INTERNATIONAL STANDARD

ISO 15011-5

First edition
2011-10-01

Health and safety in welding and allied processes — Laboratory method for sampling fume and gases —

Part 5: Identification of thermal-degradation products generated when welding or cutting through products composed wholly or partly of organic materials using pyrolysis-gas chromatography-mass spectrometry

Hygiène et sécurité en soudage et techniques connexes — Méthode de laboratoire d'échantillonnage des fumées et des gaz —

Partie 5: Identification des produits de dégradation thermique générés lors du soudage ou du coupage de produits entièrement ou partiellement constitués de matériaux organiques, par pyrolyse-chromatographie en phase gazeuse-spectrométrie de masse

Reference number
ISO 15011-5:2011(E)

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Published in Switzerland

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Foreword

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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 15011-5 was prepared by Technical Committee ISO/TC 44, *Welding and allied processes*, Subcommittee SC 9, *Health and safety*.

This first edition cancels and replaces ISO/TS 15011-5:2006, which has been technically revised.

ISO 15011 consists of the following parts, under the general title *Health and safety in welding and allied processes — Laboratory method for sampling fume and gases*:

— *Part 1: Determination of fume emission rate during arc welding and collection of fume for analysis*

— *Part 2: Determination of emission rates of carbon monoxide (CO), carbon dioxide (CO_2), nitrogen monoxide (NO) and nitrogen dioxide (NO_2) during arc welding, cutting and gouging*

— *Part 3: Determination of ozone emission rate during arc welding*

— *Part 4: Fume data sheets*

— *Part 5: Identification of thermal-degradation products generated when welding or cutting through products composed wholly or partly of organic materials using pyrolysis-gas chromatography-mass spectrometry*

— *Part 6: Procedure for quantitative determination of fume and gases from resistance spot welding* [Technical Specification]

Requests for official interpretations of any aspect of this part of ISO 15011 should be directed to the Secretariat of ISO/TC 44/SC 9, via your national standards body. A complete listing of these bodies can be found at www.iso.org.

Introduction

Welding and allied processes generate fume and gases, which, if inhaled, can be harmful to human health. Knowledge of the composition and the emission rate of the fume and gases can be useful to occupational hygienists in assessing worker exposure and in determining appropriate control measures.

ISO 15011-1[1] and ISO 15011-2[2] have been promulgated primarily to generate emission rate data when welding uncoated metals. However, it is now common practice in the welding industry to weld or cut through a variety of coatings that are composed wholly or partly of organic materials. These coatings include shop primers, paints, oils, waxes and inter-weld materials such as adhesives and sealants. When heated, these coatings give rise to a wide range of thermal degradation products, the composition of which depends upon the temperatures to which the coatings are subjected. During welding and cutting activities, the coating material is subjected to a range of temperatures due to the existence of temperature profiles within the material being processed.

The purpose of this part of ISO 15011 is to describe procedures that can be used to identify and make semi-quantitative measurements of the organic components generated when welding and cutting, preheating and straightening metal treated with the coatings mentioned above, with a view to identifying those components that are significant hygienically. The data generated can be used to provide information on degradation products for use on safety data sheets. If desired, the degradation products identified in these tests can then be measured quantitatively using existing standards for making workplace exposure measurements.

Comparative testing of various weld-through coatings has been carried out using laboratory based heating tests, pyrolysis, and different welding techniques[3][4][5]. From the results of these tests, it was decided that pyrolysis should be adopted as the basis for the testing procedure[6] prescribed in this part of ISO 15011. This was based on the following observations and conclusions:

- pyrolysis successfully identifies most of the hygienically significant components;
- despite the fact that pyrolysis tests are carried out in an atmosphere of helium, results are very comparable with those obtained in air by thermal decomposition in a furnace;
- the cost of pyrolysis testing is significantly lower than the cost of welding tests;
- pyrolysis test results show good interlaboratory consistency;
- it is easier to define standard conditions for pyrolysis tests than for welding tests; and
- in order to reduce the sampling regime required, any welding test programme would, in all likelihood, need to incorporate some pre-testing in the laboratory, probably using pyrolysis.

