# INTERNATIONAL STANDARD

Second edition 1998-03-15

# Driers for paints and varnishes

Siccatifs pour peintures et vernis

# iTeh STANDARD PREVIEW (standards.iteh.ai)

<u>ISO 4619:1998</u> https://standards.iteh.ai/catalog/standards/sist/095093ff-77a7-4975-8172-2c11cb1e47ba/iso-4619-1998



# 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.

# iTeh STANDARD PREVIEW

International Standard ISO 4619 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes.* 

This second edition cancels and replaces the first edition ((ISO)4619:1980), of which it constitutes an editorial/tevision.iteh.ai/catalog/standards/sist/095093ff-77a7-4975-8172-2c11cb1e47ba/iso-4619-1998

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# **Driers for paints and varnishes**

#### 1 Scope

This International Standard specifies the requirements and the corresponding test methods for driers for paints, varnishes and related products. The requirements relate to driers in the solid or liquid form.

CAUTION — The procedures described in this International Standard are intended to be carried out by qualified chemist or by other suitably trained and/or supervised personnel. The substances and procedures used in this method may be injurious to health if adequate precautions are not taken. This International Standard refers only to its technical suitability and does not absolve the user from statutory obligations relating to health and safety.

Attention is particularly drawn to the health hazards of heavy metals which may be a constituent of driers (e.g. cobalt, lead, cerium, zirconium, vanadium; see clauses 3, 4 and 8). (standards.iteh.ai)

#### 2 Normative references

<u>ISO 4619:1998</u>

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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 150:1980, Raw, refined and boiled linseed oil for paints and varnishes — Specifications and methods of test.

ISO 842:1984, Raw materials for paints and varnishes — Sampling.

ISO 1523:1983, Paints and varnishes — Determination of flashpoint — Closed cup method.

ISO 2431:1993, Paints and varnishes — Determination of flow time by use of flow cups.

ISO 2592:1973, Petroleum products — Determination of flash and fire points — Cleveland open cup method.

ISO 2811-1:1997, Paints and varnishes — Determination of density — Part 1: Pyknometer method.

ISO 3219:1993, Plastics — Polymers/resins in the liquid state or as emulsions or dispersions — Determination of viscosity using a rotational viscometer with defined shear rate.

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 — Specifications and test methods.

ISO 4793:1980, Laboratory sintered (fritted) filters — Porosity grading, classification and designation.

# 3 Definition

For the purposes of this International Standard, the following definition applies.

**3.1 drier:** A compound, usually a metallic soap, that is added to products drying by oxidation in order to accelerate this process.

# 4 Descriptions

# 4.1 Solid driers

Solid driers are materials which may be manufactured in a hard, soft (highly viscous) or powder form.

#### 4.2 Liquid driers

Liquid driers are materials which are supplied as solutions in organic solvents, usually white spirit.

NOTE — Emulsifiable driers are also available, but no requirements for this type are given in this International Standard.

All these types of drier, when dissolved in solvents (normally hydrocarbons), impart specific drying properties depending on the metal used.

# 4.3 Metals used iTeh STANDARD PREVIEW

The following metals are used: cobalt, manganese, lead, zinc, calcium, cerium (or other rare earths), iron, zirconium, vanadium, barium, aluminium, strontium, etc.

NOTE — In this International Standard, methods for determination of metal content are given only for those metals which are in common use. https://standards.iteh.ai/catalog/standards/sist/095093ff-77a7-4975-8172-2c11cb1e47ba/iso-4619-1998

# 4.4 Acids used

The following acids are used: fatty acids of linseed oils, tall-oil fatty acids, resinic acids, naphthenic acids, 2-ethylhexanoic acid, fatty iso-acids with 9 carbon atoms, other fatty acids with 9 to 11 carbon atoms, etc.

# 5 Requirements and test methods

**5.1** Driers for paints shall comply with the requirement given in table 1.

**5.2** Driers named according to the commercial name of the main acid used shall contain at least 90 % of this acid, except for driers based on naphthenic acids, which shall contain at least 70 % of these acids, expressed as a percentage of the total mass of acid present.

