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Plastics — Polyols for use in the production of polyurethanes — Determination of water content

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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 document 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).

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For an explanation of the voluntary nature of standards, 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 www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC61, *Plastics*, Subcommittee SC12, *Thermosetting materials*.

This third edition cancels and replaces the second edition (ISO 14897:2002), of which it constitutes a minor revision.

The changes are as follows:

— the title has been changed to plural form to read: "Plastics — Polyols for use in the production of polyurethanes — Determination of water content".

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This method is for the determination of water content in polyether polyols, which are used in the preparation of polyurethane prepolymers and polyurethane products. Knowledge of this value is important to polyurethane production.

The document is based on ASTM D 4672.

Plastics — Polyols for use in the production of polyurethanes — Determination of water content

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 of this document to establish appropriate safety and health practices and to determine applicable national regulatory conditions prior to use.

1 Scope

This document specifies methods used to measure the water content of polyols employed as polyurethane raw materials.

Method A is a manual amperometric method which has been included to better define the principles of the Karl Fischer measurement. Amperometric methods are applicable to a wide range of polyols, including those which have enough colour to obscure a visual end-point. Method B includes an automated amperometric procedure and an automated coulometric procedure.

The coulometric procedure is an absolute method that does not require calibration and gives improved sensitivity compared with amperometric methods.

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

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 terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
polyol
organic compound containing two or more hydroxyl groups suitable for reaction with isocyanates

3.2
polyurethane
polymer prepared by the reaction of an organic di- or polyisocyanate with compounds containing two or more hydroxyl groups

Note 1 to entry: Polyurethanes may be thermosetting, thermoplastic, rigid or soft and flexible, cellular or non-cellular.

4 Principle

4.1 Methods A and B are based on amperometric or coulometric titrations with Karl Fischer reagent. The sulfur dioxide in the reagent first reacts with the alcohol to form an ester which is neutralized by the base present in the reagent. The anion of the alkyl sulfurous acid is the reactive component. The titration of water present constitutes the oxidation of the alkyl sulfite to alkyl sulfate by the iodine, which consumes the water. The reaction can be formulated as follows[4]:

$$ROH + SO_2 + R'N \rightarrow (R'NH)SO^3R$$

$$H_2O + I_2 + (R'NH)SO_3R + 2R'N \rightarrow (R'NH)SO_4R + 2(R'NH)I$$

4.2 To determine water, Karl Fischer reagent [a solution of iodine, sulfur dioxide, ethylene glycol monomethyl ether ($HOCH_2CH_2OCH_3$) and pyridine or a pyridine substitute] is added to a solution of the test portion in methanol or another alcohol until all of the water present has been consumed. In an amperometric titration, this is evidenced by a current-measuring device that indicates the depolarization of a pair of platinum electrodes. In coulometric titrations, the iodine reagent is generated electrically, thus eliminating the need for standardization of the reagent.

5 Application

These test methods are suitable for quality control, as a specification test for products, and for research. The water content of a polyol is important because water reacts with isocyanates to form carbon dioxide and an amine which consumes additional isocyanate.

NOTE The description of the manual system presented below is principally for reference purposes and has been included in order to better define the principles of the Karl Fischer measurement. Commercially available automated Karl Fischer titrators of the type described in Method B are used extensively. Additional details and diagrams are available in ISO 760.

6 Interferences

6.1 Oxides, hydroxides and strongly basic compounds react with Karl Fischer reagent, producing an equivalent amount of water, thus giving falsely high results. Therefore, this method shall not be used for crude polyols containing KOH or other highly basic products unless corrections are made for the excess water produced.

6.2 Amine-based polyols can shift the pH of the Karl Fischer system into the alkaline range, causing incorrect results. This problem may be circumvented by adding salicylic or benzoic acid in greater than stoichiometric amounts before carrying out the titration. Tests should be run to determine the suitability of the procedure for a particular polyol type.

7 Reagents

7.1 Purity of reagents

Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of ISO 6353-1, ISO 6353-2 and ISO 6353-3. 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.

7.2 Purity of water

Unless otherwise indicated, references to water shall be understood to mean grade 3 water as defined in ISO 3696.

7.3 Reagents for Method A (manual titration)

7.3.1 Karl Fischer reagent, equivalent to 2,5 mg to 3,5 mg of water/ml. Dilute commercially available stabilized Karl Fischer reagent (6 mg of water/ml) with an equal volume of anhydrous ethylene glycol monomethyl ether (containing less than 0,1 % of water).

