PVC Wire Coatings: Part II Characterizations and Performance Predictions

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Theoretical background derived by the authors (1) covering the ageing processes in plasticized PVC is used to characterize the ageing processes in PVC wire coatings. The structural changes during ageing and the state of insulation at its break-down are determined. These experimental data are used to formulate a mathematical description of the ageing process in these systems and to predict the life-time of such wires in use.

Keywords: PVC; plasticized PVC; ageing processes; aircraft wiring systems; insulation break-down; prediction of insulation life-time; PVC structure at break-down

INTRODUCTION

Part 1 of this study covered the dynamics of the ageing process of plasticized PVC in applications such as wire coatings. (1) The ultimate objective of these investigations was determination of the lifetime of wire coasting systems used in modern aircraft. Considering the critical nature of this task from the point of aircraft safety, it was necessary to review the present performance specifications and introduce new analytical methods which take into consideration the ageing processes background presented in the Part 1 of this study. (1) The characterization methods which are required for determination of reliable estimates of the lifetime of PVC wire coating compositions are presented in the second Part of this study along with methods we developed to predict their performance in use.

1. ANALYTICAL TECHNIQUES

1.1. Thermoanalytical

Thermoanalyzers 1090 'Dupont Instruments' (USA) and TA 3000 'Mettler' (Switzerland) were used for the performance of thermal analyses. First of them permits the investigations in 73–1473 K temperature range, and the second only up to 1273 K. Measurements are performed in isothermic mode with a ± 1 K experimental error, and in a dynamic mode using heating rates, from 0.1 to 100 K/min.

- Thermogravimetric analyzers record the mass loss derivative curve (TG-951 'Dupont' and TG-50 'Mettler'). The mass of specimen is 25–30 mg. Usual weighing error is $\pm 0.5 \times 10^{-3}$ mg. With the differentiating scanning calorimeters the investigations were performed in air (DSC-910 'Dupont' and DSC-30 'Mettler'). The mass of samples was 10–15 mg placed in aluminium caps. Quantitative measurements were performed after preliminary calibrations using sapphire and indium specimens.
- Thermomechanical analyzer (TMA-943 'Dupont' and TMA-40 'Mettler'). Sample mass is 10–20 mg. Usual mistake of size determination is $\pm 1.0 \times 10^{-4}$ mm. Investigations were performed at 20 g load and 10 K/min rate of temperature increase.
- Dynamic mechanical analyzer (DMA-982 'Dupont'). The investigation was carried out on samples of standard $(3.0 \pm 0.1) \times (6.0 \pm 0.1)$ mm size and (1.0 ± 0.1) mm thickness.

1.2. Spectroscopy

Fourrier IR-spectrometer 'Qualimatic' Digilab (USA) was used for obtaining IR-spectra. This instrument is a single-beam spectrometer with Michelson interpherometer. Spectra were recorded in 4400–400 cm^{-1} range, the maximum resolution was ± 0.1 cm^{-1}; argon was used as the working gas phase (pressure 2 atm., flow rate 600 l/hour). IR-spectra of penetration and reflection were obtained. Sample sizes were $(2.0 \pm 0.1) \times (5.0 \pm 0.1)$ mm.

An infrared microspectrometer was used for obtaining IR-spectra (of reflection and penetration) of microsamples having areas up to 20 μm^2.

UV-spectra of samples were investigated on UV-spectrometer SP-800 Pye Unicam (UK) in 185–700 nm range.

1.3. Chromatography

Chromatographic analysis was performed using the gas-liquid chromatograph of 'Light' type. A column 1000 mm long and 3 mm in diameter, filled by Chromaton (particle diameter is 25–32 μm) containing Apieson L liquid phase, was used for plasticizer analysis. Temperature of the column was 563 K and that of evaporator and detector −623 and 573 K, respectively; current in detector was 80 A. Plasticizer solution in diethyl ester (specimen size was 50 μm) was introduced directly into the evaporator by a microinjector.

Fluid high-pressure chromatography was performed on fluid 880 Dupont chromatograph in the regime of adsorptional and gel-penetrating chromatography. Zorbax and SE-100 columns were applied, respectively, in connection with SE-500 column. The moving phase was tetrafuran of optical purity, the specimen volume was 100 μl having 0.4% concentration; the detector used was differential refractometer with 0.2 sensitivity; ultra-violent spectrometer (wavelength from 200 nm to visible range) and infra-red spectrometer (wavelength from 2.15 to 15 μm) were also used.

1.4. Mechanical

Mechanical properties were investigated on universal test-machine Instron-1122 (UK). The rate of deformation was 0.05–1000 mm/min, usual experimental error was $\pm 0.1\%$.

Microporous structure of samples was investigated on porometer Autopore 9200 Cultronics (France). The apparatus works in automatic regime and allows one to measure the total volume and surface area of pores, volumetric and specific density, and pore distribution by sizes. Mercury was used as the penetrating liquid. Pores sized from 200 to 0.003 μm are measured in the range of applied pressures from 2 to 4200 kg/cm^2. Pore radius is determined from the following expression:

$$r = \frac{2\sigma \cos \Theta}{P},$$
(1)

here r is radius of a cylindric pore; σ is mercury surface tension (480 dyn/cm); Θ is contact angle ($\sim 140°$); P is applied pressure. Sample volume is 2–5 cm^3, resolution by mercury volume is 5×10^{-4} cm^3, common error at pressure measurement is $\pm 0.5\%$.

Centrifuge T-24 Intermed (Germany) was used for determination of adhesion forces. Maximal rate is 16,000 rot/min.

Linear sizes during ageing were determined with the accuracy ± 0.1 mm on samples having initial sizes of $(20.0 \pm 0.1) \times (100.0 \pm 0.1)$ mm. Thicknesses were measured by micrometer with common error of ± 0.1 mm.

Lead salt concentration in samples was measured by atomic-absorption spectrophotometer 1000 Perkin Elmer (USA) using acetylene-air mixture. Minimal concentration was 1×10^{-4} mmol/l. Calibration was performed by standard solutions.

2. FUNDAMENTALS OF PLASTICIZED PVC INVESTIGATIONS

During storage and exploitation plasticized PVC articles are subjected to influence of temperature, humidity, air oxygen. They are also exposed to mechanical loads, aggressive media and their vapors, ozone, ionizing radiations and physical fields.

The analysis of literature data shows that the following processes contribute to ageing of the material, and decrease its performance in use: in (see Fig. 1):

● Dehydrochlorination leads to HCl extraction and formation of polyene sequences in PVC macromolecules. The Quantity and length of polyene sequences define the color of the material from light-brown to black;

● Thermoxidative degradation induces the decrease of molecular mass and formation of carbonyl-containing groups;

● Diffusional plasticizer desorption leads to the increase of vitrification temperature of the material;

Factors of ageing	Physical and chemical properties	Exploitational properties
Temperature Oxygen Humidity	Diffusional desorption of plasticizers and stabilizers	Mechanical and dielectric properties
Mechanical loads	Dehydrochlorination	Colour
Aggressive media	Thermoxidative degradation	Sorption-diffusional Properties
Ionizing radiations	Water sorption	

FIGURE 1   Ageing factors and processes taking place in plasticized PVC ageing.

● Processes of sorption of water and other low-molecular compounds by the material from the surrounding.

