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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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ISO 14932 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*.

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

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of 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 ensure compliance with any national regulatory conditions.

1 Scope

This International Standard 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 using capillary gas-chromatography.

1.1 Titration method A for group a) peroxyketals

- DTBPC: 1,1-Di(*tert*-butylperoxy)cyclohexane;
- DBPMC: 1,1-Di(*tert*-butylperoxy)-2-methylcyclohexane;
- DBPTC: 1,1-Di(*tert*-butylperoxy)-3,3,5-trimethylcylcohexane;
- DBPB: 2,2-Di(*tert*-butylperoxy)butane;
- BPV: Butyl -4,4-di(*tert*-butylperoxy)valerate.

1.2 Titration method B for group b) diacyl peroxides

- Dibenzoyl peroxide;
- Di(2,4-dichlorobenzoyl) peroxide;
- Di(4-methylbenzoyl) peroxide.

1.3 Titration method C for group c) diaralkyl and alkyl-aralkyl peroxides

- Di(*tert*-butylperoxyisopropyl)benzene;
- Dicumyl peroxide;
- *tert*-Butyl cumyl peroxide.

1.4 Capillary gas-chromatography for dialkyl peroxides

- 2,5-Dimethyl-2,5-di(*tert*-butylperoxy)hexane.

2 Normative references

The following referenced documents are indispensable for the application 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*

ISO 3696:1987, *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.

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

3.2
peroxyketal
peroxide obtained by the reaction of a ketone with *tert*-butyl hydroperoxide (TBHP) as shown in the following equation:

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

3.3
diacyl peroxide
peroxide obtained by the reaction of benzoyl chloride with hydrogen peroxide as shown in the following equation:

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

3.4
di-aralkyl peroxide
alkyl-aralkyl peroxide
peroxide obtained by the reaction of a benzyl alcohol with hydrogen peroxide in presence of sulfuric acid as shown in a simple case in the following equation:

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

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

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

4 Titration method A

4.1 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.

4.2 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:

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

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

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

4.3 General procedure

Two procedures are shown as examples depending upon the condition used for the peroxyketal oxidation-reduction reaction with potassium iodide (see methods A-1 and A-2 in Annex A).

A weighed peroxyketal test sample (m_1) is dissolved in an aqueous solution acidified with acetic acid and hydrochloric acid containing potassium iodide.

Titrate the freed iodine with sodium thiosulfate 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}) (see Annex B).

4.4 Expression of results

4.4.1 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 the following equation:

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

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.

4.4.2 Purity

Calculate the purity of the peroxyketal, P_{kt} alone, expressed as a percentage by mass to the nearest 0,1 %, by the following equation:

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

where

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

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

0,177 5 is the value obtained by dividing the theoretical amount of active oxygen in *tert*-butyl hydroperoxide by 100;

$A_{\mathrm{T,kt}}$ is the theoretical amount of active oxygen of the peroxyketal, in mass %, obtained by the following equation:

$$A_{\mathrm{T,kt}} = \frac{n_1 \times 15{,}999\,4}{M_1} \times 100$$

where

n_1 is the number of peroxide bond in the peroxyketal;

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

Table 1 — Molecular mass of peroxyketal

Peroxyketal	n_1	M_1	$A_{\mathrm{T,kt}}$
DTBPC	2	260,38	12,29
DBPMC	2	274,40	11,66
DBPTC	2	302,46	10,58
DBPB	2	234,34	13,65
BPV	2	334,46	9,57

5 Titration method B

5.1 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.

5.2 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:

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

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

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

5.3 General procedure

Two procedures are shown as examples depending upon the solvent used for the diacyl peroxide oxidation-reduction reaction with potassium iodide (see methods B-1 and B-2 in 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}).

