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Rubber compounding ingredients — Organic vulcanizing agents — Determination of organic peroxide content

Ingrédients de mélange du caoutchouc — Agents vulcanisants organiques — Détermination de la teneur en peroxyde organique

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Foreword

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This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 3, *Raw materials (including latex) for use in the rubber industry*.

This second edition cancels and replaces the first edition (ISO 14932:2012), which has been technically revised.

The main changes are as follows:

— gas chromatography using packed column has been added in 8.3;

— the solvent has been changed from chloroform to toluene and isopropyl alcohol;

— tetrahydrofuran has been removed due to toxicity;

— CAS Registry Numbers (CAS RN) have been added;

— Annex D and the former Annex E have been merged as Annex D;

— Formula (D.1) has been corrected.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Rubber compounding ingredients — Organic vulcanizing agents — Determination of organic peroxide content

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions.

1 Scope

This document specifies four methods for the determination of the content of the following groups of organic peroxides used as rubber vulcanizing agents. There are three titration methods and one gas-chromatography method.

a) titration method A for group a: Peroxyketals:

1,1-Di(*tert*-butylperoxy)cyclohexane (DTBPC; CAS Registry Number®[1]):3006-86-8)

1,1-Di(*tert*-butylperoxy)-2-methylcyclohexane (DBPMC; CAS RN 147217-40-1);

1,1-Di(*tert*-butylperoxy)-3,3,5-trimethylcylcohexane (DBPTC; CAS RN 6731-36-8);

2,2-Di(*tert*-butylperoxy)butane (DBPB; CAS RN 2167-23-9);

Butyl −4,4-di(*tert*-butylperoxy)valerate (BPV; CAS RN 995-33-5);

b) titration method B for group b: Diacyl peroxides:

Dibenzoyl peroxide (CAS RN 94-36-0);

Di(2,4-dichlorobenzoyl) peroxide (CAS RN 133-14-2);

Di(4-methylbenzoyl) peroxide (CAS RN 895-85-2);

c) titration method C for group c: Diaralkyl and alkyl-aralkyl peroxides:

Di(tert-butylperoxyisopropyl)benzene (CAS RN 2212-81-9);

Dicumyl peroxide (CAS RN 80-43-3);

tert-Butyl cumyl peroxide (CAS RN 3457-61-2);

d) gas-chromatography for dialkyl peroxides, using a capillary or packed column.

2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (CAS RN 78-63-7)

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

1) Chemical Abstracts Service (CAS) Registry Number® is a trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

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ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 6353-1, *Reagents for chemical analysis — Part 1: General test methods*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
active oxygen
oxygen-centred radicals, liberated by organic peroxide, capable of initiating vulcanization of rubber compounds

3.2
peroxyketal
peroxide obtained by the reaction of ketone with *tert*-butyl hydroperoxide (TBHP) as follows:

$$2tert-\mathrm{butyl}-\mathrm{OOH}+\mathrm{R}-\mathrm{C(O)}-\mathrm{R}'\rightarrow(tert-\mathrm{butyl}-\mathrm{OO})_2-\mathrm{CR}(\mathrm{R}')+\mathrm{H_2O}$$

3.3
diacyl peroxide
peroxide obtained by the reaction of benzoyl chloride with hydrogen peroxide as follows:

$$2\mathrm{C_6H_5}-\mathrm{C(O)}-\mathrm{Cl}+\mathrm{H_2O_2}\rightarrow\mathrm{C_6H_5}-\mathrm{C(O)}-\mathrm{OO}-\mathrm{C(O)}-\mathrm{C_6H_5}+2\mathrm{HCl}$$

3.4
alkyl-aralkyl peroxide
diaralkyl peroxide
peroxide obtained by the reaction of benzyl alcohol with hydrogen peroxide in presence of sulfuric acid as follows:

$$2\mathrm{C_6H_5}-\mathrm{C(CH_3)_2}-\mathrm{OH}+\mathrm{H_2O_2}\rightarrow\mathrm{C_6H_5}-\mathrm{C(CH_3)_2}-\mathrm{OO}-\mathrm{(CH_3)_2C}-\mathrm{C_6H_5}+2\mathrm{H_2O}$$

3.5
dialkyl peroxide
peroxide obtained by the reaction of *tert*-butyl alcohol with hydrogen peroxide in presence of sulfuric acid as follows:

$$2\mathrm{CH_3}-\mathrm{C(CH_3)_2}-\mathrm{OH}+\mathrm{H_2O_2}\rightarrow\mathrm{CH_3}-\mathrm{C(CH_3)_2}-\mathrm{OO}-\mathrm{(CH_3)_2C}-\mathrm{CH_3}+2\mathrm{H_2O}$$

4 General

Some organic peroxides are treated as diluted with an inert solvent, or mixed with an inorganic filler, a raw or an uncured rubber compound as master batches for explosion protection. The undiluted or diluted peroxides are directly used for its content analysis, however the mixed peroxides with the filler or rubber need to be pre-treated to prepare a test sample for the content analysis. The pre-treatment procedure and the determination of the peroxide content in the mixture shall be as specified in Annex D.

The choice of the properties to be determined and the values required shall be agreed between the interested parties.

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5 Titration method A for group a: Peroxyketals

5.1 Purpose

This test method specifies the procedure for the determination of the content of peroxyketals used as rubber organic vulcanizing agents and is applicable to DTBPC, DBPTC, DBPMC, DBPB and BPV.

5.2 Principle

Peroxyketales react with iodide in an acetic acid-hydrochloric acid medium, liberating an equivalent amount of iodine which is titrated with a standard sodium thiosulfate solution:

$$R-OO-R'+2\,I^-+2\,H^+\rightarrow ROH+R'OH+I_2$$

$$I_2+2S_2O_3{}^{2-}\rightarrow 2\,I^-+S_4O_6{}^{2-}$$

Peroxyketals can contain traces of *tert*-butyl-hydroperoxide (TBHP) as an impurity. The content of TBHP can be obtained by the method specified in Annex B. The amount of active oxygen of the peroxyketal alone can then be obtained by substracting of the amount of the active oxygen of TBHP and the content of the peroxyketal is obtained by dividing the value by the theoretical amount of active oxygen.

