SLOVENSKI STANDARD
SIST EN ISO 9702:2000

01-maj-2000

Polimerni materiali - Aminska utrjevala za epoksidne smole - Določanje dušika v primarnih, sekundarnih in terciarnih aminskih skupinah (ISO 9702:1996)

Plastics - Amine epoxide hardeners - Determination of primary, secondary and tertiary amine group nitrogen content (ISO 9702:1996)

Kunststoffe - Aminische Epoxidhärter - Bestimmung von primären, sekundären und tertiären Amingruppen als Stickstoffgehalt (ISO 9702:1996)

Plastiques - Durcisseurs pour résines époxy - Détermination de la teneur en azote des groupes amine primaire, secondaire, tertiaire (ISO 9702:1996)

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English version

Plastics - Amine epoxide hardeners - Determination of primary, secondary and tertiary amine group nitrogen content (ISO 9702:1996)

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Kunststoffe - Aminische Epoxidhärter - Bestimmung von primären, sekundären und tertiären Amingruppen als Stickstoffgehalt (ISO 9702:1996)

This European Standard was approved by CEN on 12 June 1998.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

The text of the International Standard from Technical Committee ISO/TC 61 "Plastics" of the International Organization for Standardization (ISO) has been taken over as an European Standard by Technical Committee CEN/TC 249 "Plastics", the secretariat of which is held by IBN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 1999, and conflicting national standards shall be withdrawn at the latest by February 1999.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Endorsement notice

The text of the International Standard ISO 9702:1996 has been approved by CEN as a European Standard without any modification.

INTERNATIONAL STANDARD

ISO 9702

First edition
1996-12-01

Plastics — Amine epoxide hardeners — Determination of primary, secondary and tertiary amine group nitrogen content

Plastiques — Durcisseurs pour résines époxy — Détermination de la teneur en azote des groupes amine primaire, secondaire, tertiaire

Reference number
ISO 9702:1996(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 9702 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

International Organization for Standardization

Plastics — Amine epoxide hardeners — Determination of primary, secondary and tertiary amine group nitrogen content

1 Scope

This International Standard specifies a method for the determination of the primary, secondary and tertiary amine group nitrogen content of aliphatic or aromatic amine hardeners for epoxy resins.

2 Principle

2.1 Aliphatic amines

2.1.1 Determination of total amine group nitrogen content (X_T)

The total alkalinity is determined by potentiometric titration against hydrobromic or perchloric acid in glacial acetic acid, as described by the following reactions:

$$RNH_2 + H^+ \rightarrow RNH_3^+$$

$$(RR'NH + H^+ \rightarrow (RR')NH_2^+$$

$$(RR'R'')N + H^+ \rightarrow (RR'R'')NH^+$$

The results are expressed as percentage nitrogen.

NOTE 1 Perchloric acid is not suitable for use with amine hardeners such as *N*-aminoethylpiperazine.

2.1.2 Determination of tertiary amine group nitrogen content (X_3)

The primary and secondary amine groups are converted into amide groups with acetic anhydride, as described by the following reactions:

$$RNH_2 + (CH_3CO)_2O \rightarrow RNHCOCH_3 + CH_3COOH$$

$$(RR')NH + (CH_3CO)_2O \rightarrow (RR')NCOCH_3 + CH_3COOH$$

The tertiary amine group alkalinity is determined by potentiometric titration against hydrobromic or perchloric acid in glacial acetic acid/acetic anhydride, as described by the following reaction:

$$(RR'R'')NH + H^+ \rightarrow (RR'R'')NH^+$$

The results are expressed as percentage nitrogen.

2.1.3 Determination of primary amine group nitrogen content (X_{L1})

The primary amine groups are reacted with a measured excess of 2,4-pentanedione (acetylacetone) in *N*,*N*-di-methylformamide to form imines, as described by the following reaction:

$$RNH_2 + CH_3COCH_2COCH_3 \rightarrow CH_3CNRCH_2COCH_3 + H_2O$$

The excess acetylacetone is determined by potentiometric titration against potassium hydroxide (the reaction products of acetylacetone and primary amine groups are neutral under these conditions).

The results are expressed as percentage nitrogen.

2.1.4 Determination of secondary amine group nitrogen content (X_{L2})

The secondary amine group nitrogen content is determined by calculating the difference between the total amine group nitrogen content and the sum of the primary and tertiary amine group nitrogen contents.

2.2 Aromatic amines

2.2.1 Determination of total amine group nitrogen content (X_T)

The total alkalinity is determined by potentiometric titration against hydrobromic or perchloric acid in glacial acetic acid, as described by the following reactions:

$$ArNH_2 + H^+ \rightarrow ArNH_3^+$$

$$(ArAr')NH + H^+ \rightarrow (ArAr')NH_2^+$$

$$(ArAr'Ar'')N + H^+ \rightarrow (ArAr'Ar'')NH^+$$

The results are expressed as percentage nitrogen.

2.2.2 Determination of tertiary amine group nitrogen content (X_3)

The primary and secondary amine groups are converted into amide groups with acetic anhydride as described by the following reactions:

$$ArNH_2 + (CH_3CO)_2O \rightarrow ArNHCOCH_3 + CH_3COOH$$

$$(ArAr')NH + (CH_3CO)_2O \rightarrow (ArAr')NCOCH_3 + CH_3COOH$$

The tertiary amine group alkalinity is determined by potentiometric titration against hydrobromic or perchloric acid in glacial acetic acid/acetic anhydride, as described by the following reaction.

$$(ArAr'Ar'')N + H^+ \rightarrow (ArAr'Ar'')NH^+$$

The results are expressed as percentage nitrogen.

