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ISO RECOMMENDATION

R 182

PLASTICS

DETERMINATION OF THE THERMAL STABILITY OF POLYVINYL CHLORIDE AND RELATED COPOLYMERS AND THEIR COMPOUNDS BY SPLITTING OFF OF HYDROGEN CHLORIDE

2nd EDITION

June 1970

This second edition supersedes the first edition

Printed in Switzerland

Also issued in French and Russian. Copies to be obtained through the national standards organizations.

BRIEF HISTORY

The ISO Recommendation R 182, *Determination of the thermal stability of polyvinyl chloride and related copolymers and their compounds by the Congo red method,* was drawn up by Technical Committee ISO/TC 61, *Plastics,* the Secretariat of which is held by the American National Standards Institute (ANSI).

Work on this question led to the adoption of Draft ISO Recommendation No. 216 which was circulated to all the ISO Member Bodies in May 1959. It was approved by 22 Member Bodies. One Member Body (France) opposed the approval of the Draft.

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in February 1961, to accept it as an ISO RECOMMENDATION.

BRIEF HISTORY RELATING TO THE 2nd EDITION

In 1964, ISO/TC 61 Secretariat decided to prepare a draft method combining the Congo red method and the pH method, and a Draft ISO Recommendation (No. 1301) was adopted for the revision of ISO Recommendation R 182-1961.

In July 1967, this Draft ISO Recommendation was circulated to all the ISO Member Bodies for enquiry and was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Argentina	Germany	Romania
Australia	Hungary	South Africa, Rep. of
Austria	India	Spain
Belgium	Iran	Sweden
Bulgaria	Israel	Switzerland
Canada	Italy	Turkey
Chile	Japan	U.A.R.
Colombia	Netherlands	United Kingdom
Czechoslovakia	New Zealand	U.S.A.
France	Poland	U.S.S.R.

No Member Body opposed the approval of the Draft.

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided to accept it as the second edition of ISO Recommendation R 182-1961, the title of which is modified as follows : *Plastics – Determination of the thermal stability of polyvinyl chloride and related copolymers and their compounds by splitting off of hydrogen chloride.*

This edition (2nd edition) cancels and replaces the first edition of ISO Recommendation R 182-1961.

ISO Recommendation R 182 June 1970

PLASTICS

DETERMINATION OF THE THERMAL STABILITY OF POLYVINYL CHLORIDE AND RELATED COPOLYMERS AND THEIR COMPOUNDS BY SPLITTING OFF OF HYDROGEN CHLORIDE

1. SCOPE

This ISO Recommendation describes two methods for the determination of thermal stability of polyvinyl chloride and related copolymers and their compounds in general :

- A : the Congo red method;
- B : the pH method.

Each of these two methods allows determination of the thermal stability with regard to splitting off of hydrogen chloride from polyvinyl chloride (PVC) and from chlorinated polymers and copolymers and their compounds in general when they are brought to a high temperature for extruding, moulding, calendering or other processing.

Purchaser and supplier have to agree which of the methods is to be used. The Congo red method is simple and rapid, but gives one value only and the attention of an observer is required. The pH method permits the use of recording equipment and gives more information.

In some circumstances other tests also can be used, for example milling.

2. DEFINITION

Thermal stability or *thermal life* of a compound of vinyl chloride polymers or copolymers means the time, in minutes, from the moment at which the material is exposed to a given temperature in a given atmosphere until the first sign of decomposition is observed. The mode of decomposition is based on the splitting off of hydrogen chloride.

3. PRINCIPLE

3.1 Congo red method

Heating of the test portion, in still air, to the test temperature recommended for the material under test.

Measurement of the time required until the hydrogen chloride split off results in a colour change from red to blue of Congo red paper placed above the test portion.

3.2 pH method

Heating of the test portion, in a moving gas medium, to the test temperature recommended for the material under test; the hydrogen chloride split off is collected in a pH measuring cell.