Chemical and physical processes proceed simultaneously during ageing of plasticized PVC. This changes the chemical composition and structure of the material. However, these processes can proceed with various rates and only some of them will have significant effect on use properties. To solve these problems it is necessary:

1. To determine processes proceeding in polymer material during ageing, which are responsible for the change of use properties,
2. To derive kinetic equations which connect the indeces of use property with time and factors of ageing.

The set of these kinetic data represents the model of ageing.

The characteristic indeces of ageing are used for quantitative estimation of polymer material properties on ageing. They are parameters which characterize the performance potential of the material in use. Indeces of exploitational properties of the material, indirectly connected to exploitational properties, are most often chosen as characteristic indexes of ageing. They are, for example, oxygen absorption at thermoxidative degradation, HCl extraction in dehydrochlorination, material mass decrease at plasticizer desorption, etc.

Characteristic indexes of ageing must:

● Uniformally characterize the present process proceeding during ageing;
● Be easily registered;
● Change when the material in article is still suitable for exploitation.

The analysis of data from literature shows that the main process in plasticized PVC-on ageing at room temperatures is, probably, the diffusional desorption of plasticizer. At temperatures over 60°C proceeding of thermoxidative degradation is also probable, and it may be accompanied by dehydrochlorination.

3. KINETICS OF PLASTICIZED PVC AGEING

3.1. Materials

The investigations were performed using the insulation of BWPV wires, used for very long time (maximal exploitation time was 28

years), and the insulation of wires of same trade marks, which were not used and were received from the manufacturer not more than a year before. In addition PVC films of the following type were also investigated: PVC C-63M-100 mass parts, DOP-24 mass parts, cadmium stearate-3 mass parts, and specially prepared samples with different di-octylphthalate concentrations.

3.2. Diffusional Desorption of Plasticizer

Plasticizer yield from plasticized PVC is a two-stage process that includes:

- Plasticizer diffusion to article surface;
- Plasticizer desorption from article surface into the surrounding.

As plasticizer concentration in the material decreases during ageing, it is wrong to use the second Fick equation for description of the diffusion process. In this case empiric equations are used, for example:

$$m_t = Kt^n, \tag{2}$$

here m_t is plasticizer amount, extracted during time t; n and K are parameters (n changes in the range $0.5 \leqslant n \leqslant 1$).

Plasticizer concentration on the material-air interface is determined according to the mass transfer laws, the simplest of which is the following:

$$m_t = \beta S(\bar{C}_0 - C_{air})t, \tag{3}$$

here β is the mass transfer coefficient.

The limiting stage of the process can be determined by m_t dependence on article thickness.

Plasticizer Amount Determination in PVC Products
Experimental Data Analysis

The following techniques were used for determination of plasticizer amount in PVC: thermogravimetric technique, chromatographic technique and UV-spectrophotometric technique.

Thermogravimetric Technique Heating of PVC samples (25–30 mg) to 400°C causes the decrease of sample mass, induced by plasticizer desorption as well as by PVC dehydrochlorination. Figure 2 shows curves of the mass change of plasticized samples with different plasticizer concentration during heating at the rate of 10 K/min. The mass decrease practically stops at 400°C, and it is possible to calculate plasticizer content in the product by total mass loss. Figure 2 also shows the linear dependence between remaining mass $^{m_0-m}400°/m_0$ and dioctylphthalate amount in the initial material.
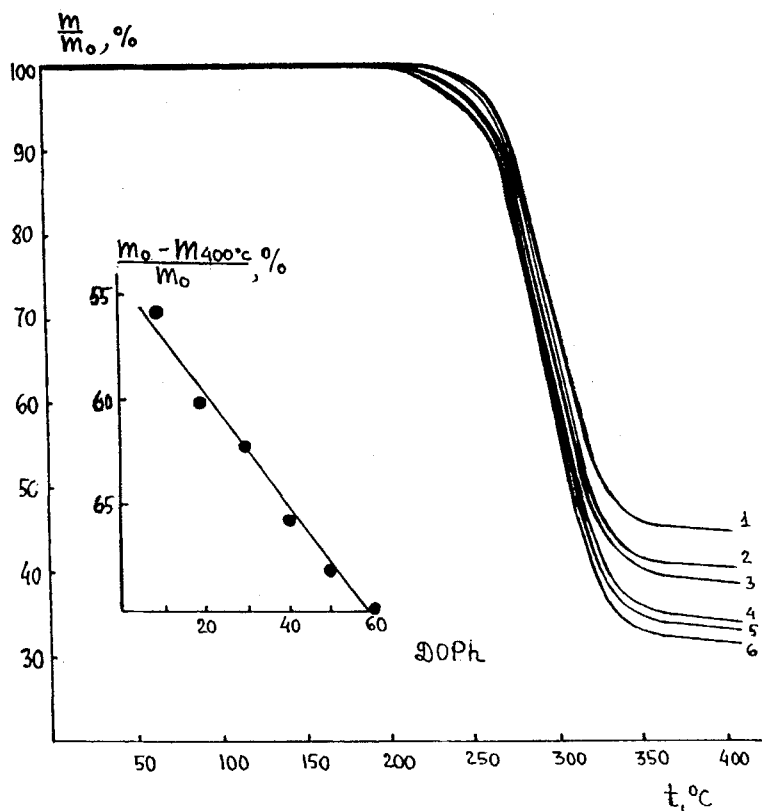

FIGURE 2 a) The change of PVC relative mass at heating at 10 K/min rate. Concentration of di-octylphthalate: 1–10; 2–20; 3–30; 4–40; 5–50; 6–60 mass parts per 100 mass parts of PVC, respectively. b) The dependence of the mass loss on di-octylphthalate concentration at heating to 400°C.

Experiments showed that if PVC sample is exposed at 300°C during 25 min, we can reliably calculate the remaining mass of the sample after plasticizer desorption and PVC dehydrochlorination.

Chromatographic Technique Extraction of plasticizers by diethyl ether was performed at 45°C during 6 hours. Solution of plasticizers in diethyl ether was analyzed on gas-fluid chromatograph.

Figure 3 shows typical chromatogram of three plasticizers and leveling lines, which correlate the peak areas with plasticizer amounts in injected probes.

The method allows one to analyze mixtures of plasticizers, however it is impossible to completely extract plasticizers under present conditions. The residue after extraction by diethyl ether amounts to 5–6%.

UV-Spectrophotometric technique PVC specimen was dissolved in optically pure tetrahydrofuran at 80°C during 1 hour. The solution was filtered by 'Millipore' filter with average pore size of 0.45 μm.