NOTE — If desired, the type and content of the acids may be determined by gas-chromatographic (GC) analysis, except in the case of naphthenic acids.

# 6 Sampling

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

Characteristic		Requirement	Test method	
			Solid driers	Liquid driers
Appearance		Clear and uniform; no suspended matter or sediment	Subclause 7.1	Subclause 8.1
Consistency, if required			To be agreed between the interested parties	_
Colour		As agreed between the interested parties	Subclause 7.2	Subclause 8.2
Solubility (miscibility) in solvent, raw linseed oil and other drying media		No separation or deposit	Subclause 7.3	Subclause 8.3
Stability of solution		Clear solution; no clouding gelation or sedimentation	Subclause 7.4	Subclause 8.4
Suspended solid matter	of liquid driers [% (m/m)]	max. 0,1	Subclause 7.5	Subclause 7.5
	of solid driers	As agreed between the		
Viscosity, only for liquid driers		interested parties	—	Subclause 8.5
Volatile matter at 105 °C			Subclause 7.6	Subclause 7.6
Flashpoint			ISO 2592	ISO 1523
Density		NDARD PR	To be agreed between the interested parties	ISO 2811-1
Acidity or basicity			Subclause 7.7	Subclause 7.7
Drying characteristics (Sta		ndards.iten.a	Subclause 7.7	e interested parties
Metal content (range)	up to 10 % ( <i>m/m</i> )	± 0,2 % 1)	Clause 9	
	above 10 % (m/m) to 20 % (m/m)	130 4619(1998 catalog/standards/sist/095093	ff-77a7-4975-8172-	
	above 20 % ( <i>m/m</i> ) to 30 % ( <i>m/m</i> )	± 0,4 % <sup>1)</sup>		
	above 30 % ( <i>m/m</i> )	± 0,5 % <sup>1)</sup>		

Table 1 — Requirements	and test methods
------------------------	------------------

# 7 Methods of test for solid driers

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity in accordance with ISO 3696.

# 7.1 Appearance and consistency

Examine the sample visually for uniformity. If the consistency is specified, a method for its determination shall be agreed between the interested parties

# 7.2 Colour

Dissolve 1 part by mass of the drier in 1 part by mass of white spirit or other agreed solvent and compare the colour against an agreed sample or colour standard.

# 7.3 Solubility (miscibility) in solvents, raw linseed oil or other drying media

Slowly heat, raising the temperature at a rate of 1 °C/min, 5 g of the drier and 20 g of an agreed solvent (or drying medium) under reflux on a sand bath, with stirring, until a homogeneous solution is obtained.

Allow to cool to room temperature and examine the solution for clarity, clouding and any separation or deposit.

#### 7.4 Stability of solution

Allow three portions of the solution obtained by the method specified in 7.3 to stand for 7 days in stoppered bottles, one at each of the following temperatures:

- a) 0 °C;
- b) ambient temperature;
- c) 50 °C.

After 1 day and again after 7 days, examine the solutions for clarity, clouding sedimentation or gelation.

The bottle used for the test at 50 °C shall be able to withstand the pressure generated.

#### 7.5 Suspended solid matter

Weigh, to the nearest 0,1 g, 5 g of solid drier (or 10 g of liquid drier) into a glass flask and dissolve in (or dilute with) 100 g of white spirit or an agreed solvent. Stopper the flask allow to stand at ambient temperature for 3 days, then filter off the sediment or suspended matter using a glass filter crucible of porosity P 16 (see ISO 4793). Wash the residue on the filter with the solvent and dry it at 105 °C for 3 h. Cool to ambient temperature and weigh to the nearest 1 mg.

Calculate the suspended solid matter, as a percentage by mass, using the formula 5-8172-

$$\frac{m_1}{m_0} \times 100$$

where

- $m_0$  is the mass, in grams, of the test portion;
- $m_1$  is the mass, in grams, of the residue.

#### 7.6 Volatile matter

Proceed according to ISO 3251, taking a flat-bottomed glass of aluminium dish and a test portion of  $(1 \pm 0,02)$  g. Place the dish with the test portion in the air oven, maintained at  $(105 \pm 2)$  °C. Leave it in the oven at this temperature for 3 h.

