
**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

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.

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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*.

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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-trimethylcyclohexane;
- 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*

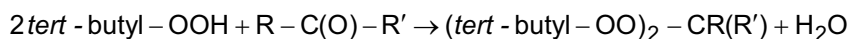
ISO 6353-1, *Reagents for chemical analysis — Part 1: General test methods*

3 Terms and definitions

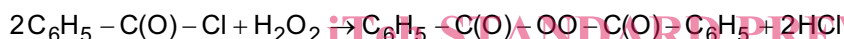
For the purposes of this document, the following terms and definitions apply.

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

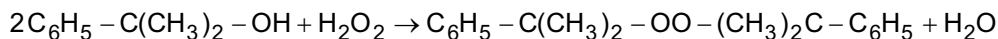
3.2 peroxyketal
peroxide obtained by the reaction of a ketone with *tert*-butyl hydroperoxide (TBHP) as shown in the following equation:



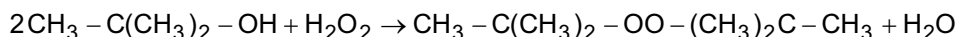
3.3 diacyl peroxide
peroxide obtained by the reaction of benzoyl chloride with hydrogen peroxide as shown in the following equation:



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:



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:



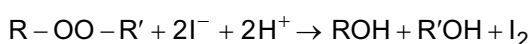
4 Titration method A

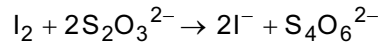
4.1 Purpose

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

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 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, $A_{\text{O,kt}}$, expressed as a percentage by mass to the nearest 0,1 %, by the following equation:

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

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:

$$P_{kt} = \frac{A_{O,kt} - C_{HPO} \times 0,1775}{A_{T,kt}} \times 100$$

where

- $A_{O,kt}$ is the total amount of active oxygen, in mass %;
- C_{HPO} is the content of TBHP (see Annex B), in mass %;
- 0,1775 is the value obtained by dividing the theoretical amount of active oxygen in *tert*-butyl hydroperoxide by 100;
- $A_{T,kt}$ is the theoretical amount of active oxygen of the peroxyketal, in mass %, obtained by the following equation:

$$A_{T,kt} = \frac{n_1 \times 15,9994}{M_1} \times 100$$

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	$A_{T,kt}$
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

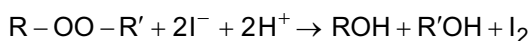
5 Titration method B

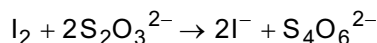
5.1 Purpose

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:





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.

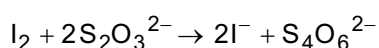
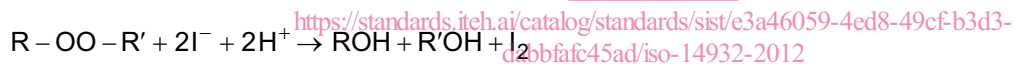
6.2 Principle

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.



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 cm³.
- 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 dm³/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 cm³ acetic acid (6.3.1) into a 300 cm³ 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 cm³ 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 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 whilst 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 (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:

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

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 <i>m</i> ₃ mg	Molar mass <i>M</i> ₃	Factor <i>f</i> _P	Number of peroxide groups <i>n</i> ₃
Di(<i>tert</i> -butylperoxyisopropyl)benzene	200	338,5	$\frac{100}{87,9} = 1,138$	2
Dicumyl peroxide	300	270,4	$\frac{100}{93} = 1,075$	1
<i>Tert</i> -Butyl cumyl peroxide	230	208,3	$\frac{100}{91} = 1,099$	1