Di-octylphthalate solution in tetrahydrofuran possesses two absorption bands at 230 and 274 nm (see Fig. 4). Absorption coefficients obtained from the leveling experiments equal 19.3 ± 0.2 and 3.2 ± 0.1 l/mg × cm, respectively. Plasticizer concentration is calculated by the
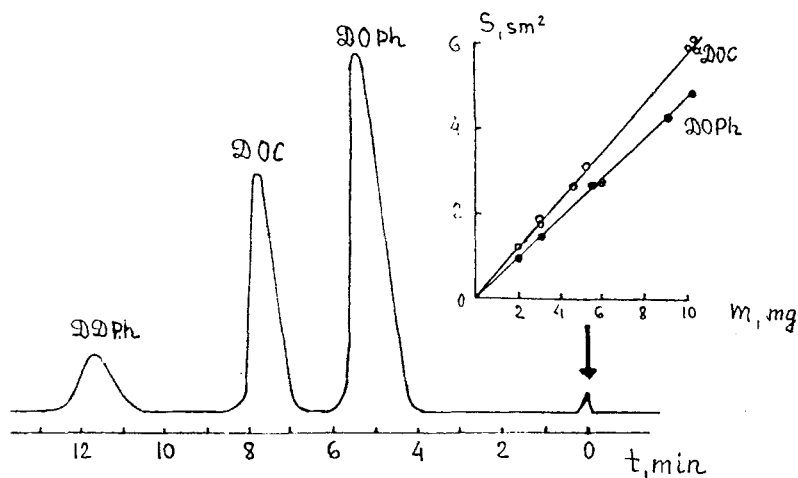
FIGURE 3 Chromatogram of the mixture of plasticizers and leveling dependence. DDP is di-isodecylphthalate, DOP is di-octylphthalate, DOC is di-octylcebacynate.
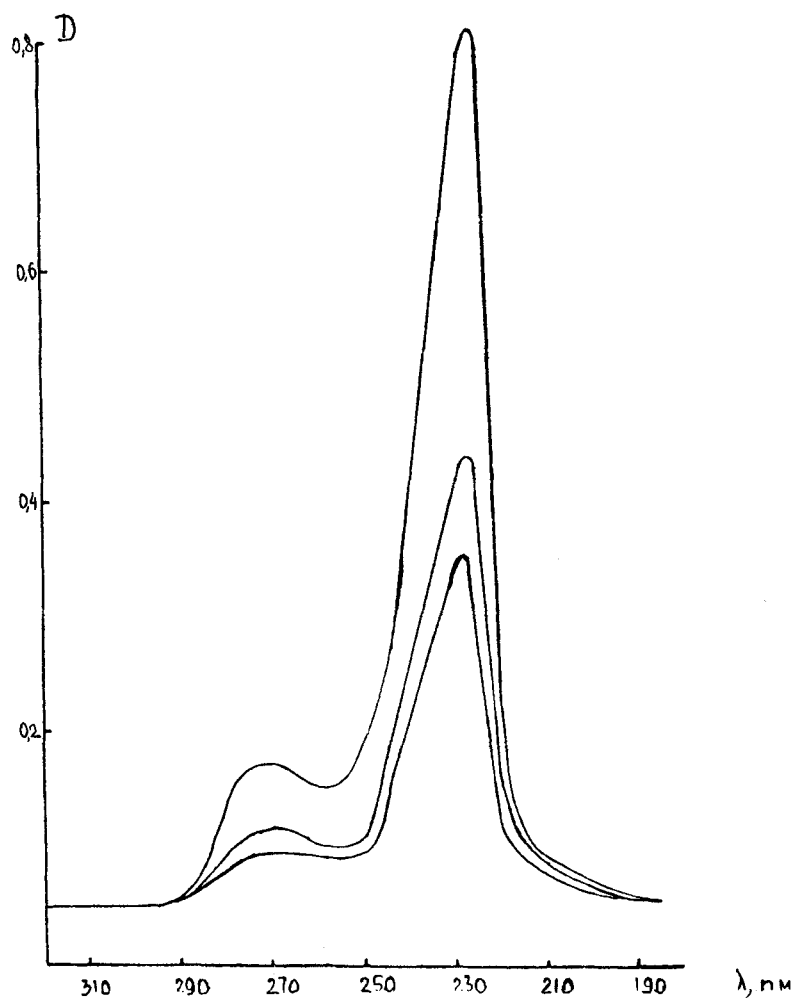
FIGURE 4   UV-spectra of di-octylphthalate in tetrahydrofuran.

following formula:

$$C = \frac{DVl}{\varepsilon m} \times 100,$$ (4)

here D is optical density; ε is absorption coefficient; V is the solution volume; m is the mass of the probe analyzed; l is optical cuvette thickness.

The method allows us to analyze the concentration of one or mixed (several) plasticizers in PVC with a 1–2% accuracy.

Description of the Plasticizer Diffusional Desorption from the Change of Sample Mass

Kinetic curves of diffusional desorption of plasticizers in 20–165°C temperature range are satisfactorily described by the following empiric equation:

$$\ln\frac{m_0}{m_t} = Kt^{0.62 \pm 0.03},$$ (5)

here K is desorption constant.

Figure 5 shows typical treatment of experimental data of di-octyl-phthalate desorption from PVC at 120 and 135°C; the data were obtained by the thermogravimetric technique.

The equation (5) describes experimental data obtained by the UV-spectrophotometric technique. However, the data obtained by the chromatographic technique (see Fig. 6) do not follow this equation. This is, probably, due to insufficient accuracy of the method.

Figure 7 shows the dependence of diffusional desorption of dioctyl-phthalate from PVC in $\ln m_0/m_t - Kt^{0.62}$ coordinates. It shows that the process probably proceeds by the same mechanism in the entire temperature range.

Changes of Linear Sizes of PVC Articles

Linear and volumetric shrinkage of thin films were determined using the following expressions

$$\Delta l = \frac{l_0 - l_t}{l_0} \times 100,$$ (6)

$$\Delta V = \frac{V_0 - V_t}{V_0} \times 100,$$ (7)

here l_0 and V_0 are initial values; l_t and V_t are values after ageing during time t.
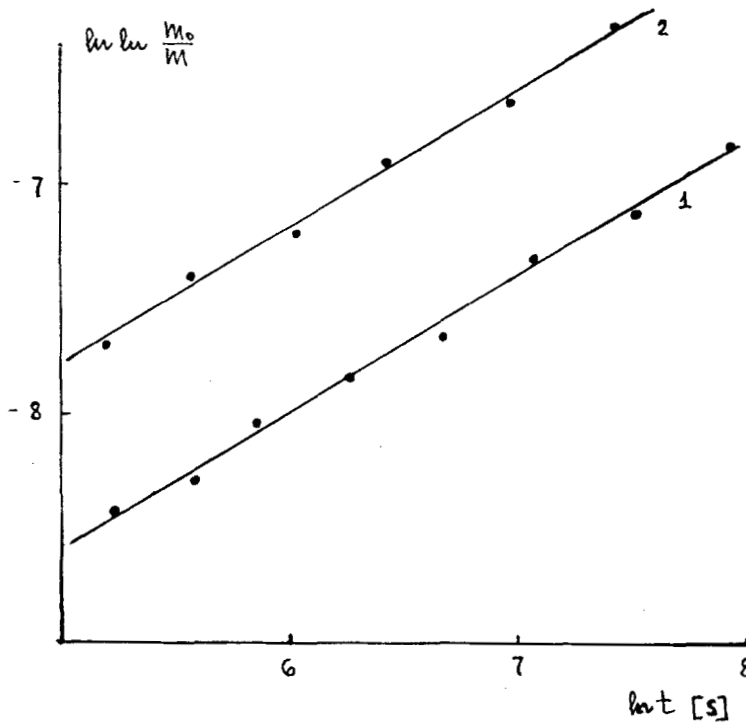
FIGURE 5 The dependence of $\ln(m_0/m)$ on $\ln t$ for diffusional desorption of di-octyl-phthalate from PVC product at 135 (1) and 120°C (2), respectively.

Shrinkage of wire insulation by length and diameter proceeded according to formulas (36) and (37) and also (38) that follows:

$$\Delta d = \frac{d_0 - d_t}{d_0} \times 100, \qquad (8)$$

here d_0 and d_t are initial and current values, respectively.

