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INTERNATIONAL STANDARD 412

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Gum spirit of turpentine and wood turpentines for paints and varnishes

Essence de térébenthine et essences de bois pour peintures et vernis

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (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 set up 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 412 was drawn up by Technical Committee ISO/TC 35, *Paints and varnishes,* and was circulated to the Member Bodies in January 1975.

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

Austria	Ireland	South Africa, Rep. of
Brazil	Israel	Sweden
Bulgaria	Mexico	Switzerland
Finland	Netherlands	Turkey
France	New Zealand	United Kingdom
Germany	Poland	Yugoslavia
India	Portugal	
Iran	Romania	

No Member Body expressed disapproval of the document.

This International Standards cancels and replaces ISO Recommendation R 412-1965, of which it constitutes a technical revision.

Printed in Switzerland

Gum spirit of turpentine and wood turpentines for paints and varnishes

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies the requirements and corresponding test methods for gum spirit of turpentine and wood turpentines for use in paints, varnishes and related products.

2 REFERENCES

ISO/R 649, *Density hydrometers for general purposes.*

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

ISO 1516, *Paints and varnishes. Determination of the danger classification by flashpoint — Closed cup method.*

ISO 3405, *Petroleum products — Determination of distillation characteristics.*

ISO 3680, *Paints and varnishes — Rapid test for determination of danger classification by flashpoint.*

3 DEFINITIONS

3.1 gum spirit of turpentine : The product obtained from oleoresins from pine trees by distillation at a temperature below 180 °C or by any other method of fractionation which does not alter the terpenic constituents of the oleoresins.

It is accepted good practice to tap only certain varieties of living pines for oleoresins for the manufacture of gum spirit of turpentine.

Gum spirit of turpentine is composed of a mixture of terpenes (with a small proportion of sesquiterpenes) and oxygenated products.

It may contain small quantities of rosin or rosin oil, arising from the method of production, as well as products of oxidation arising from ageing, provided that the product complies with the requirements given in the table, particularly with those for relative density, evaporation residue and acid value.

No other impurity can be tolerated.

3.2 wood turpentines : The volatile oils consisting primarily of a number of terpene hydrocarbons of the general formula $C_{10}H_{16}$, obtained from pine wood.

Three kinds of wood turpentine are now recognized :

3.2.1 steam-distilled wood turpentine : The wood turpentine obtained from the oleoresin within the wood of pine stumps or cuttings, either by direct steaming of the mechanically disintegrated wood or by steaming the oleoresin obtained by solvent extraction.

3.2.2 sulphate wood turpentine : The wood turpentine recovered during the conversion of wood to paper pulp by the sulphate process.

3.2.3 destructively distilled wood turpentine : The wood turpentine obtained by fractionation of certain oils recovered by condensing the vapours formed during the destructive distillation of pine wood.

Crude destructively distilled wood turpentines have generally an almost black colour and contain acids, phenols and tarry material. They should undergo a refining distillation before use. They can be immediately distinguished from the other turpentines by their odour and colour.

4 REQUIRED CHARACTERISTICS AND THEIR TOLERANCES

Gum spirit of turpentine and wood turpentines shall have the characteristics shown in the table.

5 SAMPLING

A representative sample of the product shall be taken in accordance with ISO 842.

TABLE – **Required characteristics and their tolerances**

Characteristic	Requirement				Test method
	Gum spirit of turpentine	Wood turpentines			
		Steam distilled	Sulphate	Destructively distilled	
Botanical origin	Can be stipulated at time of sale				–
Appearance	Clear, free from water and from solid matter in suspension				–
Colour	Normal or lighter or matching that of an agreed sample				Clause 6
Odour	Mild and characteristic or matching that of an agreed sample			Characteristic or matching that of an agreed sample	
Relative density d_4^{23} (d_4^{20}) (d_4^{27})	0,853 to 0,868 (0,855 to 0,870) (0,849 to 0,864)		0,858 to 0,868 (0,860 to 0,870) (0,854 to 0,864)	0,848 to 0,863 (0,850 to 0,865) (0,844 to 0,859)	Clause 7
Refractive index n_D^{23} (n_D^{20}) (n_D^{27})	1,464 to 1,477 (1,465 to 1,478) (1,462 to 1,475)			1,462 to 1,482 (1,463 to 1,483) (1,460 to 1,480)	Clause 8
Distillation 152 °C 170 °C, % (*V*/*V*)	0 min. 90			0 min. 60	Clause 9 and ISO 3405
Evaporation residue, % (*m*/*m*)	max. 2,5				Clause 10
Nitric oxidation residue, or Sulphuric polymerization residue, % (*V*/*V*)	Nil or at most a non-measurable thin film				Clause 11
	max. 12	max. 16			
Acid value	max. 1				Clause 12
Flashpoint, °C	min. 32				ISO 1516 ISO 3680

