BRITISH STANDARD

BS 4835:1973

Methods of test for

Plasticizer esters

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Co-operating organizations

The Chemicals Industry Standards Committee, under whose supervision this British Standard was prepared, consists of representatives of the following Government departments and scientific and industrial organizations:

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Chemical Industries Association*
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Department of Trade and Industry — Laboratory of the Government Chemist*
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National Sulphuric Acid Association
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Royal Institute of Chemistry
Society of Chemical Industry
Society of Motor Manufacturers and Traders Limited

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The following BSI references relate to the work on this standard:
Committee references CIC/4 and CIC/4/4
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Amendments issued since publication

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Contents

Foreword

This standard forms one of a series of British Standards for solvents and allied products; its preparation was authorized by the Chemicals Industry Standards Committee in order to provide methods of test for plasticizer esters. In the drafting of these methods account has been taken of methods adopted by the International Organization for Standardization (ISO), in the preparation of which the United Kingdom has been an active participant.

This British Standard prescribes methods of test only and should not be used or quoted as a specification defining limits of purity. Reference to the standard should be made in a form of words indicating that the methods of test used conform to BS 4835.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 6, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

1 Scope

This British Standard describes general methods of test applicable to organic ester type plasticizers containing only carbon, hydrogen and oxygen but excluding esters of phenols and esters of hydroxy-acids.

NOTE The titles of the British Standards referred to in this Standard are listed on the inside back cover.

2 Measurement of colour

2.1 Introduction This clause is technically identical with the draft of International Standard ISO 2211, modified in accordance with the comments made by the United Kingdom during its development.

2.2 Apparatus. The following apparatus is required:

1) Two *matched Nessler cylinders,* 100 ml capacity, complying with BS 612.

2) One-*mark volumetric flask,* 500 ml capacity, complying with BS 1792.

3) One-*mark volumetric flasks,* 250 ml capacity, complying with BS 1792.

2.3 Reagents. The reagents used shall be of a recognized analytical reagent quality, Water complying with BS 3978 shall be used throughout.

1) *Cobaltous chloride,* hexahydrate.

2) *Hydrochloric acid,* concentrated 36 % (m/m) (11N).

either

3) *Chloroplatinic acid reagent.* Dissolve 250 mg of platinum in a small quantity of aqua regia contained in a glass or porcelain basin by heating on a water bath. When the metal has dissolved evaporate the solution to dryness. Add 1 ml of the hydrochloric acid and again evaporate to dryness; repeat this operation twice.

or

4) *Potassium chloroplatinate.*

2.4 Preparation of colour standard. Dissolve 0.50 g of the cobaltous chloride hexahydrate and either the whole of the chloroplatinic acid (prepared as described above) or 0.623 g of potassium chloroplatinate in 50 ml of the hydrochloric acid. Warm, if necessary, to obtain a clear solution and, after cooling, pour into the 500 ml one-mark volumetric flask. Dilute with water to the mark.

From this solution prepare a series of colour standards ranging from 0 Hazen colour units upwards at intervals of 10 units. For each 10 units pipette 5.0 ml of the solution into a 250 ml one-mark volumetric flask and dilute with water to the mark. These diluted solutions should always be freshly prepared1).

2.5 Procedure. Fill one of the Nessler cylinders to the mark with the sample, and the other with the selected colour standard. If the sample is a solid, make the measurement at a temperature 10 °C above its melting point. Using a white background compare the colours viewing vertically. Repeat with other colour standards, if necessary, until the closest match is obtained.

If the colour of the sample does not match that of any of the colour standards, report, if possible, an approximate value or give a description of the colour with an appropriate note.

3 Measurement of colour after heat treatment

3.1 Introduction. This clause is technically identical with the draft of International Standard ISO 2524, modified in accordance with the comments made by the United Kingdom during its development.

3.2 Apparatus. The following apparatus is required:

1) *Boiling tube,* 200 mm × 38 mm, complying with BS 3218.

2) *Two thermometers,* No. B210C/100 complying with BS 593.

3) *Oil bath with stirrer.* A volume of about 2 litres of oil in the oil bath is suitable for testing together three samples.

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1) Permanent glass Hazen colour standards for use in the BDH Lovibond Nesslerizer are available from The Tintometer Ltd., Salisbury, Wilts.

