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TESTING OF THE HEAT RESISTANCE OF POLYVINYL CHLORIDE, PART II

J. Urbanski

ABSTRACT. The color-change and conductivity-measurement methods of determining the heat resistance of polyvinyl chloride are discussed. The conductometric method is found to be superior to the color-change methods since it permits observation of the essence of the phenomenon of material composition and quantitative changes in the service properties of a material.

2. Methods Based on Color Change

Changes in the coloration of polyvinyl chloride and similar materials /370* under the influence of heating coincide with the conductometric curves only in the event of stabilization by compounds excerting a certain inhibitory influence on this phenomena, and thus chiefly organic tin compounds. On the other hand, this agreement is not obtained when the stabilizer added to the PVC acts only as an HCl acceptor and exerts no inhibitory affect on the occurrence of polyene systems (Ca and Pb salts). Hence the need arises for parallel testing of PVC by the method based on eduction of hydrogen chloride and the color change method.

In accordance with Polish Standard PN-60/C-89064 the heat resistance of PVC is tested as follows by the color change method:

An aluminum cylinder of a diameter of 15 mm and a height of 28 mm is placed in a test tube of standardized dimensions (diameter 16 mm, length 150 mm, wall thickness 0.4 mm). One of the bases of this cylinder is rounded in shape so as to fit the bottom of the test tube, and the other, pointing to the top of the test tube, is flat. A certain number of such test tubes, depending on the duration of measurement (which is selected so that it will be possible to observe color change at five-minute intervals) are placed at a depth of five to six cm in an oil bath heated to a temperature so selected that the period of blackening of the specimen will amount to 60 to 120 minutes. After the lapse of 15 minutes a disk of the foil to be tested is introduced into each

* Numbers in the margin indicate pagination in the foreign text.

test tube, and pressed tightly against the cylinder in the test tube by means of a second aluminum cylinder with two flat bases of a diameter of 15 mm and a height of 30 mm. The test tubes are removed from the bath in succession at intervals of five minutes and left to cool for five minutes, and then the disks being tested are removed from them. These disks are placed on white paper in the sequence in which they were removed from the heating bath. A disk of unheated foil is put in first place.

The method described permits comparative evaluation of the behavior of PVC and derivative products during processing at elevated temperatures (120 - 240°).

The method proposed to the ISO by the West German delegation is quite similar to that of the Polish Standard. In this method the disk of the foil to be tested is placed on a hemisphere of aluminum resting on the bottom of a test tube. To protect the test tube against the influence of air, as in the regulation previously cited, the test tube is covered during heating with a disk of the same metal. The thermal stability is determined by two points: the time after which the first visible color change occurs and the time required for darkening of the specimen; determination of the latter quantity entails difficulties when the material darkens continuously.

Both of the methods referred to are characterized by great simplicity. The color change method developed in Caechoslovakia abandons this simplicity to a certain extent in favor of greater certainty and objectivity of the results obtained. This method permits approximate quantitative determination of the darkening of a material on heating.

Samples are heated in an air bath at a specified temperature. Every five to ten minutes the specimens are removed from the bath and compared in transmitted light from a darkening scale represented by ten standard glass plates blackened with carbon. These plates pass light over the range from 0 to 90%; the individual degrees of the scale in question differ from one another by 10% in relation to the total intensity of the incident sunlight.

A diagram is prepared with the results obtained, the time of heating being plotted on the x-axis and the degree of light absorption (%) on the y-axis. From this diagram one can determine the moment from which the changes and coloration become more rapid. A derivative function diagram is prepared in the case of continuous change in coloration.

Even more certain and more accurate results may be obtained by employing in place of the scale described a photometer, which measures the intensity of light reflected from the material subjected to heating; the specimens are then placed on hard white paper.

The results obtained by means of these quantitative and semi-quantitative methods based on color change, although more valuable than those obtained on /371
the basis of the simple visual methods described above, do not provide a simple and unambiguous answer to the question of the behavior of a specimen of material on heating, since they must be supplemented, like the results of these

methods, with information relating to the changes in dimensions and to atypical and uneven color changes.