METHODS OF TEST

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

6 COLOUR

Compare the colour of the turpentine with an agreed sample in a manner agreed between the interested parties.

7 RELATIVE DENSITY

7.1 Apparatus

Relative density hydrometer, graduated in units of 0,001, with a range from 0,840 to 0,870, conforming to ISO/R 649.

7.2 Procedure

Measure the relative density at 23 °C (if not otherwise agreed or specified, for example 20 °C, or 27 °C for tropical countries).

If this is not possible, measure the relative density at a temperature as near as possible to this temperature.

Measure the temperature of the sample immediately after reading the hydrometer.

7.3 Expression of results

The relative density $d_4^{t_1}$ at the specified temperature t_1 °C is given by the formula

$$d_4^{t_1} = d_4^t + 0{,}000\,82\,(t - t_1)$$

where d_4^t is the hydrometer reading taken at a temperature of t °C.

8 REFRACTIVE INDEX

8.1 Procedure

Determine the refractive index with a refractometer[1] which enables the temperature of the test portion to be measured to the nearest 0,2 °C and gives the refractive index[2] to within 0,000 1.

It is advisable to use a precision thermostat[3] so as to be able to regulate the temperature of the water circulating in the refractometer to the nearest 0,1 °C.

8.2 Expression of results

The refractive index $n_D^{t_1}$ at the specified temperature t_1 °C is given by the formula

$$n_D^{t_1} = n_D^t + 0{,}000\,45\,(t - t_1)$$

where n_D^t is the refractive index determined at a temperature t °C.

9 DISTILLATION

9.1 Apparatus

9.1.1 Apparatus specified in ISO 3405.

9.1.2 Low temperature range thermometer as specified in 4.8 of ISO 3405.

9.2 Preparation of apparatus

See ISO 3405, clause 6.

9.3 Procedure

Proceed according to ISO 3405, sub-clauses 7.1 to 7.3, and then proceed as follows.

When the level in the cylinder reaches 90 ml[4], record the temperature. Then, stop distilling.

9.4 Expression of results

Correct the recorded temperatures for any deviation found during calibration (see ISO 3405).

Calculate the temperatures, corrected to the standard barometric pressure of 101,3 kPa (1 013 mbar), by adding algebraically to the observed temperature the correction, in degrees Celsius, given by one of the following formulae :

$$0{,}004\,27\,(101{,}3 - p_1) \text{ or } 0{,}042\,7\,(1\,013 - p_2)$$

where

p_1 is the barometric pressure, in kilopascals;

p_2 is the barometric pressure, in millibars.

Record the quantities distilled at 152 °C and at 170 °C. Record the calculated temperatures of the initial boiling point and of the volume of 90 % distillate.[5]

NOTE — If the limiting value of 152 °C or 170 °C is obtained on the gum spirit for one of these (corrected) temperatures, it is recommended that a second distillation be carried out in order to verify this value.

10 EVAPORATION RESIDUE

10.1 Apparatus

10.1.1 Flat-bottomed cylindrical glass dish, of diameter 75 mm and depth 25 mm.

10.1.2 Oven (preferably electrically heated), capable of being maintained at 100 ± 2 °C.

10.2 Procedure

Weigh the dish (10.1.1) to the nearest 0,1 mg. Add 10 ml of turpentine and weigh the dish and test portion to the nearest 10 mg. Evaporate on a boiling water bath for 2 h. After evaporation, place the dish for 2 h in the oven (10.1.2), suitably ventilated and regulated at 100 ± 2 °C.

