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Plastics — Hardeners and accelerators for epoxide resins — Determination of free acid in acid anhydride

Plastiques — Durcisseurs et accélérateurs pour résines époxydes — Détermination de l'acide libre dans l'acide-anhydride

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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Plastics — Hardeners and accelerators for epoxide resins — Determination of free acid in acid anhydride

1 Scope

This International Standard specifies a method for the determination of free acid in acid anhydride hardeners and accelerators for epoxide resins.

NOTE 1 This method is suitable for most anhydrides except for polyester and oligomeric anhydrides which may give too wide a scatter of results.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 760:1978, *Determination of water — Karl Fischer method (General method).*

3 Principle

The small amount of free acid present in a test portion of acid anhydride hardener or accelerator is reacted with rhodamine 6G to colour the test solution pink. The absorbance of the coloured solution is measured at a wavelength of about 510 nm using a spectrometer, and the free-acid content determined from a calibration curve.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Butan-2-one (methyl ethyl ketone), dried using the following procedure:

Put 100 g of molecular sieve 4A into 1 litre of butan-2-one. After allowing to settle for 24 h, decant off the supernatant liquid, taking care that it does not contain any molecular sieve 4A particles.

Determine the water content of the dried butan-2-one by the Karl Fischer method (see ISO 760). Reject butan-2-one containing more than 20 ppm of water.

4.2 Toluene, dried using the following procedure:

Put 100 g of molecular sieve 4A into 1 litre of toluene. After allowing to settle for 24 h, decant off the supernatant liquid, taking care that it does not contain any molecular sieve 4A particles.

Determine the water content of the dried toluene using the Karl Fischer method (see ISO 760). Reject toluene containing more than 20 ppm of water.

4.3 Rhodamine 6G solution.

4.3.1 Preparation

Disperse 20 mg of rhodamine 6G in 10 ml of a buffer solution [0,1 g of sodium phosphate (Na_3PO_4) dissolved in 10 ml of water].

Pour the dispersion into a 500 ml separating funnel and add 200 ml of toluene (4.2).

Shake gently until the layer of toluene becomes yellowish brown.

After allowing to settle for 1 h, filter the organic phase through filter paper into a brown-coloured bottle. Add metallic sodium slices (grains sliced with a scalpel) to the filtrate, and allow the filtrate to stand for 12 h.

Prior to use, check the solution to ensure that the water content is less than 20 ppm and the blank value of the absorbance is in the range 0,30 to 0,50.

4.3.2 Determination of absorbance of blank solution

Determine the absorbance of a blank rhodamine 6G solution (4.3.1) by the following procedure.

Introduce, using a pipette (see 5.5), 2 ml of the rhodamine 6G solution into a 10 ml volumetric flask, and make up to the mark with a solvent mixture of 95 parts by volume of dried toluene (4.2) and five parts by volume of dried butan-2-one (4.1). Determine the absorbance of this solution as specified in 6.3.2.

4.4 Standard sample of free acid.

Boil 10 g of the acid anhydride with 60 ml of water for 3 h and allow to cool. Filter, wash the precipitate with water, and then dry it.

5 Apparatus

Ordinary laboratory apparatus, plus the following:

5.1 Balance, accurate to 0,1 mg.

5.2 Spectrometer, with absorption cells with an optical path length of 10 mm.

5.3 Conical flask, capacity 50 ml, fitted with a ground-glass stopper.

5.4 One-mark volumetric flasks, capacity 10 ml, 50 ml and 100 ml, respectively, each fitted with a ground-glass stopper.

5.5 Pipettes, capacities 1 ml, 1,5 ml, 2 ml, 2,5 ml and 10 ml.

6 Procedure

6.1 Preparation of test solution

Weigh out, to an accuracy of 0,1 mg, 0,2 g of the sample, place it in a 50 ml conical flask (5.3), add 30 ml of a solvent mixture of 95 parts by volume of dried toluene (4.2) and five parts by volume of dried butan-2-one (4.1), and dissolve at room temperature. Transfer the solution to a 50 ml volumetric flask (5.4) and make up to the mark with dried solvent mixture. (The concentration of the test solution thus prepared is between 10^{-4} mol and 10^{-5} mol of free acid per litre.)

6.2 Calibration of spectrometer

Place 20 mg of the standard sample of free acid (4.4) in a 100 ml volumetric flask (5.4) and add 50 ml of dried butan-2-one (4.1). Dissolve the free acid completely at room temperature. Then make up to the mark with dried toluene (4.2).

Using a pipette (see 5.5), transfer 10 ml of this solution to another 100 ml volumetric flask (5.4) and make up to the mark with dried toluene (4.2). (The concentration of the standard solution thus obtained is 20 mg of free acid per litre.)

Using pipettes (see 5.5), measure out 1 ml, 1,5 ml, 2 ml and 2,5 ml portions of the free-acid standard solution prepared above, react each with rhodamine 6G as specified in 6.3.1 and measure the absorbance of each calibration solution thus obtained as specified in 6.3.2.

Subtract the blank absorbance value determined in 4.3.2 from the absorbance obtained for each calibration solution and plot a graph of corrected absorbance (vertical axis) versus the mass, in micrograms, of free acid in 10 ml of the corresponding calibration solution (horizontal axis). Then draw the calibration curve, passing through the origin.

6.3 Determination

6.3.1 Formation of the absorbing compound

Using a pipette (see 5.5), introduce 2 ml of rhodamine 6G solution (4.3) into a 10 ml volumetric flask (5.4) and add between 1 ml and 5 ml of the test solution (see 6.1). Rhodamine 6G and free acid will react immediately to yield a pink colour. Make the resultant solution up to the mark with the solvent mixture of dried toluene and dried butan-2-one as used in 6.1 .

The volume of test solution taken shall be chosen to give a pink colour. The intensity of colour shall not be greater than that of the deepest-colour calibration solution.

6.3.2 Spectrometric measurements

Measure the absorbance of the solution prepared in 6.3.1 at a wavelength of 510 nm ± 10 nm using the spectrometer (5.2) and cells with an optical path length of 10 mm, having first zeroed the spectrometer with dried toluene (4.2) in the absorption cell. Since the absorbance of the test solution changes with time, measure it within 5 min of the formation of the absorbing compound.

Subtract the absorbance of the blank solution determined in 4.3.2 and read from the calibration curve plotted in 6.2 the mass of free acid in 10 ml of the solution prepared in 6.3.1.

7 Expression of results

The free-acid content of the acid anhydride, expressed as a percentage by mass, is given by the formula

$$\frac{m_1 \times r_D \times 10^{-1}}{m_0}$$

where

m_0 is the mass, in milligrams, of the test portion (see 6.1);

m_1 is the mass, in micrograms, of free acid in 10 ml of the test solution, as read off the calibration curve (see 6.2);

r_D is the dilution factor, i.e. 50 divided by the volume, in millilitres, of the test solution used in 6.3.1.

8 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

b) all details necessary for identification of the sample submitted for testing;

c) the water content of the solvents used;

d) the results of the test and the units in which they have been expressed.

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