Samples having sizes of 100×200 mm were investigated in experiments with thin films.

Figure 8 shows changes of mass and linear sizes of thin PVC films on heating in air at 150°C. The total change of mass in $(27.0 \pm 0.2)\%$ at the plateau level. The mass change is described by the equation (35), the rate constant equals $2 \times 10^{-13}\,\mathrm{s}^{-5/8}$. Linear size change is

FIGURE 6   Kinetic curves of di-octylphthalate desorption from PVC product at temperatures 1–120°C, 2–135°C, 3–150°C and 4–165°C, respectively.

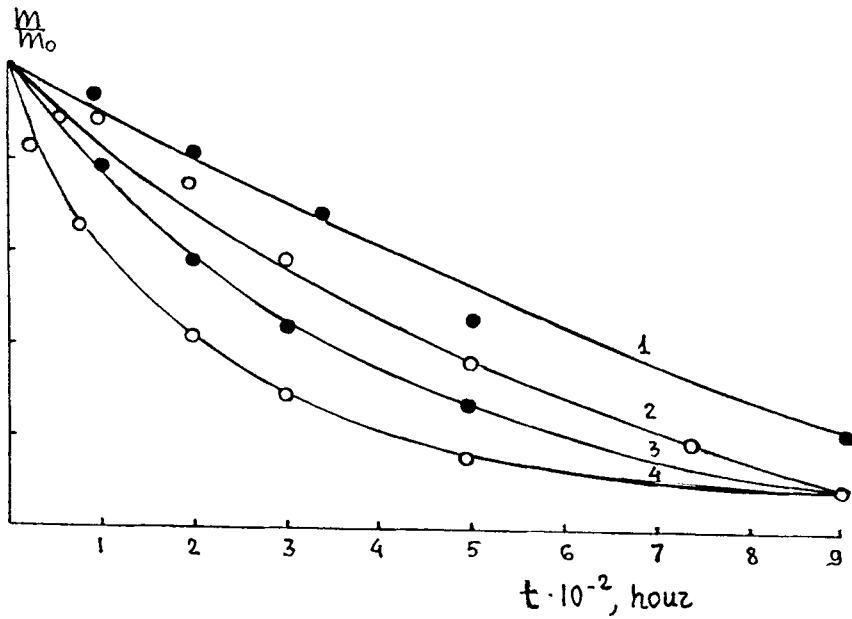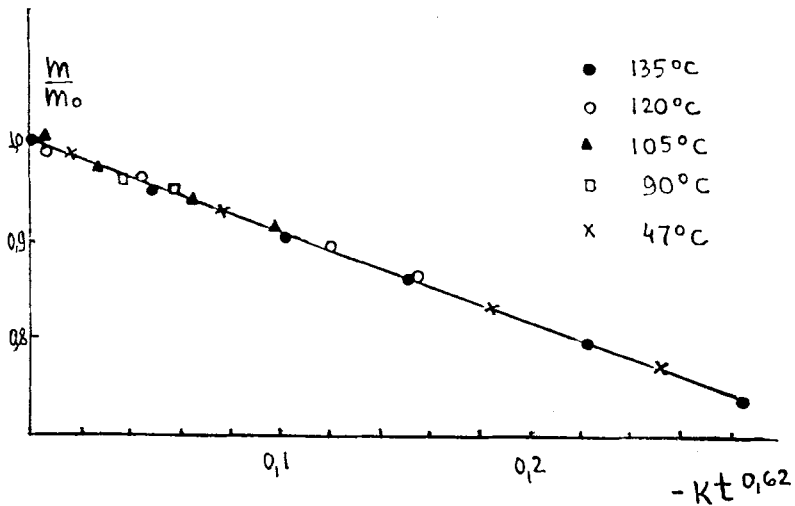FIGURE 7   Generalized kinetic dependence of the diffusional desorption of di-octylphthalate from PVC product in coordinates $(m_0/m_t) - Kt^{0.62}$.
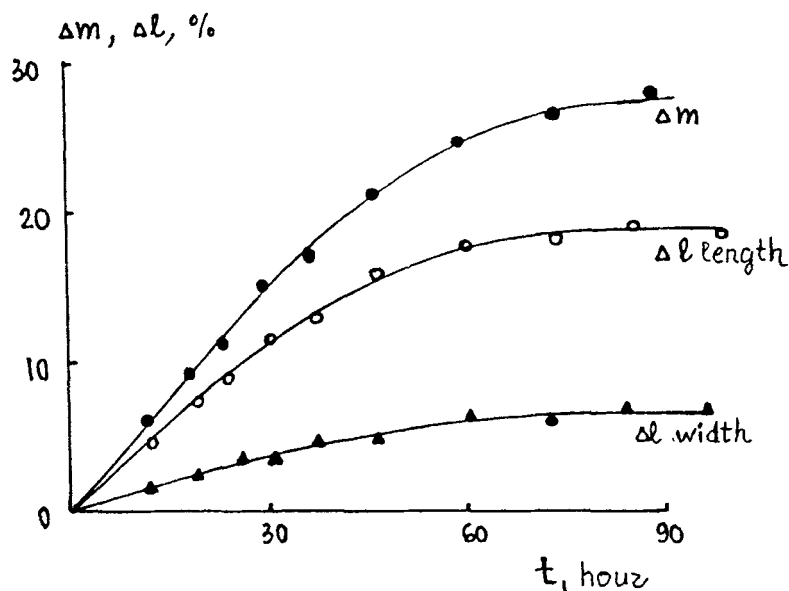
FIGURE 8 The change of mass and linear sizes of PVC product thin film at heating in air up to 150°C.

satisfactorily described by the first order equation:

$$\Delta l = \Delta l_x [1 - \exp(-Kt)]. \tag{9}$$

The value of Δl_x was $(17.0 \pm 0.3)\%$ by length and $(7.0 \pm 0.4)\%$ by width, respectively. The value of the rate constant was $(5.5 \pm 0.2) \times 10^{-6} \, \mathrm{s}^{-1}$. The limit volume change of the PVC film is $(23.0 \pm 0.4)\%$.

It should be mentioned that until the mass change reaches $\sim 25\%$ the linear dependence between Δm and ΔV takes place, and after this point the break from the above mentioned dependence occurs (see Fig. 9).

