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Rubber — Identification of polymers — Pyrolytic gas-chromatographic method using mass-spectrometric detection

Caoutchouc — Identification des polymères — Méthode par pyrolyse et chromatographie en phase gazeuse avec détection par spectrométrie de masse

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Foreword

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analyses*.

Rubber — Identification of polymers — Pyrolytic gas-chromatographic method using mass-spectrometric detection

1 Scope

This International Standard provides a qualitative method for the identification of rubbers by their pyrolysis products using tandem the gas-chromatography /mass spectrometry.

The method applies to rubbers in the raw state and to unvulcanized and vulcanized compounds. Compounds can be based on a single rubber or a blend of two or more rubbers. Where the level of a particular rubber in a blend is < 10 % detection and identification can be difficult.

A non-restrictive list of rubbers is given in Clause 3.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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*

ISO 1629, *Rubber and latices — Nomenclature*

3 List of rubbers

The following list is not restrictive.

Rubbers are presented according to ISO 1629.

3.1 Group M

3.1.1 Chloropolyethylene (CM)

3.1.2 Chlorosulfonylpolyethylene (CSM)

3.1.3 Ethylene-propylene copolymer (EPM) and Ethylene-propylene-diene terpolymer (EPDM)

The method cannot distinguish between them.

3.1.4 Fluorocarbon rubber having substituent fluoro, perfluoroalkyl, or perfluoroalkoxy groups on the polymer chain (FKM)

The method cannot distinguish between them.

3.2 Group O

3.2.1 Homopolymer of epichlorhydrin (CO), copolymer of epichlorhydrin-ethylene oxide (ECO), terpolymer of epichlorhydrin-ethylene oxide-allyl glycidyl ether (GECO)

The method cannot distinguish between them.

3.3 Group Q

3.3.1 Polysiloxanes (MQ, VMQ, PVMQ)

The method cannot distinguish MQ and VMQ, but can distinguish PVMQ from the two other polymers.

3.4 Group R

3.4.1 Butadiene rubber (BR)

3.4.2 Chloroprene rubber (CR)

3.4.3 Isobutene-isoprene rubber (IIR), chlorinated IIR (CIIR) and brominated IIR (BIIR)

The method cannot distinguish between them.

3.4.4 Natural rubber (NR) and synthetic isoprene rubber (IR)

The method cannot distinguish between them.

3.4.5 Acrylonitrile-butadiene rubber (NBR), hydrogenated NBR (HNBR) and carboxylated NBR (XNBR)

The method can only distinguish HNBR from the two other polymers (NBR and XNBR).

3.4.6 Styrene-butadiene rubber (SBR)

The method allows butadiene-α-methylstyrene rubber to be distinguished from butadiene-styrene rubber.

3.5 Rubber blends

In copolymer-homopolymer blends having one common monomer (e.g. SBR/BR, NBR/BR), the technique does not allow the homopolymer to be distinguished.

This is also valid for blends with terpolymers.

4 Principle

4.1 Raw rubbers, or vulcanized or unvulcanized compounds which previously have been solvent extracted, are pyrolysed and the pyrolysate analysed by gas chromatography with mass spectrometric detection.

4.2 The interpretation of the results is made by examining the mass spectra of the specific chromatographic peaks.

5 Reagents

All reagents shall be of an analytical grade.

5.1 Solvents, for the extraction according to ISO 1407.

5.2 Inert carrier gas.

6 Equipment

6.1 Extraction devices according to ISO 1407.

6.2 The chromatographic equipment consists of three associated parts:

a) pyrolysis system;

b) gas chromatograph equipped with chromatographic columns;

c) mass detector in electronic impact mode.

These elements are connected with an acquisition and data processing system.

A schematic diagram of the equipment is given in Annex A.

6.2.1 Pyrolysis system

Non-volatile polymers are decomposed at elevated temperature to generate volatile products able to be analysed by chromatography. In order to obtain reproducible results of decomposition, the pyrolysis parameters (temperature, time) need to be established separately.

Different types of equipment are available that give a rapid and reproducible pyrolysis. The three most common are:

— platinum filament pyrolyser;

— Curie point pyrolyser;

— micro furnace pyrolyser.

6.2.2 Chromatographic columns

6.2.2.1 General

There are several categories of chromatographic columns available in the market. They are characterized by:

— the nature of the material constituting the tube (generally silica covered with a polymer, aluminium or deactivated stainless steel, etc.);

— the column length;

— the column diameter;

— the nature, thickness, and polarity of the stationary phase placed on the internal surface of the capillary tube.

