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Third edition
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Plastics (polyester resins) and paints and varnishes (binders) — Determination of partial acid value and total acid value

Plastiques (résines de polyesters) et peintures et vernis (liants) — Détermination de l'indice d'acide partiel et de l'indice d'acide total

Reference number
ISO 2114:2000(E)

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 2114 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 12, *Thermosetting materials.*

This third edition cancels and replaces the second edition (ISO 2114:1996) as well as ISO 3682:1996, which have been technically revised.

Plastics (polyester resins) and paints and varnishes (binders) — Determination of partial acid value and total acid value

1 Scope

This International Standard specifies methods of determining the partial acid value (method A) and the total acid value (method B) of polyester resins and binders for paints and varnishes. It is not applicable to phenolic resins.

It is intended to provide quality-control data for the acceptance or rejection of such products in accordance with the terms of a specification, as well as to be used in research and development to monitor the completion of the polycondensation reaction.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

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

ISO 3251:1993, *Paints and varnishes — Determination of non-volatile matter of paints, varnishes and binders for paints and varnishes.*

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

ISO 6353-2:1983, *Reagents for chemical analysis — Part 2: Specifications — First series.*

3 Terms and definitions

For the purposes of this International Standard, the following terms and definitions apply.

3.1
acid value
the number of milligrams of potassium hydroxide (KOH) required to neutralize 1 g of resin under the test conditions

3.2
partial acid value
acid value corresponding to the neutralization of all the carboxyl-terminated groups and free acids plus half the free anhydrides in a resin

3.3
total acid value
acid value corresponding to the neutralization of all the carboxyl-terminated groups and free acids plus all the free anhydrides in a resin

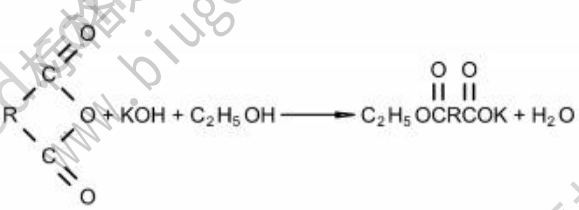
4 Principle

4.1 General

The free acids/anhydrides contained in a test portion are titrated with potassium hydroxide solution, either potentiometrically or in the presence of a colour indicator.

4.2 Method A

A weighed quantity of resin is dissolved in a solvent mixture. The solution is titrated potentiometrically (see note 1) with a standard volumetric solution of potassium hydroxide in ethanol, giving the following reaction:

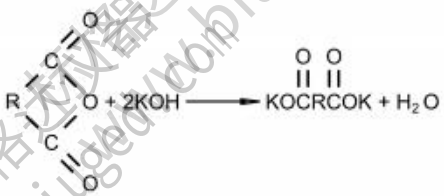


The amount, in milligrams, of potassium hydroxide used to neutralize 1 g of resin is then calculated.

Method A is recommended for binders for paints and varnishes (as generally only small amounts of free anhydrides are present) but is also suitable for unsaturated-polyester resins.

4.3 Method B

A weighed quantity of resin is dissolved in a solvent mixture including water. The free anhydrides are allowed to hydrolyse for 20 min before titrating potentiometrically (see note 1) with a standard volumetric solution of potassium hydroxide in ethanol, giving the following reaction:



The amount, in milligrams, of potassium hydroxide used to neutralize 1 g of resin is then calculated.

Method B is useful for unsaturated-polyester resins in which there are significant amounts of free anhydrides.

NOTE 1 The use of a colour indicator for the titration is an optional alternative in both methods.

NOTE 2 When titrating pure maleic polyester resins, it is better to use a methanolic solution of potassium hydroxide.

5 Reagents

During the analysis, use only reagents of recognized analytical grade in accordance with ISO 6353-2 and water of at least grade 3 as defined in ISO 3696.

5.1 Solvent for method A: solvent mixture containing 2 parts of toluene (5.7) and 1 part of ethanol (5.5) by volume.

Neutralize the solvent mixture with potassium hydroxide solution (5.3) prior to use, using phenolphthalein as indicator if the determination is to be carried out by potentiometric titration (see 7.2.2) or, if the determination is to be carried out using an indicator (see 7.2.3), using the same indicator as will be used for the determination.

5.2 Solvent for method B: solvent mixture containing 400 ml of pyridine (5.8), 750 ml of methyl ethyl ketone (5.9) and 50 ml of water.