Cool in a desiccator and weigh the dish with the residue to the nearest 0,1 mg.

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1) Abbe's refractometer, for instance.

2) Although the specifications for the refractive index are given only to three places of decimals, it is advisable to ascertain precisely the value of the refractive index of gum spirit of turpentine.

3) A thermostat of the Höppler type, for instance.

4) For destructively distilled wood turpentine, 60 ml.

5) For destructively distilled wood turpentine, the temperature for the volume of 60 % distillate.

10.3 Expression of results

The evaporation residue is given, as a percentage by mass, by the formula

$$\frac{m_2 - m_0}{m_1 - m_0} \times 100$$

where

m_0 is the mass, in grams, of the empty dish;

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

m_2 is the mass, in grams, of the dish and the evaporation residue.

11 NITRIC OXIDATION RESIDUE OR SULPHURIC POLYMERIZATION RESIDUE

The determination of the nitric oxidation residue can be replaced by that of the sulphuric polymerization residue. The purpose of these two determinations is to verify the absence of paraffinic hydrocarbons and benzene hydrocarbons, which are sometimes added to gum spirit of turpentine.

11.1 Nitric oxidation residue

11.1.1 *Reagents*

11.1.1.1 Calcium chloride, anhydrous.

11.1.1.2 Diethyl ether.

11.1.1.3 Nitric acid, concentrated fuming, $\rho \geqslant 1{,}48$ g/ml.

11.1.1.4 Nitric acid, concentrated non-fuming, ρ 1,36 g/ml.

11.1.1.5 Potassium hydroxide solution, prepared as follows :

Dissolve 50 g of potassium hydroxide in 500 ml of water and 50 ml of ethanol 95 % (*V/V*).

11.1.2 *Apparatus*

Marcusson and Winterfeld apparatus (see figure 1), consisting of a 100 ml flask with a long neck graduated in tenths of a millilitre over 10 ml. The flask is closed by a ground neck carrying a separating funnel, marked at 10 ml and terminated by a narrow stem. A small open nozzle sealed to the top of the neck allows the nitrous vapours to escape.

11.1.3 *Procedure*

WARNING — In carrying out this test, it is essential to keep the temperature of the reaction under control, otherwise an explosion may occur.

It is advisable to operate under a hood.

11.1.3.1 Place 30 ml of the concentrated fuming nitric acid (11.1.1.3) in the 100 ml flask (see 11.1.2) and cool to $-10\,^{\circ}C$ by placing it in a mixture of ice and common salt. Pour the sample into the separating funnel, with the tap OFF, to the 10 ml mark, then allow to flow very slowly, drop by drop, into the flask, shaking continuously. The turpentine shall take at least 30 min to flow into the flask. If the reaction shows a tendency to take place too quickly, slow down the addition of turpentine.

When all the turpentine has been added, stand the flask in the cooling mixture for 15 min; remove the separating funnel and add the concentrated non-fuming nitric acid (11.1.1.4), previously cooled, to the contents of the flask kept at $-10\,^{\circ}C$ throughout, until the liquid reaches the graduated part of the neck.

If the turpentine contains no paraffinic hydrocarbons, only a thin dark brown film will be observed on the surface of the liquid. Any unattacked paraffinic hydrocarbons which may be present will form a floating colourless or slightly yellow layer, the volume of which may be read.

11.1.3.2 Empty the contents of the flask into a 100 ml separating funnel. Pour off the oxidation residue, if any, and then run off the lower layer into a 500 ml flask containing 150 ml of distilled water. This dilution causes considerable heating and separation of resinous or oily substances.

11.1.3.3 Wash with water any paraffinic hydrocarbons which may be in the separating funnel. If desired, they may be identified by determining their physical properties.

11.1.3.4 Place the 500 ml flask in a water bath under a hood for 15 min, to dissolve the terpenic oxidation products completely.

If small oily drops of brownish-red colour continue to float on the surface or in the liquid, it is probable that benzene hydrocarbons, which have been transformed into nitrated derivatives, are present.

