INTERNATIONAL STANDARD

ISO 21461

Second edition
2009-03-01

Rubber — Determination of the aromaticity of oil in vulcanized rubber compounds

Caoutchouc — Détermination de l'aromaticité des huiles dans les mélanges vulcanisés

Reference number
ISO 21461:2009(E)

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Published in Switzerland

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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 21461 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 21461:2006), to which a new annex (Annex C) has been added describing a procedure for the preparation of clean samples from the various components of a tyre.

ISO 21461 is referenced in European regulation (EC) No. 1907/2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) as the method used to measure and calculate bay protons.

Rubber — Determination of the aromaticity of oil in vulcanized rubber compounds

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IMPORTANT — The electronic file of this document contains colours which are considered to be useful for the correct understanding of the document. Users should therefore consider printing this document using a colour printer.

1 Scope

This International Standard provides a method for the selective determination of polyaromaticity of oil in vulcanized rubber compounds. The method is based on nuclear magnetic resonance (NMR) spectrometry.

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 1407, *Rubber — Determination of solvent extract*

3 Terms and definitions

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

3.1
polycyclic aromatic hydrocarbon
PAH
organic compound consisting of two or more aromatic rings, certain carbon atoms of which are common to two or three rings

4 Reagents and materials

All reagents shall be of recognized analytical grade unless otherwise specified.

4.1 Extraction solvent

4.1.1 Acetone.

4.2 Sample preparation reagents

4.2.1 *n*-Hexane.

4.2.2 Methylene chloride.

4.2.3 Nitrogen, purity > 99,9 %, for protecting the extract from oxidation during drying.

4.2.4 $CDCl_3$, 99,9 %, NMR grade.

4.2.5 Hexamethyldisiloxane (HMDS), 99,5 %, NMR grade, or **tetramethylsilane (TMS)**, 99,5 %, NMR grade.

5 Apparatus

5.1 Analytical balance, accurate to 0,1 mg.

5.2 Extraction apparatus, as specified in ISO 1407.

5.3 Steam bath.

5.4 Extract purification apparatus, consisting of the items specified in 5.4.1 to 5.4.5:

5.4.1 2 cm^3, 5 cm^3 and 25 cm^3 or 30 cm^3 syringes, with conical end fittings, compatible with solid-phase extraction (SPE) columns for manual purification operations.

5.4.2 SPE cartridge containing 500 mg of silica gel. 1)

5.4.3 Laboratory glassware.

5.4.4 (Optional) **Solid-phase extraction equipment**, connected to a vacuum pump, for simultaneous purification of many extracts.

5.4.5 Disposable needles.

5.5 NMR spectrometer, at least 200 MHz, preferably with the following acquisition parameters:

probe:	^1H;
pulse phase:	30°;
spectral width:	− 2 ppm to + 12 ppm;
number of scans:	256;
relaxation delay:	2 s.

6 Procedure

6.1 Sample extraction

6.1.1 The laboratory sample shall be of sufficient size to provide at least 0,35 g of extracted oil.

Annex C gives guidance on the preparation of laboratory samples from tyres.

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1) VARIAN BOND ELUT JR-SI, 500 mg, part number 12162037B, is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product. Equivalent products may be used.

6.1.2 Pass the sample between the rolls of a laboratory mill to reduce its thickness to less than 0,7 mm or, alternatively, cut the sample in pieces smaller than 1 mm × 1 mm × 2 mm.

6.1.3 Wrap the sample in a small filter paper and insert it in the extractor (5.2), or fill the extractor with the small cut pieces. Fill the flask of the extractor with acetone (4.1.1) and extract for 8 h.

6.1.4 Evaporate the extract to dryness under a stream of nitrogen (4.2.3) to prevent oxidation.

6.2 Purification of extract

6.2.1 Weigh, to the nearest 0,1 mg, 100 mg ± 5 mg of dry extract into a vial and dissolve it in 1 cm^3 of methylene chloride (4.2.2). There may be some insoluble matter.

6.2.2 Condition the SPE cartridge (5.4.2) by injecting 5 cm^3 of *n*-hexane (4.2.1) onto it using a 5 cm^3 syringe (see 5.4.1).