5.3 Potassium hydroxide, 0,1 mol/l standard volumetric solution in ethanol (5.5) or in methanol (5.6), free from carbonates.

Check the concentration of this solution on the day of use (see annex A).

If more than 25 ml of titrant will be required with a 0,1 mol/l solution, use a 0,5 mol/l solution to avoid the additional errors involved in refilling the burette (6.3).

5.4 Acetone, containing less than 0,3 % by mass of water.

5.5 Ethanol, anhydrous, containing less than 0,2 % by mass of water.

5.6 Methanol, anhydrous, containing 99,8 % by mass.

5.7 Toluene, anhydrous, containing less than 0,005 % by mass of water.

5.8 Pyridine, containing less than 0,05 % by mass of water.

WARNING — Pyridine is toxic and flammable. Take proper precautions when handling this reagent. Avoid contact with the skin or eyes. Use only in a well ventilated area in order to avoid breathing in the vapour.

5.9 Methyl ethyl ketone, containing less than 0,01 % by mass of water.

5.10 Indicators (for optional alternative):

5.10.1 Bromothymol blue, 0,1 % solution in ethanol (5.5).

5.10.2 Phenolphthalein, 1 % solution in ethanol (5.5).

6 Apparatus

Ordinary laboratory apparatus and glassware, plus the following:

6.1 Conical flasks, of capacities 100 ml and 250 ml, with a wide neck.

6.2 Conical flask, of capacity 250 ml, with a narrow neck and fitted with a ground-glass stopper.

6.3 Burette, of capacity 25 ml (graduated in 0,05 ml divisions), complying with the requirements of ISO 385-1.

6.4 Magnetic stirrer.

6.5 Pipettes, of capacity 25 ml and 50 ml.

6.6 Automatic pipettes, of capacity 25 ml, 50 ml and 60 ml.

6.7 Analytical balance, accurate to 1 mg.

6.8 Potentiometric-titration apparatus, comprising a suitable potentiometer fitted with a glass reference electrode system and a titration stand.

7 Procedure

7.1 Test portion

By reference to Table 1, select the appropriate mass of test portion to be taken.

Table 1 — Mass of test portion

Expected acid value mg KOH/g	Approximate mass of test portion g
0 to 5	⩾ 16
> 5 to 10	8
> 10 to 25	4
> 25 to 50	2
> 50 to 100	1
> 100	0,7

7.2 Method A

7.2.1 Number of determinations

Make two determinations.

7.2.2 Potentiometric-titration procedure

Weigh each test portion into a 250 ml wide-neck conical flask (see 6.1) to the nearest 0,001 g (mass m_1). Add 50 ml of solvent mixture (5.1) using a pipette (6.5). Mix until the resin is completely dissolved.

If solubility is incomplete after 5 min, prepare another test portion, but dissolve it in 50 ml of solvent mixture (5.1) and 25 ml of acetone (5.4).

Place the conical flask on the titration stand (see 6.8) and adjust its position so that the electrode is well immersed. Titrate potentiometrically with potassium hydroxide solution (5.3) using a burette (6.3). Record the volume (V_1), in millilitres, of KOH solution used to reach the end point (the point of inflection of the titration curve).

Carry out a blank determination in the same way, using 50 ml of solvent mixture and, if needed, 25 ml of acetone. Record the volume (V_2), in millilitres, of KOH solution used. If the neutralization of the solvent mixture has been carried out correctly, the result of the blank determination will be zero.

7.2.3 Colorimetric-titration procedure

As an alternative, a colour indicator can be used instead of the potentiometric-titration apparatus, as follows:

Add at least 3 drops of phenolphthalein solution (5.10.2) to the dissolved test portion. Titrate with potassium hydroxide solution from the burette until a red coloration just appears and is stable for at least 10 s while the solution is stirred. If the colour change with phenolphthalein is not very definite, use another indicator, for example 5 drops of bromothymol blue (5.10.1) (for which the end point is when the colour remains blue for 20 s to 30 s). Record the volume (V_1), in millilitres, of KOH solution used.

Carry out a blank determination using 50 ml of solvent mixture and, if needed, 25 ml of acetone. Add the same quantity of indicator solution. Titrate to the same end point as obtained when the resin was present. Record the volume (V_2), in millilitres, of KOH solution used. If the neutralization of the solvent mixture has been carried out correctly, the result of the blank determination will be zero (use the same indicator to neutralize the solvent and to carry out the determination).