Cool and extract the nitrated derivatives with 100 ml of the diethyl ether (11.1.1.2) in a separating funnel. Run off the aqueous layer. Wash the ethereal layer with water to eliminate the acid retained, then wash with the solution of potassium hydroxide (11.1.1.5) and then again with water.

Dry the ether solution over the anhydrous calcium chloride (11.1.1.1), then filter and distil. After heating briefly on a water bath, weigh the residue.

11.2 Sulphuric polymerization residue

11.2.1 *Reagent*

Sulphuric acid, 98,5 % (*m/m*).

Dimensions in millimetres

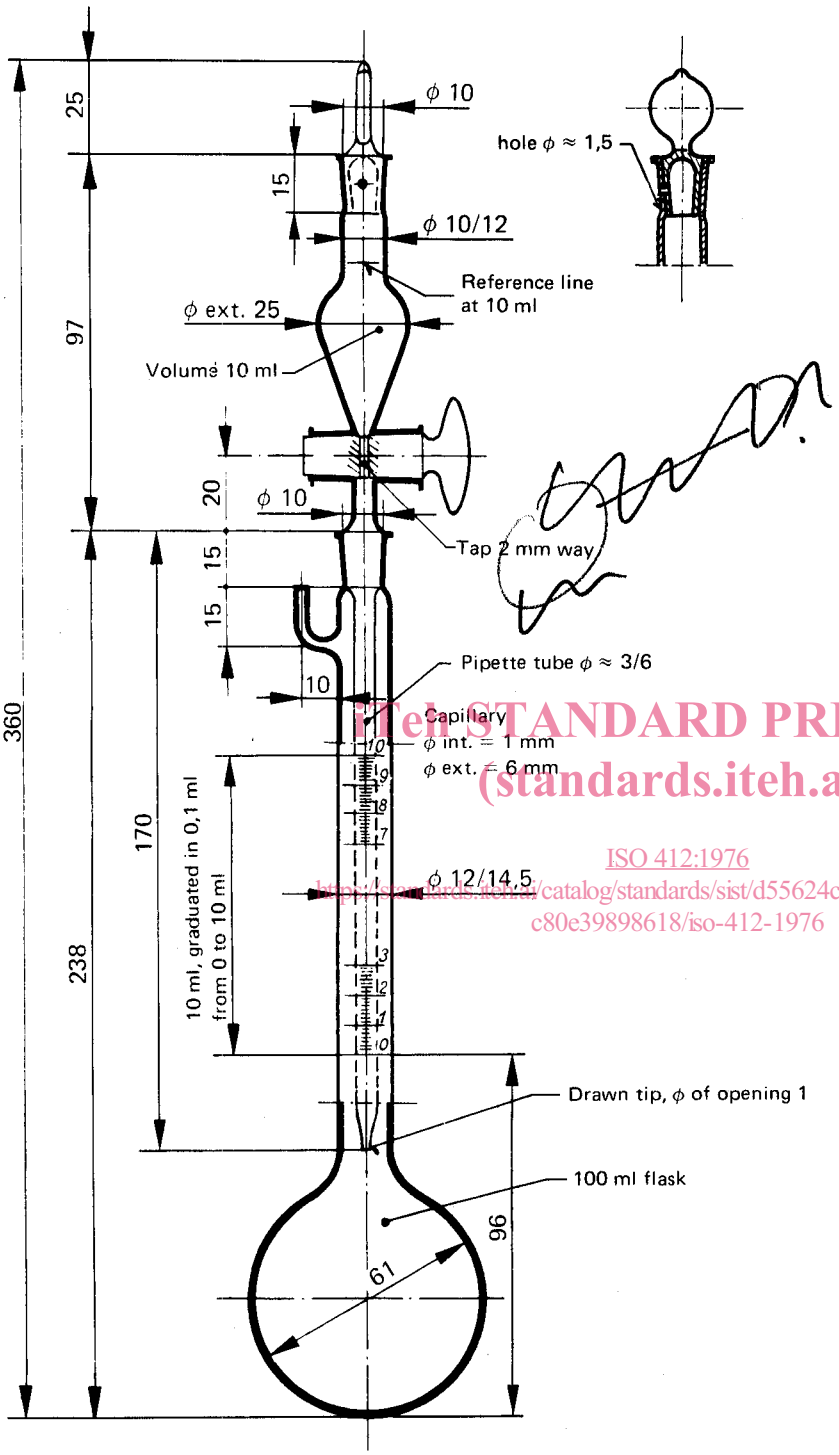

FIGURE 1 – **Marcusson and Winterfeld apparatus**

Dimensions in millimetres

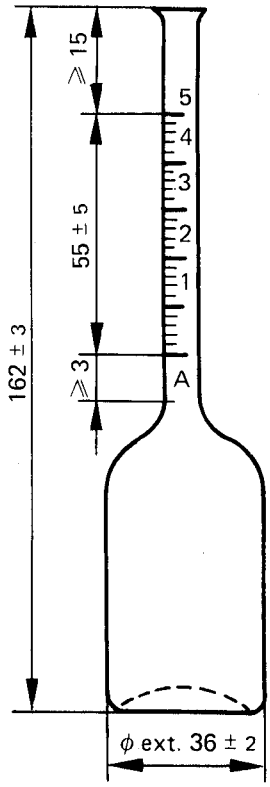

FIGURE 2 – **Flask for sulphuric polymerization test**
(The flask is graduated at 20 °C)

11.2.2 *Apparatus*

11.2.2.1 Flask, 45 ml capacity, with neck graduated up to 5 ml (see figure 2).

11.2.2.2 Burette.

11.2.3 *Procedure*

Pour 20 ml of the sulphuric acid (11.2.1) into the 45 ml flask (11.2.2.1) which is immersed in iced water. Add 5 ml of turpentine slowly, drop by drop, from the burette (11.2.2.2). Shake the flask frequently and make sure that the temperature does not exceed 60 °C. When the temperature of the mixture ceases to rise, shake the flask vigorously and heat on a water bath to between 60 and 65 °C for 10 min, carefully mixing the contents of the flask by shaking vigorously five or six times during heating.

Cool the flask to room temperature and add sufficient sulphuric acid to bring the unpolymerized residue into the graduated neck. The separation line between the residue and the sulphuric acid mixture shall be at, or slightly above, the zero graduation.

Allow the stoppered flask to stand for one night (it may also be centrifuged) and read the volume of unpolymerized residue, in millilitres.

11.2.4 *Expression of results*

The polymerization residue is given, as a percentage by volume, by the formula