3.3 Procedure. Transfer 70 ml of the sample (or, if the material is a solid, sufficient to form 70 ml when melted) to the boiling tube and close this with a vented cork, covered with aluminium foil, carrying one of the thermometers. Adjust the position of the thermometer so that the top of the bulb is 55 mm below the surface of the sample. Support the tube in the oil bath, fitted with the other thermometer and already heated to 180 ± 2 °C, at such a depth that the surface of the sample is 25 mm below the surface of the oil. Note the time at the moment of immersion of the sample. Maintain the temperature of the bath thereafter at 180 ± 2 °C.

At the end of 120 ± 2 min withdraw the tube containing the sample and allow it to cool in air to room temperature. If the sample is normally solid at room temperature, cool it to a temperature 10 °C above its melting point.

Measure the colour of the treated sample by the method described in Clause **2**, using equal volumes of the sample and colour standard in, for example, 50 ml Nessler cylinders.

4 Determination of water content

Determine the water content by one of the general methods described in BS 2511, using 20 g of the sample.

5 Determination of ash

5.1 Introduction. This clause is technically identical with the draft of International Standard ISO 2526, modified in accordance with the comments made by the United Kingdom during its development.

5.2 Apparatus. Ordinary laboratory apparatus and a furnace, capable of control at 600 ± 30 °C, is required.

5.3 Procedure. Weigh, to the nearest 1 g, about 50 g of the sample and then slowly burn it, a little at a time, in a weighed platinum or silica basin, previously heated to 600 ± 30 °C, cooled in a desiccator and weighed to the nearest 0.1 mg. Gently heat in a furnace at 600 ± 30 °C until all carbonaceous matter has disappeared. Cool in a desiccator and weigh to the nearest 0.1 mg.

5.4 Calculation. Ash, expressed as a percentage by mass = $\frac{100\ M_1}{M_2}$

where M_1 = mass, in grams, of the residue;

and M_2 = mass, in grams, of the test portion.

6 Determination of acidity to phenolphthalein

6.1 Introduction. This clause is technically identical with the draft of International Standard ISO 2525, modified in accordance with the comments made by the United Kingdom during its development.

6.2 Reagents. The reagents used shall be of a recognized analytical reagent quality. Water complying with BS 3978 shall be used throughout.

1) *Sodium hydroxide,* 0.1N standard volumetric solution.
2) *Ethanol*[2], 95 % (v/v).
3) *Phenolphthalein indicator solution,* 10 g/l, prepared as described in BS 4123.

6.3 Procedure. Weigh, to the nearest 0.5 g, about 50 g of the sample and mix with 50 ml of the ethanol previously neutralized to phenolphthalein. Titrate the mixture with the sodium hydroxide solution, using 0.5 ml of the phenolphthalein indicator solution until the pink colour remains for 5 s.

6.4 Calculation. Acidity, calculated as a percentage by mass of the acid of relative molar mass[3] m_A and basicity n_A

$$= \frac{m_A V_1}{n_A M_3} \times 10^{-2} = A$$

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[2] Ethanol may be replaced by industrial methylated spirits, 66 degrees OP, complying with BS 3591. It should be noted that the use of industrial methylated spirits is governed by The Methylated Spirits Regulations (S.I. 1952, No. 2230).

[3] Hitherto known as molecular weight.

or calculated as milliequivalents per kilogram

$$= \frac{100 V_1}{M_3} = B$$

where V_1 = volume, in millilitres, of 0.1N sodium hydroxide solution used;
M_3 = mass, in grams, of the test portion.

7 Determination of ester content and saponification and ester values

7.1 Introduction. This clause is technically identical with the draft of International Standard ISO 2527, modified in accordance with the comments made by the United Kingdom during its development.

7.2 Reagents. The reagents used shall be of a recognized analytical reagent quality. Water complying with BS 3978 shall be used throughout.

1) *Potassium hydroxide,* approximately N reagent solution in 95 % (v/v) ethanol[4].
2) *Hydrochloric acid,* N standard volumetric solution.
3) *Phenolphthalein indicator solution,* 10 g/l, prepared as described in BS 4123.

7.3 Procedure. Using the same pipette, introduce 50.0 ml of the potassium hydroxide solution into each of two dry 250 ml conical flasks with ground glass joints. Immediately add 5 ml of water to each flask. Close the flasks with their glass stoppers. Transfer into one of the flasks the mass of sample given by the following formula, weighing to the nearest milligram; and using a weighing pipette if the sample is liquid:

$$\frac{0.025 \times m_{\mathrm{E}}}{n} \pm 0.2 \text{ g}$$

where m_{E} = relative molar mass of the sample
and n_{E} = number of ester groups in the molecule.