The change of linear sizes of wire insulation (100 mm sample length) proceeds at a smaller degree than with PVC films under the same ageing conditions. At the same mass change $((27.0 \pm 0.2)\%)$ the change of length was $(9.0 \pm 0.2)\%$, and $(3.8 \pm 0.2)\%$ of diameter (see Fig. 10). Lower shrinkage value by length of wire insulation is explained by the existence of adhesion forces of polymer to metal, which inhibit the wire insulation shrinkage.
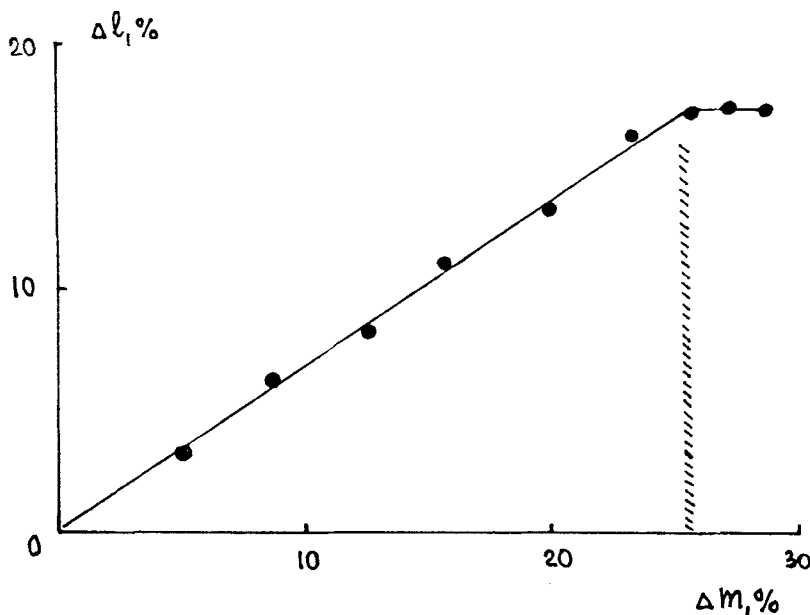
FIGURE 9 The dependence of Δm on Δl (length) of PVC product at heating in air at 150°C.

3.3. Thermoxidative Degradation

The analysis of literature data shows that thermoxidative degradation of polyvinylchloride is accompanied by dehydrochlorination. In such a manner it is advisable to follow the thermoxidative degradation by the change of molecular-mass distribution of polyvinylchloride and by double bond accumulation.

Molecular-Mass Distribution of Polyvinylchloride

Molecular-mass distribution (MMD) of polyvinylchloride was determined by gelpenetrating chromatography technique. Both initial and aged PVC samples possessed bimodal distribution with peaks corresponding to hold-back times of (4.72 ± 0.03) and (7.96 ± 0.02) min. Corresponding values of the viscosity average molecular mass of PVC are 4.8×10^4 (A) and 3.6 ± 10^3 (B), respectively.

Table I shows ratios of PVC MMD components at ageing at different temperature conditions.
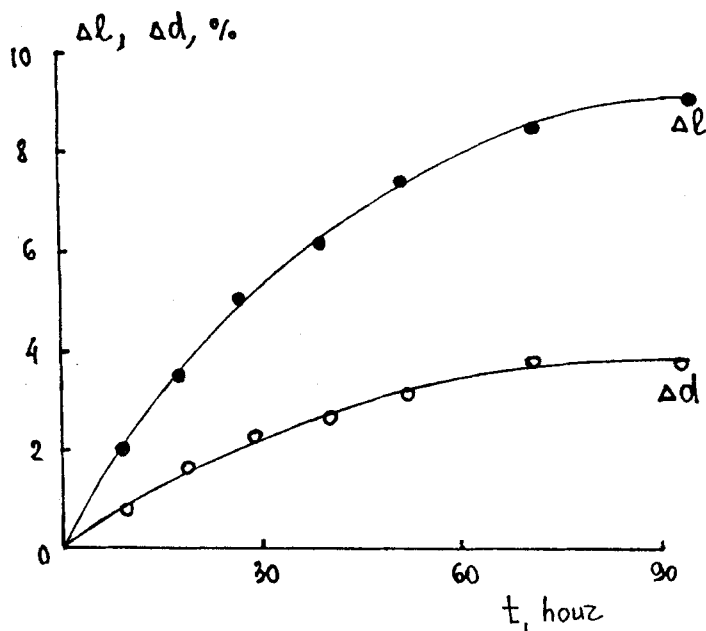
FIGURE 10   The change of length and diameter of wire insulation (sample length is 100 mm) at heating in air at 150°C.

TABLE I   Correlation of PVC MMD components in different temperature-time regimes of ageing

Time of ageing, hour	Temperature, °C	Parts of PVC MMD components,%	
		A	B
0	20	70.8	29.2
4.4×10^4	20	70.6	29.4
100	70	70.5	29.5
50	80	70.4	29.6
100	100	72.5	27.5
100	110	74.9	25.1
100	120	88.0	12.1

Concentration of high-molecular component (A) increases monotonically on ageing at 140°C, and the peak of low-molecular component (B) completely disappears at 2.5 hours after termination of ageing.

There was no significant change of MMD (> 2%) in PVC samples used under mild conditions during 20–28 years.

Therefore, we can assume that exploitation of PVC articles under mild conditions during 28 years causes no noticeable changes in polymer

MMD. At higher temperatures (> 100° C) the ageing during 100 hours causes significant changes of MMD. The observed increase of high-molecular component is probably, due to cross-linking of low-moelcular PVC fragments.

Dehydrochlorination

Concentration of polyene fragments, formed in dehydrochlorination, was measured by fluid chromatography technique. Zorbax ODS column 250×4.6 mm size was used; the flow rate was 1 ml/min; UV-detector with 333 nm wave-length was used, which sensitivity was 0,02. Tetrahydrofuran was used as the moving phase; probe volume was 50 μl, concentration of dissolved polymer was 0.05%.

The initial polymer possessed the peak (2.12 ± 0.01) min hold-back time. A new peak, possessing (1.76 ± 0.01) min hold-back time, appears on ageing. This peak corresponds to polyene fragments with five or more double bonds. Table II shows the relative amounts of peaks with hold-back times of (2.12 ± 0.01) min (A) and (1.76 ± 0.01) min (B), for different conditions of ageing.

Initial rates of dehydrochlorination were measured by accumulation of polyene fragments in 120–180°C temperature range (see Fig. 11).

The value of effective activation energy was 113 ± 5 kJ/mol, that correlates much better with the activation energy of catalytic dehydrochlorination than with the activation energy of dehydrochlorination in the presence of oxygen.

TABLE II Ratios of peaks of initial and polyene fragment-containing PVC for different temperature-time regimes of ageing

Ageing duration, hour	Temperature, °C	PVC-plasticate trade mark	Parts of peaks, %	
			A	B
0		I–40–13	100	0
1×10^4	70	I–40–13	97.2	2.8
2.2×10^5	17	I–40–13	96.4	3.6
0		I–40–12	100	0
1×10^4	70	I–40–12	97.6	2.4
1.9×10^5	17	I–40–12	97.2	2.8
0		S-70	100	0
1×10^4	70	S-70	97.8	2.2
1.9×10^5	17	S-70	97.6	2.4
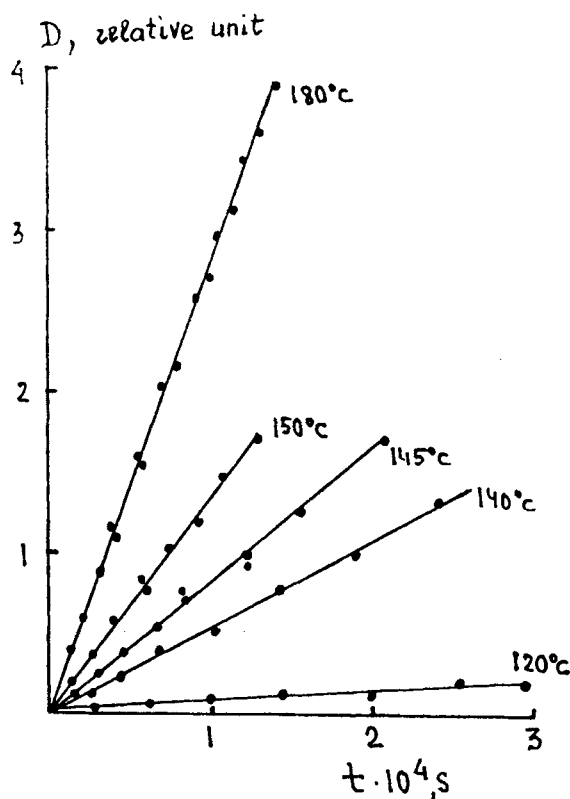
FIGURE 11 Initial rates of dehydrochlorination measured by accumulation of polyene fragments of PVC at different temperatures.