Measurement of the time required until the hydrogen chloride split off results in a decrease of pH to a value corresponding to that at which Congo red paper changes colour from red to blue.

NOTES

1. Air is a suitable gas if the process of interest implies oxidation, for example milling or calendering. On the other hand, if oxidation is essentially excluded by the process, as in extrusion, an inert gas such as nitrogen may be used.
2. The chief difference between the two methods is the fact that the measurement is made in still air in the Congo red method and in a moving gas medium, which need not necessarily be air, in the pH method.

4. SIGNIFICANCE OF TEST

4.1 The thermal decomposition of PVC is a very complex reaction which, in compounds, is greatly affected by the type and quantity of the stabilizers, other additives, and the gas medium. The decomposition which takes place with the splitting off of hydrogen chloride and with the change in colour and appearance may result in the partial or complete charring of the material.

The splitting off of hydrogen chloride is one of the most important signs of the decomposition of PVC, even if it does not proceed along parallel lines with the discoloration and with other degradation phenomena.

4.2 While the Congo red method gives one value only, the pH method provides information on the induction period of the thermal decomposition leading to splitting off of hydrogen chloride under the influence of air or another gas medium. It also gives information on part of the further decomposition process.

5. TEST PORTIONS

5.1 **A : Congo red method**

Enough material is placed in each test tube to fill it to a depth of 50 mm.

B : ph method

1.0 g of the crushed material is placed into each test tube.

5.2 If a moulding or extrusion compound, granulated or in "dry-blend" form, or a pure powdered polymer is to be tested, the material needs no processing. Plastisol should be prepared as film or sheet and treated as in clause 5.3, according to agreement between purchaser and supplier.

5.3 If the material to be tested is in the form of a sheet or film, it should be cut into pieces of approximately 5 to 6 mm^2.

6. APPARATUS AND MATERIALS

The following apparatus and materials are required (see Fig. 1, 2 and 3) :

6.1 *Timing device,* calibrated in minutes.

6.2 *Oil-bath,* fitted with stirrer and thermostatic control, capable of maintaining the temperature within ± 1 °C in the range from 120 to 210 °C. The bath should have a thermoshield at the top and should be fitted with clamps capable of holding a sufficient number of test tubes immersed to a depth of 50 mm for both the Congo red method and the pH method.

NOTE. – Baths with triethylene glycol as heating liquid are also satisfactory. A metal block and other heating devices can also be employed, provided they comply with the requirements of clause 6.2.

6.3 *Flat-bottomed test tubes,* having the following dimensions :

external diameter, approximately	17 mm
wall thickness	0.4 mm
length, minimum	150 mm

Stoppers are required, with provision for the glass tubes and cells described in clauses 6.4 and 6.6.

6.4 *Glass tubes,* as follows :

A : Congo red method – *Small glass tubes,* 2 to 3 mm in internal diameter and about 100 mm in length (see Fig. 1).

B : pH method – *Bent glass tubes* for the gas inlet, connected to the apparatus as described in clause 6.6, and for the gas outlet, connected to the measuring cell as described in clause 6.6 (see Fig. 2).

6.5 **Congo red method only**

Congo red indicator strips, 10 mm wide. The indicator paper is prepared by immersing strips of filter paper in a 0.15 % solution of Congo red in methanol, and drying.

6.6 **pH method only**

6.6.1 *Two measuring cells,* 50 mm in diameter with glass and calomel electrodes and filled with 60 ml of 0.1 N potassium chloride (reagent grade) solution of pH 6. If preferred, this solution may be held at a constant temperature, for example 20 ± 1 °C. (See Fig. 3.)

6.6.2 *Apparatus for the supply of a current of gas,* dried and free of CO_2, at a rate of 6.0 litres per hour exactly. If it is preferred, gas may be held at a constant temperature, for example 20 °C.

6.6.3 *pH meter,* which may be of the recording type.

