
**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*

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 14932:2023

<https://standards.iteh.ai/catalog/standards/sist/c0ff9242-9c69-4ab2-b0c8-6651238b1dc3/iso-14932-2023>



iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 14932:2023

<https://standards.iteh.ai/catalog/standards/sist/c0ff9242-9c69-4ab2-b0c8-6651238b1dc3/iso-14932-2023>



COPYRIGHT PROTECTED DOCUMENT

© ISO 2023

All rights reserved. Unless otherwise specified, or required in the context of its implementation, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

	Page
Foreword.....	iv
1 Scope	1
2 Normative references	1
3 Terms and definitions	2
4 General	2
5 Titration method A for group a: Peroxyketals	3
5.1 Purpose.....	3
5.2 Principle.....	3
5.3 General procedure.....	3
5.4 Expression of results.....	3
5.4.1 Total amount of active oxygen.....	3
5.4.2 Content.....	4
6 Titration method B for group b: Diacyl peroxides	5
6.1 Purpose.....	5
6.2 Principle.....	5
6.3 Measurement of active oxygen.....	5
6.3.1 General procedure.....	5
6.3.2 Calculation of amount of active oxygen.....	5
6.3.3 Calculation of theoretical active oxygen.....	6
6.4 Calculation of diacyl peroxide content.....	6
7 Titration method C for group c: Diaralkyl and alkyl-aralkyl peroxides	7
7.1 Purpose.....	7
7.2 Principle.....	7
7.3 Reagents.....	7
7.4 Apparatus.....	8
7.5 Procedure.....	8
7.5.1 Test sample analysis.....	8
7.5.2 Blank test.....	9
7.6 Expression of results.....	9
7.6.1 Assay of aralkyl peroxide.....	9
8 Determination of the assay of 2,5-dimethyl-2,5-di(<i>tert</i>-butylperoxy)hexane	9
8.1 Purpose.....	9
8.2 Principle.....	10
8.3 Gas chromatography method.....	10
8.3.1 Using capillary column.....	10
8.3.2 Using packed column.....	12
9 Precision	14
10 Test report	15
Annex A (informative) Method to determine the content of peroxyketal	16
Annex B (normative) Method to determine the content of <i>tert</i>-butyl hydroperoxide	19
Annex C (informative) Method to determine the content of diacyl peroxides	23
Annex D (normative) Pre-treatment of mixed sample with inorganic filler or uncured rubber for the determination of peroxide content	25
Annex E (informative) Precision	27
Bibliography	31

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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-trimethylcyclohexane (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

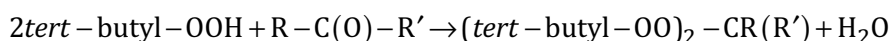
For the purposes of this document, the following terms and definitions apply.

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

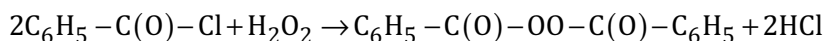
- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

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

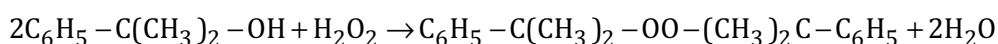
3.2 peroxyketal
peroxide obtained by the reaction of ketone with *tert*-butyl hydroperoxide (TBHP) as follows:



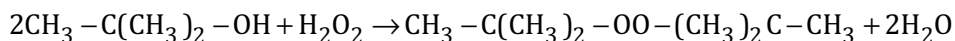
3.3 diacyl peroxide
peroxide obtained by the reaction of benzoyl chloride with hydrogen peroxide as follows:



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:



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



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.

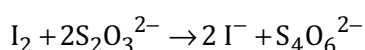
5 Titration method A for group a: Peroxyketals

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

Peroxyketals 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:



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 subtracting 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

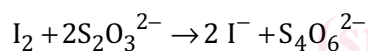
6 Titration method B for group b: Diacyl peroxides

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:



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, $A_{o,da}$, expressed as a mass fraction percentage to the nearest 0,1 %, with [Formula \(5\)](#):

$$A_{o,da} = \frac{[0,0008 \times (V_2 - V_{b2}) \times f_2] \times 100}{m_2} \times 100 \quad (5)$$

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.

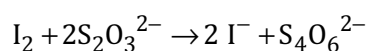
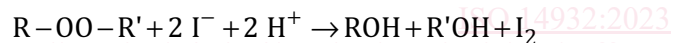
7.2 Principle

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.



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 cm³.
- 7.4.2 **Dispensettes**, 50 cm³ and 3,0 cm³ to 5,0 cm³.
- 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 dm³/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 cm³ acetic acid (7.3.1) into a 300 cm³ 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 cm³ to 5,0 cm³ of water and mix. 5 cm³ 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 dm³/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 cm³ 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 (V₃).