7.3 Method B

7.3.1 Number of determinations

Make two determinations.

7.3.2 Potentiometric-titration procedure

Weigh the test portion into a 250 ml narrow-neck conical flask (6.2) to the nearest 0,001 g (mass m_2). Add 60 ml of solvent mixture (5.2) using a pipettte (6.6). Stopper the flask and place it on the magnetic stirrer (6.4). Stir until the resin is completely dissolved, and continue stirring for 20 min to complete the hydrolysis of the anhydride groups. Heat the flask if required to obtain complete dissolution, using a water bath and a condenser on the flask. Then cool to room temperature.

Place the conical flask on the titration stand (see 6.8) and adjust its position so that the electrode is well immersed. Titrate potentiometrically with potassium hydroxide solution (5.3) from a burette (6.3). Record the volume (V_3), in millilitres, of KOH solution used to reach the end point (the point of inflection of the titration curve).

Carry out a blank determination in the same way, using 60 ml of solvent mixture. Record the volume (V_4), in millilitres, of KOH solution used. If the neutralization of the solvent mixture has been carried out correctly, the result of the blank determination will be zero.

7.3.3 Colorimetric-titration procedure

As an alternative, a colour indicator can be used, as follows:

Add at least 5 drops of phenolphthalein solution (5.10.2) to the dissolved test portion. Titrate with potassium hydroxide solution (5.3) from a burette (6.3), with stirring, until the colour remains pink for 20 s to 30 s. Record the volume (V_3), in millilitres, of KOH solution used.

Carry out a blank determination in the same way, using 60 ml of solvent mixture and adding at least 5 drops of phenolphthalein. Titrate to the same end point as obtained when the resin was present. Record the volume (V_4), in millilitres, of KOH solution used. If the neutralization of the solvent mixture has been carried out correctly, the result of the blank determination will be zero (use the same indicator to neutralize the solvent and to carry out the determination).

8 Calculation and expression of results

8.1 Calculation for method A

8.1.1 Partial acid value (PAV) calculated for the test portion [solid resin in a solvent or diluting agent (styrene)]

For each determination, calculate the partial acid value (PAV), in milligrams of KOH per gram, from the equation:

$$\mathrm{PAV} = \frac{56{,}1\,(V_1 - V_2)\,c}{m_1} \qquad (1)$$

where

56,1 is a constant (molar mass of KOH in g/mol);

m_1 is the mass, in grams, of the test portion;

V_1 is the volume, in millilitres, of KOH solution (5.3) used to neutralize the resin solution;

V_2 is the volume, in millilitres, of KOH solution (5.3) used in the blank determination;

c is the concentration, in moles per litre, of the KOH solution (5.3).

8.1.2 Partial acid value calculated for the solid resin (PAV_s)

As an alternative, the partial acid value of the solid resin may be calculated (for example in the case of alkyd resins). The non-volatile-matter content of the resin is first determined in accordance with ISO 3251. Then the partial acid value of the solid resin (PAV_s) is determined, in milligrams of KOH per gram, from the equation:

$$\mathrm{PAV_s} = \frac{\mathrm{PAV} \times 100}{\mathrm{NV}} \qquad (2)$$

where

PAV is the partial acid value as determined in 8.1.1;

NV is the non-volatile-matter content, in % by mass, determined in accordance with ISO 3251.

8.2 Calculation for method B

8.2.1 Total acid value (TAV) calculated for the test portion [solid resin in a solvent or diluting agent (styrene)]

For each determination, calculate the total acid value (TAV), in milligrams of KOH per gram, from the equation:

$$\mathrm{TAV_s} = \frac{56{,}1\,(V_3 - V_4)\,c}{m_2} \qquad (3)$$

where

56,1 is a constant (molar mass of KOH in g/mol);

m_2 is the mass, in grams, of the test portion;

V_3 is the volume, in millilitres, of KOH solution (5.3) used to neutralize the resin solution;

V_4 is the volume, in millilitres, of KOH solution (5.3) used in the blank determination;

c is the concentration, in moles per litre, of the KOH solution (5.3).

