INTERNATIONAL STANDARD

ISO 4629

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Binders for paints and varnishes — Determination of hydroxyl value — Titrimetric method

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

Reference number
ISO 4629:1996(E)

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 4629 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes,* Subcommittee SC 10, *Test methods for binders for paints and varnishes.*

This second edition cancels and replaces the first edition (ISO 4629:1978), which has been technically revised.

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Binders for paints and varnishes — Determination of hydroxyl value — Titrimetric method

1 Scope

This International Standard 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.

NOTES

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 will have to be taken into account.

2 A method for the determination of the hydroxyl value of epoxy resins is described in ISO 7142:1984, *Binders for paints and varnishes — Epoxy resins — General methods of test.*

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 842:1984, *Raw materials for paints and varnishes — Sampling.*

ISO 3682:1996, *Binders for paints and varnishes — Determination of acid value — Titrimetric method.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

3 Definition

For the purposes of this International Standard, the following definition applies:

3.1 hydroxyl value: The 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 3 Primary and secondary amines, if present, will also be acetylated. In such cases, this will have to be allowed for 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 defined in ISO 3696.

5.1 Potassium hydrogen phthalate $[C_6H_4(COO)_2HK]$.

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, $c(KOH) \approx 0{,}5$ mol/l, in methanol.

NOTE 4 Ethanol can 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 of freshly boiled and cooled water and swirl until dissolved.

Titrate with the potassium hydroxide solution prepared in 5.6.1, using phenolphthalein solution (5.7) as indicator, 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 the equation

$$c = \frac{m}{V} \times \frac{1\,000}{204{,}22}$$

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 Phenophthalein, 10 g/l solution in 95 % (*V*/*V*) ethanol, in methanol or in isopropanol.

5.8 Mixed-indicator solution.

Mix 3 volumes of a 1 g/l ethanolic solution of thymol blue with 1 volume of a 1 g/l ethanolic solution of cresol red.

6 Apparatus

Ordinary laboratory apparatus 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 fit 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 the acetylating reagent (5.5).

WARNING — If a pipette is used, this should 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 385-1, for the potassium hydroxide solution (5.6).

6.5 Heating apparatus, e.g. an oil bath or 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 8.2).

7 Sampling

Take a representative sample of the product to be tested, as described in ISO 842.

8 Procedure

Carry out the determination in duplicate.

8.1 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).

8.2 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 (8.1) is dissolved.

NOTE 5 If the test portion is not soluble in ethyl acetate, another solvent may have to be used.

Allow to cool to room temperature, add (5,00 ± 0,02) ml (see note 6) 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 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 toluene/butanol mixture (5.3) from the top of the condenser, remove the condenser and use a further 30 ml of 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 7): a few drops of phenolphthalein solution (5.7) or mixed-indicator solution (5.8)

— or determining the end point potentiometrically (see note 8), using the potentiometric titration apparatus (6.6).

NOTES

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

7 The colour changes are as follows:

— phenolphthalein: colourless (acid)/red (alkaline);

— mixed indicator: yellow (acid)/blue (alkaline).

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

8.3 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.

8.4 Determination of acid value

Determine the acid value in accordance with ISO 3682.

9 Expression of results

9.1 Calculation

Calculate the hydroxyl value HV, in milligrams of KOH per gram of product, using the equation

$$HV = \frac{(V_0 - V_1) \times c \times 56{,}1}{m} + AV$$

where

V_0 is the volume, in millilitres, of potassium hydroxide solution (5.6) required for the blank test (8.3);

V_1 is the volume, in millilitres, of potassium hydroxide solution (5.6) required for the determination (8.2);

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 hydrochloric acid, c(HCl) = 1 mol/l, to milligrams of potassium hydroxide;

m is the mass, in grams, of the test portion (8.1);

AV is the acid value (8.4), in milligrams of KOH per gram of product.

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

If the two determinations (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).

9.2 Precision

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

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

— Repeatability (r): 3,5 %

— Reproducibility (R): 8,5 %

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

— Repeatability (r): 13 %

— Reproducibility (R): 22 %

10 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 International Standard (ISO 4629);

c) the result of the test as indicated in 9.1;

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

e) any deviation from the test method specified;

f) the date of the test.