Health and safety in welding and allied processes — Laboratory method for sampling fume and gases —

Part 5: Identification of thermal-degradation products generated when welding or cutting through products composed wholly or partly of organic materials using pyrolysis-gas chromatography-mass spectrometry

1 Scope

This part of ISO 15011 specifies procedures for obtaining information about thermal degradation products generated when welding, cutting through, preheating and straightening metal treated with coatings composed wholly or partly of organic substances, e.g. shop primers, paints, oils, waxes and inter-weld materials such as adhesives and sealants. It is aimed primarily at test laboratories performing such procedures. The data generated can be used by coating manufacturers to provide information for inclusion in safety data sheets and by occupational hygienists to identify thermal degradation products of significance in the performance of risk assessments and/or workplace exposure measurements. The data cannot be used to estimate workplace exposure directly.

This part of ISO 15011 is applicable to all coatings composed partly or wholly of organic materials that can be heated during welding and cutting, preheating and straightening to temperatures at which thermal degradation products are generated and where it is not apparent what those degradation products are.

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 16000-6, *Indoor air — Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA® sorbent, thermal desorption and gas chromatography using MS/FID*

3 Terms and definitions

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

3.1

chemical agent

any chemical element or compound, on its own or admixed, as it occurs in the natural state or as produced, used or released, including release as waste, by any work activity, whether or not produced intentionally and whether or not placed on the market

[Council Directive 98/24/EC[7], Art. 2(a)]

3.2
occupational exposure limit value

limit of the time-weighted average of the concentration of a chemical agent in the air within the breathing zone of a worker in relation to a specified reference period

[Council Directive 98/24/EC[7], Art. 2(d)]

NOTE Limit values are mostly set for reference periods of 8 h, but can also be set for shorter periods or concentration excursions. Limit values for gases and vapours are stated in terms independent of temperature and air pressure variables in millilitres per cubic metre and in terms dependent on those variables in milligrams per cubic metre for a temperature of 20 °C and a pressure of 101,3 kPa. Limit values for airborne particles as well as mixtures of particles and vapours are given in milligrams per cubic metre or multiples of that unit for actual environmental conditions (temperature, pressure) at the workplace. Limit values of fibres are given in number of fibres per cubic metre or number of fibres per cubic centimetre for actual environmental conditions (temperature, pressure) at the workplace.

3.3
shop primer

material that is applied to an unpainted metal surface for protective purposes, which does not have to be removed prior to welding and does not prevent the making of an acceptable weld

NOTE Shop primers are typically applied with a thickness of between 15 µm and 30 µm.

3.4
thin organic coating

material that is applied as a very thin film to an unpainted metal surface for protective purposes, which does not have to be removed prior to welding and does not prevent the making of an acceptable weld

NOTE Thin organic coatings are typically applied with a thickness of between 1 µm and 3 µm.

3.5
weld-through adhesive

polymer that is applied prior to welding to a primed or unpainted metal surface for the purpose of bonding, which does not prevent the making of an acceptable weld

3.6
weld-through sealant

mastic, gap-filling material that is applied prior to welding to an unpainted metal surface for non-pressure sealing purposes, which does not prevent the making of an acceptable weld

3.7
weld-through oil

material composed of aliphatic and aromatic hydrocarbons that is applied to afford protection and act as a lubricant during pressing operations, which does not prevent the making of an acceptable weld

NOTE The aromatic hydrocarbon content of weld-through oils is typically less than 10 % volume fraction.

3.8
weld-through wax

material composed of esterified fatty acids that is applied to afford protection and act as a lubricant during pressing operations, which does not prevent the making of an acceptable weld

4 Principle

A sample of the coating under investigation, or a sample taken from a test piece to which the coating under investigation has been applied, is heated in a pyrolyser and the thermal degradation products generated are identified by gas chromatography–mass spectrometry (GC–MS). Analysis is carried out in an enclosed flow of carrier gas, which isolates the thermal degradation products from other airborne contaminants. Enclosing the heating operation also serves to concentrate the thermal degradation products, improving method detection limits.

5 Procedure

5.1 Identification of thermal degradation products

Perform laboratory tests to identify thermal degradation products of interest using the pyrolysis procedure specified in Annex A.

5.2 Data analysis

Evaluate the data to identify the thermal degradation products of the greatest hygienic significance. Refer to ISO 16000-6 for guidance.

6 Use of data on thermal degradation products

Refer to Annex F for information on the use of data on thermal degradation products generated using the procedures described in this part of ISO 15011.