8.2.2 Total acid value (TAV_s) calculated for the solid resin

As an alternative, the total acid value of the solid resin may be calculated (for example in the case of alkyd resins). The non-volatile-matter content of the resin is first determined in accordance with ISO 3251. Then the total acid value of the solid resin (TAV_s) is determined, in milligrams of KOH per gram, from the equation:

$$TAV_s = \frac{TAV \times 100}{NV}$$

where

TAV is the total acid value as determined in 8.2.1;

NV is the non-volatile-matter content, in % by mass, determined in accordance with ISO 3251.

8.3 Expression of results

The results may be expressed as the acid value of the solid resin or as the acid value of the resin diluted in a solvent (or diluting agent). The way in which the results are expressed shall be stated in the test report.

If the two individual results (replicates) differ by more 3 % (relative to the mean), repeat the procedure.

9 Precision

Following round-robin testing organized in France in 1995, the precision of methods A and B (with a confidence level of 95 %) is as follows:

15 < acid value < 25; $s_r = 0{,}23$; $r = 0{,}6$; $s_R = 0{,}74$; $R = 2$

where

s_r is the within-laboratory standard deviation;

s_R is the interlaboratory standard deviation;

r is the repeatability (absolute value), i.e. the value below which the absolute difference between two results, each the mean of replicates, obtained on identical material by the same operator in the same laboratory using the same equipment within a short interval of time using the standardized test method is not significant;

R is the reproducibility (absolute value), i.e. the value below which the absolute difference between two results, each the mean of replicates, obtained on identical material by operators in different laboratories using the standardized test method is not significant.

10 Test report

The test report shall include the following particulars:

a) a reference to this International Standard;

b) all details necessary for complete identification of the material tested (including type, source, manufacturer's designation, form in which supplied, etc.);

c) the type of titration carried out (potentiometric or with a colour indicator) (if an indicator was used, state which);

d) the method used (A or B);

e) the mean of two valid results (replicates), rounded to the nearest 0,1 mg KOH/g, and whether the results were determined on solid or diluted resin;

f) the place and date of the test;

g) details of any operation not specified in this International Standard and of any incident which may have affected the results.

Annex A
(informative)

Checking the concentration of the standard potassium hydroxide solution

A.1 General

This annex proposes a routine method for checking the concentration of the standard potassium hydroxide solution to ensure that it is free of carbonates.

If the concentration determined is the same as the initial one, the potassium hydroxide solution is usable for the determination of acid values.

If the concentration differs by more than 2 % from the initial one, the potassium hydroxide solution should be either discarded or the exact concentration taken into account in the calculation of the acid value.

A.2 Reagents

A.2.1 Water, of at least grade 3 as defined in ISO 3696.

A.2.2 Potassium hydrogen *o*-phthalate, reagent grade.

A.3 Apparatus

A.3.1 Analytical balance, accurate to 0,1 mg.

A.3.2 Burette, of capacity 50 ml.

A.4 Procedure

A.4.1 Colour-indicator method

Weigh, to the nearest 0,1 mg, approximately 700 mg (m) of potassium hydrogen *o*-phthalate (A.2.2) into a 250 ml conical flask (see 6.1) and dissolve in 50 cm^3 of water (A.2.1).

Add at least 5 drops of bromothymol blue indicator solution (5.10.1). Titrate with the potassium hydroxide solution (5.3) from a 50 ml burette (A.3.2) to the point where the colour remains blue for 20 s to 30 s.

Record the volume (V), in millilitres, of KOH solution used.

A.4.2 Potentiometric method

Weigh, to the nearest 0,1 mg, approximately 350 mg (m) of potassium hydrogen *o*-phthalate (A.2.2) into a 100 ml conical flask (see 6.1) and dissolve in 25 cm^3 of water (A.2.1).

Place the conical flask on the titration stand and adjust its position so that the electrode is well immersed. Titrate potentiometrically with the potassium hydroxide solution (5.3) using a 25 ml burette (6.3).

Record the volume (V), in millilitres, of KOH solution used to reach the end point (the point of inflection of the titration curve).

A.5 Calculation of the concentration

The concentration of the potassium hydroxide solution (c) is calculated, in moles per litre, from the equation:

$$c = \frac{m}{V \times 204{,}23}$$

where

m is the mass, in milligrams, of potassium hydrogen *o*-phthalate used;

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

204,23 is a constant (molar mass of potassium hydrogen *o*-phthalate).

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