5.4 Expression of results

Calculate the purity of the diacyl peroxide, P_{da} expressed as a percentage mass fraction to the nearest 0,1 %, by the following equation:

$$P_{da} = \frac{\left[0{,}000\,8 \times (V_2 - V_{b2}) \times \frac{f_2}{m_2} \right] \times 100}{A_{T,da}} \times 100$$

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;
$A_{T,da}$	is the theoretical amount of active oxygen of the diacyl peroxide, in mass %, obtained by the following equation:

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

where

n_2	is the number of peroxide bond in the diacyl peroxide;
M_2	is the molecular mass of the diacyl peroxide (see Table 2);

0,000 8	is the factor, in grams per cubic centimetre, obtained by the following equation:

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

where

15,999 4	is the atomic weight of oxygen;
0,1	is the normality of the sodium thiosulfate solution.

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 Titration method C

6.1 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.

6.2 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.

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

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

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).

6.3 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 ISO 3696:1987).

6.3.1 Acetic acid, glacial.

6.3.2 Sodium iodide, coarsely powdered.

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

6.3.4 Nitrogen or carbon dioxide, gas from a cylinder.

6.3.5 Carbon dioxide, dry ice.

6.3.6 Oxalic acid dihydrate, approximately 99,8 % mass fraction.

6.4 Apparatus

6.4.1 **Conical flask,** with ground glass joint NS 29, 300 cm^3.

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

6.4.3 **Gas inlet tube of glass,** fitted into the condensor with a considerable length.

6.4.4 **Heating mantle** or **electric hot-plate**.

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

6.4.6 **Glass beads**, diameter approximately 3 mm.

6.4.7 **Analytical balance**, accurate to within 0,1 mg.

6.5 Sample pre-treatment

6.5.1 If the sample is a homogeneous crystalline powder, a liquid or a formulation with inorganic fillers, no pretreatment is needed.

6.5.2 If the sample is in the form of flakes or granules, reduce the particle size of a representative amount of the sample by means of a pestle and mortar.

6.5.3 For formulations on rubber, see Annex D.

6.5.4 For formulations on polymers, see Annex E.

6.5.5 Homogenizing of solidified peroxide can be achieved by melting the sample in a water bath at 55 °C. The temperature of the sample shall not exceed 55 °C and the residence time in the bath shall be as short as possible.

6.6 Procedure

6.6.1 Test sample analysis

a) Transfer 50 cm^3 acetic acid (6.3.1) into a 300 cm^3 flask (6.4.1).

b) Add some dry ice (6.3.5). Dry ice shall be present until the reaction mixture boils.

c) After 2 min, add 6 g of sodium iodide (6.3.2).

d) Add exactly 3,0 cm^3 of water and mix.

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 will be insufficient for complete complexing and higher intake will cause 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 whilst 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 (6.3.3) to a colorless end point (V_3).

6.6.2 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}).

6.7 Expression of results

6.7.1 Assay of aralkyl peroxide

Calculate the assay of alkyl-aralkyl peroxide, A_{AA}, expressed as a mass fraction percentage, by the following equation:

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

where

V_3 is the volume, in cubic centimetres, of sodium thiosulfate (6.3.3) solution used for the test;

V_{b3} is the volume, in cubic centimetres, of sodium thiosulfate (6.3.3) 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	200	338,5	$\frac{100}{87,9} = 1,138$	2
Dicumyl peroxide	300	270,4	$\frac{100}{93} = 1,075$	1
Tert-Butyl cumyl peroxide	230	208,3	$\frac{100}{91} = 1,099$	1

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

7.1 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).

7.2 Principle

The technique used is capillary gas chromatography with split injection. The test sample is extracted with toluene and analyzed 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.

7.3 Reagents

7.3.1 Toluene.

7.3.2 Silicone oil 1 000.

7.3.3 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane standard, of well defined assay. Standard sample should preferably be stored in a refrigerator.

7.3.4 *n*-Pentadecane.

7.4 Apparatus

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

7.4.2 Chromatography data system.

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

7.4.4 Ultrasonic bath.

7.4.5 Mortar.

7.5 Conditions

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

7.5.4 Temperatures

Injector: 100 °C

Detector: 300 °C

Column

- **initial**: 100 °C during 2 min
- **rate**: 10 °C/min
- **final**: 150 °C

7.5.5 Injection volume: 0,5 mm^3

7.6 Procedure

7.6.1 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.

