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Plastics — Polyols for use in the production of polyurethane — Determination of hydroxyl number

Plastiques — Polyols pour la production du polyuréthanne — Détermination de l’indice d’hydroxyle

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials*.

This second edition cancels and replaces the first edition (ISO 14900:2001), of which it constitutes a minor revision. It also incorporates the Technical Corrigendum ISO 14900:2001/Cor. 1:2005. The changes compared to the previous edition are as follows:

- in Clause 2, the normative references have been updated;
- in Clause 4, it has been clarified that Method A refers to "acetylation" and Method B refers to "phthalation".

Introduction

International Standards have been published which deal with the determination of hydroxyl values of unsaturated-polyester resins (ISO 2554), non-ionic surface active agents (ISO 4326, ISO 4327), binders for paints and varnishes [ISO 4629 (all parts)] and industrial polyglycols (ISO 6796). The two methods in this document are improved versions of imidazole-catalyzed procedures specifically tailored to the determination of the hydroxyl number of many types of polyol, including those used in the production of polyurethanes. Method A is especially suited to the determination of the hydroxyl number of polyether polyols that may have steric hindrance, or are otherwise difficult to determine by phthalation. Method B is a general method based on phthalation and is applicable to a wide range of polyol types. Both of these methods are similar to procedures found in ASTM D4274.

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WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This document specifies two methods for the measurement of the hydroxyl number of polyols used as polyurethane raw materials. It is necessary to know the hydroxyl content of polyols to properly formulate polyurethane systems. Method A is primarily applicable to readily esterified polyether polyols. It is also intended for polyols which have significant steric hindrance, such as those based on sugars. Method B is intended for polyether polyols, polymer polyols and amine-initiated polyols, but may give low results for sterically hindered polyols. Other polyols can be analysed by these methods if precautions are taken to verify applicability. These methods can be used for research and for quality control and specification purposes.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

ISO 835, *Laboratory glassware — Graduated pipettes*

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

ISO 4788, *Laboratory glassware — Graduated measuring cylinders*

ISO 6353-1, *Reagents for chemical analysis — Part 1: General test methods*

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

ISO 6353-3, *Reagents for chemical analysis — Part 3: Specifications — Second series*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1

polyurethane

polymer prepared by the reaction of an organic di- or polyisocyanate with compounds containing two or more hydroxyl groups

3.2

hydroxyl number

hydroxyl value

number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of a test portion

4 Principle

4.1 Method A (Acetylation): A test portion is refluxed in a solution of acetic anhydride in pyridine to acetylate the hydroxyl groups present; the reaction is catalyzed by imidazole. The excess reagent is hydrolyzed with water and the resulting acetic acid is titrated with standardized sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the test portion and a blank solution.

CAUTION — Acetic anhydride and pyridine are toxic and flammable. In addition, acetic anhydride is corrosive. Take proper precautions when handling these reagents.

4.2 Method B (Phthalation): The hydroxyl groups in a test portion are esterified by refluxing with a solution of phthalic anhydride in pyridine; the reaction is catalyzed by imidazole. The excess anhydride is hydrolyzed with water and the phthalic acid formed is titrated with standardized sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the test portion and a blank solution.

5 Interferences

5.1 Excess water will interfere by destroying part of the esterification reagent. If the sample contains more than 0,2 % water, dry the sample with a reagent that will not add acidity or basicity to the sample.

5.2 Primary and secondary amines and long-chain fatty acids react with the reagent to form stable compounds that will be included in the result.

6 Reagents

Reagent-grade chemicals shall be used in all determinations. Unless otherwise indicated, it is intended that all reagents conform to the specifications of ISO 6353-1, ISO 6353-2 and ISO 6353-3, although other grades may be used provided that it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean grade 2 reagent water as defined by ISO 3696.

6.1 Acetylation reagent (for method A).

Mix 127 ml of acetic anhydride with 1 000 ml of dry pyridine (6.7). Add 16 g of imidazole (6.3) and swirl carefully to dissolve. Prepare the reagent fresh daily and keep it in a dark bottle. Do not use it if it is darker than pale yellow.

NOTE Some laboratories have reported that dark, resinous solids have formed when the mixture of pyridine and esterification reagent is heated. In that event, it has been found that preparing the acetylation reagent with the addition of 0,4 % water in the pyridine (6.8) will correct the problem. However, care has to be taken that sufficient reagent is present to complete the reaction quantitatively. See also 8.1.2.

CAUTION — Acetic anhydride and pyridine are eye, skin, and respiratory irritants. Avoid bodily contact with these reagents and use only in a well-ventilated area.

6.2 Phthalation reagent (for method B).

Weigh 116 g of phthalic anhydride into a 1 l brown bottle. Add 700 ml of pyridine (6.7) and shake vigorously until dissolved. Add 16 g of imidazole and swirl carefully to dissolve. The reagent shall stand overnight before use. Avoid prolonged exposure of the reagent to moisture in the air. Discard reagent that develops a colour. In the blank titration as described in the procedure for method B, exactly 25 ml of this reagent shall consume between 95 ml and 100 ml of 0,500 mol/l sodium hydroxide.