The column shall be chosen by taking into account its efficiency of separation (number of theoretical plates) and the relative polarity of the various compounds generated during rubber pyrolysis.

6.2.2.2 Examples of useful capillary columns

a) Capillary column in fused silica of 0,32 mm diameter and 30 m , of apolar type. Stationary phase - film of dimethyl polysiloxane, 1 µm thick;

b) Capillary column in fused silica of 0,32 mm diameter and 30 m , of polar type. Stationary phase - film of polyethylene glycol, 0,5 µm thick.

7 Operating conditions

7.1 General

The reproducibility is guaranteed by checking the conformity of the device and by respecting the procedure.

7.2 Gas chromatograph adjustment

Adjust the various controls of the gas chromatograph according to the retained operating conditions.

For information, typical operating conditions are given in Annex B.

7.3 Extraction

Carry out the extraction according to ISO 1407. The rubber residue is dried until constant mass.

NOTE This preliminary extraction is not mandatory but allows the elimination of compound constituents which could interfere with the pyrolysis product.

7.4 Test portion

Take a test portion of mass appropriate to the apparatus used, usually about 0,1 mg.

7.5 Pyrolysis

Place the test portion in the pyrolysis device and purge for the necessary time.

Pyrolyse at a temperature between 400 °C and 800 °C; usually the pyrolysis temperature is about 600 °C.

Record the experimental data.

8 Interpretation of results

8.1 General

The identification of rubbers is achieved by noting the presence of certain characteristic decomposition products and by consulting the mass spectra database.

Two examples of chromatograms are presented in Annex C.

The following clauses summarize all the characteristic products by family of polymer. For the interpretation of the results, refer to Annex D according to the type of column used.

8.2 Group M

8.2.1 Chloropolyethylene (CM) and chlorosulfonylpolyethylene (CSM)

— Hydrochloric acid (CAS 7647-01-0)

— Benzene (CAS 71-43-2)

It is possible, in certain case, to differentiate these two polymers by the presence of sulfur dioxide (CAS 7446-09-5).

8.2.2 Ethylene-propylene copolymer (EPM) and Ethylene-propylene-diene terpolymer (EPDM)

— Propene (CAS 115-07-1)

— 1-Hexene (CAS 592-41-6) or 2-Methyl-1-pentene (CAS 763-29-1)

— 1-Heptene (CAS 592-76-7) or 5-Methyl-1-hexene (CAS 3524-73-0)

— 2-Methyl-1-heptene (CAS 15870-10-7)

— 1,3,5-Cycloheptatriene (CAS 544-25-2)

8.2.3 Fluorocarbon rubber having substituent fluoro, perfluoroalkyl, or perfluoroalkoxy groups on the polymer chain (FKM)

— 1,1-Difluoroethene (CAS 75-38-7)

8.3 Group O

8.3.1 Homopolymer of epichlorhydrin (CO), copolymer of epichlorhydrin-ethylene oxide (ECO), terpolymer of epichlorhydrin-ethylene oxide-allyl glycidyl ether (GECO)

— Hydrochloric acid (CAS 7647-01-0)

— 1-Chloro-1-propene (CAS 590-21-6)

8.4 Group Q

8.4.1 Polysiloxanes (MQ, VMQ, PVMQ)

— Hexamethylcyclotrisiloxane (CAS 541-05-9)

— Octamethylcyclotetrasiloxane (CAS 556-67-2)

— Decamethylcyclopentasiloxane (CAS 541-02-6)

— Dodecamethylcyclohexasiloxane (CAS 540-97-6)

The presence of benzene allows the polymers PVMQ of the VMQ and MQ to be distinguished.

8.5 Group R

8.5.1 Butadiene rubber (BR)

— 1,3-Butadiene (CAS 106-99-0)

— 4-Ethenylcyclohexene or 4-Vinyl-1-cyclohexene (CAS 100-40-3)

8.5.2 Chloroprene rubber (CR)

— Hydrochloric acid (CAS 7647-01-0)

— 2-Chloro-1,3-butadiene (CAS 126-99-8)

— 1-Chloro-5-(1-chloroethenyl)-cyclohexene (CAS 13547-07-4)

— 1-Chloro-4-(1-chloroethenyl)-cyclohexene (CAS 13547-06-3)

8.5.3 Isobutene-isoprene rubber (IIR), chlorinated IIR (CIIR) and brominated IIR (BIIR)

— Isobutylene (CAS 115-11-7)