6.2.3 When nearly all the *n*-hexane has drained out, transfer quantitatively the methylene chloride solution onto the SPE cartridge and start collecting the eluate in a beaker or glass bottle. Use an additional 0,5 cm^3 of methylene chloride to rinse the vial and ensure complete transfer of the evaporation residue to the cartridge.

6.2.4 When nearly all the methylene chloride solution has been absorbed onto the SPE cartridge, start eluting the non-polar fraction with 25 cm^3 of hexane. During the elution, maintain a constant solvent flow not exceeding a rate of 5 cm^3/min.

6.2.5 Stop collecting the purified fraction when all of the 25 cm^3 of *n*-hexane has been added to the SPE cartridge.

6.2.6 Evaporate the eluate to dryness under a stream of nitrogen to prevent oxidation.

6.2.7 Weigh the dry residue to the nearest 0,1 mg and calculate the percentage recovered.

6.2.8 Repeat the extract purification procedure two more times, taking a fresh portion of extract each time.

6.2.9 Calculate the average of the three percentage recovery values. If the individual values obtained are within ± 5 % of the average, proceed to 6.3. Otherwise, repeat the sample extraction and extract purification procedure until three values within ± 5 % of the average are obtained.

6.3 NMR analysis

6.3.1 General

The aromatic character of the oil present in the dry residue obtained in 6.2.7 is determined by means of ^{1}H NMR spectroscopy.

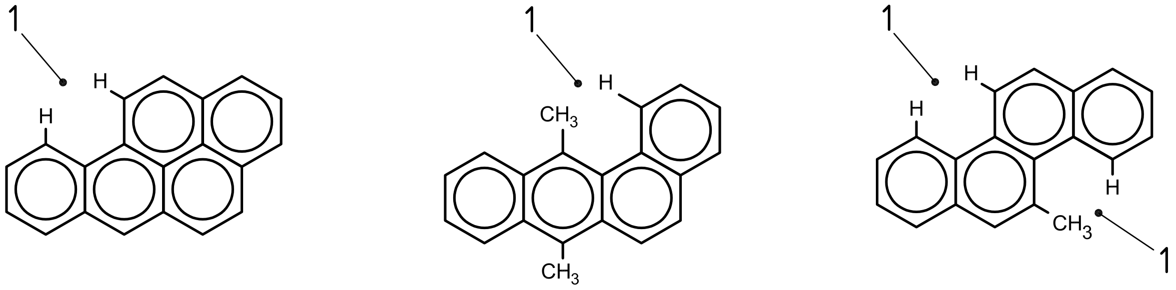
6.3.2 Principle

The molecular structure of non-linear PAHs with three or more fused rings contains a characteristic three-sided concave area, located at the periphery of the molecule. The hydrogen atoms in this area are called bay region hydrogens (see Figure 1).

^{1}H NMR spectroscopy can identify and quantify selectively the hydrogen atoms in the bay region, which are characteristic of aromatic oils.

This method describes a procedure for determining the percentage of bay region hydrogens (% H_{Bay}) in a sample solution by ^{1}H NMR, thus giving an indication of the aromatic character of the oil.

The higher the percentage of bay region hydrogens, the higher the aromaticity.



a) Benzopyrene **b) 7,12-Dimethylbenzanthracene** **c) 5-Methylchrysene**

Key

1 bay region

Figure 1

6.3.3 NMR measurement

6.3.3.1 Dissolve one of the dry residues obtained in 6.2.7 and 6.2.8 in a glass vial in about 1 cm^3 of $CDCl_3$ (4.2.4). If necessary, enhance dissolution by using a small magnetic stirrer or mechanical shaker; if this is not enough, add more $CDCl_3$.

6.3.3.2 Prepare the NMR tube by adding the sample solution prepared in 6.3.3.1 and a few drops of reference solvent, HMDS or TMS (see 4.2.5).

6.3.3.3 Acquire the free induction decay (FID) signal and apply a Fourier transform, multiplying by an exponential function (LB = 0,3 Hz) to obtain the spectrum (see the examples in Annex A). Adjust the resonance of the reference (HMDS or TMS) peak to 0,0 ppm.

