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Binders for paints and varnishes — Determination of hydroxyl value —

Part 1:
Titrimetric method without using a catalyst

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

Partie 1: Méthode titrimétrique sans catalyseur

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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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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*.

This first edition of ISO 4629-1 cancels and replaces ISO 4629:1996, which has been technically revised with the following changes:

a) the standard has been numbered as ISO 4629-1;

b) the standard has been editorially revised and the normative references have been updated;

c) the concentration of the phenolphthalein-indicator solution has been changed.

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*

Binders for paints and varnishes — Determination of hydroxyl value —

Part 1:
Titrimetric method without using a catalyst

1 Scope

This part of ISO 4629 specifies a titrimetric method for determining the free hydroxyl groups in binders and binder solutions for paints and varnishes. The hydroxyl groups may be present as polyhydric alcohols, partial esters, polyester end groups or hydroxylated fatty acids.

This method is not applicable to resins containing both hydroxyl groups and epoxy groups, because the latter will also be included in the result. Also the method is not applicable to cellulose nitrate or to phenolic resins.

NOTE 1 If, in the case of binder solutions, the hydroxyl value of the binder only is to be determined, the possibility that other constituents of the binder solution may contain hydroxyl groups has to be taken into account.

NOTE 2 A method for the determination of the hydroxyl value of epoxy resins is specified in ISO 7142[1].

2 Normative references

The following referenced 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 385, *Laboratory glassware — Burettes*

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

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

3 Terms and definitions

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

4 Principle

The hydroxyl groups contained in a test portion are acetylated with acetic anhydride. The excess acetic anhydride is hydrolysed and the resulting acetic acid is titrated with potassium hydroxide solution, either in the presence of a colour indicator or potentiometrically.

NOTE Primary and secondary amines, if present, will also be acetylated. In such cases, this will have to be allowed when calculating the hydroxyl value.

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 Potassium hydrogen phthalate [C_6H_4 (COOH) (COOK)].

5.2 Ethyl acetate, anhydrous.

5.3 Toluene/butanol mixture, 1 + 2 by volume.

5.4 Pyridine/water mixture, 3 + 1 by volume.

5.5 Acetylating reagent.

Dissolve 4,0 g of p-toluenesulfonic acid monohydrate ($CH_3C_6H_4SO_3H{\cdot}H_2O$) in 100 ml of ethyl acetate (5.2), preferably using a magnetic stirrer.

To this solution, add slowly, while stirring, 33 ml of acetic anhydride. Check that 5 ml of this reagent requires on titration a volume of between 40 ml and 50 ml of potassium hydroxide solution (5.6) for neutralization.

5.6 Potassium hydroxide, standard volumetric solution, $c(\text{KOH}) \approx 0{,}5$ mol/l, in methanol.

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

5.6.1 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.

5.6.2 Standardization

Weigh, to the nearest 0,01 g, 2,5 g of potassium hydrogen phthalate (5.1), 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 5.6.1, using phenolphthalein solution (5.7) 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.

5.7 Phenolphthalein, 0,5 g/l solution in 95 % (by volume) ethanol, in methanol or in isopropanol.

5.8 Mixed-indicator solution.

Mix three volumes of a 1 g/l ethanolic solution of thymol blue with one volume of a 1 g/l ethanolic solution of cresol red.

6 Apparatus

Ordinary laboratory equipment and glassware, together with the following.

6.1 Conical flask, capacity about 250 ml, with a ground-glass joint.

6.2 Reflux condenser, with a ground-glass joint to the conical flask (6.1).

6.3 Microburette or **pipette**, complying with the requirements of class A of ISO 648, of capacity 5 ml, for acetylating reagent (5.5).

WARNING — If a pipette is used, this shall not be a mouth pipette in view of the corrosive nature of the reagent.

6.4 Burette, of capacity 50 ml, complying with the requirements of ISO 385, for the potassium hydroxide solution (5.6).

6.5 Heating apparatus, e.g. an oil bath or a sand bath, capable of being maintained at (50 ± 1) °C.

6.6 Potentiometric titration apparatus, fitted with a glass electrode and a reference electrode. The use of this apparatus is an optional alternative (see 8.3).