— Diisobutylene or 2,4,4-trimethyl-1-pentene (CAS 107-39-1)

— Triisobutylene or 2-methylpropane (CAS 7756-94-7)

8.5.4 Natural rubber (NR) or synthetic isoprene rubber (IR)

— Isoprene (CAS 78-79-5)

Isomers of the limonene:

— 1-Methyl-5-(1-methylethenyl)-cyclohexene (CAS 13898-73-2)

— 1-Methyl-4-(1-methylethenyl)-cyclohexene (CAS 138-86-3)

8.5.5 Acrylonitrile-butadiene rubber (NBR), hydrogenated NBR (HNBR) and carboxylated NBR (XNBR)

8.5.5.1 NBR and XNBR

— 1,3-Butadiene (CAS 106-99-0)

— 4-Ethenylcyclohexene or 4-Vinyl-1-cyclohexene (CAS 100-40-3)

— 2-Propenenitrile or Acrylonitrile (CAS 107-13-1)

8.5.5.2 HNBR

— 2-Propenenitrile or Acrylonitrile (CAS 107-13-1)

— Hexanenitrile or Capronitrile (CAS 628-73-9)

8.5.6 Styrene-butadiene rubber (SBR)

— 1,3-Butadiene (CAS 106-99-0)

— 4-Ethenylcyclohexene or 4-Vinyl-1-cyclohexene (CAS 100-40-3)

— Ethenylbenzene or Styrene (CAS 100-42-5)

In case of butadiene-alpha-methylstyrene copolymers, there is a strong peak of alpha-methylstyrene or isopropenylbenzene (CAS 98-83-9).

9 Test report

The test report shall include the following particulars:

a) sample details: a full description of the sample;

b) test method:

   — a reference to this International Standard, (i.e. ISO 17257:2013);

   — characteristics of the column, if necessary thermal program and spectral condition;

   — identification of the pyrolyser GC-MS equipment used;

c) test details: details of any procedures not specified in this International Standard, if any;

d) test results:

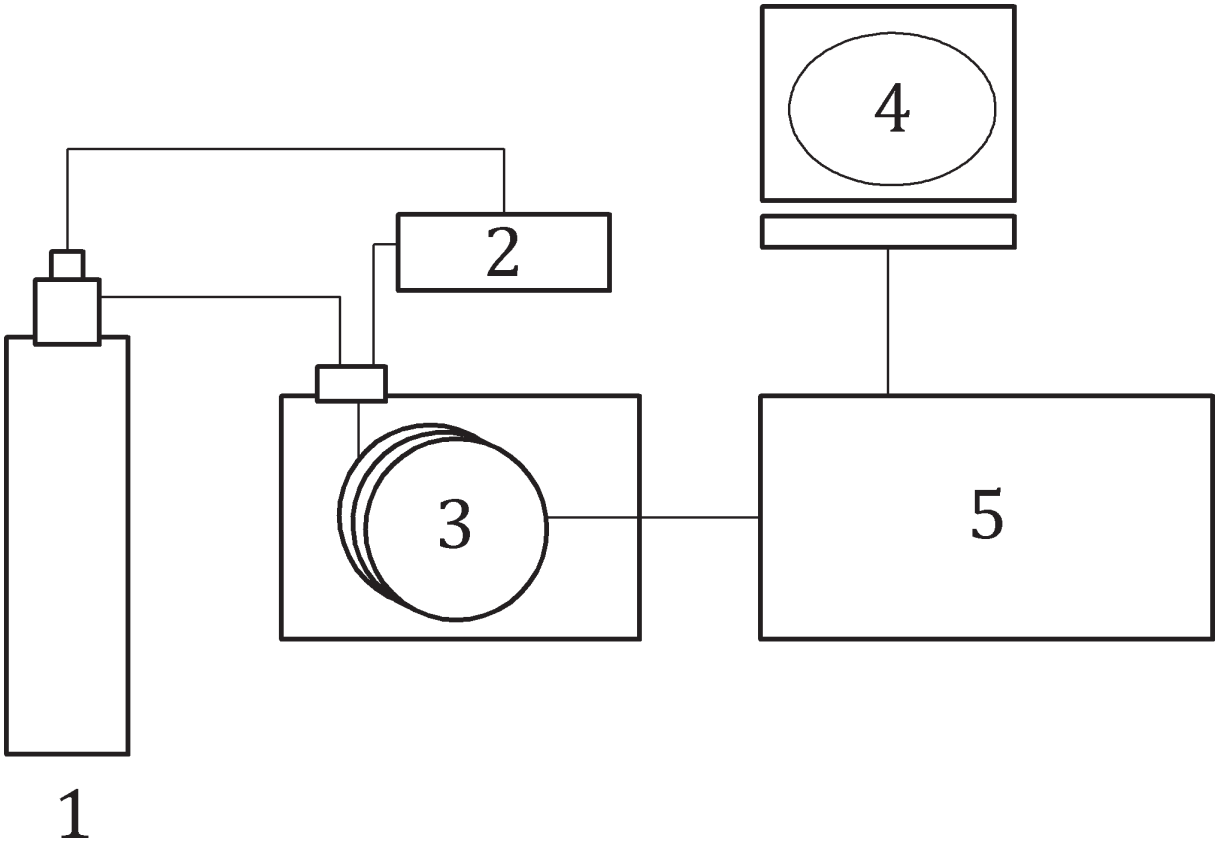
— chromatogram of sample;

