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# International Standard



# 3681

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

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

Second edition — 1983-03-01

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UDC 667.6 : 543.851.5

Ref. No. ISO 3681-1983 (E)

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

Price based on 3 pages

## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized 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.

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 3681 was developed by Technical Committee ISO/TC 35, *Paints and varnishes*.

The first edition (ISO 3681-1976) had been approved by the member bodies of the following countries:

Austria	India	South Africa, Rep. of
Brazil	Iran	Spain
Bulgaria	Israel	Sweden
Canada	Netherlands	Switzerland
Czechoslovakia	New Zealand	Turkey
France	Portugal	United Kingdom
Germany, F.R.	Romania	Yugoslavia

No member body had expressed disapproval of the document.

This second edition, which cancels and replaces ISO 3681-1976, incorporates draft Amendment 1, which was circulated to the member bodies in December 1981 and has been approved by the member bodies of the following countries:

Australia	India	Romania
Austria	Israel	South Africa, Rep. of
Belgium	Kenya	Sri Lanka
Brazil	Korea, Rep. of	Sweden
Canada	Netherlands	Switzerland
China	New Zealand	United Kingdom
Czechoslovakia	Norway	USSR
Egypt, Arab Rep. of	Poland	
Hungary	Portugal	

The member body of the following country expressed disapproval of the document on technical grounds:

Germany, F.R.

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

## 1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of the esterified acid content in binders for paints and varnishes whereby free acids and acid anhydrides are necessarily included.

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

The annex to this International Standard specifies a procedure adapted to binders which saponify with difficulty.

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

## 2 References

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

ISO 3251, *Paint media — Determination of volatile and non-volatile matter*.

## 3 Definitions

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

**3.1 saponification:** The formation of alkali salts from 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 non-volatile matter of the product.

## 4 Sampling

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

## 5 Reagents

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

**5.1 Toluene, or other suitable unsaponifiable solvent.**

**5.2 Potassium hydroxide,**  $c(\text{KOH}) = 0,5 \text{ mol/l}$  ethanolic or methanolic solution.

NOTE — 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 7 and the annex).

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

Check the concentration of this solution on the day of use.

**5.4 Phenolphthalein, or thymolphthalein,** indicator solution, 10 g/l in ethanol 95 % (V/V), methanol or 2-propanol.

## 6 Apparatus

Ordinary laboratory apparatus and

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

**6.2 Reflux condenser,** with ground-glass joint.

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

If required,

**6.4 Device for potentiometric titration,** with glass electrode and reference electrode.

**6.5 Magnetic stirrer.**

## 7 Preliminary test

If no special saponification conditions are specified or agreed, use 25 ml of the 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 final 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 value is obtained using the more intense conditions, the test may be carried out according to this International Standard. If an increased value is obtained which is not further increased by again intensifying the test, 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.

## 8 Procedure

### 8.1 Test portion

The mass of the test portion depends on the saponification value to be expected (see the table for guidance in selecting the appropriate mass). 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.

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

Table

Expected saponification value	Mass of test portion
mg KOH/g	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

### 8.2 Determination

Carry out the determination in duplicate.

Dissolve the test portion (8.1), if necessary, in a measured volume of the 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:

- 25 ml of the 0,5 mol/l potassium hydroxide solution (5.2);
- 25 ml of a different potassium hydroxide solution (see clause 7 and the note to 5.2);
- the specified or agreed volume of a potassium hydroxide solution.

Heat the contents of the flask to boiling and maintain at boiling point under reflux for 1 h or the specified or agreed time, or the time found necessary in the preliminary test (see clause 7).

Titrate the hot solution with the hydrochloric acid solution (5.3) after addition of 3 drops of the phenolphthalein or thymolphthalein indicator solution (5.4), or using a potentiometric method.

NOTE — If the potentiometric titration is used, the glass electrode should have a suitable response time.

### 8.3 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, but omitting the test portion.

## 9 Expression of results

### 9.1 Calculation

Calculate the saponification value,  $S$ , by the equation

$$S = 56,1 \frac{(V_0 - V_1) \times c}{m \times NV} \times 100$$

where

$S$  is the saponification value, in milligrams of KOH per gram;

$V_0$  is the volume, in millilitres, of the hydrochloric acid solution (5.3), used for the blank test;

$V_1$  is the volume, in millilitres, of the hydrochloric acid solution (5.3), used for the determination;

$c$  is the actual concentration, in moles of HCl per litre, of the hydrochloric acid solution (5.3) at the time of use;

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

$NV$  is the non-volatile matter content, expressed as a percentage by mass, determined according to ISO 3251.

Calculate the arithmetic mean of two determinations, and report the result to one decimal place.

### 9.2 Precision

No precision data are currently available.

## 10 Test report

The test report shall contain at least the following information:

- the type and identification of the product tested;
- a reference to this International Standard (ISO 3681);
- the solvent and the concentration and volume of the potassium hydroxide solution used;
- the period of boiling;
- the type of titration: potentiometric or by indicator (phenolphthalein, thymolphthalein);
- the saponification value, expressed in milligrams of KOH per gram of the non-volatile matter of the product (mg KOH/g);
- the temperature and period of heating for the determination of the non-volatile matter content according to ISO 3251;
- any deviation, by agreement or otherwise, from the procedure specified;
- the date of the test.

## Annex

### 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 distilled water or water of equivalent purity.

**A.1.1 Hydrochloric acid**, standard volumetric aqueous solution,  $c(\text{HCl}) = 0,25 \text{ mol/l}$ .

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

Weigh about 6 g of potassium hydroxide into a 100 ml conical flask (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 (A.2.1) containing 75 ml of 1,2-ethanediol. Shake the resultant liquor carefully and allow it to cool.

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

#### A.2 Apparatus

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

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

The pipette shall be recalibrated before use.

**A.2.3 Oil-bath**, capable of being controlled to within  $\pm 1 \text{ }^\circ\text{C}$ .

#### A.3 Preliminary test

See clause 7.

#### A.4 Procedure

##### 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 (A.2.1).

##### A.4.2 Determination

Carry out the determination in duplicate.

By means of the pipette (A.2.2), add 10 ml of the 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 on the oil-bath (A.2.3) to 70 to 80 °C and maintain at this temperature for 2 to 3 min.

Swirl the contents of the flask as before during heating.

Then 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 to 130 °C.

Heat for 3 min at this temperature, cool the flask to 80 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 the phenolphthalein indicator solution (A.1.3). Titrate the mixture, whilst swirling, with the hydrochloric acid solution (A.1.1).

##### A.4.3 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, but omitting the test portion.

#### A.5 Expression of results

See clause 9.

#### A.6 Test report

See clause 10.

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