INTERNATIONAL STANDARD

ISO 2114

Second edition
1996-12-15

Plastics — Unsaturated polyester resins — Determination of partial acid value and total acid value

Plastiques — Résines de polyesters non saturés — Détermination de l'indice d'acide partiel et de l'indice d'acide total

Reference number
ISO 2114:1996(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 2114 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This second edition cancels and replaces the first edition (ISO 2114:1974), which has been technically revised (see the introduction for details).

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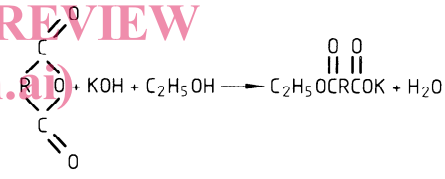
Introduction

This International Standard was developed for unsaturated polyester resins and specifies the methods that are applicable for the determination of the acid values: total acid value and partial acid value.

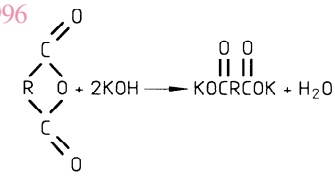
The previous edition determined only the partial acid value, which corresponds to the neutralization of only half of the free anhydride present. In the case of resins based on maleic anhydride/tetrahydrophthalic acid, the error involved is very small. In the case of resins based on maleic anhydride/orthophthalic acid or maleic anhydride/tetrabromophthalic acid, however, the error is significant.

Hence, this edition includes methods for the determination of both partial and total acid values, using the chemical reactions given below:

Method A



Method B



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Plastics — Unsaturated polyester resins — Determination of partial acid value and total acid value

1 Scope

This International Standard specifies methods of determining the partial acid value (method A) and the total acid value (method B) of unsaturated polyester resins.

It is intended to provide quality-control data for the acceptance or rejection of resins in accordance with the terms of a specification, as well as to be used in research and development to monitor the completion of the polycondensation reaction.

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

ISO 6353-2:1983, *Reagents for chemical analysis — Part 2: Specifications — First series.*

3 Definitions

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

3.1 acid value: The number of milligrams of potassium hydroxide (KOH) required to neutralize 1 g of unsaturated polyester resin under the test conditions.

3.2 partial acid value: The acid value corresponding to the neutralization of all the carboxyl-terminated groups and free acids plus half the anhydride groups in an unsaturated polyester resin.

3.3 total acid value: The acid value corresponding to the neutralization of all the carboxyl-terminated groups and free acids plus all the anhydride groups in an unsaturated polyester resin.

4 Principle

4.1 Method A

A weighed quantity of resin is dissolved in a solvent mixture and the resin solution is titrated potentiometrically (see note 1) with a standard volumetric solution of potassium hydroxide in ethanol. The partial acid value is the number of milligrams of potassium hydroxide required to neutralize 1 g of resin.

4.2 Method B

A weighed quantity of resin is dissolved in a solvent mixture including water. The free anhydride groups are allowed to hydrolyse for 20 min before titrating potentiometrically (see note 1) with a standard volumetric solution of potassium hydroxide in ethanol. The total acid value is the number of milligrams of potassium hydroxide required to neutralize 1 g of resin.

NOTES

1 Titration using a colour indicator is an optional alternative in both methods.

2 When titrating pure maleic polyester resins, it is better to use a standard volumetric solution of potassium hydroxide in methanol.

5 Reagents

During the analysis, use only reagents of recognized analytical grade in accordance with ISO 6353-2 and water of at least grade 3 as defined in ISO 3696.

5.1 Solvent for method A: solvent mixture containing 2 parts of toluene (5.7) and 1 part of ethanol (5.5) by volume.

5.2 Solvent for method B: solvent mixture containing 400 ml of pyridine (5.8), 750 ml of methyl ethyl ketone (5.9) and 50 ml of water.

5.3 Potassium hydroxide, 0,1 mol/l standard volumetric solution in ethanol (5.5) or in methanol (5.6), free from carbonates.

Check the concentration of this solution on the day of use.

5.4 Acetone, containing less than 0,3 % (m/m) of water.

5.5 Ethanol, containing less than 0,2 % (m/m) of water.

5.6 Methanol, at least 99,8 % (m/m) pure.

5.7 Toluene, containing less than 0,005 % (m/m) of water.

5.8 Pyridine, containing less than 0,05 % (m/m) of water.

5.9 Methyl ethyl ketone, containing less than 0,01 % (m/m) of water.

5.10 Indicators (optional):

5.10.1 Thymol blue, 0,1 % solution in ethanol (5.5).

5.10.2 Phenolphthalein, 1 % solution in ethanol (5.5).

6 Apparatus

Ordinary laboratory apparatus, plus the following:

6.1 Conical flask, of capacity 250 ml, with a wide neck.

6.2 Conical flask, of capacity 250 ml, with a narrow neck and fitted with a ground-glass stopper.

6.3 Burette, of capacity 25 ml, graduated in 0,05 ml divisions.

6.4 Magnetic stirrer.

6.5 Automatic pipettes, of capacity 25 ml, 50 ml and 60 ml.

6.6 Analytical balance, accurate to 1 mg.

6.7 Potentiometric-titration apparatus, comprising a suitable potentiometer fitted with a combined glass/reference electrode and a titration stand.

