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Binders for paints and varnishes — Determination of hydroxyl value —

Part 2: Titrimetric method using a catalyst

Liants pour peintures et vernis — Détermination de l'indice d'hydroxyle —

Partie 2: Méthode titrimétrique utilisant un catalyseur

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Contents

Page

Foreword ..... **iv**
Introduction ..... **v**
1 Scope **1**
2 Normative references **1**
3 Terms and definitions **1**
4 Principle **1**
5 Reagents **2**
6 Apparatus **2**
7 Sampling **3**
8 Procedure **3**
8.1 Number of determinations 3
8.2 Test portion 3
8.3 Determination 3
8.4 Blank test 4
8.5 Determination of acid value 4
9 Expression of results **4**
10 Precision **4**
10.1 Repeatability 4
10.2 Reproducibility 4
11 Test report **5**
Bibliography **6**

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).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 35, *Paints and varnishes*, Subcommittee SC 10, *Test methods for binders for paints and varnishes*.

ISO 4629 consists of the following parts, under the general title *Binders for paints and varnishes — Determination of hydroxyl value*:

— *Part 1: Titrimetric method without using a catalyst*

— *Part 2: Titrimetric method using a catalyst*

Introduction

There are several different methods standardized for determining the hydroxyl value of resins. The classic method using pyridine without a catalyst is specified in ISO 4629-1. The advantages of the method using a catalyst are the following:

— the solvents used are less hazardous to health;

— the solvent consumption is lower;

— the method is faster due to shorter reaction times;

— the end point of the titration is easier to see;

— polyols are more readily soluble.

Binders for paints and varnishes — Determination of hydroxyl value —

Part 2: Titrimetric method using a catalyst

1 Scope

This part of ISO 4629 specifies a titrimetric method for determining the hydroxyl value of resins, binders for paints and varnishes, primary alcohols, glycols and fats. Whether it can be applied for hydro carboxylic acids, phenolic hydroxyl groups, polyols such as trimethyl propane and substances containing aromatic groups have been activated for Friedel-Crafts acylation shall be decided on case-to-case basis.

Under the right conditions, the method is also applicable for determining the hydroxyl value of castor oil and its derivatives.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 660, *Animal and vegetable fats and oils — Determination of acid value and acidity*

ISO 2114:2000, *Plastics (polyester resins) and paints and varnishes (binders) — Determination of partial acid value and total acid value*

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

ISO 4618, *Paints and varnishes — Terms and definitions*

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.

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 hydroxyl groups in polyols are acetylated with acetic anhydride. The excess acetic anhydride is titrated with alcoholic potassium hydroxide solution.

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 N-Methylpyrrolidone (NMP).

NOTE Commission chemists' workgroup validate methodologies using less dangerous substances such as dioxolane and other hetero cycles.

5.2 Potassium hydroxide solution, c = 0,5 mol/l in methanol.

Ethanol may also be used if the product to be tested is soluble in ethanol.

5.2.1 Preparation

Weigh, to the nearest 0,05 g, 28 g of potassium hydroxide, dissolve in the minimum quantity of water in a 1 000 ml one-mark flask, dilute to the mark with methanol and mix well.

5.2.2 Standardization

Weigh, to the nearest 0,01 g, 2,5 g of potassium hydrogen phthalate, previously dried at about 120 °C to constant mass and allowed to cool in a desiccator, into a 250 ml flask. Add 150 ml freshly boiled and cooled water and swirl until dissolved.

Titrate the potassium hydroxide solution prepared in 5.2.1, using phenolphthalein solution as indication, until a red coloration that remains for at least 10 s appears.

Calculate the actual concentration, c, in moles of hydroxyl ions (OH^-) per litre, of the potassium hydroxide solution using Formula (1):

$$c = \frac{m}{V} \cdot \frac{1\,000}{204,22} \qquad (1)$$

where

m is the mass, in grams, of potassium hydrogen phthalate taken;

V is the volume, in millilitres, of potassium hydroxide solution used for the titration;

204,22 is the relative molecular mass, in grams per mole, of potassium hydrogen phthalate.