6.3.3.4 Integrate the spectrum and record the following areas:

I_0	the aromatic area, from 6,0 ppm to 9,5 ppm, including the $CHCl_3$ signal (impurity contained in $CDCl_3$);
I_{CHCl_3}	the $CHCl_3$ signal (located around 7,2 ppm);
I_1	the pure aromatic area (= $I_0 - I_{CHCl_3}$);
I_2	the area of the bay region from 8,3 ppm to 9,5 ppm;
I_3	the area of the aliphatic and ethylenic regions from 0,2 ppm to 5,8 ppm.

6.3.3.5 Perform NMR measurements on each of the three purified extracts obtained in 6.2.7 and 6.2.8.

7 Calculation

For each of the three purified extracts, calculate the percentage of bay region hydrogens (% H_{Bay}) to two decimal places using the following equation:

$$\% \, H_{Bay} = \frac{I_2}{I_1 + I_3} \times 100$$

where the symbols are as defined in 6.3.3.4.

8 Precision

An interlaboratory test programme was carried out in which five laboratories participated. The percentage of bay region hydrogens was determined for three different rubber samples. The number of within-laboratory replicates was two, and the time span for repeatability was 7 days. The precision calculations to express repeatability and reproducibility were performed in accordance with ISO/TR 9272, *Rubber and rubber products — Determination of precision for test method standards*. A type 2 interlaboratory precision was determined.

The results are given in Table 1.

Table 1 — Precision data for % H_{Bay} determined by NMR

Sample	Mean level	Within-laboratory			Between laboratories		
	%	s_r	r	(r)	s_R	R	(R)
Compound No. 1: 20 phr of distilled aromatic (DAE) oil	0,48	0,045	0,13	26,7	0,047	0,13	27,9
Compound No. 2: 20 phr of treated distilled aromatic (TDAE) oil	0,19	0,036	0,1	55,2	0,045	0,13	69,5
Compound No. 3: 20 phr of mild extract solvent (MES) oil	0,07	0,033	0,09	142	0,046	0,13	197,9
Pooled values		0,038	0,11	74,6	0,046	0,13	98,4
Number of laboratories p = 5, number of materials q = 3, number of replicates n = 2							

s_r is the within-laboratory standard deviation;

s_R is the between-laboratories standard deviation;

r is the repeatability, in measurement units;

(r) is the repeatability, in percent (these values represent percent relative, i.e. percent of a percent);

R is the reproducibility, in measurement units;

(R) is the reproducibility, in percent (these values represent percent relative, i.e. percent of a percent).

9 Test report

The test report shall include the following information:

a) a reference to this International Standard (ISO 21461);

b) all details necessary for the identification of the rubber sample(s) tested;

c) details of the silica gel used in the solid-phase extraction cartridge (5.4.2);

d) the three percentage recovery values calculated in 6.2.7 and 6.2.8;

e) the average values of I_0, I_{CHCl_3}, I_1, I_2, I_3 and % H_{Bay};

f) any unusual features noted during the determination;

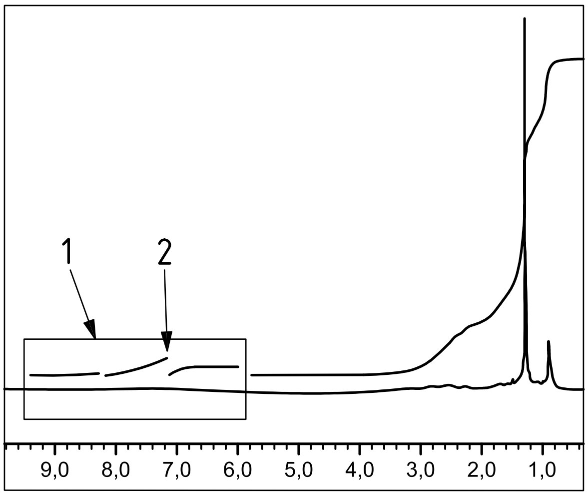
g) details of any operation not included in this International Standard, as well as details of any aspect regarded as optional, such as the NMR parameters in 5.5 if different from those specified;

h) the date of the test.