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 duplicate.

8.2 Test portion

By reference to Table 1, select the appropriate mass of test portion to be taken. If the hydroxyl value cannot be predicted, take a test portion of 2,0 g and carry out a preliminary determination.

Table 1 — Mass of test portion

Expected hydroxyl value mg KOH/g	**Approximate mass of test portion** g
40	7,0
50	5,6
60	4,7
70	4,0
80	3,5
90	3,1
100	2,8
140	2,0
180	1,6
200	1,4
250	1,1
280	1,0
350	0,8
400	0,7
500	0,6
1 000	0,3

Weigh to the nearest 1 mg, the test portion into the conical flask (6.1).

8.3 Determination

Add 5 ml of ethyl acetate (5.2) to the contents of the conical flask and shake, if necessary, with gentle warming, until the test portion (8.2) is dissolved.

If the test portion is not soluble in ethyl acetate, another solvent may be used.

Allow to cool to room temperature, add (5,00 ± 0,02) ml (see Note 1) of the acetylating reagent (5.5) by means of the microburette or pipette (6.3) and fit the reflux condenser (6.2) on the conical flask.

Heat the flask in the heating apparatus (6.5), maintained at (50 ± 1) °C, for 20 min, shaking every 5 min.

Cool the contents of the flask to room temperature, remove the condenser, add 2 ml of water, replace the condenser and vigorously shake the flask. Add 10 ml of the pyridine/water mixture (5.4) from the top of the condenser so as to rinse down the condenser tube. Mix the contents of the flask and allow to stand for 5 min at room temperature. Add 30 ml of the toluene/butanol mixture (5.3) from the top of the condenser and use a further 30 ml of the toluene/butanol mixture to rinse the condenser/flask joint.

Titrate with potassium hydroxide solution (5.6)

- either in the presence of a colour indicator (see Note 2), a few drops of phenolphthalein solution (5.7) or mixed-indicator solution (5.8), or
- determining the end point potentiometrically (see Note 3), using the potentiometric titration apparatus (6.6).

NOTE 1 The tolerance of 0,02 ml on the volume of the acetylating reagent is necessary to obtain the required precision of the test result.

NOTE 2 The colour changes are as follows:

- phenolphthalein: colourless (acid)/red (alkaline);
- mixed indicator: yellow (acid)/blue (alkaline).

NOTE 3 For hydroxyl values below 10 or dark-coloured solutions, potentiometric determination of the end point is desirable.

8.4 Blank test

Carry out a blank test, following the same procedure and using (5,00 ± 0,02) ml of the acetylating reagent (5.5), but omitting the test portion.

8.5 Determination of acid value

Determine the acid value in accordance with ISO 2114:2000, Method A.

9 Expression of results

Calculate the hydroxyl value HV, in milligrams of KOH per gram of the product, using Formula (2):

$$\mathrm{HV} = \frac{(V_0 - V_1)\cdot c\cdot 56{,}1}{m} + \mathrm{AV} \qquad (2)$$

where

V_0 is the volume, in millilitres, of potassium hydroxide solution (5.6) required for the blank test (8.4);

V_1 is the volume, in millilitres, of potassium hydroxide solution (5.6) required for the determination (8.3);

c is the actual concentration, in moles per litre, of the potassium hydroxide solution (5.6);

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.

If primary or secondary amines are present, they shall be considered when calculating the hydroxyl value.

If two determination (duplicates) differ by more than 5 % (relative to the mean), repeat the procedure described in Clause 8.

Report as the final result the mean, to the nearest 1 mg KOH/g, of two valid results (replicates).

10 Precision

The precision of the test method depends on the size of the hydroxyl value. The following precision data were obtained in a round-robin test.

Poly(ethylene glycerol) with a hydroxyl value about 30 mg KOH/g:

- Repeatability limit (r): 3,5 %
- Reproducibility limit (R): 8,5 %

Trimethylolpropane with a hydroxyl value about 1 200 mg KOH/g:

- Repeatability limit (r): 13 %
- Reproducibility limit (R): 22 %