5.3 General procedure

Two procedures are shown as examples depending upon the condition used for the peroxyketal oxidation-reduction reaction with potassium iodide (CAS RN 7681-11-0) (see methods A1 and A2 in Annex A).

A weighed peroxyketal test sample (m_1) is dissolved in an aqueous solution acidified with acetic acid (CAS RN 64-19-7) and hydrochloric acid (CAS RN 7647-01-0) containing potassium iodide.

Titrate the freed iodine with sodium thiosulfate (CAS RN 10102-17-7) of standard concentration and determine the volume required to complete the titration (V_1).

Repeat the same procedure without the peroxyketal as a blank test and determine the volume of sodium thiosulfate required to complete the titration (V_{b1}).

Determine the content of TBHP in the sample (C_{HPO}) as specified in Annex B.

The content of TBHP can be zero as it is negligible in the calculation of peroxyketal content determination when agreed between the interested parties (see 5.4.2). This shall be recorded in the test report.

5.4 Expression of results

5.4.1 Total amount of active oxygen

Calculate the total amount of active oxygen, $A_{O,kt}$, expressed as a percentage by mass to the nearest 0,1 %, by Formula (1):

$$A_{O,kt}=\frac{0{,}000\,8\times(V_1-V_{b1})\times f_1}{m_1}\times 100 \quad (1)$$

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where

V_1 is the volume, in cubic centimetres, of sodium thiosulfate solution used for the test;

V_{b1} is the volume, in cubic centimetres, of sodium thiosulfate solution used for the blank test;

f_1 is the factor of sodium thiosulfate solution, which is the ratio of the actual concentration to the theoretical concentration (the normality is 0,1);

m_1 is the mass, in grams, of the test sample;

0,000 8 is the factor, in grams per cubic centimetre obtained as follows:

$$0{,}000\ 8 = \frac{15{,}999\ 4}{2} \times 0{,}1 \times \frac{1}{1\ 000}$$

where

15,999 4 is the atomic weight of oxygen;

0,1 is the normality of the sodium thiosulfate solution.

5.4.2 Content

Calculate the content of the peroxyketal, P_{kt}, expressed as a percentage by mass to the nearest 0,1 %, by Formula (2):

$$P_{kt} = \frac{A_{O,kt} - C_{HPO} \times 0{,}177\,5}{A_{T,kt}} \times 100 \quad (2)$$

where

$A_{O,kt}$ is the total amount of active oxygen, in mass %;

C_{HPO} is the content of TBHP (as specified in Annex B), in mass %;

0,177 5 is the value obtained by dividing the theoretical amount of active oxygen in TBHP by 100;

$A_{T,kt}$ is the theoretical amount of active oxygen of the peroxyketal, in mass %, obtained by Formula (3):

$$A_{T,kt} = \frac{n_1 \times 15{,}999\ 4}{M_1} \times 100 \quad (3)$$

where

n_1 is the number of peroxide bond in the peroxyketal;

M_1 is the molecular mass of the peroxyketal (see Table 1).

As a simple method, TBHP (C_{HPO}) may be assumed to be zero and the total amount of organic peroxide may be used as the amount of ketal-based organic peroxide by Formula (4):

$$P_{kt} = \frac{A_{O,kt}}{A_{T,kt}} \times 100 \quad (4)$$

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Table 1 — Molecular mass of peroxyketal

Peroxyketal	n_1	M_1	$A_{T,kt}$
DTBPC	2	260,37	12,29
DBPMC	2	274,40	11,66
DBPTC	2	302,45	10,58
DBPB	2	234,33	13,65
BPV	2	334,45	9,57

6 Titration method B for group b: Diacyl peroxides

6.1 Purpose

This test method specifies the procedure for the determination of the content of diacyl peroxides such as dibenzoyl peroxide used as rubber organic vulcanizing agents.

6.2 Principle

Diacyl peroxides react with iodide in a solvent medium, liberating an equivalent amount of iodine which is titrated with a standard sodium thiosulfate solution:

$$R-OO-R'+2\ I^{-}+2\ H^{+}\rightarrow ROH+R'OH+I_2$$

$$I_2+2S_2O_3{}^{2-}\rightarrow 2\ I^{-}+S_4O_6{}^{2-}$$

The content of the diacyl peroxide is obtained by dividing the amount of active oxygen measured by the theoretical amount of active oxygen.

6.3 Measurement of active oxygen

6.3.1 General procedure

Two procedures are shown as examples depending upon the solvent used for the diacyl peroxide oxidation-reduction reaction with potassium iodide (see Annex C).

A weighed diacyl peroxide test sample (m_2) is dissolved in dilute acetic acid containing potassium iodide.

Titrate the freed iodine with sodium thiosulfate of standard concentration and determine the volume required to complete the titration (V_2).

Repeat the same procedure without the diacyl peroxide as a blank test and determine the volume of sodium thiosulfate required to complete the titration (V_{b2}).

6.3.2 Calculation of amount of active oxygen

Calculate the amount of active oxygen of the diacyl peroxide, $Ao_{,da}$, expressed as a mass fraction percentage to the nearest 0,1 %, with Formula (5):

$$A_{O,da}=\frac{[0{,}000\,8\times(V_2-V_{b2})\times f_2]\times 100}{m_2}\times 100 \tag{5}$$

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where

V_2 is the volume, in cubic centimetres, of sodium thiosulfate solution used for the test;

V_{b2} is the volume, in cubic centimetres, of sodium thiosulfate solution used for the blank test;

f_2 is the factor of sodium thiosulfate solution, which is the ratio of the actual concentration to the theoretical concentration (the normality is 0,1);

m_2 is the mass, in grams, of the test sample;

0,000 8 is the factor, in grams per cubic centimetre, obtained by Formula (6);

$$0{,}000\ 8 = \frac{15{,}999\ 4}{2} \times 0{,}1 \times \frac{1}{1\ 000} \quad (6)$$

where

15,999 4 is the atomic weight of oxygen;

0,1 is the normality of the sodium thiosulfate solution.