#### 7.7 Acidity or basicity

#### 7.7.1 Principle

A solution of the drier in toluene/propan-2-ol is passed through a strong acid cation exchanger and the total acid in the eluate is determined. From the total acid determined, the acid combined with the metal is subtracted.

If a negative value for the acidity is obtained, the drier tested is a basic drier.

The method is suitable for driers containing barium, calcium, cobalt, lead or zinc as metals, but is not applicable to driers containing cerium, iron, manganese or zirconium as metals.

In such cases, the method shall be agreed between the interested parties.

#### 7.7.2 Reagents

**7.7.2.1 Cation exchanger:** a strong-acid, ring-sulfonated polystyrene resin (for example, Merck 1, Dowex 50, Amberlite IR 120) <sup>1</sup>).

- 7.7.2.2 Propan-2-ol.
- 7.7.2.3 Toluene.
- 7.7.2.4 Hydrochloric acid, approximately 5 % (*m/m*) solution.
- 7.7.2.5 Potassium hydroxide, approximately 0,2 mol/l standard volumetric solution in 96 % (V/V) ethanol.
- **7.7.2.6** Phenolphthalein, 1 % (m/m) solution in 96 % (V/V) ethanol.

#### 7.7.3 Apparatus

Ordinary laboratory apparatus and glassware, together with the following:

# 7.7.3.1 Suitable ion-exchange column, as shown in figure 1, for instance. (Standards.itch.al)

**7.7.4** Preparation of the ion-exchange column SO 4619:1998 https://standards.iteh.ai/catalog/standards/sist/095093ff-77a7-4975-8172-

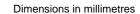
Fill the ion-exchange column (7.7.3) with a quantity of the swollen ion-exchange resin (7.7.2.1) so that the height of resin in the column is about 170 mm. Pour 250 ml of the hydrochloric acid solution (7.7.2.4) gradually into the exchange column in order to change the resin into the hydrogen form. Drain off slowly, at about 1 or 2 drops/s (= 5 ml/min). When the acid has drained off completely, wash the resin successively with several 350 ml portions of water. The final washings shall not be acid to litmus paper. Then displace the water in the exchange column by 50 ml of the propan-2-ol (7.7.2.2) and finally displace the propan-2-ol with 50 ml of a mixture (1 + 1) of the propan-2-ol and the toluene (7.7.2.3).

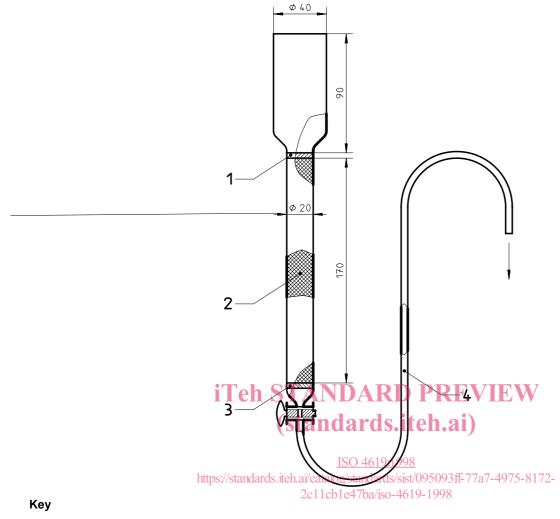
Do not use this column for more than about 50 milliequivalents of total metal.

#### 7.7.5 Procedure

Weigh, to the nearest 1 mg, about 8 g of the drier to be tested into a 100 ml one-mark volumetric flask and dissolve it in 50 ml of the toluene (7.7.2.3). Dilute to the mark with the propan-2-ol (7.7.2.2) and mix well. Pipette 25 ml of the solution into the ion-exchange column (7.7.4) and adjust the rate of flow to 5 ml/min. Collect the eluate in a 500 ml conical flask. When all the liquid has soaked through the resin, wash the exchange column with 150 ml of a mixture (1 + 1) of the propan-2-ol and the toluene, and collect the washings in the 500 ml conical flask, allowing them to drain of completely. Add a few drops of the phenolphthalein solution (7.7.2.6) to the eluate and titrate with the potassium hydroxide solution (7.7.2.5) to the end-point.