NOTE Improved, pyridine-free Karl Fischer reagents have been made available and are highly recommended as a replacement for the previous reagents.

7.3.2 Titration solvent (anhydrous methanol): Unless the methanol is extremely dry, it will require a large amount of dilute Karl Fischer reagent to react with its residual water. For this reason, dry the solvent further by adding undiluted Karl Fischer reagent (6 mg of water/ml) to a bottle of methanol until a light red-brown colour persists. Then add methanol until the solution is a pale yellow. A 100 ml portion of the treated solvent should require 1 ml to 10 ml of dilute Karl Fischer reagent.

7.4 Reagent for Method B

7.4.1 Karl Fischer reagent: Commercial reagents and reagent systems of various types are available for use with autotitrators for water determination. These pyridine-free reagents have improved stability and a less objectionable odour than the conventional Karl Fischer reagent. Reagents can be purchased in split or composite forms in different concentrations to fit various ranges of water content. A composite reagent contains all of the components required for a Karl Fischer titration in a single solution. A split reagent implies separate solutions of the solvent and titrant.

8 Apparatus

8.1 Apparatus for Method A (manual titration)

8.1.1 Titration vessel: A vessel of approximately 300 ml capacity, such as a tall-form, lipless beaker provided with a tight-fitting closure to protect the reaction mixture from atmospheric moisture. The vessel shall also be fitted with a nitrogen inlet tube, a 10 ml burette, a stirrer (preferably magnetic) and a port that may be opened momentarily for sample and solvent addition, or removal of electrodes. It is convenient to provide a vacuum line leading to a 1 l trap bottle for drawing off the titrated solution. Pass the nitrogen through a drying tube containing anhydrous calcium sulfate before it enters the titration vessel.

8.1.2 Instrument electrodes, platinum, with a surface equivalent of two No. 26 wires, 4,76 mm long. The wires shall be 3 mm to 8 mm apart and inserted in the vessel so that 75 ml of solution will cover them.

8.1.3 Instrument depolarization indicator, having an internal resistance of less than 5 000 Ω, consisting of a means of applying and indicating a voltage of 20 mV to 50 mV across the electrodes, and capable of indicating a current flow of 10 µA to 20 µA by means of a galvanometer or ratio tuning circuit.

8.1.4 Burette assembly, for Karl Fischer reagent, consisting of a 10 ml burette with 0,05 ml subdivisions and connected by means of glass or polyethylene (not rubber) connectors to a source of reagent. Various types of automatic dispensing burette may be used. Since the reagent loses strength when exposed to moist air, all vents shall be protected against atmospheric moisture by adequate drying tubes containing anhydrous calcium sulfate. All stopcocks and joints shall be lubricated with an inert lubricant.

8.1.5 Weighing pipette, approximately 1 ml.

8.1.6 Syringes, 1 ml and 10 ml, suitable for weighing and delivering viscous liquid samples.

8.1.7 Analytical balance, capable of weighing to 0,1 mg.

8.2 Apparatus for Method B (automated titration)

8.2.1 Autotitrator: Several commercial autotitrators are available for amperometric or coulometric titrations and provide results equivalent to or better than those of the manual procedure described in Method A. These instruments consist of an automated burette assembly, a sealed titration vessel with appropriate electrodes and associated circuitry, and a means for removal of solution after analysis. These automated systems provide several advantages. Atmospheric-moisture contamination can be more closely controlled, calibration is simplified and the preneutralization step is automatic. Titrations are rapid and reagent consumption is low. The newer autotitrators automatically calculate and display or print out the water concentration.

8.2.2 Syringes, 1 ml and 10 ml, suitable for weighing and delivering viscous liquid samples.

8.2.3 Analytical balance, capable of weighing to 0,1 mg.

9 Sampling

9.1 It is essential to avoid changes in the water content of the material during sampling operations. Many polyols are quite hygroscopic, and errors from this source are particularly significant in the determination of the small amount of water usually present. It has been demonstrated that increases in the water content of hygroscopic liquids will occur, even when the analyses are carried out in an air-conditioned laboratory, without using special precautions to exclude atmospheric moisture. Therefore, use almost-filled, tightly capped containers and limit as much as possible contact of the sample with air when transferring the sample to the titration vessel. Notable improvements in accuracy can be expected from placing the entire titration equipment in a nitrogen (or dry air) purged enclosure. Avoid intermediate sample containers, if possible. If several different analyses are to be performed on the same sample, determine the water content first and do not open the sample prior to the actual analysis. If possible, keep the laboratory humidity low, preferably under 50 % relative humidity.