6.3.3 Calculation of theoretical active oxygen

The theoretical amount of active oxygen of the diacyl peroxide $A_{T,da}$, in mass fraction %, is calculated from Formula (7). The diacyl peroxy bond number, molecular weight and theoretical active oxygen is calculated from Formula (7):

$$A_{T,da} = \frac{n_2 \times 15{,}999\ 4}{M_2} \times 100 \quad (7)$$

where

n_2 is the number of peroxide bond in the diacyl peroxide (see Table 2);

M_2 is the molecular mass of the diacyl peroxide (see Table 2);

15,999 4 is the atomic weight of oxygen.

Table 2 — Molecular mass of the diacyl peroxide

Diacyl peroxide	n_2	M_2	$A_{T,da}$
Dibenzoyl peroxide	1	242,23	6,61
Di(2,4-dichlorobenzoyl) peroxide	1	380,01	4,21
Di(4-methylbenzoyl) peroxide	1	270,29	5,92

6.4 Calculation of diacyl peroxide content

Calculate amount of content of the diacyl peroxide, P_{da} expressed as a percentage mass fraction to the nearest 0,1 %, by Formula (8):

$$P_{da} = \frac{A_{o,da}}{A_{T,da}} \times 100 \quad (8)$$

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where

$A_{O, da}$ is the total amount of active oxygen, in mass fraction %;

$A_{T, da}$ is the total amount of theoretical oxygen, in mass fraction %.

7 Titration method C for group c: Diaralkyl and alkyl-aralkyl peroxides

7.1 Purpose

This test method specifies the procedure to determine the content of alkyl-aralkyl peroxides such as dicumyl peroxide used as rubber organic vulcanizing agents.

7.2 Principle

The alkyl aralkyl peroxide is refluxed in an inert atmosphere with acetic acid and a specified amount of water containing sodium iodide. Water is added to the reaction mixture to prevent side reactions taking place between iodide and decomposition products of the alkyl aralkyl peroxide.

After refluxing for 30 min, the reaction mixture is cooled to room temperature to prevent side reactions between the liberated iodine and decomposition products of the alkyl aralkyl peroxide and to avoid loss of iodine through volatilization. After dilution with water, the liberated iodine is titrated with a standard sodium thiosulfate solution.

This procedure gives a reproducible but not quantitative reaction because of the side reactions. For this reason, a peroxide specific factor is introduced into the calculation (see Table 3).

As the method is empirical, the procedure shall be followed exactly, otherwise the factors are not valid.

$$R-OO-R' + 2\ I^- + 2\ H^+ \rightarrow ROH + R'OH + I_2$$

$$I_2 + 2S_2O_3{}^{2-} \rightarrow 2\ I^- + S_4O_6{}^{2-}$$

The content of the alkyl-aralkyl peroxides is obtained by multiplying the active oxygen content with the molecular mass and a peroxide specific factor (see Table 3).

7.3 Reagents

Use only reagents of recognized analytical grade and only distilled water (CAS RN 7732-18-5) or water of equivalent purity (grade 3 or higher grade in accordance with ISO 3696).

7.3.1 Acetic acid, glacial.

7.3.2 Sodium iodide (CAS RN 7681-82-5), coarsely powdered.

7.3.3 Sodium thiosulfate solution, 0,1 N standard solution.

7.3.4 Nitrogen (CAS RN 7727-37-9) or **carbon dioxide**, gas from a cylinder.

7.3.5 Carbon dioxide (CAS RN 124-38-9), dry ice.

7.3.6 Oxalic acid dihydrate (CAS RN 6153-56-6), approximately 99,8 % mass fraction.

7.3.7 Hydrochloric acid, analytical grade.

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7.4 Apparatus

7.4.1 Conical flask, with ground glass joint NS 29 or similar, 300 cm^3.

7.4.2 Dispensettes, 50 cm^3 and 3,0 cm^3 to 5,0 cm^3.

7.4.3 Liebig condenser, with ground glass joint NS 29, length approximately 40 cm.

7.4.4 Gas inlet tube of glass, fitted into the condenser with a considerable length.

7.4.5 Heating mantle or **electric hot-plate** or **hot water bath**.

7.4.6 Flow-meter, capable of measuring 10 dm^3/h.

7.4.7 Glass beads, diameter approximately 3 mm or boiling bubble stones.

7.4.8 Analytical balance, accurate to within 0,1 mg.

7.5 Procedure

7.5.1 Test sample analysis

a) Transfer 50 cm^3 acetic acid (7.3.1) into a 300 cm^3 flask (7.4.1) with dispensette (7.4.2).

b) Add some dry ice (7.3.5). Dry ice shall be present until the reaction mixture boils.

c) After 2 min, add 6 g of sodium iodide (7.3.2).

d) Add exactly 3,0 cm^3 to 5,0 cm^3 of water and mix. 5 cm^3 of hydrochloric acid (7.3.7) may be added to increase the acidity to make the end point easier to see.

e) If the dicumyl peroxide formulation contains calcium carbonate or clay, add 600 mg ± 25 mg of oxalic dihydrate to the solution mixture and mix.

NOTE Oxalic acid dihydrate is added to neutralize the effect of calcium carbonate or clay. Lower intake is insufficient for complete complexing and higher intake causes side reactions resulting in incorrect factors.

f) Weigh a test sample to the nearest 0,1 mg into a weighing cap, the amount to be as indicated in Table 3.

g) Transfer the cap into the flask and mix.

h) Add some glass beads.

i) Connect the condenser to the gas inlet tube.

j) Adjust the gas flow to approximately 10 dm^3/h and maintain this flow for the remainder of the procedure.

k) Heat the contents of the flask rapidly to boiling and maintain a moderate boiling for 30 min.

l) Cool the contents rapidly to approximately 20 °C by placing the flask in an ice-water bath for about 5 min while maintaining the gas flow.

m) Add 100 cm^3 water through the condenser.

n) Remove the condenser from the flask and titrate immediately with the sodium thiosulfate solution (7.3.3) to a colourless end point (V_3).