In order not to omit any of the more important methods of testing the heat resistance of PVC based on color change, mention should be made here of technological tests [1]. In these tests stabilized mixtures are subjected either to protracted rolling, the external appearance and coloration of foil specimens being determined at certain intervals, or to brief intermixing on cylinders (for about five minutes) followed by heating in a thermostat-controlled drier.

The technological methods permit practical evaluation of the effectiveness of action of the stabilizers employed during the processing of the material tested. They are applied chiefly in the case of suspension PVC.

3. Method Based on Measurement of Conductivity of Material

Although the methods based on color changes permits satisfactory observation of the changes occurring in a material during processing, as was pointed out above, it is difficult to select any universal formula for these changes, since the most widely varying colorations may occur, depending on the class of product: bronze, violet, yellow, yellow-green, or orange. The methods based on eduction of hydrogen chloride, in turn, do not give a true picture of the relationships prevailing during the processing of the material.

In a search for a better method of testing the thermal stability of PVC, J. Novak (Vyzkumny Ustav Gumarenske a Plastikarske Technologie in Gottwald) has in recent years developed a method of testing the thermal stability of PVC based on the phenomenon of change in the electrical conductivity of a heated material [2]. Judging by the results presented by this author, this method is a combination of the best methods of the groups described above, since it permits observation both of the essence of the phenomenon of decomposition of a material and of the accompanying quantitative changes in its service properties.

The curves obtained by J. Novak in testing PVC by the method described (curve 1) are shown in Figure 1. A certain drop in conductivity is observed during the initial period. This effect is caused by the occurrence of bubbles due to release of water vapor or softener. The central section of the curve corresponds to the period of action of the stabilizer inhibiting decomposition of the material up to the moment of total deactivation. The terminal, nearly vertical, section of the curve corresponds to the abrupt decomposition of the material following total depletion of the stabilizer.

This method has been used to investigate both pure polymers and the most varied mixtures based on PVC, agreement between variations in electrical conductivity and color change always being found.

On the other hand, higher results are usually obtained by the method of measuring the electrical conductivity of an aqueous solution of decomposition products, as recently demonstrated by the investigations of J. Novak [3], the

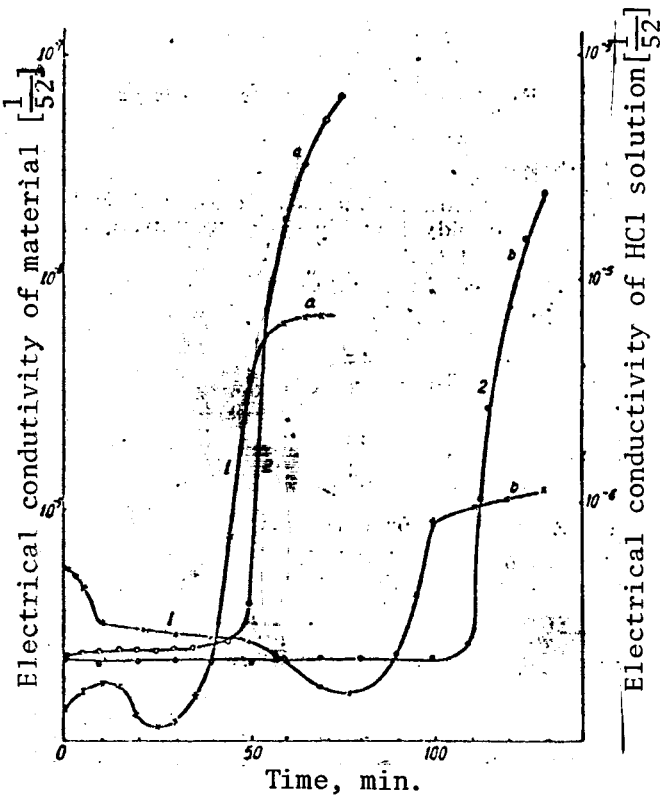

Fig. 1. Comparison of Results of Conductometric Methods: a - Unstabilized Suspension PVC, Temperature 175°; b - Suspension PVC - 100 parts, Palatinol AH-20 parts, dibutyl 10 two- (2-ethylohexylomaleate) - 2 parts, Temperature 175°. 1 - Results of Measurements of Electrical Conductivity of PVC. 2 - Results of Measurements of Electrical Conductivity of Aqueous Solution of HCl from Decomposition Products.

results of which are shown by curve 2 (Fig. 1). This permits the assumption that the material undergoes substantial internal transformations before the eduction of hydrogen chloride begins.

