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International Standard 6796

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Polyglycols for industrial use — Determination of hydroxyl number — Phthalic anhydride esterification method

Polyglycols à usage industriel — Détermination de l'indice d'hydroxyle — Méthode par estérification à l'anhydride phtalique

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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 6796 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in January 1980.

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

Australia	Germany, F. R.	Poland
Austria	Hungary	Romania
Belgium	India	South Africa, Rep. of
Brazil	Italy	Switzerland
China	Korea, Rep. of	Thailand
Czechoslovakia	Netherlands	United Kingdom
France	Philippines	USSR

No member body expressed disapproval of the document.

This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

Printed in Switzerland

Polyglycols for industrial use — Determination of hydroxyl number — Phthalic anhydride esterification method

1 Scope and field of application

This International Standard specifies an esterification method for the determination of the hydroxyl number of the following polyglycols for industrial use :

— poly(ethylene glycol) $[HO(C_2H_4O)_nH]$, where n is greater than 3;

— poly(propylene glycol) $[HO(C_3H_6O)_nH]$, where n is greater than 3.

The method is not recommended for products containing more than 0,2 % (m/m) of water, unless the sample is first dried.

2 References

ISO 1389/6, *Phthalic anhydride for industrial use — Methods of test — Part 6 : Determination of phthalic anhydride content — Titrimetric method.*

ISO 2211, *Liquid chemical products — Measurement of colour in Hazen units (platinum-cobalt scale).*

3 Definition

hydroxyl number $I(OH)$: The number of milligrams of potassium hydroxide corresponding to the hydroxy groups (OH) content of 1 g of product.

4 Principle

Esterification of hydroxy groups present in a test portion with phthalic anhydride. Hydrolysis of the excess phthalic anhydride and neutralization of the phthalic acid formed with standard volumetric sodium hydroxide solution.

5 Reagents

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

5.1 Phthalic anhydride, assay at least 99 % (m/m) as determined by the method specified in ISO 1389/6.

WARNING — Irritating to eyes, respiratory system and skin.

5.2 Pyridine.

WARNING — Pyridine is highly toxic, highly flammable and harmful by inhalation, contact with skin and if swallowed. In case of contact with skin or eyes, rinse immediately with plenty of water.

The reagent shall pass the following quality test.

Place 7 g of the phthalic anhydride (5.1) and 50 ml of the pyridine in a glass-stoppered flask. Shake vigorously until the phthalic anhydride has dissolved and heat at 50 to 60 °C for 30 min. Allow to stand at room temperature in the dark for 24 h. Measure the colour of the solution by the method specified in ISO 2211. The pyridine is acceptable if the colour of the solution is lighter than 200 Hazen units.

If the pyridine marginally fails this test, it may be refined by distilling with 5 % of its volume of the phthalic anhydride (5.1), discarding the fraction boiling below 114 °C and collecting the fraction distilling between 114 and 116 °C.

5.3 Phthalic anhydride/pyridine solution (see **warnings** in 5.1 and 5.2).

Weigh 111 to 116 g of the phthalic anhydride (5.1) into a 1 000 ml, brown, ground glass-stoppered bottle. Add 700 ml of the pyridine (5.2) and shake vigorously until the phthalic anhydride has dissolved. Allow the reagent to stand overnight before use.

In the blank test (8.2), 25,0 ml of this reagent shall be equivalent to between 47,5 and 50,0 ml of the standard volumetric sodium hydroxide solution (5.5).

Check the colour of the solution periodically by the method specified in ISO 2211 and discard it if the value exceeds 200 Hazen units.

5.4 Phenolphthalein, 10 g/l solution in pyridine (see **warning** in 5.2).

Dissolve 1 g of phenolphthalein in 100 ml of the pyridine (5.2) and make faintly pink by addition of the sodium hydroxide solution (5.6).

5.5 Sodium hydroxide, standard volumetric solution, $c(NaOH) = 1$ mol/l.

5.6 Sodium hydroxide, standard volumetric solution, c(NaOH) = 0,1 mol/l.

5.7 Hydrochloric acid, approximately 3,6 g/l solution.

6 Apparatus

Ordinary laboratory apparatus and

6.1 Conical flasks, of borosilicate glass, capacity 250 ml, fitted with ground glass stoppers.

6.2 Water-cooled reflux condensers, with ground glass joints to fit the flasks (6.1). Each condenser shall be fitted with a guard tube containing anhydrous calcium chloride.

7 Sampling

Methods of sampling liquid chemical products will form the subject of a future International Standard.

Place the laboratory sample, representative of the material taken from the bulk, in a clean, dry, stoppered bottle of such size that it is nearly filled by the sample. If it is necessary to seal this bottle, take care to avoid any risk of contamination.

8 Procedure

WARNING — Prevent contact of reagents 5.1, 5.2, 5.3 and 5.4 (see warnings) with skin and eyes. Avoid breathing the vapours. Do not pipette by mouth.