— identification of the rubber(s) in the sample;

e) date of test.

Annex A
(informative)

Schematic diagram of the chromatographic equipment



Key

1 carrier gas
2 pyrolyser
3 gas chromatograph
4 acquistion and data processing system
5 mass spectrometer

Figure A.1 — Schematic diagram of a gas-chromatograph equipped with a pyrolyser coupled with a mass spectrometer

Annex B
(informative)

Examples of operating conditions

Examples of operating conditions are given in Table B.1

Table B.1 — Examples of operating conditions

Apolar column	Polar column
— Initial temperature at 40 °C — Isothermal for 2 min at 40 °C — Increase to 140 °C (10 °C per minute) — Increase to 290 °C (20 °C per minute) — Isothermal for 5 min at 290 °C	— Initial temperature at 30 °C — Isothermal for 2 min 30 °C — Increase to 200 °C (5 °C per minute) — Isothermal for 10 min in 200 °C
Injector temperature: 250 °C Carrier gas: He The flow rate output of the carrier gas in the column is adjusted between 1 ml/min and 2 ml/min. Calibration of the mass spectrometer: Interface temperature: 250 °C to 290 °C Ionization mode: electronic impact mode (70 eV) Track of acquisition covering at least the range m/z: 29 to 500	

Annex C
(informative)

Chromatogram examples

Chromatogram examples, obtained under operation conditions stated in Table B.1 with an apolar column, are given in Figures C.1 and C.2.