7 Test report

The test report shall contain at least the following information:

a) the test method used, with reference to this part of ISO 15011 (ISO 15011-5:2011);

b) the name and address of the product manufacturer or supplier;

c) the type of product and/or the trade name of the product tested;

d) the name and address of the test laboratory;

e) the date the test report was issued;

f) the lot number of the coating tested;

g) any deviation from the procedures specified in this part of ISO 15011, unusual occurrences or other notable observations;

h) full details of each set of conditions under which the coatings were tested;

i) semi-quantitative data on the chemical composition of the thermal degradation products generated under each set of test conditions.

See Annex E for an example of a test report sheet.

Annex A
(normative)

Test procedure

A.1 Equipment

A.1.1 Pyrolyser

The pyrolyser used shall be capable of heating to a temperature of at least 800 °C.

NOTE Two of the main types of pyrolyser, the filament-type pyrolyser and the oven-type pyrolyser, which differ in the method used to heat the sample, have been found to produce satisfactory results. See Annex B for details.

A.1.2 GC–MS system

The GC–MS system shall include the following components:

a) a suitable capillary column held in a temperature-controlled oven;

b) a split-splitless injector;

c) a detector with a mass range of at least 25 u to 400 u;

d) a software control package incorporating peak area measurement and library search facilities.

A 30 m length, non-polar, capillary column with a diameter of around 0,25 µm and a film thickness of 0,25 µm to 0,50 µm is recommended. Other columns can also be used, if suitable. See Annex D for information on system and performance checks that can be used to determine if suitable resolution can be obtained.

A.2 Sample preparation

A.2.1 Filament-type pyrolyser

A.2.1.1 Shop primers and thin organic coatings

Obtain a suitable quantity of test material, typically a few tens of micrograms, from a piece of coated metal by means of light scraping. Place the scrapings directly on the pyrolyser filament.

A.2.1.2 Weld-through sealants, weld-through adhesives, and weld-through waxes

Place a suitable quantity of test material, typically a few tens of micrograms, directly on the pyrolyser filament.

A.2.1.3 Weld-through oils

For oil-coated metal plates, extract the oil from a piece of coated metal with dichloromethane. For neat oils, prepare a test solution of approximately 100 g/l of the oil in dichloromethane. Place 2 µl of the test solution on the pyrolyser filament and leave the solvent to evaporate at room temperature.

A.2.2 Oven-type pyrolyser

A.2.2.1 Shop primers and thin organic coatings

Obtain a suitable quantity of test material, typically 0,5 mg to 2 mg, from a piece of coated metal by means of light scraping. Lower the scrapings directly into the pyrolyser tube or inject them using a suitable syringe.

A.2.2.2 Weld-through sealants, weld-through adhesives, and weld-through waxes

Lower a suitable quantity of test material, typically 0,5 mg to 2 mg, directly into the pyrolyser tube or inject it using a suitable syringe. If the test material is too soft or sticky at room temperature, place it in a fridge to harden.

A.2.2.3 Weld-through oils

For oil-coated metal plates, extract oil from a piece of coated metal with dichloromethane and then evaporate the solvent. For neat oils, no sample pre-treatment is required. Lower approximately 1 µl of oil into the heating tube of the pyrolyser or inject it using a suitable syringe.

A.3 Analysis

Carry out tests at temperatures between 600 °C and 800 °C, using chromatographic conditions optimized for separation of components with carbon numbers ranging from 2 to 30. Refer to Annex C for a set of conditions appropriate for use with the column recommended in A.1.2.