5.3 Methyl ethyl ketone (MEK).

5.4 Demineralized water.

5.5 Acetylating reagent, make up a 10 % solution of acetic anhydride in NMP (5.1).

5.6 Catalyst solution, make up a 1 % (by mass) solution of 4-N-dimethylaminopyridine in NMP (5.1).

5.7 Indicator solution, make up a 1 % (by mass) solution of either thymolphthalein or 0,05 % (by mass) solution of phenolphthalein in NMP (5.1).

6 Apparatus

Ordinary laboratory equipment and glassware, together with the following.

6.1 Automatic titrator.

6.2 Analytical balance.

6.3 250 ml conical flask with grounded joint.

6.4 50 ml motorized piston burette.

6.5 Hot plate.

6.6 Magnetic stirrer.

7 Sampling

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

8 Procedure

8.1 Number of determinations

Carry out the determination in triplicate by titrating the sample potentiometrically or using a colour indicator.

8.2 Test portion

The initial sample mass required for the determination depends on the expected hydroxyl value and shall be calculated using Formula (2):

$$m = \frac{300}{HV_e} \tag{2}$$

where

m is the initial sample mass, in grams;

HV_e is the expected hydroxyl value, in milligrams of KOH per gram, of the product.

Weigh, to the nearest 1 mg, the test portion into the 250 ml conical flask (6.3).

8.3 Determination

Add 30 ml of catalyst solution (5.6) and 10 ml of acetylating reagent (5.5). Close the flask with the stopper and dissolve the sample by stirring and, if necessary, by heating the mixture. Then, while stirring continuously on the magnetic stirrer (6.6), allow the reaction to take place for at least 15 min at ambient temperature (23 ± 2) °C.

All products containing secondary OH–groups require a reaction time of at least 60 min, and that is also found to be the case for polyols containing secondary OH–groups.

Stop the reaction by adding 3 ml of demineralized water (5.4) and stir for a further 12 min.

All products containing secondary OH–groups require a hydrolysis time of at least 30 min.

Remove the flask from the stirrer, rinse the stopper and wall with methyl ethyl ketone (5.3), add two to three drops of indicator solution (5.7) and titrate with potassium hydroxide solution (5.2) until the colourless solution becomes blue (thymolphthalein) or pink (phenolphthalein).

8.4 Blank test

Carry out a blank test, following the same procedure, but omitting the test portion.

It shall be redetermined on a daily basis.

NOTE The value for the blank is around 40 ml.

8.5 Determination of acid value

Determine the acid value of the sample separately as specified in ISO 2114:2000, Method A. For determination of the acid value of animal and vegetable fats and oils, ISO 660 may be used.

9 Expression of results

Calculate the hydroxyl value, HV, in milligrams of KOH per gram, of the product using Formula (3):

$$\mathrm{HV} = \frac{(V_0 - V_1) \cdot c \cdot 56,1}{m} + \mathrm{AV} \tag{3}$$

where

V_0 is the volume, in millilitres, of potassium hydroxide solution (5.2) required for the blank test (8.4);

V_1 is the volume, in millilitres, of potassium hydroxide solution (5.2) required for the determination (8.3);

c is the actual concentration, in moles per litre, of the potassium hydroxide solution (5.2);

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 (8.2);

AV is the acid value (8.5), in milligrams of KOH per gram, of the product.

Report as the final result the hydroxyl value (individual values and mean) to the nearest 1 mg KOH/g.

10 Precision

10.1 Repeatability

Two determinations made consequently on the same day under repeatability conditions with different masses of the final sample shall not differ by more than 0,84 mg KOH/g for hydroxyl values less than 20 and not more than 1,72 mg KOH/g for hydroxyl values between 20 and 200.

10.2 Reproducibility

Two determinations made with the same sample under reproducibility conditions shall not differ by more than 1,36 mg KOH/g for hydroxyl values less than 20 and not more than 3,28 mg KOH/g for hydroxyl values between 20 and 200.

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 part of ISO 4629, i.e. ISO 4629-2;

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

d) the acetylation time;

e) the type of titration: in the presence of a colour indicator (thymolphthalein or phenolphthalein) or potentiometric;

f) any deviation from the test method specified;

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

h) the date of the test.

Bibliography

[1] ISO 4629-1:2016, *Binders for paints and varnishes — Determination of hydroxyl value — Part 1: Titrimetric method without using a catalyst*

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