<sup>1)</sup> These are examples of suitable products available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.





- 1 Layer of glass wool
- 2 Ion-exchange resin
- 3 Sintered-glass disc 4
- Capillary tubing Ø 2

$$56,1\left(\frac{4\times V\times T}{m}-\frac{10\times c\times n}{A}\right)$$

where

- Vis the volume, in millilitres, of the potassium hydroxide solution (7.7.2.5) required for the titration;
- Т is the exact concentration of the potassium hydroxide solution (7.7.2.5), in moles of KOH per litre;
- is the metal content, as a percentage by mass, of the drier, as determined in clause 9; С
- is the valency of the metal in the drier; п
- is the mass, in grams, of the test portion; т
- A is the relative atomic mass of the metal in the drier.

For mixed drivers the factor  $\frac{c \times n}{A}$  shall be calculated, taking into account the composition of the mixed driver.

# 8 Methods of test for liquid driers

#### 8.1 Appearance

Examine the sample visually for uniformity, clarity, suspended matter or sediment.

#### 8.2 Colour

Compare the colour of the liquid drier against that of an agreed sample or colour standard.

#### 8.3 Solubility (miscibility) in solvents, raw linseed oil or other drying media

Prepare a mixture as follows:

Raw linseed oil, complying with ISO 150 (see the note): 16 parts by volume

Mineral solvents. e.g. white spirit with an aromatic contentof approximately 25 % (V/V) (see below):4 parts by volume

The drier under test (at standard strength) (see below):

NOTE — In the case of driers containing calcium, barium or rare earths, it is recommended that an air-drying alkyd resin [non-volatile content at least 60 % (*m/m*)] be used instead of linseed oil

1 part by volume

Allow the mixture to stand at room temperature for 6 h and then examine it for clarity, noting any clouding, separation or deposit.

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The exact aromatic content of the solvent shall be agreed between the interested parties.

For the purpose of this test, the standard strength of the drier is defined, in % (m/m), as

6	Со	6	Ce (or other rare earths)
6	Mn	6	Fe
24	Pb	6	Zr
8	Zn	12,5	Ва
4	Ca		

Dilute driers of higher concentration than those above with mineral solvent until the standard strength is obtained.

#### 8.4 Stability of solution

Prepare three mixtures of 10 g of liquid driers and 10 g of mineral solvent (the exact aromatic content of which shall be agreed between the interested parties), and allow to stand for 7 days in stoppered bottles, one at each of the following temperatures:

a) 0 °C;

- b) ambient temperature;
- c) 50 °C.

After this period, examine the solutions for clarity, noting any clouding, sedimentation or gelation.

The bottle used for the test at 50 °C shall be able to withstand the pressure generated.

# 8.5 Viscosity

A suitable method shall be agreed between the interested parties, for example by the procedure specified in ISO 2431 (flow cup method), ISO 3219 (rotational viscometer working at known shear rate) or falling-ball methods.

# 9 Methods for determination of metal content of driers containing only one metal

NOTE — The methods are not selective for only one metal. In case of doubt, a qualitative test for the presence of other metals may be carried out. Other methods, e.g. atomic absorption spectrometry (AAS), may be used by agreement between the interested parties.

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity as defined in ISO 3696. All indicator solutions should preferably be freshly prepared but shall in no case be older than 2 weeks.

#### 9.1 Cobalt (EDTA titrimetric method)

- 9.1.1 Reagents
- **9.1.11** Hydroxylammonium chloride (OHNH<sub>3</sub>Cl).
- 9.1.1.2 Propan-2-ol.
- 9.1.1.3 Ethanol, 96 % (V/V) solution STANDARD PREVIEW
- 9.1.1.4 Hydrochloric acid,  $c(HCI) \approx 1 \mod \frac{1}{3}$
- **9.1.1.5** Hexamethylenetetramine, 40 % (*m*/*m*) aqueous solution.

