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Binders for paints and varnishes — Determination of hydroxyl value —

Part 3: Rapid test

Liants pour peintures et vernis — Détermination de l'indice d'hydroxyle —
Partie 3: Méthode rapide

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Foreword

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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).

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This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*.

A list of all parts in the ISO 4629 series can be found on the ISO website.

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

The most frequently described method for determining the hydroxyl number is conversion with acetic anhydride in pyridine with subsequent titration of the released acetic acid.

$$H_3C\text{-}CO\text{-}O\text{-}CO\text{-}CH_3 + R\text{-}OH \rightarrow R\text{-}O\text{-}CO\text{-}CH_3 + CH_3COOH$$

However, this method suffers from the following disadvantages:

— the sample is boiled under reflux for 1 h;

— the method cannot be automated;

— small hydroxyl numbers cannot be determined exactly;

— unpleasant and toxic pyridine is used.

For these reasons, a far simpler method was selected for automation. The (primary and secondary) hydroxyl groups are converted to acidic carbamate groups using toluene-4-sulfonyl-isocyanate.

$$H_3C\text{-}(C_6H_4)\text{-}SO_2\text{-}NCO + R\text{-}OH \rightarrow H_3C\text{-}(C_6H_4)\text{-}SO_2\text{-}NH\text{-}COOR$$

The carbamate can then be titrated with the strong base tetrabutylammonium hydroxide (TBAOH) under non-aqueous conditions, i.e. in an organic solvent.

Binders for paints and varnishes — Determination of hydroxyl value —

Part 3:
Rapid test

1 Scope

This document specifies a titrimetric method for determining the hydroxyl groups in resins and binders for paints and varnishes.

This method is primarily suitable for neutral media. Acidic products provide higher values; neutral products provide, through neutralization of the acidic carbamates, lower values. For these products, preliminary tests are performed to ensure the applicability of the method.

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 4618, *Paints and varnishes — Terms and definitions*

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

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4618 and the following apply.

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

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

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

3.1
hydroxyl value
number of milligrams of potassium hydroxide (KOH) corresponding to hydroxyl groups that have been acetylated under specified test conditions in 1 g of the product tested

[SOURCE: ISO 4629-1:2016, 3.1]

4 Principle

The primary and secondary hydroxyl groups of the sample are converted to acidic carbamate groups using toluene-4-sulfonyl-isocyanate. The carbamate can then be titrated with the strong base tetrabutylammonium hydroxide (TBAOH) under non-aqueous conditions, i.e. in an organic solvent.

5 Reagents

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

5.1 Solution of tetrabutylammonium hydroxide (TBAOH) in isopropanol/methanol, *c*(TBAOH) = 1,0 mol/l.

5.2 Reaction solution.

Place approximately 250 ml acetonitrile in a 500 ml volumetric flask and titrate with 20 ml toluene-4-sulfonyl-isocyanate. Make up the solution to the mark with acetonitrile and mix thoroughly. The reaction solution has a shelf life of approximately 1 month.

5.3 Acetonitrile, HPLC-Grade.

5.4 Toluene, analytical grade.

6 Apparatus

Ordinary laboratory equipment and glassware, together with the following.

6.1 Conical flask, capacity about 250 ml.

6.2 Watch glass.

6.3 Burette.

6.4 Potentiometric titration apparatus.

7 Sampling

Take a representative sample of the product to be tested, as specified in ISO 15528.

8 Procedure

Depending on the expected hydroxyl number, weigh out 1 g to 15 g[1)] of the product under test in the conical flask (6.1), dissolve with 3 ml toluene and 7 ml acetonitrile and heat to 30 °C to 35 °C.

Add 10 ml reaction solution (5.2) and cover the flask with the watch glass (6.2). Allow the reaction to proceed for 5 min under gentle stirring. Then add 1,5 ml distilled water (to hydrolyse the excess reaction solution) and stir for an additional 3 min.

Add 30 ml acetonitrile (5.3) and titrate the mixture with the tetrabutylammonium hydroxide solution (5.1) until after the second point of change.

The electrode should be immersed in the solution immediately before the measurement. The electrode and burette shall be rinsed with acetone before each use.

After each titration rinse the electrode and burette tip with acetone followed by distilled water. Then place the electrode in distilled water for 1 min.

1) The optimum sample mass, in grams, can be calculated as follows: 40/expected hydroxyl number (numerical value equation).

9 Expression of results

Calculate the hydroxyl value, HV, in milligrams of KOH per gram, of the product using Formula (1):

$$\mathrm{HV} = \frac{(V_2 - V_1) \cdot c \cdot 56{,}1}{m} \tag{1}$$

where

V_1 is the volume, in millilitres, of tetrabutylammonium hydroxide solution (5.1) at the first point of change;

V_2 is the volume, in millilitres, of tetrabutylammonium hydroxide solution (5.1) at the second point of change;

c is the actual concentration, in moles per litre, of the tetrabutylammonium hydroxide solution (5.1);

56,1 is the factor for the conversion of millilitres of potassium hydroxide, c(KOH) = 1 mol/l, to milligrams of potassium hydroxide;

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

10 Precision

No precision data are currently available.

11 Test report

The test report shall contain at least the following information:

a) all details necessary to identify the product tested;

b) a reference to this document, i.e. ISO 4629-3:2018;

c) the result of the test as indicated in Clause 9;

d) any deviation (by agreement or otherwise) from the test method specified;

e) any unusual features (anomalies) observed during the test;

f) the date of the test.