INTERNATIONAL STANDARD

ISO 3681

Third edition
1996-06-01

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

Liants pour peintures et vernis — Détermination de l'indice de saponification — Méthode titrimétrique

Reference number
ISO 3681:1996(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 3681 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes,* Subcommittee SC 10, *Test methods for binders for paints and varnishes.*

This third edition cancels and replaces the second edition (ISO 3681:1983), which has been technically and editorially revised. The main change is that the saponification value is no longer related to 1 g of non-volatile matter of the product but to 1 g of the product itself.

Annex A forms an integral part of this International Standard.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

INTERNATIONAL STANDARD © ISO ISO 3681:1996(E)

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

1 Scope

This International Standard specifies a titrimetric method for determining the esterified-acid content in binders for paints and varnishes, free acids and acid anhydrides being necessarily included in the result obtained.

Because different binders vary in their resistance to saponification, this International Standard is of limited applicability. If necessary, completeness of saponification may be checked by repeating the test under more severe conditions achieved by the use of longer saponification time, more concentrated potassium hydroxide solution, or a higher-boiling alcohol as solvent.

Annex A specifies a procedure suitable for binders that saponify with difficulty.

The method is not applicable to those materials that show further reaction with alkalis beyond normal saponification.

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

3 Definitions

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

3.1 saponification: The formation of the alkali metal salts of derivatives of organic acids.

3.2 saponification value: The number of milligrams of potassium hydroxide (KOH) required for the saponification of 1 g of the product tested.

4 Principle

After a preliminary test to determine the saponification conditions (concentration of potassium hydroxide solution, saponification time, etc.) for the product to be tested, a test portion is boiled under reflux with potassium hydroxide solution under these conditions. The hot solution is titrated with standard volumetric hydrochloric acid, either in the presence of a colour indicator or potentiometrically.

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 Toluene, or other suitable unsaponifiable solvent.

5.2 Potassium hydroxide solution, in isopropanol, ethanol or methanol, c(KOH) = 0,5 mol/l.

NOTE 1 If more severe conditions for saponification are needed, 2 mol/l ethanolic potassium hydroxide solution may be used, or 1,2-ethanediol (ethylene glycol) or 2,2'-oxydiethanol (diethylene glycol) may be used as the solvent (see clause 8 and annex A).

Where isopropanol can be used instead of ethanol or methanol, it shall be used. The applicability of the solution in isopropanol is comparable to that of an ethanolic solution and its toxicity is less than that of a methanolic solution.

5.3 Hydrochloric acid, standard volumetric solution, c(HCl) = 0,5 mol/l, in a mixture of 4 parts by volume of methanol and 1 part by volume of water or in water.

5.4 Phenolphthalein or **thymolphthalein,** 10 g/l solution in 95 % (*V/V*) ethanol, in methanol or in isopropanol (see note 1).

6 Apparatus

Ordinary laboratory apparatus and glassware, complying with the requirements of ISO 385-1 and ISO 648, together with the following:

6.1 Conical flask, of capacity 250 ml, with a ground-glass joint.

6.2 Reflux condenser, with a ground-glass joint.

6.3 Burette or **pipette,** of capacity 25 ml or 50 ml.

6.4 Potentiometric titration apparatus, fitted with a glass electrode and a reference electrode. The use of this apparatus is an optional alternative (see 9.2).

6.5 Magnetic stirrer.

6.6 Water bath or **oil bath.**

7 Sampling

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

8 Preliminary test

If no special saponification conditions are specified or agreed, carry out the procedure specified in clause 9 using 25 ml of potassium hydroxide solution (5.2) and a boiling time of 1 h. To test whether the saponification value can be determined under these conditions, intensify the conditions by increasing the saponification time to at least 2 h and/or by using a 2 mol/l potassium hydroxide solution or a solution of potassium hydroxide in an alcohol that has a boiling point distinctly higher than that of ethanol, for example 1,2-ethanediol (ethylene glycol) or 2,2'-oxydiethanol (diethylene glycol).

If no increase in the final (i.e mean) result (see 10.1) is obtained using the more intense conditions, the test may be carried out using this International Standard. If a higher value is obtained which is not further increased by again intensifying the test conditions, this International Standard may be followed but using and noting the intensified conditions applied. If a constant result is not obtained even under the most severe conditions of saponification, the method to be used shall be agreed between the interested parties.

9 Procedure

Carry out the determination in duplicate.

9.1 Test portion

By reference to table 1, select the appropriate mass of test portion to be taken. This mass shall be chosen so that less than half of the volume of potassium hydroxide solution added is sufficient to saponify the test portion.

Table 1 — Mass of test portion

Expected saponification value mg KOH/g	Approximate mass of test portion g
up to 10	20
above 10 to 20	10
above 20 to 50	5
above 50 to 100	2,5
above 100 to 200	1,5
above 200 to 300	1
above 300 to 500	0,5
above 500	0,2

Weigh, to the nearest 1 mg, the test portion into the conical flask (6.1).

