximum 60 g/ 100 g and a molar ratio SiO/Al_2O_3 ranging between 1.6 and 2.2; coloidal aluminium oxide with maximum humidity of 10%, an oil index of 140 g/ 100 g, a maximum content of 3% Fe_2O_3 and a minimum content of 44% Al_2O_3; (c) 2,4,6-tris-(dimethylaminoethyl)phenol as hardener and (d) cyclohexanone/ isopropanol in a volume ratio of 1/1 as thinner.

The films were applied by spraying on 200 x 100 x 1 (mm) metallic plates cleaned previously with sandpaper and degreased in order to obtain a thickness as uniform as possible. To remove the solvents better, more layers were applied and every layer was dried.To obtain a wide range of thicknesses 1 to 5 layers were applied.Film cross-linking was obtained by heating for 30 minutes at 160 ºC.

RESULTS AND DISCUSSION

The experimental data was treated by the statistical method of linear regression implemented on an IBM compatible PC. The dependence of the volume electric resistivity on the film thickness, ℓ , and temperature , T, was analysed. The two parameters were considred independent and the third one - the nature of the filler - interferes implicitly for each sample.

To find the best correlation between ρ_v and the two parameters ℓ and T, six equations were introduced into the program:

$$Y = C_o + C_1 + X_1 \quad (2)$$

$$Y = C_o \times \exp(C_1/X_1) \quad (3)$$

$$Y = C_o + C_1/X_1 \quad (4)$$

$$Y = C_o \times X_1^{C_1} \quad (5)$$

$$Y = C_o \times C_1^{X_1} \quad (6)$$

$$Y = C_o + C_1 \times X_1 + C_2 \times X_2 \quad (7)$$

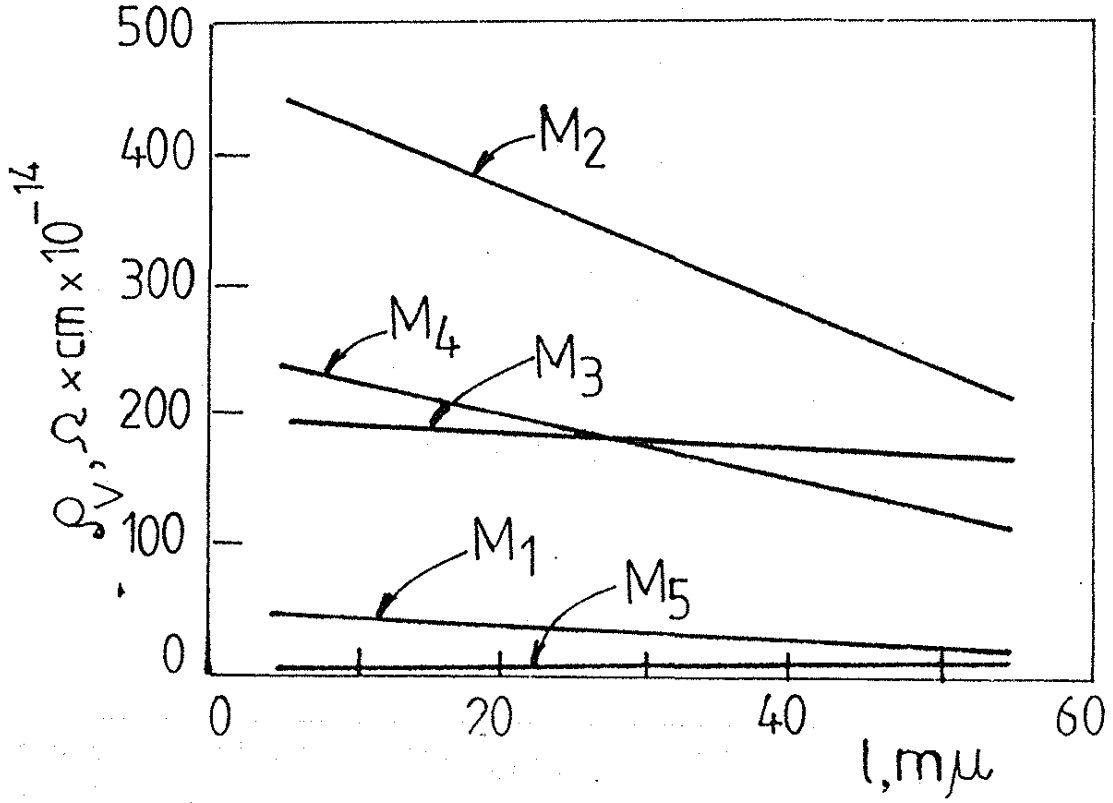
where Y represents the volume electric resistivity and $X_{1,2}$ are either the film thickness or the temperature. Forty-nine pairs of points (ρ_v, ℓ and ρ_v, T) were introduced in each equation and the coefficients C_o, C_1 and C_2 were determined. More complex equations were not used because, besides the complication in the calculation, the phenomenological interpretation becomes practically impossible.