The table below gives the mass of sample to be taken of a number of esters.

	Relative molar mass	Mass of sample		Relative molar mass	Mass of sample
		g			g
Dimethyl phthalate	194	2.4 ± 0.2	Ditridecyl phthalates	531	6.6 ± 0.2
Diethyl phthalate	222	2.8 ± 0.2	Dibutyl adipates	254	3.2 ± 0.2
Dibutyl phthalates	278	3.5 ± 0.2	Dioctyl adipates	371	4.6 ± 0.2
Dimethoxyethyl phthalate	280	3.5 ± 0.2	Diononyl adipates	399	5.0 ± 0.2
Benzyl Butyl phthalates	312	3.9 ± 0.2	Didecyl adipates	427	5.3 ± 0.2
Diheptyl phthalates	362	4.5 ± 0.2	Diundecyl adipates	455	5.7 ± 0.2
Dibutoxyethyl phthalates	366	4.6 ± 0.2	Didodecyl adipates	483	6.0 ± 0.2
Dioctyl phthalates	390	4.9 ± 0.2	Ditridecyl adipates	511	6.4 ± 0.2
Dinonyl phthalates	418	5.2 ± 0.2	Dibutyl sebacates	314	3.9 ± 0.2
Didecyl phthalates	447	5.6 ± 0.2	Dioctyl sebacates	426	5.4 ± 0.2
			Dioctyl azelates	412	5.3 ± 0.2

Attach the flasks to water-cooled reflux condensers fitted with ground glass joints and heat for 1 h in a boiling water bath. Withdraw the flasks, still carrying their condensers, and immerse them in cold running water. When cool, wash down the inside of each condenser with two 20 ml portions of water. Disconnect the flasks and wash each joint with a further 20 ml of water. Add 0.5 ml of the phenolphthalein indicator solution and titrate the mixture immediately with the hydrochloric acid solution until the pink colour is just discharged.

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[4] Ethanol may be replaced by industrial methylated spirits, 66 degrees OP, complying with BS 3591. It should be noted that the use of industrial methylated spirits is governed by The Methylated Spirits Regulations (S.I. 1952, No. 2230).

7.4 Calculation

7.4.1 *Ester content.* The ester content, expressed as a percentage by mass of the ester concerned

$$= \frac{m_E(V_2 - V_3)}{10M_4 n_A} - \frac{m_E \times A}{m_A}$$

where V_2 = volume, in millilitres, of N hydrochloric acid solution required by the blank;

V_3 = volume, in millilitres, of N hydrochloric acid solution required by the test sample;

M_4 = mass, in grams, of the test portion;

A = acidity of phenolphthalein, expressed as a percentage by mass of the acid, and determined by the method described in Clause **6**;

m_A = relative molar mass of the acid concerned;

m_E = relative molar mass of the ester concerned;

n_A = basicity of the acid concerned.

7.4.2 *Saponification and ester values.* Especially in the case of mixed alcohol esters, for which the relative molecular mass can only, at best, be estimated, saponification or ester values are used to express the result.

7.4.2.1 *Saponification value.* Saponification value, expressed as milligrams of potassium hydroxide per gram

$$= \frac{56.10\ (V_2 - V_3)}{M_4}$$

NOTE 56.10 is the relative molar mass of potassium hydroxide.

7.4.2.2 *Ester value.* Ester value, expressed as milligrams of potassium hydroxide per gram

$$= \frac{56.10\ (V_2 - V_3)}{M_4} - 0.0561\ B$$

where B = acidity to phenolphthalein, expressed as milliequivalents per kilogram, and determined by the method described in Clause **6**.

NOTE The ester content, as a percentage by mass of the ester concerned, may be estimated from the ester value by multiplication by the factor:

$$\frac{m_E}{561.0\ n_A}$$

8 Determination of viscosity

Determine the viscosity at a temperature of 20 ± 0.1 °C by one of the methods described in BS 188.

9 Determination of matter oxidizable by potassium dichromate

9.1 Reagents. The reagents used shall be of recognized analytical reagent quality. Water complying with BS 3978 shall be used throughout.