3.4. Microporous Structure

The microporous structure of PVC samples was investigated by mercury porometry. Three samples were investigated. The initial sample produced in 1985; the sample treated by ageing in air at 70°C for 8949 hours; and the sample used for 30 years at ambient temperature of ~ 20°C.

Main characteristics of the microstructure are shown in the Table III.

It is seen that a significant increase of the total pore volume occurs during ageing. It should be noted that the average pore diameter remains practically unchanged, but the pore size distribution changes significantly. For example, if pore content in the inital sample is several percents, the sample treated by 30 year ageing contains 20% of pores, and pores possessing 2–3 μm radius represent a significant fraction.

4. APPLICATION

4.1. Characteristics of Board Wires (BW) with Plasticized PVC Insulation and Application Conditions

BWPV wires are used as a part of board electric network (BEN). These wires are designed to junction under conditions of the environment temperature from -60 to $+70°C$ for voltage below 220 V. Contrary to industrial wires, aviation electric wires must reliably work in a wide range of temperatures, pressures, mechanical loads, in aggressive media and their vapours. The conditions to which the wires are exposed are presented in the Table IV.

The wire insulation is also exposed to air oxygen and ozone, but there is no exposure to ultra-violet radiation.

4.2. Test Results of Board Cable Inspection with Plasticized PVC Insulation Striped from Articles

The following tests of board cables with PVC insulation removed from articles, were performed:

TABLE III

Characteristics	Initial sample	Ageing at 70°C during 8949 hours	Natural ageing at 20°C during 30 years
1. Total pore volume, cm³/g	0.172	0.0381	0.0656
2. Total pore surface, m²/g	4.54	7.64	24.1
3. Average pore diameter, μm	0.015	0.020	0.011
4. Capillarity	4.6	18.1	6.2

TABLE IV   Exploitation factors treating BEN wires of articles '3' and '4'

Sort of treatment	Level of influence
1. The environment temperature, °C	From -60 to $+70°C$
2. Relative humidity, %	98 (at 20°C)
3. Rarefaction, mm Hg	To 140
4. Net voltage, V	
–direct current	Up to 30
–alternate current	Up to 115
5. Alternate current frequency, Hz	400

- Measurements of insulation mass after heating at 350°C for 25 min, % (see Tab. V)

$$\frac{m_0 - m_{350°}}{m_0} = \Delta G;$$

- Measurements of cable diameter;
- Determination of electrical resistance of cable insulation at 70% relative humidity in air and in water;
- Visual inspection in order to find mechanical damages (breaks), color change, soilings, etc.

Tests were carried using 30–50 cm long cable fragments. Values of ΔG parameter were determined as a arithmetic mean of three measurements, with noting in some cases the maximal and minimal values of ΔG. Values of ΔG were measured at the beginning and at the end of cables. In some samples theses values are sufficiently different, which is attributed to differences in use temperatures Typical ΔG parameter values are presented in Table V.

Figure 12 shows the change of relative plasticizer mass in insulation of cables, dismounted from articles after different periods of exploitation.

Plasticizer mass in insulation samples was measured using the following techniques:

- Thermogravimetrically by heating insulation sample at 350°C for 25 min. Plasticizer concentration in the material was calculated by the following equation:

$$C_{pl} = \Delta G - 0.58\,C_{PVC} - \beta C_{ad}, \tag{10}$$

There C_{PVC} and C_{ad} are concentrations of PVC and industrial additives in the initial material, respectively, in mass parts; β is the rate of additive thermodecomposition in the corresponding temperature regime.

- By spectral technique; using UV-spectra of samples desolved in tetrahydrofuran and calculating plasticizer concentration by the equation (34), and IR-spectra by measuring the absorption band intensity at 1720 cm^{-1}.

These investigations allowed us to formulate methods to predict the performance of PVC insulation in use. These methods are described in the section below.

G. E. ZAIKOV *et al.*

TABLE V   Typical results of ΔG measurements for BWPV cables

| No.	Braid label	Cable label	Parameter ΔG values, %				
			Average	Minimum	Maximum	At the beginning of the cable	At the end of the cable
1	2	3	4	5	6	7	8
1	2 END 26						
	(art. '4')	1	72.7	71.2	74.2	71.5	74.0
	The same	2	72.4	70.9	73.4	71.4	73.3
	The same	3	73.2	71.1	76.0	71.7	74.8
2	CL-28						
	(art. '3')						
	4SW8	4	65.5	64.1	66.6	65.3	65.6
	1UW31	5	66.3	64.8	68.6	65.0	67.6
	1UW26	6	66.8	64.8	68.8	65.8	67.8
	1UW24	7	64.8	63.6	66.3	65.1	64.5
	1UW30	7	66.6	64.8	67.5	66.0	67.3
	1UW46	8	66.2	65.1	67.1	66.1	66.4
	2SW1	9	66.0	64.1	67.7	66.1	65.9
	1UW3	10	65.9	64.03	66.9	65.4	66.5
	2SW8	11	66.9	66.2	67.6	67.2	66.7
	1UW26	12	66.5	65.5	67.7	66.5	66.6
	1SW1	13	66.5	64.4	68.3	65.0	68.0
3	CL-4	14	64.5	62.6	65.3	65.0	63.9
	(art. '3')	15	66.9	65.2	68.2	68.1	65.7
		16	66.5	65.6	67.3	66.0	67.1
		17	67.7	65.6	69.8	68.7	6.8
		18	62.3	61.9	62.6	62.5	62.2
		19	65.2	64.5	66.4	65.4	65.0
		20	68.2	65.2	70.7	70.3	66.1
		21	66.9	66.1	69.2	66.2	67.6
		22	68.4	65.5	70.5	70.1	66.8
4	C-265	23	67.4	66.9	67.8	67.3	67.4
	(art. '3')	24	66.4	63.5	68.7	68.0	64.9
		25	64.9	60.5	67.3	66.4	63.3
		26	65.1	64.0	66.4	65.1	65.2
		27	66.9	63.2	75.8	63.9	69.9
		28	74.6	67.3	88.3	81.9	67.3
		29	65.7	64.4	66.9	66.4	65.1
5	CL-59	30	67.0	66.1	67.5	67.2	66.8
	(art. '3')	31	66.6	65.7	67.5	66.2	66.6
6	2 END 20	32	72.7	71.6	73.8	72.7	72.8
	(art. '4')	33	73.3	70.9	75.3	71.7	75.0
7	1 END 17	35	68.2	61.7	73.4	67.5	68.9
	(art. '4')	36	70.2	66.6	73.5	72.8	67.6
8	2 END 18	37	72.8	72.1	74.6	73.3	72.3
	(art. '4')	38	74.6	72.2	79.0	72.4	76.8