8.1 Test portion

Weigh, to the nearest 0,001 g, a mass (m) of the laboratory sample, as calculated from either of the following formulae

$$m = \frac{561}{I(\mathrm{OH})} \quad \text{or} \quad m = \frac{M_r}{100\ n}$$

where

I(OH) is the expected hydroxyl number;

M_r is the expected mean relative molecular mass;

n is the number of hydroxy groups per molecule [n = 2 for poly(ethylene glycol) and poly(propylene glycol)].

NOTE — If the water content exceeds 0,2 % (m/m), take the test portion from part of the laboratory sample which has been dried as follows.

Take a mass of the laboratory sample that is about five times the mass required for the test portion and spread it in a thin layer on a watch glass. Place the watch glass and its content in a desiccator containing an efficient drying agent [for example, concentrated sulphuric acid or phosphorus(V) oxide] and leave to stand under vacuum for at least 12 h.

This procedure is also recommended if doubts exist as to the magnitude of the water content of the laboratory sample.

8.2 Blank test

Carry out a blank test at the same time as the determination using the same procedure and the same reagents, but omitting the test portion.

8.3 Determination

Place the test portion (8.1) in one of the conical flasks (6.1). Introduce, from a one-mark pipette, 25,0 ml of the phthalic anhydride/pyridine solution (5.3).

Add some anti-bumping granules (see the note), attach the flask to one of the condensers (6.2) and reflux for about 30 min on an electric hot plate. Withdraw the flask, still fitted with its condenser, and allow to stand at room temperature for about 15 min. Wash down the inside of the condenser, first with 25 ml of the pyridine (5.2) and then with 15 ml of water. Disconnect the flask and wash the joints with a further 10 ml of water.

NOTE — The anti-bumping granules should be neutral. In case of doubt, boil the granules with water.

Add a few drops of the phenolphthalein solution (5.4) and titrate immediately with the standard volumetric sodium hydroxide solution (5.5) until the first appearance of a pink coloration which persists for at least 15 s. It is essential that the difference between the titration values for the blank test (8.2) and the determination (8.3) is between 9 and 11 ml; if not, repeat the procedure, adjusting the mass of the test portion accordingly.

8.4 Acidity or alkalinity correction

8.4.1 Preparation of the solution

Weigh into a 250 ml conical flask the same mass of laboratory sample as in 8.1. Add 50 ml of the pyridine (5.2), 15 ml of water and a few drops of the phenolphthalein solution (5.4).

8.4.2 Acidity correction

If the solution (8.4.1) is colourless, titrate with the standard volumetric sodium hydroxide solution (5.6) until the first appearance of a faint pink coloration that persists for at least 15 s.

Carry out a blank test on the reagents mixture specified in 8.4.1, but omitting the laboratory sample.

8.4.3 Alkalinity correction

If the solution (8.4.1) is pink, add the hydrochloric acid solution (5.7) until the pink colour is just discharged and then add 1,0 ml in excess. Back titrate with the standard volumetric sodium hydroxide solution (5.6) until the first appearance of a faint pink coloration that persists for at least 15 s.

Carry out a blank test on the reagents mixture (8.4.1), less the laboratory sample, by adding the same amount of the hydrochloric acid solution (5.7) as was added to the solution (8.4.1) and back titrating the mixture with the standard volumetric sodium hydroxide solution (5.6).

9 Expression of results

9.1 Neutral samples

The hydroxyl number, expressed as milligrams of potassium hydroxide per gram of sample [dried or with a water content which does not exceed 0,2 % (m/m)], is given by the formula

$$\frac{56{,}1 \times (V_1 - V_2) \times c_1}{m_0}$$

where

V_1 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (5.5) required for the blank test (8.2);

V_2 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (5.5) required for the determination (8.3);

c_1 is the exact concentration, in moles of NaOH per litre, of the standard volumetric sodium hydroxide solution (5.5);

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

56,1 is the relative molecular mass of potassium hydroxide (KOH).

9.2 Acidic or alkaline samples

If the sample contains free acidity or alkalinity, as determined in 8.4, correct the result in 9.1 by adding the correction for acidity or subtracting the correction for alkalinity, as follows :

— *acidity correction :*

$$\frac{56{,}1 \times (V_3 - V_4) \times c_2}{m_1}$$

— *alkalinity correction :*

$$\frac{56{,}1 \times (V_4 - V_3) \times c_2}{m_1}$$

where

V_3 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (5.6) required for the acidity/alkalinity correction sample titration (8.4);

V_4 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (5.6) required for the acidity/alkalinity correction blank titration (8.4);

c_2 is the exact concentration, in moles of NaOH per litre, of the standard volumetric sodium hydroxide solution (5.6);

m_1 is the mass, in grams, of the test portion taken for the acidity/alkalinity correction (8.4);

56,1 has the same meaning as in 9.1.

9.3 Apparent relative molecular mass

From the corrrected hydroxyl number, the apparent relative molecular mass may be calculated by the formula

$$\frac{56{,}1 \times n}{I(\mathrm{OH})} \times 1\,000$$

where

I(OH) is the hydroxyl number corrected in accordance with 9.2;

n is the number of hydroxy groups per molecule [$n = 2$ for poly(ethylene glycol) and poly(propylene glycol)];

56,1 has the same meaning as in 9.1.

10 Test report

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or in the International Standards to which reference is made, or regarded as optional.