6.6.4 *Balance,* weighing to an accuracy of ± 10 mg.

7. PROCEDURE A – CONGO RED METHOD

7.1 Place the material to be tested in the test tube and gently shake it down, taking care to ensure that the pieces do not form a compact mass.

7.2 Close the test tube with a stopper having at its centre the glass tube with a Congo red paper strip 30 mm long and 10 mm wide. The Congo red strip is folded or rolled at one end, which is inserted into the glass tube. The tube is made to slide in such a way that the lower edge of the paper will be placed 25 mm above the top of the specimen.

7.3 Immerse the test tube thus prepared in the oil-bath – which is already brought to the given temperature – to the level of the upper surface of the test portion.

7.4 For each sample, at least two determinations should be carried out, in two separate test tubes, which are immersed in the oil-bath at the same time.

7.5 The preferred temperature is 180 ± 1 °C. Other temperatures may be used, provided that the duration of the test is not less than 20 minutes and not more than 5 hours.

NOTE. – A temperature of 200 °C is recommended for particularly stable materials and a temperature of 170 °C for less stable materials. The test temperature should be selected according to the processing conditions employed for the material. Thus, rigid PVC which is processed by injection moulding or extrusion should be tested at 200 °C in an inert gas. On the other hand, a material should be tested at 170 °C in air if it is processed on a roll mill or calender. Adherence to the test temperatures recommended is advisable in order to simplify the experimental operations and to provide a satisfactory basis for a comparison of the results. The recommended test temperatures cannot be employed in all cases. Thus much lower temperatures are necessary for a number of copolymers in order to simulate the conditions employed in processing the material.

7.6 The time, in minutes, for the two values determined from the insertion of the test tube in the hot oil to the time when the indicator paper shows the first clear signs of a change from red to blue, is recorded. When two values are more than ± 10 % apart from their average, the test should be repeated.

7.7 Sometimes, with certain stabilizers, the colour change is only slow and not very distinct; in these cases, two different times should be recorded, corresponding both to the first sign of colour changing from red to violet and to the permanent change from violet to blue.

8. PROCEDURE B – pH METHOD

8.1 Place the material to be tested in the test tube and gently shake it down, taking care to ensure that the pieces do not form a compact mass.

8.2 Close the test tube with a stopper (see Fig. 2).

8.3 Connect to the gas supply, start the gas current and keep it flowing for at least one minute, then connect the measuring cell.

8.4 Immerse the test tube thus prepared to a depth of 50 mm in the oil-bath – which has already been brought to the given temperature.

8.5 For each sample, at least two determinations should be made preferably simultaneously in the same oil-bath.

8.6 The preferred temperature is 180 ± 1 °C. Other temperatures may be used provided that the duration of the test is not less than 20 minutes and not more than 5 hours. The period between the pH measurements should be adjusted according to the decomposition of the specimen. A curve should then be plotted of the pH values obtained as a function of the time.

8.7 The time in minutes should be measured from the immersion of the tube in the bath until a pH of 3.9 ± 0.1 is achieved. When the two values are more than ± 10 % apart from their average, the test should be repeated. An alternative value of pH may be used if included in the specification for the material or by agreement between the two parties.

9. EXPRESSION OF RESULTS

The thermal stability is expressed by the time, in minutes, from the immersion of the tube containing the test portion in the oil-bath until either the indicator paper shows a change in colour (method A) or a pH of 3.9 ± 0.1, or other specified value (method B), is reached.

10. TEST REPORT

The test report should give the following information :

(*a*) Method used.

(*b*) The complete identification of the material tested and, if desired, the formulation of the compound and the thermal treatment during the preparation of the test specimens.

(*c*) Test temperature.

(*d*) pH method only : nature of the gas medium and temperature of the solution in the measuring cell.

(*e*) The results obtained; in the case of slow changing in colour when the Congo red method is used, the two times obtained according to clause 7.7 should be recorded.

(*f*) Date of test.