7.6.2 Preparation of the standard solution

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

7.6.3 Preparation of the sample solution

7.6.3.1 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane in formulations containing silicone oil and silica

Weigh 160 mg ± 20 mg of silicone oil (7.3.2) into a 25 cm^3 volumetric flask. Weigh approximately 120 mg of the 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane standard (7.3.3) and 125 mg of *n*-pentadecane (7.3.4) to the nearest 0,1 mg into the same volumetric flask. Make up to volume with toluene (7.3.1) and mix well.

7.6.3.2 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 to the nearest 0,1 mg into a 25 cm^3 volumetric flask. Make up to volume with toluene and mix well.

7.6.4 Analysis

Inject 0,5 mm^3 of the standard solution and record the chromatogram. Inject 0,5 µl 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.

7.6.5 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.

7.7 Expression of results

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

$$f_\text{R} = \frac{I_\text{st}}{S_\text{st}} \times \frac{s_\text{st}}{i_\text{st}} \times \frac{C_\text{st}}{100}$$

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.

7.7.2 The content of 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane C_PO is calculated from:

$$C_\text{PO} = f_\text{R} \times \frac{S_\text{sa}}{I_\text{sa}} \times \frac{i_\text{sa}}{m_\text{sa}} \times 100$$

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 Precision

See Annex F.

9 Test report

The test report shall include the following information:

a) a reference to this International Standard;

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

c) the individual results and their average;

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

e) date(s) of testing.

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 A-1

A.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 ISO 3696:1987).

A.2.1.1 2-Propanol, analytical grade.

A.2.1.2 Acetic acid, glacial.

A.2.1.3 Sodium hydrogen carbonate, 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).

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.

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), 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 50 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).

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 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.

A.2.3.8 Detach the flat bottom pear-shaped 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 A-2

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 ISO 3696:1987).

A.3.1.1 Acetic acid, glacial.

A.3.1.2 Nitrogen or carbon dioxide, gas from a cylinder.

A.3.1.3 Potassium iodide solution, prepared by dissolving 500 g of potassium iodide in 500 cm^3 of water and storing in a dark place.

A.3.1.4 Concentrated hydrochloric acid, 36 % to 38 % mass fraction.

A.3.1.5 Sodium thiosulfate solution, 0,1 N standardized.

A.3.1.6 Starch solution, 5 g/dm^3.

A.3.2 Apparatus

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

A.3.2.2 Dispensettes, 50 cm^3, 15 cm^3, and 3 cm^3 for water, acetic acid, potassium iodide and starch addition.

A.3.2.3 Pipette, 2,5 cm^3.

A.3.2.4 Weighing caps, approximately 5 cm^3.

A.3.2.5 Burette, 20 cm^3 capacity, graduated in 0,01 cm^3, in accordance with the general specifications given in ISO 385.

A.3.2.6 Analytical balance, accurate to within 0,1 mg.

A.3.2.7 Mortar and pestle.

A.3.3 Sample pretreatment

A.3.3.1 Peroxides formulated on powder and in solvents

Homogenize completely.

A.3.3.2 Peroxides formulated as granules with silica or whiting

Weigh approximately 5 g of granules into a mortar and grind to a fine powder.

A.3.3.3 Peroxide formulated on whiting, silica and EPDM

Grind with a cryogenic milling equipment in accordance with the method in Annex D.

A.3.4 Procedure

A.3.4.1 Transfer 15 cm^3 of acetic acid (A.3.1.1) into a 200 cm^3 conical flask with stopper (A.3.2.1) using a 15 cm^3 dispensette (A.3.2.2).

A.3.4.2 Pass nitrogen or carbon dioxide gas (A.3.1.2) 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.3.4.3 After 2 min, add 3 cm^3 of potassium iodide solution (A.3.1.3) using a 3 cm^3 dispensette (A.3.2.2).

