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Plastics — Unsaturated polyester resins — Determination of hydroxyl value

~~Matières~~ Plastiques — Résines de polyesters non saturés — Détermination de l'indice d'hydroxyle

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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.

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It has been approved by the Member Bodies of the following countries:

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Belgium	India	South Africa, Rep. of
Brazil	Israel	Sweden
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Egypt, Arab Rep. of	Netherlands	Turkey
Finland	New Zealand	United Kingdom
France	Poland	U.S.A.
Germany	Portugal	U.S.S.R.

No Member Body expressed disapproval of the document.

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Plastics — Unsaturated polyester resins — Determination of hydroxyl value

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method for determining the hydroxyl value of unsaturated polyester resins.

In fact, this method determines the difference between the hydroxyl value and the acid value; it is therefore necessary to determine the acid value separately, in order to calculate the hydroxyl value.

NOTE – The hydroxyl value of saturated polyester resins (for example, polyester resin used for the manufacture of polyurethanes and polymeric plasticizers) and of certain types of alkyd resins may also be determined by this method.

2 REFERENCE

ISO 2114, *Plastics — Unsaturated polyester resins — Determination of acid value.*

3 DEFINITION

hydroxyl value : The number of milligrams of potassium hydroxide necessary to neutralize the acetic acid which will combine by acetylation with 1 g of the unsaturated polyester resin.

4 PRINCIPLE

Acetylation of the hydroxyl groups by acetic anhydride is carried out on an ethyl acetate solution of the resin in the presence of toluene-4-sulphonic acid catalyst. The excess acetic anhydride is hydrolyzed by a pyridine/water mixture and the resultant acetic acid titrated with standard volumetric methanolic potassium hydroxide solution.

In this titration, the free acid groups which exist in the resin are also neutralized by the potassium hydroxide. The hydroxyl value is finally calculated by taking into account the acid value determined separately.

5 REAGENTS

5.1 Acetic anhydride acetylating solution, approximately 1 M, in ethyl acetate.

Dissolve 1,4 g of pure, dry toluene-4-sulphonic acid in 111 ml of anhydrous ethyl acetate. When completely dissolved, slowly add, while mixing, 12 ml of freshly distilled acetic anhydride and store in a dry atmosphere.

5.2 Ethyl acetate, anhydrous.

5.3 Pyridine/water mixture, 3 + 2 (*V*/*V*).

Mix 3 volumes of pyridine, analytical reagent quality, with 2 volumes of water.

5.4 Butanol-1/toluene mixture, 2 + 1 (*V*/*V*).

5.5 Mixed indicator solution.

Mix 3 volumes of a 0,1 % ethanolic solution of thymol blue with 1 volume of a 0,1 % ethanolic solution of cresol red.

5.6 Potassium hydroxide, 0,5 N standard volumetric solution in methanol.

6 APPARATUS

Ordinary laboratory apparatus, and

6.1 Conical flask, capacity 250 ml, with a ground glass stopper.

6.2 Magnetic stirrer, with a magnetic bar covered with a corrosion-resistant material (for example PTFE).

6.3 Burette, capacity 50 ml, graduated in 0,05 ml.

6.4 Water bath, controlled at a temperature of 50 ± 1 °C.

6.5 Pipette, capacity 10 ml (for the acetylating solution).

6.6 If necessary : **Apparatus for potentiometric titration.**

7 PROCEDURE

Weigh, to the nearest 1 mg, in the 250 ml conical flask (6.1), a test portion of the resin containing approximately 5 milli-equivalents of OH (the mass in grams of the sample = 280/hydroxyl value).

NOTE – If the approximate hydroxyl value is not known, preliminary tests should be made.

Add exactly 10 ml of the acetylating solution (5.1) and the magnetic bar (see 6.2).

Stopper the conical flask after moistening the stopper with ethyl acetate (5.2) and dissolve the test portion, using the magnetic stirrer (6.2).

NOTE – Should the sample not dissolve completely on warming, 5 or 10 ml of the acetylating solution may be added.

Place the conical flask in the water bath at 50 ± 1 °C, taking care to immerse it only about 10 mm, and leave it for 45 min.

NOTE – This time may be reduced, for example to 30 min or less, provided it can be shown that equivalent results are obtained.

Remove the conical flask from the bath, cool, place on the magnetic stirrer and add 2 ml of distilled water. When the solution has been thoroughly mixed, add 10 ml of the pyridine/water mixture (5.3) and stir for 5 min.

Rinse the stopper and inner surface of the conical flask with 60 ml of the butanol-1/toluene mixture (5.4) and add 5 drops of the mixed indicator solution (5.5).

Continue stirring and titrate with the methanolic potassium hydroxide solution (5.6). When the colour change is observed, add a further 1 to 2 drops of the mixed indicator. The solution changes from yellow to clear; note the volume V_1, in millilitres, of potassium hydroxide solution used. Add a further drop of the potassium hydroxide solution : the indicator colour should turn to blue. If it does not, note the burette reading and add a further drop of the mixed indicator solution; continue in this way until the blue colour is obtained.

The value of V_1 to be used for the calculation is the one noted before adding the drop which produced the blue colour.

Carry out a blank test under the same conditions, but without the test portion, and note the volume V_2, in millilitres, of potassium hydroxide solution used.

At least two tests should be carried out. The results of the two tests should not differ by more than 2 units of the hydroxyl value. If this is not the case, further tests should be carried out until the results of two consecutive tests fulfil the requirement.

NOTE – It is possible, as an alternative, especially when dealing with densely coloured products, to replace the titration in the presence of an indicator by a potentiometric titration. Use a calomel reference electrode with a bridge containing a saturated solution of potassium chloride in methanol and a glass electrode connected to a pH meter or to a millivoltmeter.

8 EXPRESSION OF RESULTS

From each of the two results obtained, calculate the hydroxyl value by the formula

$$\frac{(V_2 - V_1) \times N \times 56{,}1}{m} + \mathrm{Av}$$

where

Av is the acid value[1];

V_1 is the volume, in millilitres, of standard volumetric potassium hydroxide solution used in the determination;

V_2 is the volume, in millilitres, of standard volumetric potassium hydroxide solution used in the blank test;

N is the normality of the standard volumetric potassium hydroxide solution (usually 0,5 N);

m is the mass, in grams, of the test portion.

Calculate the average of the two values obtained to the nearest unit.

NOTE – The value of $(V_2 - V_1)$ can be positive or negative.

9 TEST REPORT

The test report shall include the following particulars :

a) a reference to this International Standard;

b) the individual results and their mean;

c) any special features noted during the determination;

d) any operations not specified in this International Standard, or that document to which reference is made, and all incidents that may have affected the results.

1) Determine the acid value in accordance with ISO 2114.

It should be noted however that the results obtained correspond to only half of the free anhydrides. In the case of resins based on maleic anhydride/hexachloro-endomethylene-tetrahydrophthalic acid and maleic anhydride/tetrahydrophthalic acid, the error is very small, being slightly greater in the case of resins of maleic anhydride/orthophthalic acid type.