9.1.1 *Oxidizing solution.* Dissolve approximately 1 g of potassium dichromate in 100 ml of water. Then cautiously add 150 ml of concentrated nitric acid, 70 % (m/m) (16N). Cool the flask during the addition of the nitric acid. Store the solution in a dark-coloured bottle.

9.1.2 *Potassium iodide,* 50 g/l solution. Dissolve 50 g of potassium iodide in 1 litre of water.

9.1.3 *Sodium thiosulphate,* 0.1N standard volumetric solution.

9.1.4 *Cyclohexane.* Wash 1 litre of cyclohexane with three 100 ml portions of water.

9.1.5 *Starch indicator solution.* Prepare as described in BS 4123.

9.2 Procedure

9.2.1 *Calibration.* Weigh, to the nearest 1 mg, 500 mg of the pure alcohol (corresponding to the alcohol component of the ester) into a 50 ml one-mark volumetric flask. Dilute to the mark with the cyclohexane and mix.

1 ml of solution ≡ 10.0 mg of alcohol.

To four 100 ml stoppered separating funnels add 20, 19, 18 and 17 ml of the cyclohexane respectively, followed by 0, 1, 2 and 3 ml of the alcohol solution (corresponding to 0, 10, 20 and 30 mg of alcohol). Add, by pipette, 25.0 ml of the oxidizing solution into each separating funnel.

On no account pipette the oxidizing solution by mouth.

Shake each funnel vigorously for exactly 5 min. Allow to settle and then run off the (lower) potassium dichromate layer into a 250 ml conical flask. Wash the cyclohexane layer with two 25 ml portions of water and add the washings (lower layer) to the dichromate solution. Add 100 ml of the potassium iodide solution, swirl to mix and allow the flask to stand in the dark for 10 min. Titrate the liberated iodine with the 0.1N sodium thiosulphate solution using starch as indicator. The end-point is the discharge of the dark blue of the starch to the light bluish-green of the resultant solution.

From the differences in titre between the blank and the calibration standards, draw a graph of the volume of the 0.1N sodium thiosulphate solution against free alcohol content, in milligrams.

9.2.2 *Test portion.* Use the following volumes of sample depending upon the expected oxidizable matter content:

Oxidizable matter	Volume of sample
%	ml
< 0.2	20
0.2 to 0.5	10
0.5 to 1.0	5

9.2.3 *Determination.* Place 20 ml of the washed cyclohexane in a 100 ml stoppered separating funnel. Add the test portion (**9.2.2**) and then pipette 25.0 ml of the oxidizing solution into the funnel. Then follow the procedure given in **9.2.1**.

9.2.4 *Blank test.* Carry out a blank determination as described in **9.2.3**, but omitting the test portion.

9.3 Calculation. Content of oxidizable matter, expressed as a percentage (mass/volume) of the free alcohol

$$= \frac{M_5}{10V_5}$$

where M_5 = mass, in milligrams, of alcohol corresponding to the difference between the volumes of standard volumetric sodium thiosulphate solution used for the determination and for the blank test;

V_5 = volume, in millilitres, of the test portion.

10 Determination of density at 20 °C (for liquid samples only)

Use the method described in BS 4522.

11 Determination of crystallizing point (for solid samples only)

Use the method described in BS 4633.

12 Determination of refractive index (for liquid samples only)

Use a refractometer that enables the refractive index for the sodium D line at 20 °C to be determined to four decimal places.

13 Determination of flash point

Use, as appropriate, the open cup Pensky-Martens method described in BS 4688 or the Cleveland open cup method described in BS 4689.

Publications referred to

This standard makes reference to the following British Standards:

BS 188, *Methods for the determination of the viscosity of liquids in c.g.s. units.*

BS 593, *Laboratory thermometers.*

BS 612, *Nessler cylinders.*

BS 1792, *One-mark volumetric flasks.*

BS 2511, *Methods for the determination of water (Karl Fischer method).*

BS 3218, *Test tubes and boiling tubes.*

BS 3978, *Water for laboratory use.*

BS 4123, *Schedule of preferred chemical indicators.*

BS 4522, *Method for the determination of density of liquids at 20 °C.*

BS 4633, *Method for the determination of crystallizing point.*

BS 4688, *Method for determination of flash point (open) and fire point of petroleum products by the Pensky-Martens apparatus.*

BS 4689, *Method for determination of flash and fire points of petroleum products and other liquids by the Cleveland open cup.*

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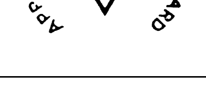

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