A.3.4.4 Add 2,5 cm^3 of hydrochloric acid (A.3.1.4) with a pipette (A.3.2.3).

A.3.4.5 Weigh to the nearest 0,1 mg an amount of sample containing approximately 0,003 mol of peroxide into a weighing cap (A.3.2.4).

A.3.4.6 Transfer the cap into the conical flask, stopper the flask and swirl to dissolve the peroxide.

A.3.4.7 Allow to stand in the dark for 20 min at 25 °C ± 5 °C.

A.3.4.8 Add 50 cm^3 of water using a 50 cm^3 dispensette (A.3.2.2).

A.3.4.9 Titrate with the sodium thiosulfate solution (A.3.1.5) to a colourless end point, adding 3 cm^3 of starch solution (A.3.1.6) towards the end of the titration (V_1).

A.3.4.10 Carry out the procedure in duplicate.

A.3.4.11 In addition, carry out a blank test without the sample in accordance with the same procedure (V_{b1}).

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.

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:

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

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 ISO 3696:1987).

B.2.2.1 Acetic acid, glacial.

B.2.2.2 Sulfuric acid, which concentration $c(H_2SO_4) = 3$ mol/dm^3.

B.2.2.3 Ferroin solution, 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 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 though 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.

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) whilst 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) whilst 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 the following equation:

$$C_{\mathrm{HPO}} = \frac{V_4 \times f_4 \times 0{,}009\,0}{m_4} \times 100$$

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 the following equation:

$$0{,}009\,0 = 90{,}12 \times 0{,}1 \times \frac{1}{1\,000}$$

where

90,12 is the molecular weight of TBHP;

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

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:

$$\mathrm{ROOH} + \mathrm{SO_2} \rightarrow \mathrm{RHSO_4}$$

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

B.3.2 Reagents

B.3.2.1 Imidazole.

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 solution, prepared by mixing 50 cm^3 of Karl Fischer solvent with 50 g of imidazole and diluting to 1 dm^3 with methanol 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).

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 the following equation:

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

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 the following equation:

$$0{,}009\,0 = 90{,}12 \times 0{,}1 \times \frac{1}{1\,000}$$

where

90,12 is the molecular weight of TBHP;

0,1 is the normality of the iodine solution.

Annex C
(informative)

Method to determine the content of diacyl peroxides

C.1 General

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

C.2 Method B-1

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 ISO 3696:1987).

C.2.1.1 Chloroform.

WARNING — Chloroform is a harmful solvent.

C.2.1.2 Acetic acid, glacial.

C.2.1.3 Potassium iodide solution (1+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.2.1.4 Methanol, analytical grade.

C.2.1.5 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, 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 Conical flask with stopper, 100 cm^3.

C.2.3 Procedure

C.2.3.1 Weigh approximately 0,001 mol of sample 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 chloroform (C.2.1.1) using a 20 cm^3 capacity graduated measuring cylinder (C.2.2.3) and dissolve it.

C.2.3.3 Add 5 cm^3 of acetic acid (C.2.1.2) with a pipette (C.2.2.4).

C.2.3.4 Add 2 cm^3 of potassium iodide solution (C.2.1.3) with a pipette (C.2.2.4).

C.2.3.5 Add 20 cm^3 of methanol (C.2.1.4) using a 20cm^3 capacity graduated measuring cylinder (C.2.2.3).

C.2.3.6 After stirring the flask gently to mix the contents, stopper hermetically and leave it to stand in a dark place for 10 min.

C.2.3.7 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.2.3.8 Carry out the procedure in duplicate.

C.2.3.9 In addition, carry out a blank test without adding the sample in accordance with the same procedure (V_{b2}).

C.3 Method B-2

C.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 ISO 3696:1987).

C.3.1.1 Tetrahydrofuran solution, prepared by adding 30 cm^3 of glacial acetic acid to 900 cm^3 of tetrahydrofuran.

C.3.1.2 Acetic acid, glacial.