9.2 Determination

Dissolve the test portion, if necessary, in a measured volume of toluene or other suitable, unsaponifiable solvent (5.1), warming, if necessary, under the reflux condenser (6.2). Add, from the burette or pipette (6.3), one of the following:

a) 25 ml of 0,5 mol/l potassium hydroxide solution (5.2);

b) 25 ml of a different potassium hydroxide solution (see clause 8 and note 1 to 5.2);

c) the specified or agreed volume of a potassium hydroxide solution.

Heat, while stirring, the contents of the flask to boiling in a water bath or oil bath (6.6) and reflux for 1 h or the specified or agreed time, or the time found necessary in the preliminary test (see clause 8).

Titrate the hot solution with hydrochloric acid (5.3) after addition of 3 drops of phenolphthalein or thymolphthalein solution (5.4).

If the potentiometric titration is used, the glass electrode shall have a suitable response time.

If precipitation occurs, bring the precipitate back into solution by the addition of water, which acts as a solvent.

9.3 Blank test

Carry out a blank test, following the same procedure but omitting the test portion.

10 Expression of results

10.1 Calculation

Calculate the saponification value SV, in milligrams of KOH per gram of product, using the equation

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

where

V_0 is the volume, in millilitres, of hydrochloric acid (5.3) required for the blank test (9.3);

V_1 is the volume, in millilitres, of hydrochloric acid (5.3) required for the determination (9.2);

c is the actual concentration, in moles per litre, of the hydrochloric acid (5.3);

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 (9.1).

If the two results (duplicates) differ by more than 3 % (relative to the mean), repeat the procedure described in clause 9.

Report as the final result the mean, rounded to the nearest 0,1 mg KOH/g, of two valid results (replicates).

10.2 Precision

No precision data are currently available.

11 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 3681);

c) the result of the test as indicated in 10.1;

d) the solvent and the concentration and volume of the potassium hydroxide solution used;

e) the period of boiling;

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

g) any deviation from the test method specified;

h) the date of the test.

Annex A
(normative)

Binders which are saponifiable with difficulty — Determination of saponification value

A.1 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.

A.1.1 Hydrochloric acid, aqueous standard volumetric solution, c(HCl) = 0,25 mol/l.

A.1.2 Potassium hydroxide, solution in 1,2-ethanediol.

Weigh about 6 g of potassium hydroxide into a 100 ml conical flask (see A.2.1) and add 25 ml of 1,2-ethanediol. Warm until the potassium hydroxide is dissolved. It is advisable to insert a thermometer in the solution whilst carrying out the dissolving procedure in order to avoid exceeding a temperature of 130 °C. If this occurs, a deep yellow colour develops in the solution.

When the potassium hydroxide is completely dissolved, transfer the solution to a 150 ml conical flask (see A.2.1) containing 75 ml of 1,2-ethanediol. Shake the resultant solution carefully and allow it to cool.

A.1.3 Phenolphthalein, 10 g/l solution in 95 % (*V/V*) ethanol.

A.2 Apparatus

A.2.1 Conical flasks, of capacity 100 ml and 150 ml, with ground-glass stoppers.

A.2.2 Pipette, capacity 10 ml, the delivery end of which has been modified so that its internal diameter is between 2 mm and 3 mm in order to facilitate the delivery of the potassium hydroxide solution.

The modified pipette shall be recalibrated before use.

A.2.3 Oil bath, capable of being maintained at temperatures to 150 °C to within 1 °C.

A.2.4 Magnetic stirrer.

A.3 Preliminary test

See clause 8.

A.4 Procedure

Carry out the determination in duplicate.

A.4.1 Test portion

Weigh, to the nearest 0,1 mg, about 0,5 g of the sample into a 100 ml conical flask (see A.2.1).

A.4.2 Determination

By means of the pipette (A.2.2), add 10 ml of potassium hydroxide solution (A.1.2) to the flask containing the test portion (A.4.1).

Stopper the flask and mix the contents by swirling.

Secure the stopper and heat the contents in the oil bath (A.2.3) to 70 °C to 80 °C. Maintain this temperature for 2 min to 3 min.

Swirl the contents of the flask, as before, during heating.

Remove the flask from the oil bath. Shake the contents vigorously and allow the flask to stand. Remove the stopper carefully so as to permit air to escape.

Again secure the stopper in the flask and return the flask to the oil bath heated to 120 °C to 130 °C.

NOTE 2 If necessary, a temperature higher than 130 °C may be used. Saponification under pressure is also possible.

Heat for 3 min at this temperature, cool the flask to 80 °C to 90 °C, remove the stopper and rinse it with water, collecting the washings in the flask.

Add a further 15 ml of water to the flask and a few drops of phenolphthalein solution (A.1.3). Titrate the mixture, whilst stirring, with hydrochloric acid (A.1.1).

A.4.3 Blank test

Carry out a blank test, using the same procedure but omitting the test portion.

A.5 Expression of results

See clause 10.

A.6 Test report

See clause 11.

ICS 87.060.20

Descriptors: paints, varnishes, binders (materials), tests, chemical tests, determination, saponification number, volumetric analysis.

Price based on 5 pages