7 Procedure

7.1 Method A

7.1.1 Make at least two determinations. Use test portions of 0,5 g to 3,0 g, depending on the estimated acid value (the higher the acid value expected, the smaller the mass of the test portion).

7.1.2 Weigh the test portion in a 250 ml wide-neck conical flask (6.1) to the nearest 1 mg (mass m_1). Add 50 ml of solvent mixture (5.1) using a pipette (see 6.5). Mix until the resin is completely dissolved.

If solubility is incomplete after 5 min, prepare another test portion, but dissolve it in 50 ml of solvent mixture (5.1) and 25 ml of acetone (5.4).

7.1.3 Place the conical flask on the titration stand (see 6.7), adjust its position so that the electrode is well immersed and titrate potentiometrically with potassium hydroxide solution (5.3) from a burette (6.3) (see 7.1.4 for an alternative procedure using a colour indicator). Record the volume (V_1), in millilitres, of KOH solution used.

Carry out a blank determination in the same way, using 50 ml of solvent mixture and, if needed, 25 ml of acetone. Record the volume (V_2), in millilitres, of KOH solution used.

7.1.4 As an alternative, a colour indicator can be used instead of the potentiometric-titration apparatus, as follows:

Add at least 5 drops of thymol blue indicator solution (5.10.1) to the dissolved test portion. Titrate with potassium hydroxide solution from the burette until the colour remains blue for 20 s to 30 s. Record the volume (V_1), in millilitres, of KOH solution used.

Carry out a blank determination using 50 ml of solvent mixture and, if needed, 25 ml of acetone. Add at least 5 drops of thymol blue. Titrate to the same end point as obtained when the resin was present. Record the volume (V_2), in millilitres, of KOH solution used.

7.2 Method B

7.2.1 Make at least two determinations. Use test portions of about 0,5 g to 3 g depending on the estimated acid value (the higher the acid value expected, the smaller the mass of the test portion).

7.2.2 Weigh the test portion in a narrow-neck conical flask (6.2) to the nearest 1 mg (mass m_2). Add 60 ml of solvent mixture (5.2) using a pipette (6.5). Stopper the flask and place it on the magnetic stirrer (6.4). Stir until the resin is completely dissolved, and continue stirring for 20 min to complete the hydrolysis of the anhydride groups. Heat the flask if required, using a water bath and a condenser on the flask. Then cool to room temperature.

7.2.3 Place the conical flask on the titration stand (see 6.7), adjust its position so that the electrode is well immersed and titrate potentiometrically with potassium hydroxide solution (5.3) from a burette (6.3) (see 7.2.4 for an alternative procedure using a colour indicator). Record the volume (V_3), in millilitres, of KOH solution used.

Carry out a blank determination in the same way, using 60 ml of solvent mixture. Record the volume (V_4), in millilitres, of KOH solution used.

7.2.4 As an alternative, a colour indicator can be used instead of the potentiometric-titration apparatus, as follows:

Add at least 5 drops of phenolphthalein indicator solution (5.10.2) to the dissolved test portion. Titrate with potassium hydroxide solution from the burette, with stirring, until the colour remains pink for 20 s to 30 s. Record the volume (V_3), in millilitres, of KOH solution used.

Carry out a blank determination using 60 ml of solvent mixture, and adding at least 5 drops of phenolphthalein. Titrate to the same end point as obtained when the resin was present. Record the volume (V_4), in millilitres, of KOH solution used.

8 Calculation and expression of results

8.1 Calculation

8.1.1 Method A

For each determination, calculate the partial acid value AV_P from the equation

$$AV_P = \frac{56{,}1 \times (V_1 - V_2) \times c}{m_1}$$

where

m_1 is the mass, in grams, of the test portion;

V_1 is the volume, in millilitres, of KOH solution (5.3) required to neutralize the resin solution;

V_2 is the volume, in millilitres, of KOH solution (5.3) required in the blank determination;

c is the concentration, in moles per litre, of the KOH solution (5.3).

8.1.2 Method B

For each determination, calculate the total acid value AV_T from the equation

$$AV_T = \frac{56{,}1 \times (V_3 - V_4) \times c}{m_2}$$

where

m_2 is the mass, in grams, of the test portion;

V_3 is the volume, in millilitres, of KOH solution (5.3) required to neutralize the resin solution;

V_4 is the volume, in millilitres, of KOH solution (5.3) required in the blank determination;

c is the concentration, in moles per litre, of the KOH solution (5.3).

8.2 Expression of results

Express the result as the mean value of at least two determinations that do not differ by more than 2 %.

9 Precision

Following round-robin testing organized in France in 1995, the precision of these methods (with a confidence level of 95 %) is as follows:

15 < acid value < 25; $s_r = 0{,}23$; $r = 0{,}6$;
$s_R = 0{,}74$; $R = 2$

s_r Within-laboratory standard deviation;

s_R Interlaboratory standard deviation;

r Repeatability (absolute value);

R Reproducibility (absolute value).

10 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

b) all details necessary for the identification of the material tested (including type, source, manufacturer's designation, form in which supplied, etc.);

c) the type of titration carried out (potentiometric or with a colour indicator);

d) the individual results and their mean;

e) the place and date of the test;

f) details of any operation not specified in this International Standard and of any incident which may have affected the results.

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