C, % mass
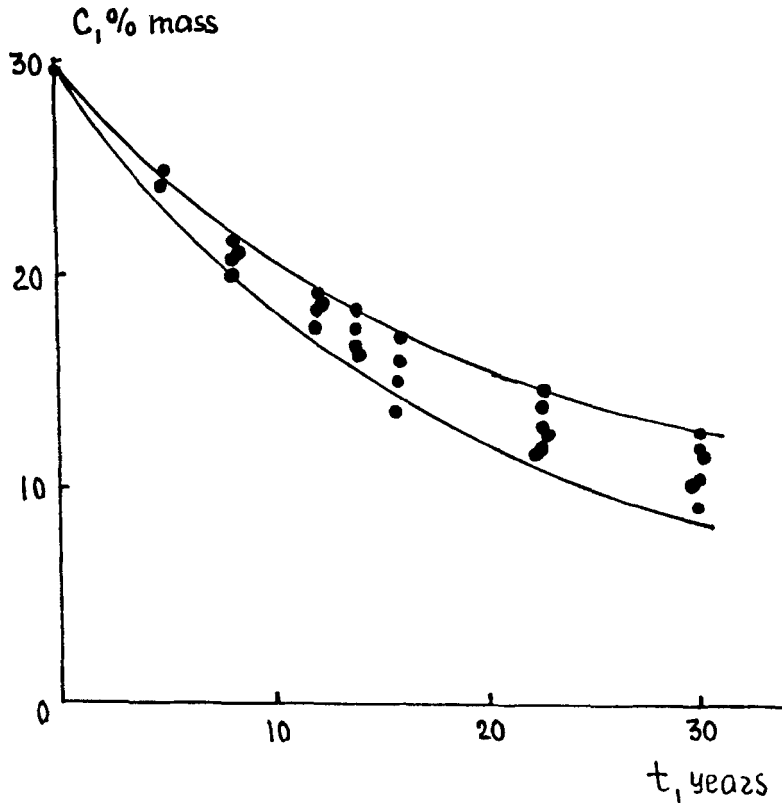
FIGURE 12 The change of plasticizer concentration in mass % in cable isolation dismounted from articles after different periods of exploitation.

5. PERFORMANCE PREDICTIONS

5.1. Mathematical Description and Determination of Plasticized PVC Insulation Break-down

The break-down state is experimentally determined by placing a 1 meter section of cable into water and applying electric current of 10 V to cable. Shorting testifies the insulation break-down caused by the existence of connected holes (channels) filled with water. Such measurements, require a great amount of wires and cannot be used for rapid estimation of board electric network capability.

To solve this problem it was necessary to develop:

- A method of mathematical description of the break-down state, i.e. to characterize this state by parameters of physical and chemical properties, which can be determined experimentally;
- Methods of experimental determination of the break-down state using microamounts of cable insulation, i.e. to provide a fast method for determination of the break-down state;
- A method for predicting the remaining life-time of cables with plasticized PVC insulation based on the established mechanism of ageing.

Plasticized PVC represents a molecular network, incorporated in a plasticizer. Crystallites or globules are lattice points. The predominant process of PVC ageing under exploitation conditions (< 40°C), which causes the change of use properties, is diffusional desorption of plasticizer accompanied by shrinkage of the isolating covering. However, the volume decrease of plasticized PVC is limited by a kinetic factor and article geometry. This leads to formation of pores and accumulation of elastic deformation energy in the material. The pore volume will grow in the material during ageing leading to a connected pore system and the insulation break-down.

The break-down state can be explained using the flow theory, which assumes the existence of a critical fraction of pores, at which the pores form a connected system.

Let us formulate the model of PVC and derive some relevant mathematical results.

1. Initially a Poisson distribution (with intensity μ_0) of O_i centers of 'congenital' pores is set in the volume V with R^3. The pores S_i connected with O_i centers are independent distributed. The initial pore set $D_c = \cup_i^{S_i}$ is divided into linearly connected components, which we consider as 'congenital' pores.

Volumetric concentration of the pore set at time $t = 0$ equals:

$$\lambda_0 = \lim_{V \to R^3} \frac{\mathrm{Vol}(D_v)}{\mathrm{Vol}(V)}. \tag{11}$$

The limit can be easily calculated in terms of μ_0 and distribution S_i. For example, if $S_i = \{X : |X - O_i| \leqslant \xi_i\}$ and $P\{\xi_i E(r_1 r + dr)\} = P(r) dr$,

$$\lambda_0 = \exp\left\{ -\mu_0 \int_0^\infty 4\pi r^2 P(r) dr \right\}. \tag{12}$$

2. The pore development during ageing is more suitable for characterization by the following function:

$$\lambda(t) = \lim \frac{\mathrm{Vol}(D_v(t))}{\mathrm{Vol}(V)}, \qquad (13)$$

here $D_v(t)$ is the set of pores at time t. Time dependence of the distribution S_i should also be taken into account.

The most simple ageing model looks as follows. Micropores appear in the material with the rate V_0, in addition, all pores existing in the volume at time t grow (by normal to $\partial D_j(t)$) with the rate v_1. Initial pores $S_i(0)$ are spheres possessing radius distribution density $P(r)$ and intensity μ_0 at the center.

Diffusional desorption proceeds at constant temperature T, and rates v_0 and v_1 depend on T according to Arrhenius law:

$$v_0(T) = C_0 \exp\left(-\frac{E_0}{T}\right), \qquad (14)$$

$$v_1(T) = C_1 \exp\left(-\frac{E_1}{T}\right). \qquad (15)$$

It can be shown that

$$\lambda(t) = \exp\left\{-P_4(t)\right\}, \qquad (16)$$

here $P_4(t)$ is the order four polynomial, whose coefficients are clearly expressed by μ_0, v_0, v_1 and $P(r)$.

If $v_1 \gg v_0$ and t is not too long, the main role is played by linear terms of the polymonial, which depend on μ_0, v_1 and $P(r)$.

3. Regardless of the mechanism of pore development, the volumetric concentration of pores $\lambda(t)$ grows. Using combinatorial methods, contour technique in particular, we can find that at some critical value λ^*, the flow channels will occur. The correspondent moment $t^*; \lambda(t^*) = \lambda^*$ is the time at which flow threshold is reached.

Mathematical modelling shows that coordination number of pores does not depend on shape of pores and falls in the range of 3.0 ± 0.2. The however volumetric concentration of pores, however,

may change in a wide range, when the flow threshold is reached: from 0.28 for spheres of equal radii to > 0.01 for needle-shaped pores.

4. The result of 3 means that the time of the PVC insulation break-down must be close to t^* and corresponding function defining this state are:

$$P_\xi(x) = 0 \text{ for } x < t^* \text{ and } P_\xi(x) = 1 \text{ for } x > t^*.$$

Deviations from this law indicate the existence of 'congenital' pores.

5. When the critical concentration λ^* is reached, the mechanical and physical properties of PVC system change abruptly.

When the critical pore volume is reached, the system of connected flow channels is formed causing the break-down. The value of critical pore volume can be theoretically calculated taking into account the pores formed and the amount of initial 'congenital' pores.

Taking into account that insulating covering contacts metal wire of a cable, shrinkage due to plasticizer desorption will proceed in radial direction only. The pores formed will, therefore, possess the form of rotation ellipsoids stretched along the interface of polymer contact with metal. The break-down state displays ratio of rotation ellipsoid axises as 2:1. Such pores have a critical value of volumetric concentration of $\sim 5\%$.