The composition of the samples studied is shown in Table I.

TABLE I. COMPOSITION OF THE SAMPLES STUDIED IN PERCENT BY WEIGHT.

Sample	Epoxy resin	Amine curing agent	Titanium dioxide	Micronized mica	Colloidal aluminium oxide	Aluminium silicate
M_1	77.67	2.91	-	-	-	-
M_2	77.67	2.91	19.42	-	-	-
M_3	77.67	2.91	-	19.42	-	-
M_4	77.67	2.91	-	-	19.42	-
M_5	77.67	2.91	-	-	-	19.42

The experimental dependence of ρ_v on film thickness is represented, for each sample, in Figure 2. As can be seen, a linear decrease of the volume electric resistivity with film thickness is observed for all samples with the exception of sample M_5 that contains aluminium silicate as filler and presents a slightly positive slope.



M_1 - EPOXY RESIN

M_2 - TITANIUM DIOXIDE

M_3 - MICRONIZED MICA

M_4 - COLLOIDAL ALUMINIUM OXIDE

M_5 - ALUMINIUM SILICATE

FIGURE 2. PLOT OF THE VOLUME ELECTRIC RESISTIVITY AS A FUNCTION OF FILM THICKNESS FOR THE SAMPLES STUDIED.

The equations that fit the best the experimental values for each sample are:

$$\rho_v = 42.818 - 0.422 \times \ell \quad (M_1) \quad (8)$$

$$\rho_v = 458.703 - 4.449 \times \ell \quad (M_2) \quad (9)$$

$$\rho_v = 188.168 - 0.410 \times \ell \quad (M_3) \quad (10)$$

$$\rho_v = 247.732 - 2.481 \times \ell \quad (M_4) \quad (11)$$

$$\rho_v = 4.108 + 0.017 \times \ell \quad (M_5) \quad (12)$$

The dependence of the volume electric resistivity on temperature is represented, for each sample, in Figure 3 and a linear or hyperbolic decrease of ρ_v can be seen when the temperature increases. It may be stated that, within the limits of experimental error, the resistivity dependence on temperature follows the theoretical equation (1).

The equations obtained for the dependence of ρ_v on T using the regression method are:

$$\rho_v = -14.915 + 2635/T \quad (M_1) \quad (13)$$

$$\rho_v = 940.750 - 7.063 \times T \quad (M_2) \quad (14)$$

$$\rho_v = -67.625 + 14018.357/T \quad (M_3) \quad (15)$$

$$\rho_v = 472.282 - 3.465 \times T \quad (M_4) \quad (16)$$

$$\rho_v = -3.654 + 483.038/T \quad (M_5) \quad (17)$$

The simultaneous dependence of volume electric resistivity on the two parameters shows a decrease for both film thickness and temperature, with the exception of sample M_5 for which, as mentioned before, resistivity decreases with film thickness.

The following equations were obtained for the dependence of ρ_v on thickness and temperature:

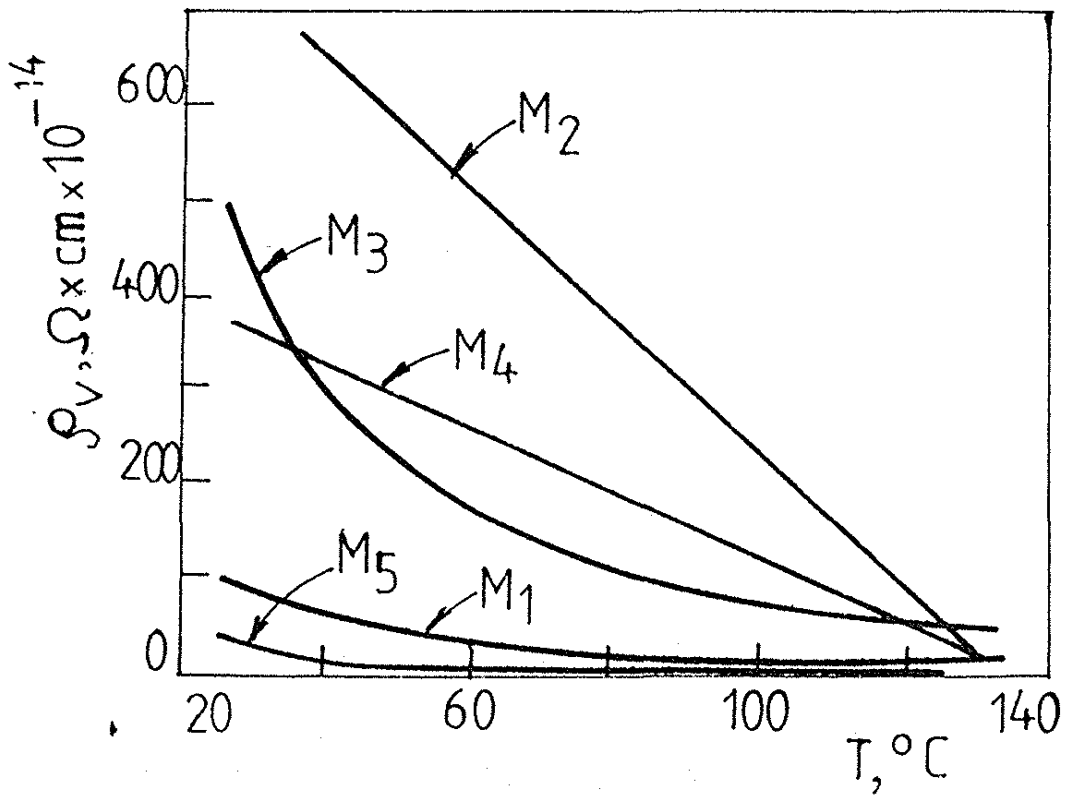
$$\rho_v = 100.588 - 0.422 \times \ell - 0.732 \times T \quad (M_1) \quad (18)$$

$$\rho_v = 1027.933 - 4.458 \times \ell - 7.063 \times T \quad (M_2) \quad (19)$$

$$\rho_v = 487.038 - 0.395 \times \ell - 3.720 \times T \quad (M_3) \quad (20)$$

$$\rho_v = 526.882 - 2.482 \times \ell - 3.465 \times T \quad (M_4) \quad (21)$$

$$\rho_v = 14,648 + 0.017 \times \ell - 0.131 \times T \quad (M_5) \quad (22)$$



M_1 - EPOXY RESIN

M_2 - TITANIUM DIOXIDE

M_3 - MICRONIZED MICA

M_4 - COLLOIDAL ALUMINIUM OXIDE

M_5 - ALUMINIUM SILICATE

FIGURE 3. VARIATION OF VOLUME ELECTRIC RESISTIVITY AS A FUNCTION OF TEMPERATURE FOR THE SAMPLES STUDIED.

The experimental data and the equations obtained using the statistical analysis of the dependence of the volume electric resistivity on film thickness show that ρ_v can not be considered a material constant at a given temperature, because it decreases continuously when film thickness dimishes. This may be explained by the higher quantity of solvents or by reaction byproducts that remain within a thick film when compared to a thin one, for which removal of these compounds is more complete. Another explanation is that the thicker films crosslink more slowly than thinner ones, which means that the crosslinking process is more advanced for thin films and this produces a higher resistivity.[4]

Regarding the composition of the samples (Table I), the only difference is the nature of the inorganic fillers.

The independence of the volume electric resistivity on film thickness within the temperature range studied when aluminium silicate was the filler is difficult to explain. A constant value might indicate a complete removal of solvents and byproducts. Fillers can alter the volume electric resistivity only at temperatures higher than 200 ºC, when the conduction phenomemon can appear. For titanium dioxide, for example, the electric conductance appears at about 500 ºC.[5]

Figures 2 and 3 show that titanium dioxide gives the highest resistivities for the compositions studied; micronized mica and aluminium oxide have lower but very close performance. The filler free varnish has lower resistivity; the worst filler is aluminium silicate, that decreases the value of resistivity under that measured for the varnish.

The volume electric resistivity does no seem to be a material constant for a given insulator deposited from solution at a given temperature in the range of film thicknesses of practical use because they contain solvents and byproducts resulting from the crosslinking process, in quantities increasing with film thickness.

Titanium dioxide as a filler gives the highest volume electric resitivity. Colloidal aluminium oxide and micronized mica also increase resistivity, but their effect is less pronounced. The lowest value was obtained using aluminium silicate, that decreases the resistivity to values less than those measured for the varnish.

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