Annex A
(informative)

^{1}H NMR spectra of extracts from compounds containing aromatic oil (Figures A.1 and A.3) and MES oil (Figures A.2 and A.4)

A.1 Complete spectra

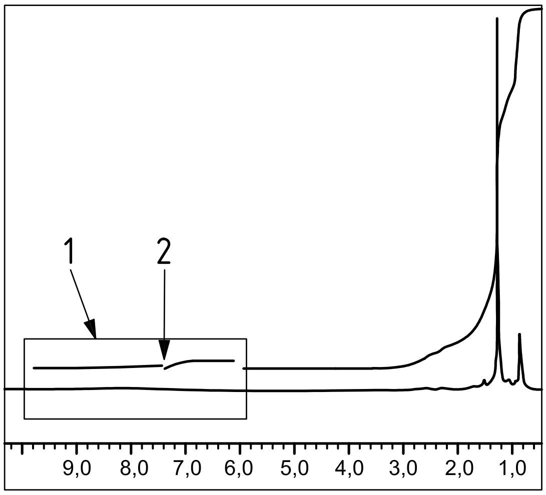


Key

1 aromatic region

2 $CHCl_3$ impurity

Figure A.1 — ^{1}H NMR spectrum of an extract from a compound containing aromatic oil



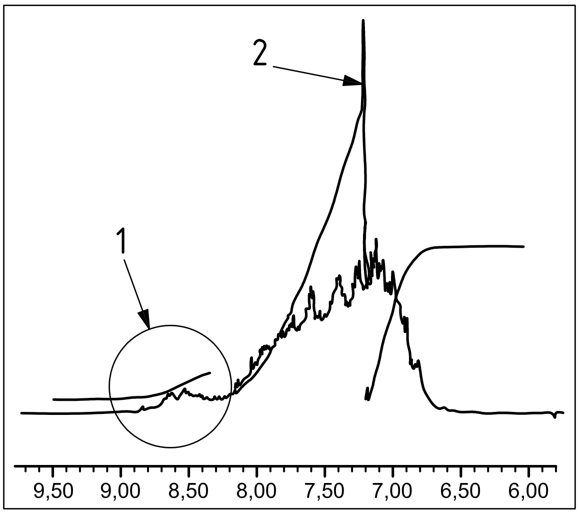
Key

1 aromatic region

2 $CHCl_3$ impurity

Figure A.2 — ^{1}H NMR spectrum of an extract from a compound containing MES oil

A.2 Zoom-in on aromatic region with (circled) the specific "bay region"

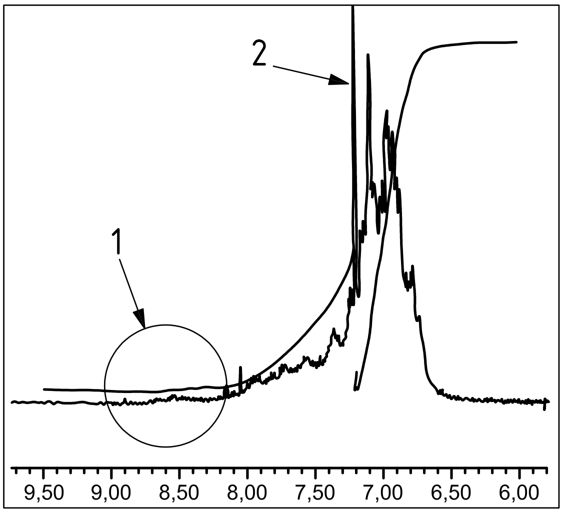


Key

1 bay region (8,3 ppm to 9,5 ppm)

2 $CHCl_3$ impurity

Figure A.3 — Aromatic region of the ^1H NMR spectrum of an extract from a compound containing aromatic oil (% H_{Bay} = 0,46)



Key

1 bay region (8,3 ppm to 9,5 ppm)

2 $CHCl_3$ impurity

Figure A.4 — Aromatic region of the ^1H NMR spectrum of an extract from a compound containing MES oil (% H_{Bay} = 0,04)

Annex B
(informative)

^{1}H NMR analysis results for typical rubber compounds
(those used for the interlaboratory trial described in Clause 8)

Composition in phr (parts per 100 parts of rubber by mass)