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7.5.2 Blank test

Repeat the same procedure without the peroxide test sample as a blank test and determine the volume of sodium thiosulfate required to complete the titration (V_{b3}).

7.6 Expression of results

7.6.1 Assay of aralkyl peroxide

Calculate the assay of alkyl-aralkyl peroxide, $A_{AA,}$ expressed as a mass fraction percentage, by Formula (9):

$$A_{AA} = \frac{(V_3 - V_{b3}) \times N \times f_P \times M_3 \times 100}{m_3 \times n_3 \times 2} \tag{9}$$

where

V_3	is the volume, in cubic centimetres, of sodium thiosulfate (7.3.3) solution used for the test;
V_{b3}	is the volume, in cubic centimetres, of sodium thiosulfate (7.3.3) solution used for the test;
N	is the normality of the sodium thiosulfate solution;
f_P	is the peroxide specific factor (see Table 3);
M_3	is the molar mass of the alkyl-aralkyl peroxide concerned (see Table 3);
m_3	is the mass of the sample, in milligrams;
n_3	is the number of peroxide groups of the peroxide concerned (see Table 3).

Table 3 — Required mass of test sample, molar mass, factor and number of peroxide groups for alkyl-aralkyl peroxides

Product	Mass of test sample m_3 mg	Molar mass M_3	Factor f_P	Number of peroxide groups n_3
Di(*tert*-butylperoxyisopropyl)benzene CAS RN 25155-25-3	200	338,49	$\frac{100}{87{,}9} = 1{,}138$	2
Dicumyl peroxide CAS RN 80-43-3	300	270,37	$\frac{100}{93} = 1{,}075$	1
tert-Butyl cumyl peroxide CAS RN 3457-61-2	230	208,30	$\frac{100}{91} = 1{,}099$	1

8 Determination of the assay of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane

8.1 Purpose

This test method specifies the procedure to determine a mass fraction of 35 % to 55 % of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane in formulations containing silicone oil and silica, a mass fraction of 40 % to 55 % of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane in formulations containing silica and/or whiting, and/or ethylene propylene diene rubber (EPDM).

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8.2 Principle

The technique used is gas chromatography methods with capillary column or packed column. The test sample is extracted with toluene and analysed on a chemically bonded non-polar stationary phase. The content of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane is determined according to the internal standard method using *n*-pentadecane.

8.3 Gas chromatography method

8.3.1 Using capillary column

8.3.1.1 Reagents

Use only reagents of recognized analytical grade.

8.3.1.1.1 Toluene (CAS RN 108-88-3).

8.3.1.1.2 Silicone oil 1 000 (CAS RN 63148-62-9).

8.3.1.1.3 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane standard, of well-defined assay. Standard sample should preferably be stored in a refrigerator.

8.3.1.1.4 *n*-Pentadecane (CAS RN 629-62-9).

8.3.1.2 Apparatus

8.3.1.2.1 Capillary gas chromatograph equipped with a split injector and a flame ionization detector.

8.3.1.2.2 Chromatography data system.

8.3.1.2.3 Injection syringe, 5 µl, plunger-in-barrel type.

8.3.1.2.4 Ultrasonic bath.

8.3.1.2.5 Mortar.

8.3.1.3 Conditions

8.3.1.3.1	**Column:**	fused silica WCOT, 16 m × 0,32 mm ID
	Stationary phase:	Sil 5 CB, 100 % polydimethylsiloxane, cross-linked
	Film thickness:	0,12 µm
8.3.1.3.2	**Carrier gas:**	helium
	Flow rate:	so that methane is eluted with a retention time of 35 s ± 2 s (at 100 °C)
8.3.1.3.3	**Injector:**	split
	Split flow rate:	60 cm^3/min
	Glass insert:	filled with some silanized glass wool

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8.3.1.3.4 Temperatures

Injector: 100 °C

Detector: 300 °C

Column
— initial: 100 °C during 2 min
— rate: 10 °C/min
— final: 150 °C

8.3.1.3.5 Injection volume: 0,5 mm^3

8.3.1.4 Procedure

8.3.1.4.1 Conditioning of equipment

Condition the column at 200 °C until a stable baseline is attained. It is advised to condition newly mounted injector glass liners.

8.3.1.4.2 Preparation of the standard solution

Weigh approximately 100 mg of the 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane standard (8.3.1.1.3) and 125 mg of *n*-pentadecane (8.3.1.1.4) to the nearest 0,1 mg into a 10 cm^3 volumetric flask. Make up to volume with toluene (8.3.1.1.1) and mix well.

8.3.1.4.3 Preparation of the sample solution

8.3.1.4.3.1 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane in formulations containing silicone oil and silica

Weigh 160 mg ± 20 mg of silicone oil (8.3.1.1.2) into a 25 cm^3 volumetric flask. Weigh approximately 120 mg of the sample and 125 mg of *n*-pentadecane (8.3.1.1.4) to the nearest 0,1 mg into the same volumetric flask. Make up to volume with toluene (8.3.1.1.1) and mix well.

8.3.1.4.3.2 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane in formulations containing silica and/or whiting, and/or ethylene propylene diene rubber

The sample shall be homogeneous. Cut a representative test sample from the sample into small granules using a pair of scissors or reduce the particle size by grinding a representative test sample from the sample in a mortar.

Weigh approximately 280 mg of the sample and 125 mg of *n*-pentadecane (8.3.1.1.4) to the nearest 0,1 mg into a 25 cm^3 volumetric flask. Make up to volume with toluene (8.3.1.1.1) and mix well.

8.3.1.5 Analysis

Inject 0,5 mm^3 of the standard solution and record the chromatogram. Inject 0,5 mm^3 of the sample solution and record the chromatogram. Determine the areas of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane and *n*-pentadecane peaks. Verify that these peaks have been recorded and integrated correctly.

8.3.1.6 Maintenance

Replace an injector glass liner which has become contaminated with deposited silicone oil on a daily basis. Then, clean the column by raising its temperature to 290 °C at a rate of 30 °C/min and maintaining this temperature for 20 min.