2.2.3 Determination of the sum of the secondary and tertiary amine group nitrogen contents (X_{R2+3})

The primary amine groups are converted into Schiff bases by salicylaldehyde in glacial acetic acid, as described by the following reaction:

$$ArNH_2 + C_6H_4(OH)CHO \rightarrow ArN{=}CHC_6H_4(OH) + H_2O$$

With strongly basic amines, the secondary and tertiary amine group alkalinity is determined by potentiometric titration against hydrochloric acid in glacial acetic acid, as described by the following reactions:

$$(ArAr')NH + H^+ \rightarrow (ArAr')NH_2^+$$

$$(ArAr'Ar'')N + H^+ \rightarrow (ArAr'Ar'')NH^+$$

The results are expressed as percentage nitrogen.

NOTE 2 Weakly basic amines, such as 4,4'-diaminodiphenylsulfone, are titrated with hydrobromic or perchloric acid in glacial acetic acid.

2.2.4 Determination of primary amine group nitrogen content (X_{R1})

The primary amine group nitrogen content is determined by calculating the difference between the total amine group nitrogen content and the sum of the secondary and tertiary amine group nitrogen contents.

2.2.5 Determination of secondary amine group nitrogen content (X_{R2})

The secondary amine group nitrogen content is determined by calculating the difference between the sum of the secondary and tertiary amine group nitrogen contents and the tertiary amine group nitrogen content.

3 Reagents

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

3.1 Acetic acid, glacial.

3.2 Acetic anhydride.

3.3 2,4-Pentanedione (acetylacetone).

3.4 *N,N*-diamethylformamide.

3.5 Acetylacetone, 1,5 mol/l solution in *N,N*-dimethylformamide.

Dissolve 15 ml of acetylacetone (3.3) in 90 ml of *N,N*-dimethylformamide (3.4).

3.6 Salicylaldehyde.

3.7 Ethan-1,2-diol (ethylene glycol).

3.8 Propan-2-ol.

3.9 Ethylene glycol/propan-2-ol mixed solvent.

Mix 500 ml of ethylene glycol (3.7) and 500 ml of propan-2-ol (3.8).

3.10 Potassium hydrogen phthalate.

3.11 Hydrobromic acid, 250 g/l solution in acetic acid.

3.12 Perchloric acid, 70 % or 60 % solution in water.

3.13 Potassium hydroxide.

3.14 Hydrochloric acid, concentrated.

3.15 Sodium carbonate.

3.16 Hydrobromic acid, 0,1 mol/l standard volumetric solution in glacial acetic acid.

3.16.1 Preparation

Add 25 ml of hydrobromic acid (3.11) slowly to 100 ml of glacial acetic acid (3.1) in a 1 000 ml brown-glass volumetric flask (4.9) and stir carefully. Dilute to the mark with glacial acetic acid.

3.16.2 Standardization

Weigh out, to the nearest 0,1 mg, 0,1 g to 0,2 g of potassium hydrogen phthalate (3.10) and dissolve in 50 ml of glacial acetic acid (3.1).

Titrate this solution potentiometrically against the solution of hydrobromic acid prepared in 3.16.1 (V_1).

Perform a blank test by titrating 50 ml of glacial acetic acid against the solution of hydrobromic acid prepared in 3.16.1 (V_2).

Calculate the concentration c_1 of the hydrobromic acid solution, expressed in moles of HBr per litre to the nearest 0,001 mol HBr/l, using the equation

$$c_1 = \frac{1\,000 \times m_0}{204{,}23\,(V_1 - V_2)}$$

where

m_0 is the mass, in grams, of potassium hydrogen phthalate used;

V_1 is the volume, in millilitres, of the solution of hydrobromic acid prepared in 3.16.1 required to reach the end point in the titration;

V_2 is the volume, in millilitres of the above solution (3.16.1) required in the blank test.

3.17 Perchloric acid, 0,1 mol/l standard volumetric solution in glacial acetic acid.

3.17.1 Preparation

Mix 8,5 ml of 70 % perchloric acid (or 9,9 ml of 60 % perchloric acid) (3.12) with 500 ml of glacial acetic acid (3.1) in a 1 000 ml brown-glass volumetric flask (4.9). Add 30 ml (or 35 ml if 60 % perchloric acid was used) of acetic anhydride (3.2) and mix well. Dilute to the mark with glacial acetic acid.

3.17.2 Standardization

Use the same procedure as that in 3.16.2, calculating the concentration using the same equation. In this case, c_1 is the concentration of the perchloric acid solution prepared in 3.17.1.

3.18 Potassium hydroxide, 0,5 mol/l standard volumetric solution in propan-2-ol.

3.18.1 Preparation

Take 1 000 ml of propan-2-ol (3.8) in a round-bottomed flask and add 30 g of potassium hydroxide (3.13). Reflux for several hours to dissolve completely. Leave the solution in a carbon-dioxide-free atmosphere for a few days, then transfer the clear upper solution to a polyethylene bottle and keep it in the bottle equipped with a guard tube filled with soda lime. Take care that the solution does not touch a cork or rubber stopper or stopper grease, which may be saponified.

3.18.2 Standardization

Weigh, to the nearest 0,1 mg, 0,5 g to 1,0 g of potassium hydrogen phthalate (3.10) and dissolve in 100 ml of water.

Titrate this solution potentiometrically against the potassium hydroxide solution prepared in 3.18.1 (V_3).

Perform a blank test separately (V_4).

Calculate the concentration c_2 of the potassium hydroxide solution, expressed in moles of KOH per litre to the nearest 0,001 mol KOH/l, using the equation

$$c_2 = \frac{1\,000 \times m_1}{204{,}23\,(V_3 - V_4)}$$