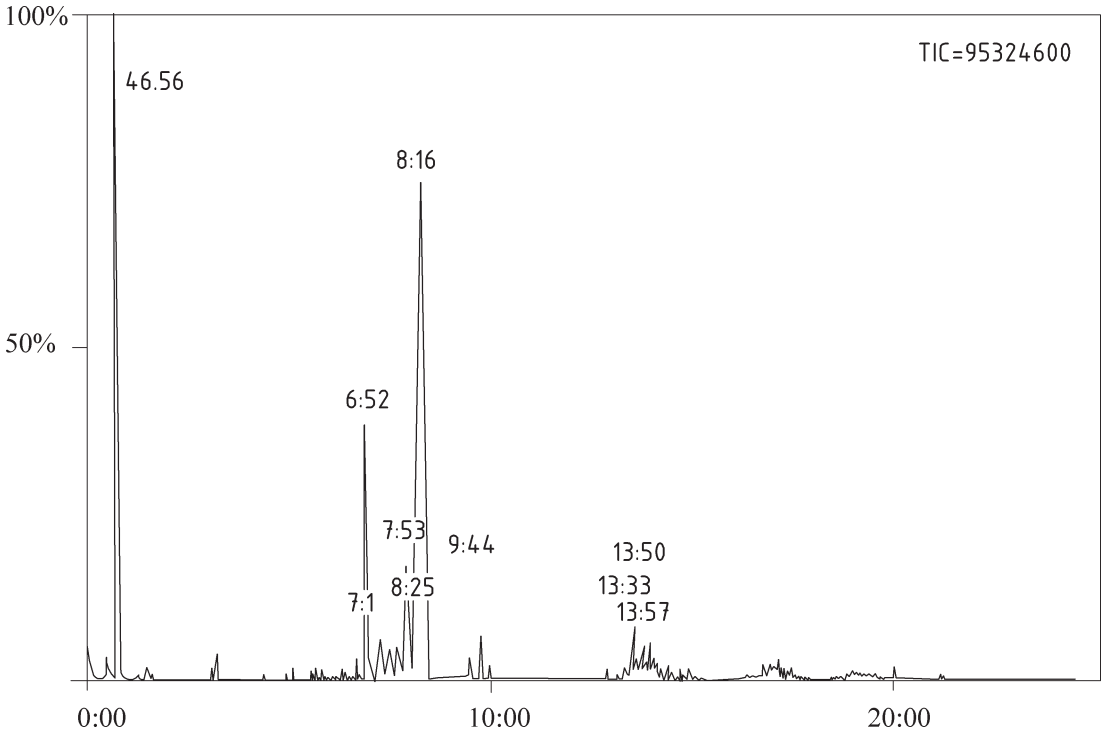


Figure C.1 — Chromatogram of a natural rubber (NR)

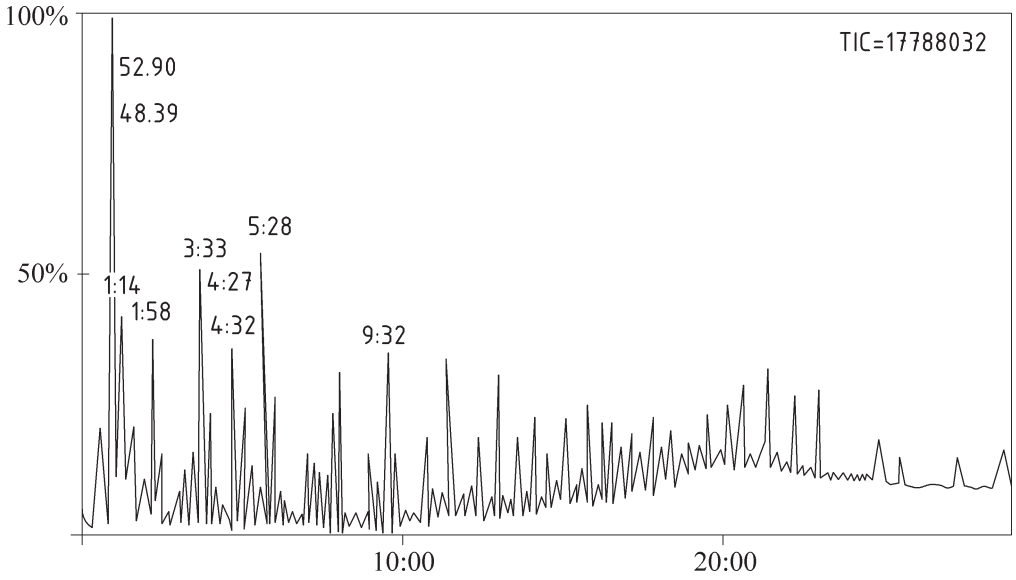


Figure C.2 — Chromatogram of an ethylene-propylene-diene terpolymer (EPDM)

Annex D
(informative)

Chemical compounds identified in rubber pyrolysates

The chemical compounds are given for information in Tables D.1 and D.2 in order of retention time. The black boxes correspond to the characteristic pyrolysis products. Products-highlighted by a circle are less characteristic.

Table D.1 — Chemical compounds identified in rubber pyrolysates — Apolar column

MW	Chemical compounds	N CAS	NR / IR	BR	SBR	αMSBR	IIR / BIIR / CIIR	NBR	HNBR	CR	CM	CSM	EPM / EPDM	VMQ / MQ	PVMQ	CO / ECO
36	HCl	7647-01-0								■	■	■				■
64	SO2	7446-09-5										■				
42	Propene	115-07-1											■			
56	2-Methyl-1-propene or Isobutylene	115-11-7					■									
84	1-Hexene	592-41-6											■			
54	1,3-Butadiene	106-99-0		■	■	■		■			■	■				
88	2-Chloro-1,3-butadiene	126-99-8								■						
53	2-Propenenitrile or Acrylonitrile	107-13-1						■	■							
68	2-Methyl-1,3-butadiene or Isoprene	78-79-5	■													
76	1-Chloro-1-propene-	590-21-6														■
98	1-Heptene	592-76-7											■			
78	Benzene	71-43-2									■	■			■	
94	2-Methyl-1,3,5-hexatriene	19264-50-7											○			
112	2-Methyl-1-heptene	15870-10-7											■			
112	2,4,4-Trimethyl-1-pentene or Diisobutylene	107-39-1					■									
97	Hexanenitrile or Capronitrile	628-73-9							■							
108	4-Ethenylcyclohexene or 4-Vinyl-1-cyclohexene	100-40-3		■	■	■		■			○	○				
222	Hexamethylcyclotrisiloxane	541-05-9												○	○	
104	Ethenylbenzene or Styrene	100-42-5			■											
118	Isopropenylbenzene or α-methylstyrene	98-83-9				■										
296	Octamethylcyclotetrasiloxane	556-67-2												■	■	
168	2-Methylpropane or Triisobutylene	7756-94-7					■									
136	1-Methyl-5-(1-methylethenyl)-	13898-73-	○													