$$\frac{5 - V}{5} \times 100$$

where V is the volume, in millilitres, of the unpolymerized residue.

12 ACID VALUE

12.1 Reagents

12.1.1 Ethanol, 95 % (*V*/*V*), neutral to the phenolphthalein solution (12.1.3).

12.1.2 Potassium hydroxide, 0,1 M standard volumetric solution in ethanol 95 % (*V*/*V*).

12.1.3 Phenolphthalein, 1 % (*m*/*m*) solution in ethanol 95 % (*V*/*V*).

12.2 Test portion

Using a pipette, transfer 10 ml of turpentine to a 100 ml conical flask which has been previously weighed.

Determine the mass of this test portion to the nearest 0,1 mg.

12.3 Procedure

Add 20 ml of the ethanol (12.1.1) and a few drops of the phenolphthalein solution (12.1.3) to the conical flask.

Titrate cold with the standard volumetric ethanolic potassium hydroxide solution (12.1.2) from a burette, until the mixture becomes pink.

12.4 Expression of results

The acid value is given by the formula

$$56{,}1 \times \frac{T\,V}{m}$$

where

T is the concentration, in moles per litre, of the ethanolic potassium hydroxide solution (12.1.2);

V is the volume, in millilitres, of the ethanolic potassium hydroxide solution (12.1.2) used;

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

13 TEST REPORT

The test report shall contain at least the following information :

a) a reference to this International Standard or to a corresponding national standard;

b) the type and identification of the product tested;

c) the results of the tests and whether or not the product tested complies with the relevant specification limits;

d) any deviation, by agreement or otherwise, from the procedures specified;

e) the date of the tests.

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INTERNATIONAL STANDARD ISO 412-1976 (E)/ERRATUM

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ERRATUM

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Sub-clause 11.2.4 : the formula should read

$$\frac{5 - V}{5} \times 100$$