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8.3.1.7 Expression of results

8.3.1.7.1 The response factor of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane f_R is calculated from Formula (10):

$$f_R = \frac{I_{st}}{S_{st}} \times \frac{s_{st}}{i_{st}} \times \frac{C_{st}}{100} \qquad (10)$$

where

S_{st} is the peak area of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane obtained from the standard solution;

I_{st} is the peak area of *n*-pentadecane obtained from the standard solution;

s_{st} is the 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane standard used to prepare the standard solution in milligrams;

i_{st} is the *n*-pentadecane used to prepare the standard solution, in milligrams;

C_{st} is the assay (% area/area) of the 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane standard.

8.3.1.7.2 The content of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane C_{PO} is calculated from Formula (11):

$$C_{PO} = f_R \times \frac{S_{sa}}{I_{sa}} \times \frac{i_{sa}}{m_{sa}} \times 100 \qquad (11)$$

where

S_{sa} is the peak area of 2,5 dimethyl-2,5-di(*tert*-butylperoxy)hexane obtained from the sample solution;

I_{sa} is the peak area of *n*-pentadecane obtained from the sample solution;

f_R is the response factor of 2,5 dimethyl-2,5-di(*tert*-butylperoxy)hexane;

i_{sa} is the *n*-pentadecane used to prepare the sample solution, in milligrams;

m_{sa} is the sample used to prepare the sample solution, in milligrams.

8.3.2 Using packed column

8.3.2.1 Reagents

Use only reagents of recognized analytical grade.

8.3.2.1.1 Toluene.

8.3.2.1.2 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane standard, of well-defined assay. Standard sample should preferably be stored in a refrigerator.

8.3.2.1.3 *n*-Dodecane (CAS RN 112-40-3).

8.3.2.2 Apparatus

8.3.2.2.1 Gas chromatograph equipped a flame ionization detector.

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8.3.2.2.2 Chromatography data system.

8.3.2.2.3 Micro syringe.

8.3.2.2.4 Ultrasonic bath.

8.3.2.2.5 Mortar and pestle.

8.3.2.3 Conditions

8.3.2.3.1	**Column:**	glass column, from 0,5 m to 1,1 m × 3 mm ID
	Stationary phase:	a mass fraction from 1,5 % to 10 % of methylsilicon
	Support:	diatomite of a particle size of from 60 mesh to 100 mesh treated with acid and silane
8.3.2.3.2	**Carrier gas:**	helium
8.3.2.3.3	**Injector:**	split less
8.3.2.3.4	**Temperatures**	
	Injector:	110 °C
	Detector:	190 °C
	Column	— initial: 95 °C during 9 min — rate: 40 °C/min — final: 190 °C
8.3.2.3.5	**Injection volume:**	0,4 mm^3

8.3.2.4 Procedure

8.3.2.4.1 Conditioning of equipment

Condition the column at 200 °C until a stable baseline is attained. It is advised to condition newly mounted injector glass liners.

8.3.2.4.2 Preparation of the standard solution

Weigh approximately 400 mg of the 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane standard (8.3.2.1.2) and 150 mg of *n*-dodecane (8.3.2.1.3) to the nearest 0,1 mg into a 30 cm^3 volumetric flask. Make up to volume with toluene (8.3.2.1.1) and mix well.

8.3.2.4.3 Preparation of the sample solution

The sample shall be homogeneous. Cut a representative test sample from the sample into small granules using a pair of scissors or reduce the particle size by grinding a representative test sample from the sample in a mortar.

Weigh approximately 5 g of the sample and 2 g of *n*-dodecane (8.3.2.1.3) to the nearest 0,1 mg into a 100 cm^3 volumetric flask. Make up to volume with toluene (8.3.2.1.1) and mix well.

WARNING — Toluene is a harmful solvent, so avoid inhaling vapours, and avoid instances where it can adhere to mucous membranes and skin.

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In addition to *n*-dodecane, the same internal standard material used when preparing the standard solution can be used.

8.3.2.4.4 Analysis

Inject 0,4 mm^3 of the standard solution and record the chromatogram. Inject 0,4 mm^3 of the sample solution and record the chromatogram. Determine the areas of 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane and *n*-dodecane peaks. Verify that these peaks have been recorded and integrated correctly.

8.3.2.5 Expression of results

8.3.2.5.1 The response factor of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane, f_R, is calculated from Formula (12):

$$f_R = \frac{I_{st}}{S_{st}} \times \frac{s_{st}}{i_{st}} \times \frac{C_{st}}{100} \tag{12}$$

where

S_{st} is the peak area of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane obtained from the standard solution;

I_{st} is the peak area of *n*-pentadecane obtained from the standard solution;

s_{st} is the 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane standard used to prepare the standard solution in milligrams;

i_{st} is the *n*-pentadecane used to prepare the standard solution, in milligrams;

C_{st} is the assay (% area/area) of the 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane standard.

8.3.2.5.2 The content of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane, C_{PO}, is calculated from Formula (13):

$$C_{PO} = f_R \times \frac{S_{sa}}{I_{sa}} \times \frac{i_{sa}}{m_{sa}} \times 100 \tag{13}$$

where

S_{sa} is the peak area of 2,5 dimethyl-2,5-di(*tert*-butylperoxy)hexane obtained from the sample solution;

I_{sa} is the peak area of *n*-pentadecane obtained from the sample solution;

f_R is the response factor of 2,5 dimethyl-2,5-di(*tert*-butylperoxy)hexane;

i_{sa} is the *n*-pentadecane used to prepare the sample solution, in milligrams;

m_{sa} is the sample used to prepare the sample solution, in milligrams.

9 Precision

See Annex E.

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10 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 14932:2023;

b) all details necessary for complete identification of the material or product tested;

c) the method used (if the standard includes several);

d) any deviations from the procedure;

e) the individual results and their average;

f) any unusual observations or incidents likely to have affected the results;

g) date(s) of testing.

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Annex A
(informative)

Method to determine the content of peroxyketal

A.1 General

This annex gives two methods to determine the content of peroxyketals used as rubber organic vulcanizing agents. These methods are applicable to DTBPC, DBPTC, DBPMC, DBPB and BPV.