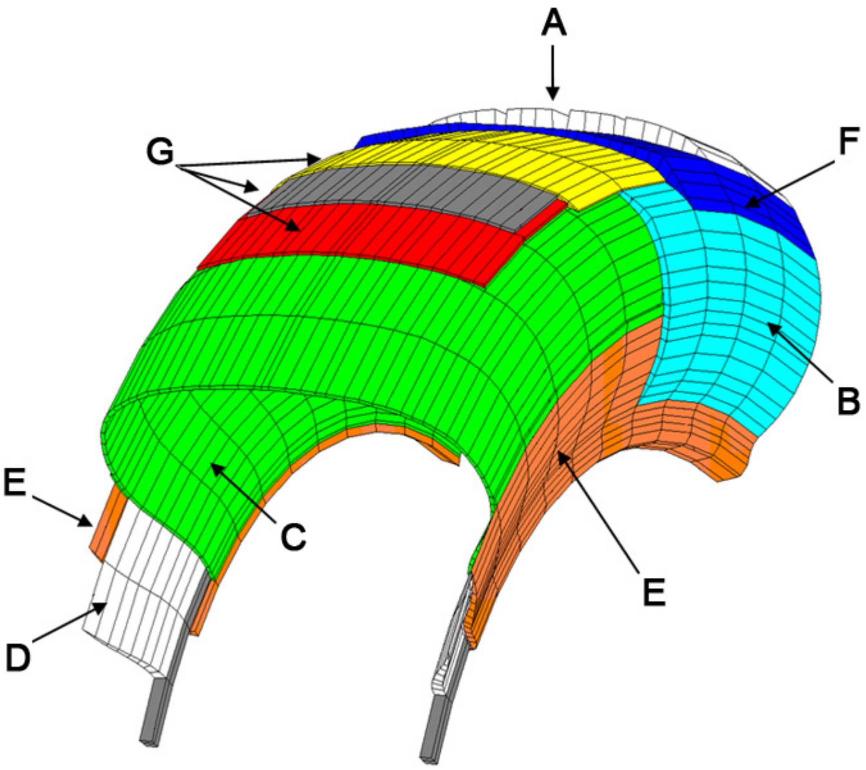
Constituent	**Compound No. 1**	**Compound No. 2**	**Compound No. 3**
Polymer: NR	50	50	50
SBR1500	50	50	50
Carbon black (N330)	65	65	65
Process oil: DAE	20	—	—
TDAE	—	20	—
MES	—	—	20
Antioxidant (6PPD)	2	2	2
Zinc oxide	3	3	3
Stearic acid	2	2	2
Accelerator (CBS)	1,5	1,5	1,5
Sulfur	1,5	1,5	1,5
Results			
Average of: I_0	$2{,}63 \times 10^7$	$1{,}91 \times 10^7$	$1{,}34 \times 10^7$
I_{CHCl_3}	$0{,}10 \times 10^7$	$0{,}08 \times 10^7$	$0{,}08 \times 10^7$
I_1	$2{,}53 \times 10^7$	$1{,}83 \times 10^7$	$1{,}26 \times 10^7$
I_2	$13{,}3 \times 10^5$	$5{,}5 \times 10^5$	$1{,}49 \times 10^5$
I_3	$2{,}61 \times 10^8$	$3{,}16 \times 10^8$	$3{,}34 \times 10^8$
% H_{Bay}	0,46	0,16	0,04

Annex C
(informative)

Preparation of clean samples of rubber compounds from tyres

C.1 General

Taking samples of rubber compounds from tyres is complicated by the intrinsic complexity of the tyre construction, which includes many different components as shown in Figure C.1. In addition, the visual inspection of tyre sections requires some degree of skill to identify the different components. The aim of this annex is to provide basic guidance on how to section the tyre and take samples from the sections thus produced.



Key

A tread
B sidewall
C innerliner and carcass ply
D bead filler/apex
E chafer/abrasion gum strip
F under-tread
G rubberized belts

Figure C.1 — Tyre construction

The structure shown in Figure C.1 is an example showing the main components of a tyre, but some components may be absent or others present, depending on the particular design.

