INTERNATIONAL STANDARD

ISO 2554

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Plastics — Unsaturated polyester resins — Determination of hydroxyl value

Plastiques — Résines de polyesters non saturés — Détermination de l'indice d'hydroxyle

Reference number
ISO 2554:1997(E)

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.

International Standard ISO 2554 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This second edition cancels and replaces the first edition (ISO 2554:1974), of which it constitutes a minor (editorial) revision.

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Plastics – Unsaturated polyester resins – Determination of hydroxyl value

1 Scope

This International Standard specifies a method for determining the hydroxyl value of unsaturated polyester resins.

In fact, this method determines the difference between the hydroxyl value and the acid value; it is therefore necessary to determine the total acid value separately, in order to calculate the hydroxyl value.

NOTE 1 The hydroxyl value of saturated polyester resins (for example, polyester resin used for the manufacture of polyurethanes and polymeric plasticizers) and of certain types of alkyd resins may also be determined by this method.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were 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 editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 2114:1996, *Plastics — Unsaturated polyester resins — Determination of partial acid value and total acid value.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

3 Definitions

For the purposes of this International Standard, the following definitions apply:

3.1 hydroxyl value: The number of milligrams of potassium hydroxide necessary to neutralize the acetic acid which will combine, by acetylation, with 1 g of an unsaturated polyester resin.

3.2 acid value: The number of milligrams of potassium hydroxide required to neutralize 1 g of a test sample under the test conditions.

3.3 total acid value: The acid value corresponding to the neutralization of all carboxyl-terminated groups and free acids and free anhydrides of a polyester.

4 Principle

The hydroxyl groups in the resin are acetylated by reacting an ethyl acetate solution of the resin with acetic anhydride in the presence of toluene-4-sulfonic acid catalyst. The excess acetic anhydride is hydrolysed by a pyridine/water mixture and the resultant acetic acid is titrated with methanolic potassium hydroxide solution.

In this titration, the free acid and free anhydride groups which exist in the resin are also neutralized by the potassium hydroxide.

The hydroxyl value is finally calculated by taking into account the total acid value determined separately by ISO 2114.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and water of grade 3 purity as defined in ISO 3696.

5.1 Acetic anhydride acetylating solution, approximately 1 mol/l, in ethyl acetate.

Dissolve 1,4 g of pure, dry toluene-4-sulfonic acid in 111 ml of anhydrous ethyl acetate. When completely dissolved, slowly add, while mixing, 12 ml of freshly distilled acetic anhydride. Store in a dry atmosphere.

5.2 Ethyl acetate, anhydrous.

5.3 Pyridine/water mixture, 3+2 (*V*/*V*).

Mix 3 volumes of pyridine with 2 volumes of water.

WARNING — Pyridine is toxic. Do not inhale the vapour and avoid all contact with the skin and eyes. Work under a fume-extraction hood or in a well ventilated space.

5.4 1-Butanol/toluene mixture, 2+1 (*V*/*V*).

Mix 2 volumes of 1-butanol with 1 volume of toluene.

5.5 Mixed-indicator solution.

Mix 3 volumes of a 0,1 % ethanolic solution of thymol blue with 1 volume of a 0,1 % ethanolic solution of cresol red.

5.6 Potassium hydroxide, 0,5 mol/l standard volumetric solution in methanol.

6 Apparatus

Ordinary laboratory apparatus plus the following:

6.1 Conical flask, capacity 250 ml, with a ground-glass stopper.

6.2 Magnetic stirrer, with a stirrer bar covered with a corrosion-resistant material (for example PTFE).

6.3 Burette, capacity 50 ml, graduated at 0,05 ml intervals.

6.4 Water bath, controlled at a temperature of 50 °C ± 1 °C.

6.5 Pipettes, capacity 5 ml and 10 ml (for the acetylating solution).

6.6 Apparatus for potentiometric titration: a suitable potentiometer equipped with a calomel reference electrode/glass electrode system, with a titration stand.

6.7 Analytical balance, having an accuracy of 1 mg.

7 Procedure

Weigh, to the nearest 1 mg, into the 250 ml conical flask (6.1), a test portion of the resin containing approximately 5 milli-equivalents of OH (the mass in grams of the test portion = 280 divided by the hydroxyl value). If the approximate hydroxyl value is not known, carry out preliminary tests.

Add exactly 10 ml of the acetylating solution (5.1) and the stirrer bar (see 6.2). Stopper the conical flask after moistening the stopper with ethyl acetate (5.2), and dissolve the test portion using the magnetic stirrer (6.2). Should the sample not dissolve completely on warming, add another 5 ml or 10 ml of acetylating solution.

Place the conical flask in the water bath (6.4) at 50 °C ± 1 °C, taking care to immerse it only about 10 mm, and leave it for 45 min. (This time may be reduced, for example to 30 min or less, provided it can be shown that equivalent results are obtained.)

Remove the conical flask from the bath, cool, place on the magnetic stirrer and add 2 ml of water. When the solution has been thoroughly mixed, add 10 ml of pyridine/water mixture (5.3) and stir for 5 min.

Rinse the stopper and inner surface of the conical flask with 60 ml of 1-butanol/toluene mixture (5.4) and add 5 drops of mixed-indicator solution (5.5).

Continue stirring and titrate with methanolic potassium hydroxide solution (5.6). When the colour change is observed, add a further 1 or 2 drops of the mixed indicator. The solution changes from yellow to clear; note the volume V_1, in millilitres, of potassium hydroxide solution used. Add a further drop of potassium hydroxide solution; the indicator should turn blue. If it does not, note the burette reading and add a further drop of the mixed-indicator solution, continuing in this way until the blue colour is obtained.

The value of V_1 to be used for the calculation is the one noted before adding the drop which produced the blue colour.

Carry out a blank test under the same conditions, but without the test portion, and note the volume V_0, in millilitres, of potassium hydroxide solution used.

Carry out at least two determinations. The results of the two determinations should not differ by more than 2 hydroxyl-value units. If this is not the case, carry out further determinations until the results of two consecutive determinations meet this requirement.

An alternative method consists in carrying out the determination by potentiometric titration instead of using a colour indicator. This method, which is usable in all cases, is recommended especially with densely coloured products. Use a calomel reference electrode, with a bridge containing a saturated solution of potassium chloride in methanol, and a glass electrode connected to a pH-meter or to a millivoltmeter.

8 Expression of results

For each of the two determinations, calculate the hydroxyl value HV from the equation

$$\mathrm{HV} = \frac{(V_0 - V_1) \times c \times 56{,}1}{m} + \mathrm{AV}$$

where

V_1 is the volume, in millilitres, of standard volumetric potassium hydroxide solution (5.6) used in the determination;

V_0 is the volume, in millilitres, of standard volumetric potassium hydroxide solution (5.6) used in the blank test;

c is the exact concentration, in moles per litre, of the standard volumetric potassium hydroxide solution used;

m is the mass, in grams, of the test portion;

AV is the total acid value, determined in accordance with ISO 2114.

NOTE 2 The value of $(V_0 - V_1)$ may be positive or negative.

Calculate the average of the two values obtained and round to the nearest whole number.

9 Precision

The precision of this method is not known because interlaboratory data are not available. Interlaboratory data are being obtained, and a precision statement will be added at the next revision.

10 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

b) all details necessary for the complete identification of the sample;

c) the individual results and their mean;

d) details of any operation not specified in this International Standard, as well as any incident which may have affected the results;

e) the date and place of the test.

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