A.2 Method A1

A.2.1 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity. Use a grade 3 or higher grade as specified in accordance with ISO 3696.

A.2.1.1 2-Propanol, analytical grade.

A.2.1.2 Acetic acid, glacial.

A.2.1.3 Sodium hydrogen carbonate (CAS RN 144-55-8), analytical grade.

A.2.1.4 Saturated solution of potassium iodide, prepared by adding approximately 250 cm^3 of water to approximately 500 g of potassium iodide, then warming at approximately 40 °C to dissolve, cooling to room temperature and preserving in a dark place.

A.2.1.5 Concentrated hydrochloric acid, analytical grade.

A.2.1.6 Sodium thiosulfate solution, 0,1 N standardized.

A.2.1.7 Nitrogen or carbon dioxide, gas from a cylinder.

A.2.2 Apparatus

A.2.2.1 Flat bottom pear-shaped flask, 300 cm^3 capacity, with an interchangeable ground joint (T29/32 or similar).

A.2.2.2 Hot plate.

A.2.2.3 Reflux condenser, of top open, with an interchangeable ground joint (T29/32) of male mouth.

A.2.2.4 Burette, 25 cm^3 capacity, graduated in 0,1 cm^3, in accordance with the general specifications given in ISO 385.

A.2.2.5 Graduated measuring cylinder, 50 cm^3, 30 cm^3 and 10 cm^3 capacity.

A.2.2.6 Pipette, two of 2 cm^3 capacity and 5 cm^3 capacity.

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A.2.2.7 Analytical balance, accurate to within 0,1 mg.

A.2.2.8 Conical flask, 200 cm^3 with stopper.

A.2.3 Procedure

A.2.3.1 Weigh approximately 0,000 5 mol of sample into the flat bottom pear-shaped flask (A.2.2.1) or the conical flask with stopper (A.2.2.8), and weigh to the nearest 0,1 mg.

A.2.3.2 Add 30 cm^3 of 2-propanol (A.2.1.1) using a graduated measuring cylinder of 30 cm^3 capacity (A.2.2.5).

A.2.3.3 Add 2 cm^3 of acetic acid (A.2.1.2) with a pipette (A.2.2.6). In addition, nitrogen or carbon dioxide may be bubbled for 2 min to reduce the effect of oxygen.

A.2.3.4 Add 1,5 g of sodium hydrogen carbonate (A.2.1.3).

A.2.3.5 Add 2 cm^3 of potassium iodide saturated solution (A.2.1.4) with a pipette (A.2.2.6).

A.2.3.6 Fix the reflux condenser (A.2.2.3) to the flat bottom pear-shaped flask or the conical flask and boil it on a hot plate (A.2.2.2) gently for 5 min.

A.2.3.7 Add approximately 8 cm^3 of concentrated hydrochloric acid (A.2.1.5) using a graduated measuring cylinder of 10 cm^3 capacity (A.2.2.5) from the upper part of the reflux condenser, and boil it for 3 min to 10 min.

A.2.3.8 Detach the flat bottom pear-shaped flask or the conical flask.

A.2.3.9 Add approximately 1,5 g of sodium hydrogen carbonate (A.2.1.3) and approximately 50 cm^3 of water using a graduated measuring cylinder of 50 cm^3 capacity (A.2.2.5). Immediately titrate with sodium thiosulfate solution (A.2.1.6) until the colour of iodine disappears (V_1).

A.2.3.10 Carry out the procedure in duplicate.

A.2.3.11 In addition, carry out a blank test without the sample in accordance with the same procedure (V_{b1}).

A.3 Method A2

A.3.1 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity (grade 3 or higher grade as specified in accordance with ISO 3696).

A.3.1.1 2-Propanol (CAS RN 67-63-0), analytical grade.

A.3.1.2 Acetic acid, glacial.

A.3.1.3 Nitrogen or carbon dioxide, gas from a cylinder.

A.3.1.4 Potassium iodide solution, prepared by dissolving 500 g of potassium iodide in 500 cm^3 of water and storing in a dark place.

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A.3.1.5 Concentrated hydrochloric acid, 36 % to 38 % mass fraction.

A.3.1.6 Sodium thiosulfate solution, 0,1 N standardized.

A.3.1.7 Starch solution (CAS RN 9005-84-9), 5 g/dm^3.

A.3.2 Apparatus

A.3.2.1 Conical flask, 200 cm^3 with stopper.

A.3.2.2 Graduated measuring cylinder, 50 cm^3 and 30 cm^3, capacity.

A.3.2.3 Pipette, two of 2 cm^3 and two of 5 cm^3 capacity.

A.3.2.4 Burette, 25 cm^3 capacity, graduated in 0,1 cm^3, in accordance with the general specifications given in ISO 385.

A.3.2.5 Analytical balance, accurate to within 0,1 mg.

A.3.3 Procedure

A.3.3.1 Transfer 30 cm^3 of 2-propanol (A.3.1.1) into a 200 cm^3 conical flask with stopper (A.3.2.1) using a graduated measuring cylinder of 30 cm^3 (A.3.2.2).

A.3.3.2 Pass nitrogen or carbon dioxide gas (A.3.1.3) over the liquid; adjusting the flow rate, so that the gas causes a slight dimple on the surface of the liquid. Maintain this flow rate during further additions.

A.3.3.3 After 30 s, weigh to the nearest 0,1 mg an amount of sample containing approximately 0,003 mol of peroxide.

A.3.3.4 Add 2 cm^3 of acetic acid (A.3.1.2) with a pipette (A.3.2.3).

A.3.3.5 Add 2 cm^3 of potassium iodide saturated solution (A.3.1.4) with a pipette (A.3.2.3).

A.3.3.6 After swirl to dissolve the peroxide, allow to stand in the dark for 15 min at 25 °C ± 5 °C.

A.3.3.7 Add 2,5 cm^3 of hydrochloric acid (A.3.1.5) with a pipette (A.3.2.3).

A.3.3.8 Allow to stand in the dark for 15 min at 25 °C ± 5 °C again.

A.3.3.9 Add 50 cm^3 of water using a graduated measuring cylinder of 50 cm^3 capacity (A.3.2.2).