A.4 Data collection

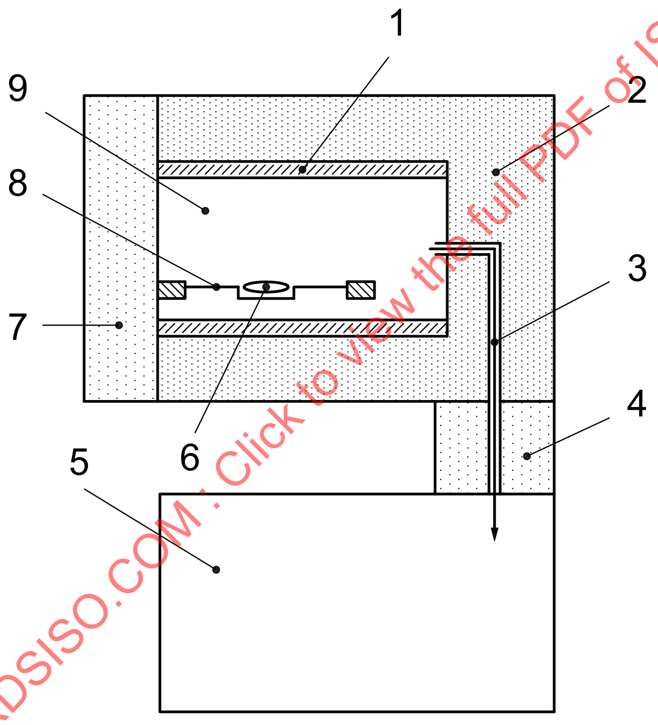
Collect mass spectral data, in total ion current (TIC) mode over the entire run time (some systems could require a short detector delay of a few seconds at the beginning of the run).

Annex B
(informative)

Pyrolysers

B.1 Filament-type pyrolyser

A filament-type pyrolyser comprises a metal (typically platinum) filament on to which the test sample is placed. The filament is positioned inside a heated pyrolysis chamber that is attached to the inlet of the GC–MS system via a heated transfer line. The sample is heated in a flow of helium carrier gas for a few seconds (typically 2 s) and any pyrolysis products are transported to the inlet of the GC–MS system through the heated transfer line for separation and detection. The equipment should be capable of heating to a temperature of at least 800 °C. A schematic representation of a typical system is shown in Figure B.1.



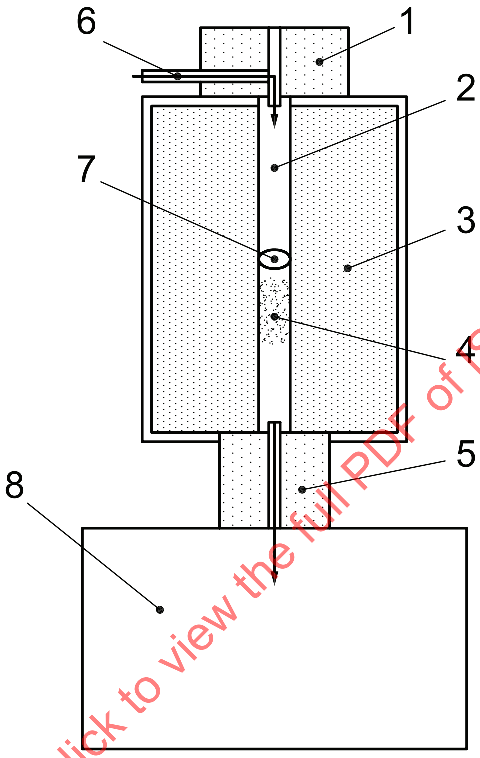
Key

1 glass liner
2 heated pyrolysis chamber block
3 capillary transfer line
4 heated transfer line block
5 GC–MS system
6 sample
7 pyrolyser chamber door
8 platinum filament
9 pyrolysis chamber

Figure B.1 — Schematic representation of a filament-type pyrolyser

B.2 Oven-type pyrolyser

An oven-type pyrolyser comprises a vertical heating tube held in an oven into which the sample is placed. The heating tube is attached to the inlet of the GC–MS system via a heated transfer line. The sample is introduced into the heating tube by injection, or by lowering, via a port at the top and heated in a flow of helium carrier gas for a few seconds (typically 3 s). Any pyrolysis products are transported to the inlet of the GC–MS system through the heated transfer line for separation and detection. The equipment should be capable of heating to a temperature of at least 800 °C. A schematic representation of a typical system is shown in Figure B.2.



Key

1 injection port
2 quartz tube
3 furnace block
4 quartz wool
5 heated transfer line
6 carrier gas inlet
7 sample
8 GC–MS system

Figure B.2 — Schematic representation of an oven-type pyrolyser

Annex C
(informative)

Chromatographic conditions

A carrier gas flow of around 1 ml/min of helium is recommended. The split-splitless injector should be set to split mode. A split flow of around 50 ml/min has been found to be suitable. The oven programme can be optimized as required. A typical oven programme, with a run time of 30 min, is to:

a) set the initial oven temperature at 50 °C and hold for 5 min;

b) increase the oven temperature to 75 °C at a rate of 5 °C/min;

c) increase the oven temperature to 200 °C at a rate of 12,5 °C/min;

d) increase to a final oven temperature of 300 °C at a rate of 25 °C/min and hold for 6 min.