The measurements of the conductivity of a material are made in special equipment the fundamental components of which are two aluminum electrodes heated to a constant and the same temperature (Fig. 2). One of them is fixed and the other may be displaced within the limits of 30 mm.

A specimen of PVC in the form of a disk of a diameter of 3.5 cm and approximately 1 mm thick is secured between aluminum rings, cellophane disks of a thickness of 0.02 to 0.05 mm first being inserted between the rings and the material tested. If the material /372 tested is in the form of a paste or fine grains, a teflon ring is placed on the first disk, then the interior is filled and covered with another disk. The entire arrangement together with the specimen is suspended between electrodes previously heated to the proper measuring temperature and a stop watch is set in operation. It should be noted that accurate knowledge of the thickness of the layer of material tested is not necessary, since its behavior is characterized by the changes in conductivity and not by the absolute value of the latter.

The resistance of the heated material is measured at intervals of three to five minutes by means of an ohmmeter with a measuring range of 10^5 to 10^{11} ohms and a curve is drawn in the conductivity-time logarithmic system. The time after which the conductivity of the material begins to rise abruptly constitutes a gage of the thermal stability of the material.

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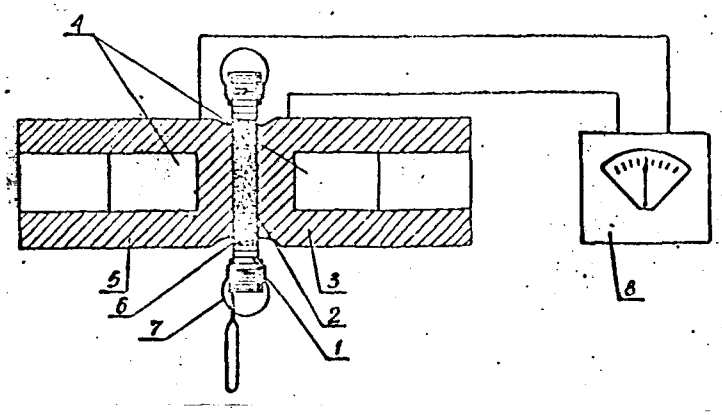

Fig. 2a. Diagram of Equipment for Measurement of Electrical Conductivity of Heated PVC: 1 - Teflon Ring; 2 - Material Tested; 3 - Fixed Electrode; 4 - Moving Electrode; 5 - Resistance Heater; 6 - Cellophane (foil) Spacer; 7 - Clamp; 8 - Ohmmeter.

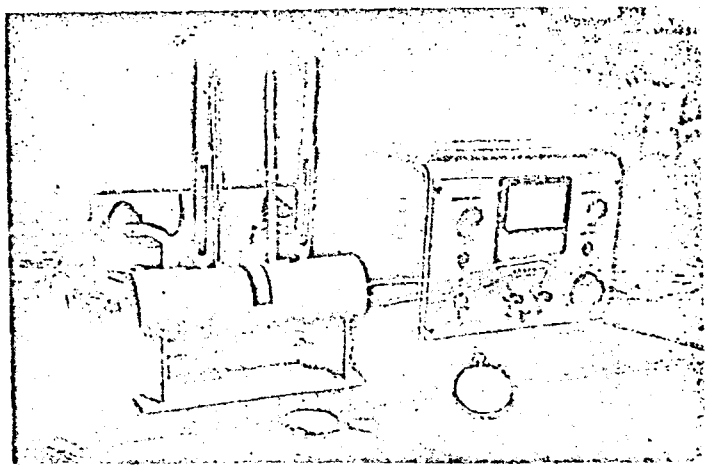

Fig. 2b. Equipment for Measuring Electrical Conductivity of Heated PVC.

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