A.3.3.10 Titrate with the sodium thiosulfate solution (A.3.1.6) to a colourless end point, adding 3 cm^3 of starch solution (A.3.1.7) towards the end of the titration (V_1).

A.3.3.11 Carry out the procedure in duplicate.

A.3.3.12 In addition, carry out a blank test without the sample in accordance with the same procedure (V_{b1}).

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Annex B
(normative)

Method to determine the content of *tert*-butyl hydroperoxide

B.1 General

This annex specifies two methods to determine the content of *tert*-butyl hydroperoxide (TBHP) in peroxyketal. The determination of TBHP content may be skipped upon agreement between the interested parties as described in 5.3.

B.2 Method HPO-1

B.2.1 Principle

The amount of TBHP is obtained by utilizing oxidation by Ce^{4+} under acidic condition as shown in the following reaction:

$$2\ Ce^{4+} + SO_4^{\ 2-} + ROOH \rightarrow 2\ Ce^{3+} + RHSO_4 + O_2$$

B.2.2 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity (grade 3 or higher grade as specified in accordance with ISO 3696).

B.2.2.1 Acetic acid, glacial.

B.2.2.2 Sulfuric acid (CAS RN 7664-93-9), which concentration $c(H_2SO_4)$ = 3 mol/dm^3.

B.2.2.3 Ferroin solution (CAS RN 14708-99-7), in accordance with the method to prepare indicator specified in ISO 6353-1.

B.2.2.4 0,1 mol/dm^3 tetra ammonium cerium (IV) sulfate solution, prepared as follows.

Pour about 1 500 cm^3 of water into a 5 l beaker contained within an ice bath. Carefully add approximately 90 cm^3 of sulfuric acid. Add 201 g of tetra ammonium cerium (IV) sulfate dihydrate (CAS RN 10378-47-9) and allow to dissolve. After cooling, make up to approximately 3 000 cm^3 with water. If a precipitate is produced on standing, remove it by filtering through a No. 5 A. The standardization shall be carried out as specified in ISO 6353-1, and the factor (f_4) shall be rounded off to the fourth decimal.

B.2.3 Apparatus

B.2.3.1 Erlenmeyer flask, 300 cm^3 capacity.

B.2.3.2 Burette, 2 cm^3 capacity, graduated in 0,01 cm^3, in accordance with the general specifications given in ISO 385.

B.2.3.3 Graduated measuring cylinder, 50 cm^3 and 10 cm^3 capacity.

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B.2.3.4 Pipette, 2 cm^3 and 10 cm^3 capacity.

B.2.3.5 Analytical balance, accurate to within 0,01 mg.

B.2.4 Procedure

B.2.4.1 Add approximately 100 g of ice made with water (B.2.2), 50 cm^3 of acetic acid (B.2.2.1) and 6 cm^3 of sulfuric acid (B.2.2.2) into a 300 cm^3 Erlenmeyer flask (B.2.3.1) using a graduated measuring cylinder and mix well.

B.2.4.2 Add five to six drops of ferroin solution (B.2.2.3) with a pipette (B.2.3.4).

B.2.4.3 Titrate it with tetra ammonium cerium (IV) sulfate solution (B.2.2.4) while mixing vigorously until the colour changes to pale blue.

B.2.4.4 In addition, weigh 3 g to 5 g of the peroxyketal sample to the nearest 0,01 g (m_4) and add it into the Erlenmeyer flask.

B.2.4.5 Add five drops of ferroin solution (B.2.2.3) with a pipette (B.2.3.4).

B.2.4.6 Titrate it with tetra ammonium cerium (IV) sulfate solution (B.2.2.4) while mixing vigorously until the colour changes to pale blue.

B.2.4.7 Add one more drop of ferroin solution (B.2.2.3), regard the point where the pale blue colour is kept for 30 s as the end point and read the titration amount to the nearest 0,01 cm^3 (V_4).

B.2.5 Expression of results

The content of TBHP, C_{HPO}, expressed as a percentage mass fraction, is calculated by Formula (B.1):

$$C_{HPO} = \frac{V_4 \times f_4 \times 0{,}009\ 0}{m_4} \times 100 \quad \text{(B.1)}$$

where

V_4 is the volume, in cubic centimetres, of tetra ammonium cerium (IV) sulfate solution (B.2.2.4) required for titration after taking the sample;

f_4 is the factor of tetra ammonium cerium (IV) sulfate solution (B.2.2.4), which is the ratio of the actual concentration to the theoretical concentration (the normality is 0,1);

m_4 is the mass, in grams, of the test sample;

0,009 0 is the factor, in grams per cubic centimetre, obtained by Formula (B.2):

$$0{,}009\ 0 = 90{,}12 \times 0{,}1 \times \frac{1}{1\ 000} \quad \text{(B.2)}$$

where

90,12 is the molecular weight of TBHP;

0,1 is the normality of tetra ammonium cerium (IV) sulfate solution.

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B.3 Method HPO-2

B.3.1 Principle

In a toluene-methanol medium hydroperoxides are quantitatively reduced by an excess of sulfur dioxide in the presence of imidazole:

$$ROOH + SO_2 \rightarrow RHSO_4$$

The excess of sulfur dioxide is titrated with a standardized iodine solution.

B.3.2 Reagents

B.3.2.1 Imidazole (CAS RN 288-32-4).

B.3.2.2 Karl Fischer solvent, e.g. Hydranal Solvent of Riedel de Haen (1 to 2 molar of SO_2 in methanol with imidazole as amine).

B.3.2.3 Sulfur dioxide (CAS RN 7446-09-5) **solution**, prepared by mixing 50 cm^3 of Karl Fischer solvent with 50 g of imidazole and diluting to 1 dm^3 with methanol (CAS RN 67-56-1) and dissolve.

B.3.2.4 Iodine solution, 0,1 N standardized.

B.3.2.5 Methanol.

B.3.2.6 Toluene.

B.3.3 Apparatus

B.3.3.1 Conical flask with stopper, 100 cm^3.

