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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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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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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.

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.

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:

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

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

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

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:

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

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

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

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.

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):

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

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):

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

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):

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

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);

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

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):

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

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):

$$P_{da} = \frac{A_{o,da}}{A_{T,da}} \times 100 \tag{8}$$

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.

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).