5.2. Development of Methods for Experimental Break-down Determination

Analysis of the experimental data showed that two parameters can be recorded with a satisfactory accuracy at PVC plasticized ageing; the remaining amount of plasticizer in the material and, the total volume of pores and their size distribution. Both these parameters can be applied for quantitative characterization of the break-down state.

The following two methods are recommended for detemination of the remaining amount of plasticizer in insulation samples removed from the articles:

- *Thermogravimetric technique*: is used with sample heated to 350°C for 25 min. The calculation of plasticizer amount is performed using the equation (40). The average duration of analysis is 30 min, the relative error is $\pm 4\%$, the minimum of the material amount is 50 mg.
- *IR-spectrum technique*: The intensity of absorption band at 1720 cm^{-1} is used . Preliminary calibration is required. The average duration of analysis is 5 min, the relative error is $\pm 5\%$, the minimal material are is 20 μm^2.

Figure 13 shows the curves of mass change and total pore volume in PVC insulation as a function of exploitation time under normal ambient conditions. The pore volume was calculated from the difference
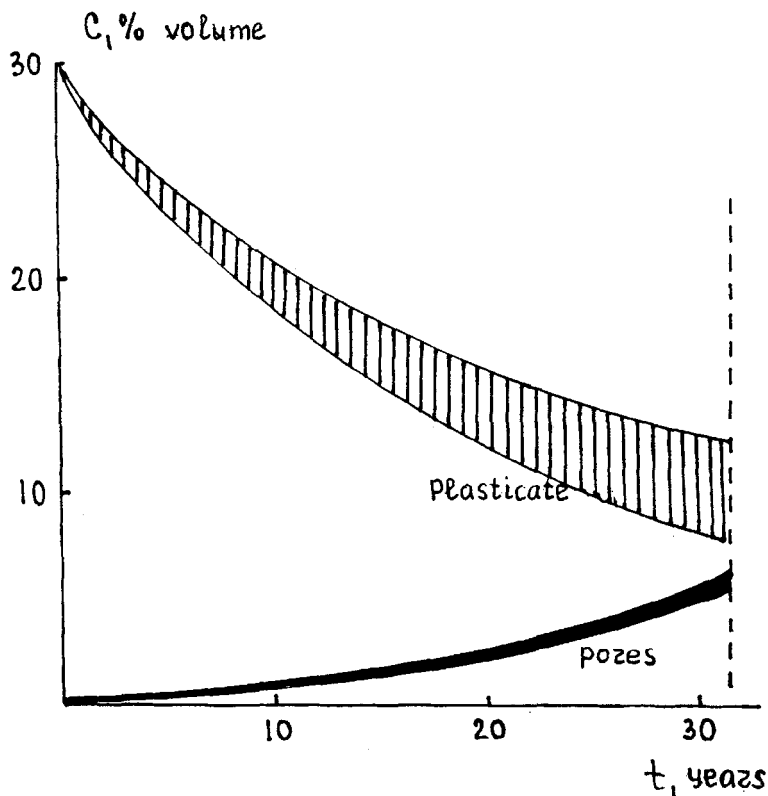

FIGURE 13 Kinetic curves of the change of mass and volume of pores in PVC plasticate isolation depending on exploitation time.

between the mass loss and insulation volume decrease at shrinkage:

$$V_{pour} = \frac{\Delta m_{pl}}{\rho_{pl}} - \Delta V, \qquad (17)$$

here V_{pore} is the pore volume; Δm_{pl} and ρ_{pl} are the mass desorbed plasticizer and plasticizer density, respectively; ΔV^1 is the change of article volume.

This Figure 1 also shows the straight broken line , corresponding to 10% of break-downs obtained in cables removed from articles. To this line correspond 8–11% of remaining plasticizer mass and 5–6% of pore volume.

Consequently, the critical value of volumetric pore concentration (λ^*), to which the break-down state relates, is $5.5 \pm 0.5\%$.

Total volume of pores in the break-down state can be directly determined by mercury pormetry.

As it is seen in the Table III total pore volume in the break-down state is 6.5%, which agrees well with the value obtained from the determinations of plasticizer mass losses and calculation of sample shrinkage. Thus, the experimentally determined critical value of the pore concentration equals the value, calculated theoretically by taking into account the form of pores formed and the amount of initial 'congenital' pores.

5.3. Prediction of the Residual Wire Life-time of Plasticized PVC Insulation

In the previous parts we determined that the break-down state contains 8–11% of residual plasticizer mass and 5–6% of the formed pore volume. Based on these data we can estimate the remaining life-time of the cable according to the Figure 5. If the mass of plasticizer in the material is known, we can calculate the remaining life-time, corresponding to the accepted equivalent temperature (15–20°C). If the calculated exploitation time equals to the real one, the remaining life-time represents the difference of t^* (the break-down state time) and the time of previous exploitation. If calculated exploitation time differs

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[1]The value of ΔV was determined for a part of insulation samples only dismounted from articles.

from the real one by more than 5%, it is necessary to adjust again the equivalent temperature (T_e) by the following equation, derived from the equation (5):

$$T_e = -\frac{E}{R}\left\{\ln\left[\frac{1}{\tau_0^{0.62}}\sum_{j=1}^{n}\Delta\tau_0^{0.62}\exp\left(-\frac{E}{RT_j}\right)\right]\right\}^{-1}, \qquad (18)$$

here E is activation energy of diffusional desorption of plasticizer; τ_0 is mean-statistic time (in hours) of the present exploitation duration; $\Delta\tau_j$ is duration of temperature range with average temperature T_j.

Thus determined T_e must be applied in further calculations.

CONCLUSIONS

1. We demonstrated that at temperatures below 40°C, the diffusional desorption of plasticizer is the key ageing process taking place in the plasticized PVC insulation which ultimately leads to the insulation break-down. At use temperatures exceeding 100°C, dehydrochlorination and thermoxidative degradation also play a significant role in the ageing process.

2. We developed a set of techniques to determine the remaining amount of Plasticizer in PVC: with the thermogravimetric method we determine the material mass after heating the samples to 350°C for 25 min; UV absorption bands at 230 and 270 nm of PVC product solution in tetrahydrofurane and 1720 cm^{-1} band in 1R spectra are also suitable for the determination of the residual plasticizer.

3. It was shown that diffusional desorption of plasticizer at ageing under normal conditions and in rapid tests (> 100°C) is accompanied by a decrease insulation volume. This shrinkage does not completely correspond to the insulation mass loss because of pore formation in the material. Mercury porometry technique is used to determine the total pore volume and pore diameter distribution in PVC samples. It was shown that pore volume and their sizes increase during ageing from 100 to 500 nm. Pores with 3 μm sizes were observed at the break-down state, which is a characteristic feature of the break-down state.

4. A mathematical description of the break-down in plasticized PVC insulation was developed on the basis of the flow theory. It was shown that the break-down state is characterized by critical pore volume, at which the formation of connected flow channel system occurs. These channels provide phase water transfer. The value of the critical pore volume was calculated taking into account the shape of formed pores and the amount of initial pores was also determined.

5. The methods were developed to predict the remaining life-time of cables covered by PVC type insulation. These methods were developed with the help of kinetic equation describing the mass change of plasticizer with the ageing time at an "equivalent" exploitation temperature.

References

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