Visual inspection of a cleanly cut cross-section, if necessary with the help of a magnification glass, can be useful to determine the actual structure before starting the sampling operations.

C.2 Apparatus

C.2.1 Sectioning machine, for cutting the materials taken from the tyre into layers down to 0,1 mm to 0,2 mm in thickness.

Any suitable machine [2] designed for rubbery materials may be used.

C.2.2 Knife and **cutters**, together with suitable **safety gloves and clothes**.

C.2.3 Magnifying glass.

C.3 Procedure

This sampling procedure is designed to be carried out only on new tyres cut into sections of suitable dimensions (dependent on the size of the tyre). With minor modifications, the procedure can be used for tyres of all the types and sizes currently on the market (passenger car tyres, truck tyres, motorcycle tyres, etc.).

As stated in 6.1.1, at least 0,35 g of oil has to be recovered from each component. This implies a minimum sample size ranging from about 2 g to 20 g, depending on the extractable-matter content. Moreover, due to practical limitations, with tyre components made up of vulcanized-rubber layers less than 1 mm thick (e.g. rubberized belts and carcass plies in passenger car tyres), it may be difficult to obtain a sample of sufficient size for the analysis.

The sampling operation is based on the following steps:

a) **Step 1:** Using a suitable cutter, a piece of the tread assembly, i.e. the tread, the under-tread, if present, and the rubberized belts (A, F and G in Figure C.1), is cut from the tyre. The cross-section of the piece is visually inspected to confirm the absence of any materials which could contaminate the sample. A clean sample is now taken of the tread and, if present, the under-tread, using the sectioning machine. The first 0,1 mm to 0,5 mm of the surface of the sample is removed and discarded to avoid contamination by foreign matter.

b) **Step 2:** A piece of the sidewall assembly, i.e. the sidewall itself, the chafer, the bead filler, the innerliner and the rubberized carcass ply embedded between the innerliner and the sidewall (B, C, D and E in Figure C.1), is cut from the tyre. The steel beads are removed from the assembly and the assembly is subsequently separated into its various components as described in the following sub-steps:

    1) **Sub-step 2A:** The material between cutting line 1 and cutting line 2 shown in Figure C.2 is cut out with a knife and clean samples are taken of the sidewall and the innerliner using the sectioning machine, setting the cutting depth at the required thickness as determined by visual inspection of the cross-section of the piece of sidewall assembly originally cut out. The first 0,5 mm to 1 mm of the surface of the sidewall sample is removed and discarded to avoid contamination by foreign matter. This is not normally possible for the innerliner, due to its small thickness. In this case, a careful examination is carried out under a magnifying glass to exclude the possibility of contamination with material from the ply coating.

    2) **Sub-step 2B:** The material between cutting line 2 and cutting line 3 shown in Figure C.2 is cut out with a knife and clean samples are taken of the chafer and the bead filler by carefully removing all the other components which are not of interest by means of the sectioning machine, setting the cutting depth of the machine at the required thickness as determined by visual inspection of the cross-section of the piece of sidewall assembly originally cut out.

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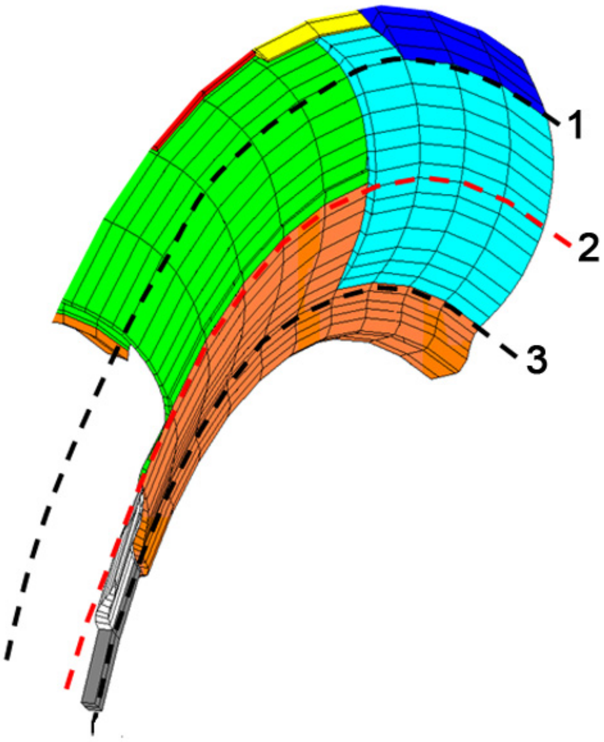
2) Suitable machines can be obtained from Fortuna Spezialmaschinen GmbH, Eisenbahnstraβe 15, D-71263 Weil der Stadt, Germany, www.fortuna-werke.net. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these machines.