C.3.1.3 Potassium iodide solution, prepared by dissolving 45 g of potassium iodide in 60 cm^3 of water and storing in a dark place.

C.3.1.4 Sodium thiosulfate solution, 0,1 N standardized solution.

C.3.2 Apparatus

C.3.2.1 Conical flask with stopper, 100 cm^3.

C.3.2.2 Burette, 20 cm^3 capacity, graduated in 0,01 cm^3, in accordance with the general specifications given in ISO 385.

C.3.2.3 Dispensettes, 30 cm^3, 25 cm^3 and 2,5 cm^3.

C.3.2.4 Analytical balance, accurate to within 0,1 mg.

C.3.3 Sample pretreatment

The sample should be completely homogeneous.

C.3.4 Procedure

C.3.4.1 Sample analysis

C.3.4.1.1 Weigh to the nearest 0,1 mg an amount of sample containing approximately 1,5 meq [1] of active oxygen into a 100 cm^3 conical flask (C.3.2.1) with stopper.

C.3.4.1.2 Add 30 cm^3 of THF solution (C.3.1.1) with a dispensette (C.3.2.3) and swirl to dissolve.

C.3.4.1.3 Add 2,5 cm^3 of potassium iodide solution (C.3.1.3) with a dispensette (C.3.2.3), stopper the flask and swirl.

C.3.4.1.4 Allow to stand in the dark for 1 min at 25 °C ± 5 °C.

C.3.4.1.5 Titrate with the sodium thiosulfate solution (C.3.1.4) to a colourless end point while vigorous swirling of the flask near the end point at a low titration rate (V_2).

C.3.4.2 Blank analysis

C.3.4.2.1 Transfer 30 cm^3 of THF solution (C.3.1.1) into a 100 cm^3 of conical flask (C.3.2.1) with stopper.

C.3.4.2.2 Add 2,5 cm^3 of potassium iodide solution (C.3.1.3) with a dispensette (C.3.2.3), stopper the flask and swirl.

C.3.4.2.3 Allow to stand in the dark for 1 min at 25 °C ± 5 °C.

C.3.4.2.4 Add 25 cm^3 of water with a dispensette (C.3.2.3).

C.3.4.2.5 Titrate with the sodium thiosulfate solution (C.3.1.4) to a colourless end point while vigorous swirling of the flask near the end point at a low titration rate (V_{b2}).

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1) meq = milliequivalents, determined according to the relation, (mol) = (Eq) × (valence of ion). The valence of ion depends on the type of peroxides.

Annex D
(normative)

Sample preparation for the determination of peroxide in peroxide masterbatches

D.1 General

Peroxide becomes accessible for iodometric determination after cryogenic grinding of the peroxide masterbatch. Cryogenic grinding shall be used for peroxyketals, because potential extraction solvents such as toluene interfere with the iodometric determination.

D.2 Principle

D.2.1 Solution

An adequate amount of sample is dissolved in toluene (see D.2.3.1) by means of ultrasonic vibration at a maximum temperature of 60 °C. An aliquot from this solution is taken for the iodometric determination.

D.2.2 Cryogenic grinding

An amount of sample together with silica, to avoid caking, is ground cryogenically in a ball mill. Liquid nitrogen is used as the cooling medium. The ground sample is used for the iodometric determination once it has returned to room temperature.

D.2.3 Reagents

D.2.3.1 Toluene, analytical grade.

D.2.3.2 Liquid nitrogen.

D.2.3.3 Silica, hydrophylic [2].

D.2.4 Apparatus

D.2.4.1 Ultrasonic bath.

D.2.4.2 Disposable syringe with a volume of 10 cm^3.

D.2.4.3 Ball mill [3] provided with liquid nitrogen feeding device.

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[2] An example of a suitable silica available commercially is Perkasil SM 500 produced by W. R. Grace & Co. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

[3] An example of a suitable ball mill available commercially is Retsch MM2 produced by Retsch GmbH. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

D.2.5 Sample

When the sample is in masterbatch form the particle size shall be reduced to a minimum of 0,4 cm × 0,4 cm × 0,4 cm both for the solution and cryogenic grinding method.