6.3 Imidazole, reagent grade or equivalent.

6.4 Hydrochloric acid, standard solution, 0,1 mol/l.

Prepare and standardize to four significant figures in accordance with good practice, using potassium acid phthalate (6.6) as a primary standard. Determine and record the temperature at which the standardization was performed. The concentration of the solution shall be corrected to the temperature at which the determination is performed, as described in 6.9. This solution is required only if a correction is to be applied for the presence of strong base in the sample being analysed.

6.5 Phenolphthalein indicator solution, 10 g/l.

Prepare a solution of 1 g of phenolphthalein in 100 ml of pyridine (6.7).

6.6 Potassium acid phthalate.

Use a certified primary standard.

6.7 Pyridine, reagent grade, containing less than 0,1 % water.

If purification is required, distil from phthalic anhydride, discarding the fraction boiling below 114 °C to 115 °C.

6.8 Pyridine, containing from 0,30 % to 0,45 % water (used for special cases: see the note to 6.1).

Determine the water content of the pyridine using ISO 760. Add the required amount of water. The required volume of water to add per litre of pyridine may be calculated as follows:

$$\text{Water to add, in ml} = 4{,}0 - 9A$$

where A is the percent water already in the pyridine.

6.9 Sodium hydroxide, standard solution, 0,5 mol/l.

Prepare and standardize to four significant figures in accordance with good practice. Determine and record the temperature at which the standardization was performed. The factor for thermal expansion of this solution is 0,000 14. For calculation of the hydroxyl content, the concentration of the solution shall be corrected to the temperature at which the determination was performed by the following:

$$c_{\theta 2} = c_{\theta 1} + F(\theta_1 - \theta_2)$$

where

$c_{\theta 1}$ is the concentration of the solution when standardized, in mol/l;

$c_{\theta 2}$ is the concentration during analysis of samples, in mol/l;

θ_1 is the temperature of the solution during standardization, in °C;

θ_2 is the temperature of the solution during analysis of samples, in °C;

F is the factor to correct for thermal expansion of the solution.

7 Apparatus

7.1 Potentiometric titrator or pH-meter, accurate to 0,1 mV or better, equipped with a pair of electrodes or a combination glass-calomel electrode and a piston burette having a 100 ml capacity or capability for multiple automatic refilling.

7.2 Syringes, 2 ml, 5 ml and 10 ml, with an orifice suitable for handling viscous polyols.

7.3 Magnetic stirrer.

7.4 Analytical balance, accurate to 0,1 mg.

7.5 Volumetric pipette, 20 ml, conforming to ISO 648.

7.6 Measuring pipette, 1 ml, conforming to ISO 835.

7.7 Graduated cylinder, 100 ml, conforming to ISO 4788.

7.8 Beakers, 250 ml, 500 ml.

7.9 Burette (for colorimetric titration), 100 ml total capacity, range of graduated portion 50 ml, with 0,1 ml graduations, and conforming to ISO 385. If a 100 ml burette is not available, the first 50 ml of titrant may be added by pipette and the titration completed with a 50 ml burette.

7.10 Conical flasks, 300 ml, with standard taper 24/40 joint.

7.11 Condenser, West type, 400 mm, drip-tip, standard taper 24/40 joint with cooling extending to the joint.

7.12 Oil bath, maintained at 115 °C ± 2 °C.

8 Method A — Acetylation

8.1 Procedure

8.1.1 If the sample does not contain an appreciable amount of water, determine the test portion size required using one of the following formulae:

$$\text{Test portion size, in g} = \frac{561 \times 0{,}98}{\text{Expected hydroxyl number}}$$

or

$$\text{Test portion size, in g} = \frac{0{,}009\,8 \times M_\mathrm{r}}{n}$$

where

M_r is the molecular mass of the hydroxyl-containing compound;

n is the number of hydroxyl groups in the molecule.

NOTE In each case, the calculation is based on the assumption that a maximum of 9,8 meq of hydroxyl is present.

Since the calculated test portion size will be near the maximum permitted by the method, adhere closely to the amount calculated.

If the sample contains an appreciable amount of water, the test portion size shall be adjusted to accommodate this interference. In this case, determine the test portion size using one of the following formulae:

$$\text{Test portion size, in g} = \frac{0{,}170\,1 \times 0{,}98}{0{,}009\,4R + [0{,}01S \times (n \times 17{,}01) / M_\mathrm{r}]}$$

or

$$\text{Test portion size, in g} = \frac{550}{\text{Expected hydroxyl number} + (31{,}2 \times R)}$$

where

R is the water in the sample, in mass %;

S is the purity of the sample, in mass %;

M_r is the molecular mass of the hydroxyl-containing compound;

n is the number of hydroxyl groups present in the molecule.

Precision and accuracy may be decreased when appreciable amounts of water are present because of the required decrease in test portion size.

8.1.2 Having calculated the appropriate size, weigh the test portion into a clean, dry conical flask (7.10).

8.1.3 Pipette 25,0 ml of the acetylation reagent (6.1) into each flask (7.10) used for test portion and blank determinations, using a uniform drainage time for all aliquots. If necessary, swirl the test portion flask to dissolve the test portion. Connect each flask to a condenser (7.11) (if the surrounding atmosphere