TC35

INTERNATIONAL STANDARD ISO 4629

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Binders for paints and varnishes

~~Paint media~~ — Determination of hydroxyl value — Titrimetric method

Liants pour peintures — Détermination de l'indice d'hydroxyle — Méthode titrimétrique

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FOREWORD

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 4629 was developed by Technical Committee ISO/TC 35, *Paints and varnishes*, and was circulated to the member bodies in July 1976.

It has been approved by the member bodies of the following countries :

Australia	Ireland	Portugal
Austria	Israel	Romania
Brazil	Italy	South Africa, Rep. of
Canada	Korea, Rep. of	Sweden
Chile	Mexico	Switzerland
Czechoslovakia	New Zealand	Turkey
France	Norway	United Kingdom
Germany, F.R.	Peru	Yugoslavia
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INTERNATIONAL STANDA ISO 4629-1978 (E)/ERRATUM

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Paint media — Determination of hydroxyl value — Titrimetric method

ERRATUM

Page 1

Sub-clause 5.6.2 : The formula shoud read as follows :

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

Paint media — Determination of hydroxyl value — Titrimetric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a titrimetric method for the determination of the free hydroxyl groups in paint media. The hydroxyl groups may be present as polyhydric alcohols, partial esters, polyester end groups or hydroxylated fatty acids.

The method is not applicable to resins containing both hydroxyl groups and epoxide groups, because the latter will also be attacked and included in the result. It is also not applicable to cellulose nitrate or phenolic resins.

NOTE — If the hydroxyl value of the binder only is to be determined, the possibility that other constituents of the paint medium may contain hydroxyl groups should be taken into account.

2 REFERENCES

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

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

ISO 3682, *Paint media — Determination of acid value — Titrimetric method.*

3 DEFINITION

For the purpose of this International Standard, the following definition applies.

hydroxyl value : The number of milligrams of potassium hydroxide corresponding to the hydroxyl groups in 1 g of the material.

4 PRINCIPLE

Acetylation of the hydroxyl groups contained in a test portion with acetic anhydride, hydrolysis of the excess acetic anhydride and titration of the resulting acetic acid with potassium hydroxide solution, either in the presence of a colour indicator or potentiometrically.

5 REAGENTS

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

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

5.2 Ethyl acetate, anhydrous.

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

Neutralize this mixture with the potassium hydroxide solution (5.6), in the presence either of the phenolphthalein solution (5.7) or of the mixed indicator solution (5.8) or potentiometrically.

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

5.5 Acetylating reagent

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

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

5.6 Potassium hydroxide, ~~0,5 N~~ standard volumetric methanolic solution, $c(KOH) \approx 0{,}5$ mol/l.

5.6.1 *Preparation*

Weigh, to the nearest 0,001 g, 28,05 g of potassium hydroxide, dissolve in the minimum quantity of water in a 1 000 ml one-mark volumetric flask, dilute to the mark with methanol and mix well.

5.6.2 *Standardization*

Weigh, to the nearest 0,000 1 g, 2,5 g of the potassium hydrogen phthalate (5.1), previously dried at about 120 °C for 2 h and allowed to cool in a desiccator, into a 250 ml conical flask. Add 150 ml of freshly boiled and cooled water and swirl until dissolved.

Titrate with the potassium hydroxide solution (5.6.1), using the phenolphthalein solution (5.7) as indicator.

The ~~exact normality~~ concentration c ~~T~~, in moles of ~~hydroxyl ions (OH^-)~~ KOH per litre, of the solution is given by the formula

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

where

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

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

204,22 is the relative molecular mass of potassium hydrogen phthalate.

5.7 Phenolphthalein, 10 g/l solution in 95 % (*V*/*V*) ethanol, or

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

6.1 Conical flask, of capacity about 250 ml, with ground glass neck.

6.2 Reflux condenser, with ground glass joint, fitting on 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).

NOTE – The pipette should not be a mouth pipette in view of the corrosive nature of the reagent.

6.4 Burette, of capacity 50 ml, for the potassium hydroxide solution (5.6).

6.5 Oil bath or **sand bath** or other suitable heating device, capable of being maintained at 50 ± 1 °C.

If required :

6.6 Device for potentiometric titration, fitted with a glass electrode and a reference electrode.

7 SAMPLING

Take a representative sample of the product to be tested by the method specified in ISO 842.

8 PROCEDURE

8.1 Test portion

Choose the mass of the test portion so that 5 to 6 mmol of hydroxyl groups are present; this corresponds to a mass, in grams, of

$$\frac{280}{\text{expected hydroxyl value}}$$

Do not, however, take a test portion of more than 10 g.

Weigh, to the nearest 0,001 g, the appropriate mass of test portion into the conical flask (6.1).

8.2 Determination

Add 5 ml of the 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.

Allow to cool to ambient temperature, add 5,00 ± 0,02 ml (see 9.1) of the acetylating reagent (5.5) by means of the microburette or the pipette (6.3), and fit the reflux condenser (6.2) onto the conical flask.

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

Cool the contents of the flask to ambient 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 the condenser tube. Mix the contents of the flask and allow to stand for 5 min at ambient temperature. Add 30 ml of the toluene/butanol mixture (5.3) from the top of the condenser, remove the condenser and use a further 30 ml of the toluene/butanol mixture to rinse the condenser/flask glass joint.

Titrate with the potassium hydroxide solution (5.6) either

– in the presence of a colour indicator (see 9.2) : a few drops of the phenolphthalein solution (5.7) or of the mixed indicator solution (5.8), or

– by determining the end-point potentiometrically (see 9.3), using the device (6.6).

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.

9 NOTES ON PROCEDURE

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

9.2 The colour changes are as follows :

– Phenolphthalein : colourless (acid)/red (alkaline).

– Mixed indicator : yellow (acid)/blue (alkaline).

9.3 For the potentiometric titration, use glass electrodes having a suitable response time.

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

10 EXPRESSION OF RESULTS

10.1 Calculation

The hydroxyl value is given, in milligrams of potassium hydroxide per gram of sample, by the formula

$$\frac{(V_0 - V_1) \times T \times 56{,}1}{m_0} + AV$$

where

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

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

T is the exact normality of the potassium hydroxide solution (5.6);

AV is the acid value of the sample, in milligrams of potassium hydroxide per gram of product, determined by the method specified in ISO 3682;

m_0 is the mass, in grams, of the test portion (8.1).

10.2 Precision

Under consideration.

11 TEST REPORT

The test report shall contain at least the following information :

a) the type and identification of the product tested;

b) a reference to this International Standard or to a corresponding national standard;

c) the type of titration : potentiometric or in the presence of an indicator;

d) the hydroxyl value, expressed in milligrams of potassium hydroxide per gram of product (mg KOH/g);

e) any deviation, by agreement or otherwise, from the procedure specified;

f) the date of the test.