D.2.6 Procedure

D.2.6.1 Solution

D.2.6.1.1 Weigh 5 g to 6 g of sample (m_{s1}) to the nearest 1 mg into a 200 cm^3 conical flask with stopper.

D.2.6.1.2 Weigh 100 cm^3 of toluene (m_t) to the nearest 10 mg into the flask and stopper the flask.

D.2.6.1.3 Dissolve the sample using ultrasonic vibration at a temperature of 50 °C to 60 °C.

D.2.6.1.4 Homogenize the sample solution.

D.2.6.1.5 Charge a syringe with 10 cm^3 of sample solution and weigh it to the nearest 1 mg.

D.2.6.1.6 Use the contents of the syringe as a sample (m_3) in the procedure of the relevant standard method of analysis.

D.2.6.1.7 Reweigh the syringe to the nearest 1 mg.

D.2.6.2 Cryogenic grinding

D.2.6.2.1 Weigh 1 g of sample (m_{s2}) to the nearest 0,1 mg and also 0,2 g of silica (m_c) to the nearest 0,1 mg into the grinding chamber.

D.2.6.2.2 Add two grinding balls. Place the lid on the chamber and place the chamber into the cooling unit.

D.2.6.2.3 Fill the supply vessel of the ball mill with liquid nitrogen.

D.2.6.2.4 Cool the sample for 2,5 min, keeping the vessel filled with liquid nitrogen.

D.2.6.2.5 Grind the test sample with maximum frequency (1 800 rotations per minute) for 30 s and stop the grinding for 30 s to allow the heat from grinding to dissipate.

D.2.6.2.6 Repeat this procedure five times. Ensure that the supply vessel is kept filled with liquid nitrogen throughout this operation.

D.2.6.2.7 Allow the liquid nitrogen in the cooling unit to evaporate (approximately two minutes).

D.2.6.2.8 Remove the chamber.

D.2.7 Expression of results

D.2.7.1 Solution

Multiply the result of the peroxide determination according to the relevant standard method of analysis by a factor F_c:

$$F_c = \frac{m_{s1} + m_t}{m_{s1}}$$

where

m_{s1} is the mass of sample, in grams;

m_t is the mass of toluene, in grams.

D.2.7.2 Cryogenic grinding

Multiply the result of the peroxide determination according to the relevant standard method of analysis by a factor F_c:

$$F_c = \frac{m_{s2} + m_c}{m_{s2}}$$

where

m_{s2} is the mass of sample, in milligrams;

m_c is the mass of added silica, in milligrams.

Annex E
(normative)

Sample preparation for the determination of alkyl-aralkyl peroxide on polymers

E.1 General

After extraction of the alkyl-aralkyl peroxide from the polymer, the peroxide is accessible for the iodometric determination.

E.2 Principle

An adequate amount of sample is stirred in toluene for 1 h at 25 °C ± 5 °C. From the toluene layer, an aliquot is used for the iodometric determination.

E.3 Reagents

E.3.1 **Toluene**, analytical grade.

E.4 Apparatus

E.4.1 **Magnetic stirrer**.

E.4.2 **Disposable syringe**, with a volume of 10 cm^3.

E.5 Procedure

E.5.1 Weigh 5 g of sample (m_{s3}) to the nearest 1 mg into a 200 cm^3 conical flask with stopper.

E.5.2 Weigh 100 cm^3 of toluene (m_t) to the nearest 10 mg into the flask and stopper the flask.

E.5.3 Stir for 1 h at a temperature of 25 °C ± 5 °C.

E.5.4 Stop stirring and let the polymer settle.

E.5.5 Charge a syringe with 10 cm^3 of toluene solution and weigh it to the nearest 1 mg.

E.5.6 Use the contents of the syringe as a sample (m_3) in the procedure for the determination of peroxide.