B.3.3.2 Burettes, 20 cm^3 capacity, graduated in 0,01 cm^3, in accordance with the general specifications given in ISO 385.

B.3.3.3 Dispensettes, 50 cm^3 and 20 cm^3.

B.3.3.4 Analytical balance, accurate to within 0,1 mg.

B.3.4 Procedure

B.3.4.1 Weigh to the nearest 0,1 mg an amount of sample containing less than 0,000 4 mol of TBHP into a 100 cm^3 conical flask (B.3.3.1). The test sample weight (m_5) shall not exceed 3 g.

B.3.4.2 Dissolve the sample in 20 cm^3 of toluene (B.3.2.6) using a dispensette (B.3.3.3).

B.3.4.3 Add exactly 10,00 cm^3 of sulfur dioxide solution (B.3.2.3) with a burette (B.3.3.2), stopper the flask and mix.

B.3.4.4 Dilute with 50 cm^3 of methanol using a dispensette (B.3.3.3).

B.3.4.5 Titrate with the standardized iodine solution (B.3.2.4) until the colour changes to yellow while swirling vigorously (V_5).

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B.3.4.6 Run a blank (V_{b5}).

B.3.5 Expression of results

The content of the TBHP, C_{HPO} in mass %, is calculated by Formula (B.3):

$$C_{HPO} = \frac{(V_5 - V_{b5}) \times f_5 \times 0{,}009\ 0}{m_5} \times 100 \tag{B.3}$$

where

V_5 is the volume, in cubic centimetres, of tetra iodine solution (B.3.2.4) required for titration after taking the sample;

V_{b5} is the volume, in cubic centimetres, of tetra iodine solution (B.3.2.4) required for titration after taking the blank;

f_5 is the factor of tetra iodine solution (B.3.2.4), which is the ratio of the actual concentration to the theoretical concentration (the normality is 0,1);

m_5 is the mass, in grams, of the test portion;

0,009 0 is the factor, in grams per cubic centimetre, obtained by Formula (B.4):

$$0{,}009\ 0 = 90{,}12 \times 0{,}1 \times \frac{1}{1\ 000} \tag{B.4}$$

where

90,12 is the molecular weight of TBHP;

0,1 is the normality of the iodine solution.

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Annex C
(informative)

Method to determine the content of diacyl peroxides

C.1 General

This annex gives a method to determine the content of diacyl peroxides used as rubber organic vulcanizing agents.

C.2 Method

C.2.1 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity (grade 3 or higher grade as specified in accordance with ISO 3696).

C.2.1.1 Toluene.

C.2.1.2 2-Propanol.

C.2.1.3 Acetic acid, glacial.

C.2.1.4 Potassium iodide solution (2+1), prepared by adding approximately 250 g of potassium iodide to approximately 250 cm^3 of water, then warming at approximately 40 °C to dissolve, cooling to room temperature and storing in a dark place.

C.2.1.5 Methanol, analytical grade.

C.2.1.6 Sodium thiosulfate, standardized solution, the concentration of sodium thiosulfate $c(Na_2S_2O_3)$ = 0,1 mol/dm^3.

C.2.2 Apparatus

C.2.2.1 Erlenmeyer flask with ground-in stopper, 200 cm^3 capacity.

C.2.2.2 Burette, 20 cm^3 and 25 cm^3 capacity, graduated in 0,1 cm^3, in accordance with the general specifications given in ISO 385.

C.2.2.3 Graduated measuring cylinder, 30 cm^3 and 20 cm^3 capacity.

C.2.2.4 Pipette, 2 cm^3 and 5 cm^3 capacity.

C.2.2.5 Analytical balance, accurate to within 0,1 mg.

C.2.2.6 Reflex condenser, capacity approximately 30 cm^3.

C.2.2.7 Hot water bath.

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C.2.3 Procedure

C.2.3.1 Weigh the mass of sample concerned (see Table C.1) into a 200 cm^3 Erlenmeyer flask (C.2.2.1) with ground-in stopper and read the scale to the nearest 0,1 mg.

C.2.3.2 Add 15 cm^3 of toluene (C.2.1.1) using a 20 cm^3 capacity graduated measuring cylinder (C.2.2.3) and dissolve it. A volume of 20 cm^3 of 2-propanol may be used instead of toluene.

WARNING — Toluene is a harmful solvent, so avoid inhaling vapour, and avoid instances where it can adhere to mucous membranes and skin.

C.2.3.3 Add 5 cm^3 of acetic acid (C.2.1.3) with a pipette (C.2.2.4). If 2-propanol is used, add 2 cm^3 of glacial acetic acid (C.2.1.3) with a pipette (C.2.2.4).

C.2.3.4 Add 2 cm^3 of potassium iodide solution (C.2.1.4) with a pipette (C.2.2.4).

C.2.3.5 Add 20 cm^3 of methanol (C.2.1.5) using a 20 cm^3 capacity graduated measuring cylinder (C.2.2.3). If 2-propanol is used, add 10 cm^3 of methanol (C.2.1.5) using a 20 cm^3 capacity graduated measuring cylinder (C.2.2.3).

C.2.3.6 In the case of benzoyl peroxide, heat the flask at 30 °C ± 3 °C for 15 min with a stopper. In the case of Di(4-methylbenzoyl) peroxide and Di(2,4-dichlorobenzoyl) peroxide, attach a reflux condenser to the flask and heat it in a water bath at 80 °C ± 3 °C for 15 min.

C.2.3.7 After stirring the flask gently to mix the contents, stopper hermetically and leave it to stand in a dark place for 10 min.

C.2.3.8 Titrate the solution with sodium thiosulfate solution (C.2.1.5) until the colour of iodine disappears and read the scale to the nearest 0,01 cm^3 (V_2).

C.2.3.9 Carry out the procedure in duplicate.

C.2.3.10 In addition, carry out a blank test without adding the sample in accordance with the same procedure (V_{b2}).

Table C.1 — Required mass of test sample for diacyl peroxide

Diacyl peroxide	Mass of test sample g
Benzoyl peroxide	0,24
Di(2,4-dichlorobenzoyl) peroxide	0,38
Di(4-methylbenzoyl) peroxide	0,27

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