Key

1 cutting line 1

2 cutting line 2

3 cutting line 3

Figure C.2 — Cutting the sidewall assembly

C.4 Photographs

Figures C.3 to C.15 give examples illustrating the various steps in the procedure.

Figure C.3 — Step 1: Cutting the tread assembly using a knife and cutting groove

Figure C.4 — Step 1: Removing a piece of tread assembly from the tyre

Figure C.5 — Step 1: Visual inspection before removing the belts
(no under-tread is present in this case)

Figure C.6 — Step 1: Tread sample, after removal of the surface layer, ready for analysis

Figure C.7 — Step 2: Removing the bead by cutting along cutting line 3 in Figure C.2

Figure C.8 — Step 2: Removing the sidewall assembly by cutting along cutting line 1 in Figure C.2

Figure C.9 — Step 2: Sidewall assembly cut from tread assembly and bead

Figure C.10 — Sub-step 2A: Sidewall assembly after cutting along cutting line 2 in Figure C.2

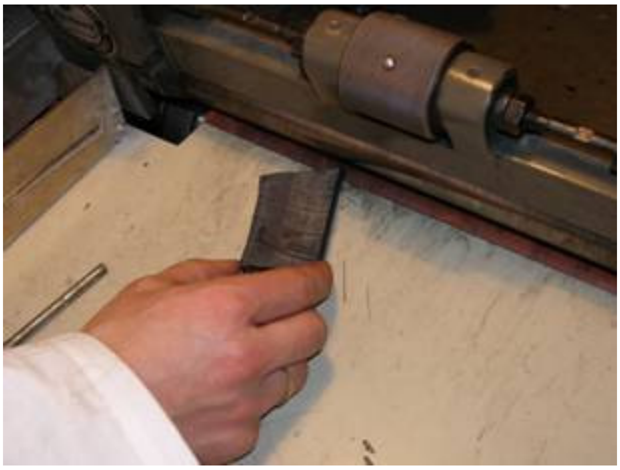


Figure C.11 — Sub-step 2A: Upper part of sidewall assembly being sectioned with the sectioning machine to obtain a clean sample of the sidewall

Figure C.12 — Sub-step 2A: Sidewall sample, after removal of the surface layer, ready for analysis

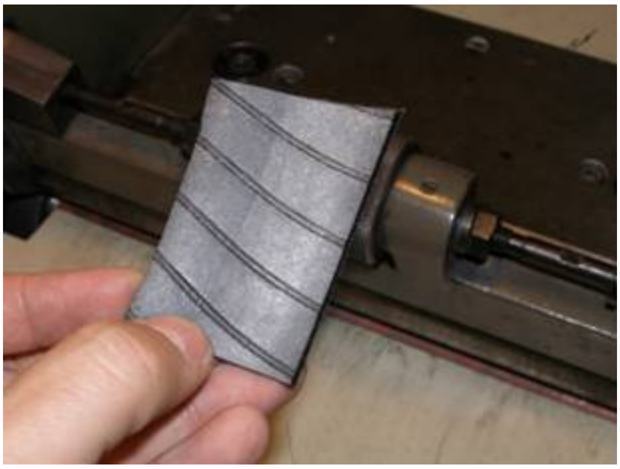


Figure C.13 — Sub-step 2A: Innerliner sample taken from the sidewall assembly

Figure C.14 — Sub-step 2B: Chafer and bead filler cut from the sidewall assembly
(between cutting lines 2 and 3 in Figure C.2)

a) Tread b) Sidewall c) Chafer d) Bead filler e) Innerliner

Figure C.15 — Samples ready for analysis

ICS 83.040.10

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