Table D.1 — *(continued)*

	cyclohexene	2														
136	1-Methyl-4-(1-methylethenyl)-cyclohexene or Limonene	138–86–3	■													
176	1-Chloro-5-(1-chloroethenyl)-cyclohexene	13547–07–4								■						
176	1-Chloro-4-(1-chloroethenyl)-cyclohexene	13547–06–3								■						
370	Decamethylcyclopentasiloxane	541–02–6												■	■	
224	2,2,4,4,6,6,8-Heptamethylnonane or Tetraisobutylene	15220–85–6					0									
444	Dodecamethylcyclohexasiloxane	540–97–6												■	■	

Table D.2 — Chemical compounds identified in rubber pyrolysates — Polar column

MW	Chemical compounds	N CAS	NR / IR	BR	SBR	αMSBR	IIR / BIIR / CIIR	NBR	HNBR	CR	CM / CSM	EPM / EPDM	FKM	VMQ / MQ	PVMQ
36	HCl	7647-01-0								■	■				
64	1,1-Difluoroethene	75-38-7											■		
42	Propene	115-07-1										■			
58	Isobutane	75-28-5										O			
56	2-Methyl-1-propene or Isobutylene	115-11-7					■								
56	2-Butene	107-01-7						O							
68	Isoprene	78-79-5	■												
54	1,3-Butadiene	106-99-0		■	■	■		■							
84	1-Hexene or 2-Methyl-1-pentene	592-41-6 or 736-29-1									O	■			
68	1,3-Pentadiene	504-60-9		O	O			O							
68	Cyclopentene	142-29-0									O				
112	2,4,4-Trimethyl-1-pentene or Diisobutylene	107-39-1					■								
98	5-Methyl-1-hexene	3524-73-0										O			
66	3-Pentene-1-yne	2206-23-7									O				
222	Hexamethylcyclotrisiloxane	541-05-9												■	■
112	1,2-Diethylcyclobutane trans	61141-83-1										O			
88	2-Chloro-1,3-butadiene	126-99-8								■					
80	Cyclohexadiene	29797-09-9		O							O				
94	2-Methyl-1,3,5-hexatriene	19264-50-7										O			
94	Methyl-1,3,5-hexatriene											O			
78	Benzene	71-43-2		O	O			O			O				■
296	Octamethylcyclotetrasiloxane	556-67-2												■	■

Table D.2 — *(continued)*

108	4-Ethenylcyclohexene or 4-Vinyl-1-cyclohexene	100–40–3		■	■	■		■			O				
53	2-Propenenitrile or Acrylonitrile	107–13–1						■	■						
168	2-Methylpropane or Triisobutylene	7756–94–7					■								
92	Methylbenzene or Toluene	108–88–3								O	O	O			
92	1,3,5-Cycloheptatriene	544–25–2										■			
136	1-Methyl-5-(1-methylethenyl)-cyclohexene	13898–73–2	O												
370	Decamethylcyclopentasiloxane	541–02–6												■	■
136	1-Methyl-4-(1-methylethenyl)-cyclohexene or Limonene	138–86–3	■												
136	2,5-Dimethyl-1,5-heptadiene-3-methyl alcohol		O												
136	3,7-Dimethyl-1,3,6-octatriene		O												
104	Ethenylbenzene or Styrene	100–42–5			■						O				
444	Dodecamethylcyclohexasiloxane	540–97–6												■	■
97	Hexanenitrile or Capronitrile	628–73–9							■						
118	Isopropenylbenzene or α-methylstyrene	98–83–9				■									
224	2,2,4,4,6,6,8-Heptamethylnonane or Tetraisobutylene	15220–85–6					■								
134	1-Hexene –1,6-dinitrile								■						
116	1-Ethynyl-4-methylbenzene	766-97-2									O				
176	1-Chloro-5-(1-chloroethenyl)-cyclohexene	13547–07–4								■					
176	1-Chloro-4-(1-chloroethenyl)-cyclohexene	13547–06–3								■					
158	4-Phenylcyclohexene	4994–16–5			■										

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