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9.1.1.6 EDTA, standard volumetric solution h0;100 lmol/lndards/sist/095093ff-77a7-4975-8172-

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Dissolve 37,225 0 g of ethylene diaminetetraacetatic acid (EDTA) dihydrate, disodium salt, in water in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix well.

Store the solution in a polyethylene bottle.

9.1.1.7 Zinc sulfate, approximately 0,05 mol/l standard volumetric solution.

a) Preparation

Dissolve 14,38 g of zinc sulfate heptahydrate ( $ZnSO_4$ ·7 $H_2O$ ) in water in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

b) Standardization

Pipette 20 ml of the zinc sulfate solution into a 250 ml conical flask. Dilute to about 100 ml with water and add successively 10 ml of buffer solution (9.1.1.8) and 5 or 6 drops of Mordant black solution (9.1.1.9). Titrate with EDTA solution (9.1.1.6) until the first change of the red colour to blue.

c) Calculation of concentration

The concentration  $T_1$  of the zinc sulfate solution, in moles of ZnSO<sub>4</sub> per litre, is given by the equation

$$T_1 = \frac{V_1 \times T_0}{20}$$

where

- $V_1$  is the volume, in millilitres, of EDTA solution (9.1.1.6) required for the titration;
- $T_0$  is the concentration of the EDTA solution (9.1.1.6), in moles of EDTA per litre.

### 9.1.1.8 Buffer solution, pH 10.

Add 54 g of ammonium chloride and 350 g of ammonia solution ( $\rho$  approximately 0,91 g/ml) to water in a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix well.

Store the solution in a polyethylene bottle.

9.1.1.9 Mordant black 11<sup>2)</sup>, indicator solution.

Dissolve 0,5 g of Mordant black and 2,25 g of hydroxylammonium chloride (9.1.1.1) in 100 ml of ethanol (9.1.1.3).

9.1.1.10 Xylenol orange/potassium nitrate mixture, 1 + 100, for use as indicator.

#### 9.1.2 Procedure

Weigh, to the nearest 1 mg, a test portion of the drier containing approximately 120 mg of cobalt into a 250 ml conical flask. Add 25 ml of hydrochloric acid (9.1.1.4) and heat to boiling.

Dilute with 100 ml of propan-2-ol (9.1.1.2), add 15 ml of hexamethylenetetramine solution (9.1.1.5) and 0,050 g of xylenol orange/potassium nitrate mixture (9.1.1.10). Titrate with EDTA solution (9.1.1.6) until the violet colour just changes to yellow.

If desired, back-titrate with zinc sulfate solution (9.1.1.7) until the first change of the yellow colour to red.

# 9.1.3 Expression of results Teh STANDARD PREVIEW

The cobalt content, expressed as a percentage by mass of Co, is given by the formula

$$\frac{\left[\left(V_{2} \times T_{0}\right) - \left(V_{3} \times T_{1}\right)\right] \times 0,058 \ 94}{m_{2} \ \text{https://standards.iteh.ai/catalog/standards/sist/095093ff-77a7-4975-8172}} \times 100 \qquad \text{ISO 4619:1998} \\ = \frac{\left(V_{2} \times T_{0}\right) - \left(V_{3} \times T_{1}\right)}{m_{2}} \times 5,894$$

where

- $V_2$  is the volume, in millilitres, of EDTA solution (9.1.1.6) required;
- $V_3$  is the volume, in millilitres, of zinc sulfate solution (9.1.1.7) required (if used);
- $T_0$  is the concentration of the EDTA solution (9.1.1.6), in moles of EDTA per litre;
- $T_1$  is the concentration of the zinc sulfate solution (9.1.1.7), in moles of ZnSO<sub>4</sub> per litre;

 $m_2$  is the mass, in grams, of the test portion.

# 9.2 Manganese (EDTA titrimetric method)

# 9.2.1 Reagents

**9.2.1.1** Ascorbic acid or hydroxylammonium chloride (OHNH<sub>3</sub>Cl).

# 9.2.1.2 Toluene.

<sup>2)</sup> Listed in Colour Index as C.I. 14645. Trade names include "Chrome Fast Black CAT, KIT & TS", "Eriochrome Black DW, T and TDW", "Potting Black C", etc. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.