Using this temperature programme and a chromatographic column such as that recommended in A.1.2, the most volatile components have retention times of approximately 1 min.

Annex D
(informative)

System and performance checks

D.1 Aspects to be monitored

The following aspects should be monitored for quality assurance purposes, either through the use of internal system checks or by the analysis of quality assurance materials:

a) overall system performance (to ensure adequate sensitivity and consistency of results);

b) consistent recovery, particularly of semi-volatile components such as bisphenol-A or polycyclic aromatic hydrocarbons;

c) chromatographic resolution, particularly of highly volatile components such as formaldehyde and butadiene;

d) optimum sample loading;

e) interlaboratory or equipment variations.

Quality assurance is of particular importance when setting up, or making significant changes to, test equipment, for example when changing to a different chromatographic column.

D.2 Quality assurance materials

D.2.1 General. Many common substances can be used as quality assurance materials. Examples are given in D.2.2 to D.2.4.

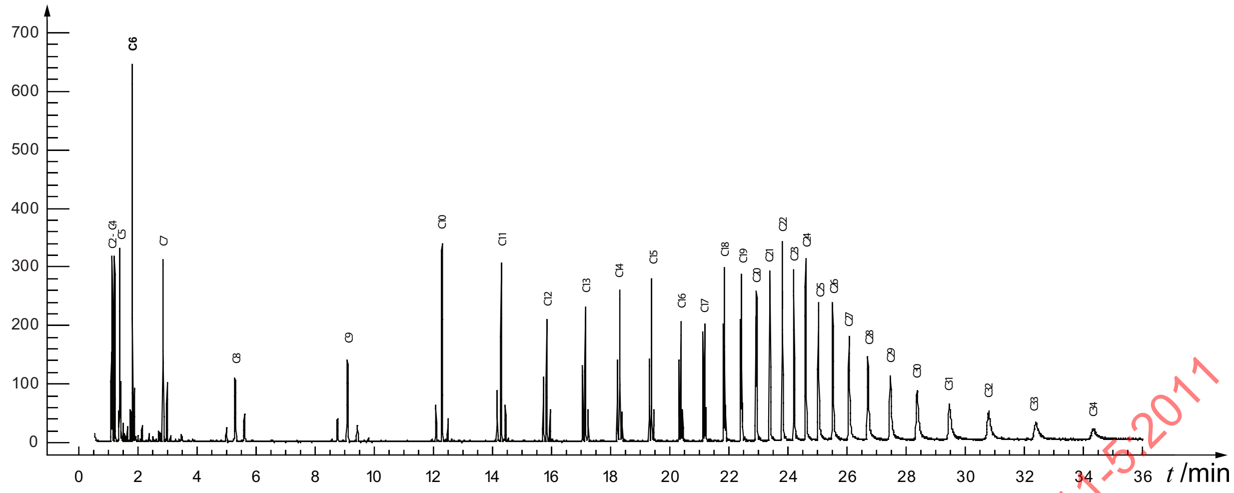
D.2.2 High-density polyethylene (HDPE). This material, when pyrolysed, generates a series of aliphatic hydrocarbons with carbon numbers from 2 to beyond 30. HDPE is therefore useful as a quality assurance material to check for consistent recovery of pyrolysis products over a wide range of volatilities. An example chromatogram obtained from pyrolysis of HDPE is shown in Figure D.1.

D.2.3 Polystyrene solution. This material, typically a 1 mg/ml solution prepared in a suitable solvent, such as dichloromethane, is useful for monitoring system response and sensitivity. A 1 µl aliquot of such a solution, containing 1 µg of polystyrene, can be used as a semi-quantitative check of peak area (see the example test report in Annex E). An example chromatogram obtained from pyrolysis of 1 µg of polystyrene in shown in Figure D.2.

D.2.4 Other substances that can be used as quality control materials for specific components, or groups of components, include epoxy resin (for phenolic components such as phenol or bisphenol-A), polyester resin (for components such as phthalic anhydride) and polyurethane [for isocyanate components such as tolylene diisocyanate (TDI) or methylenediphenyl diisocyanate (MDI)].

D.3 Procedure

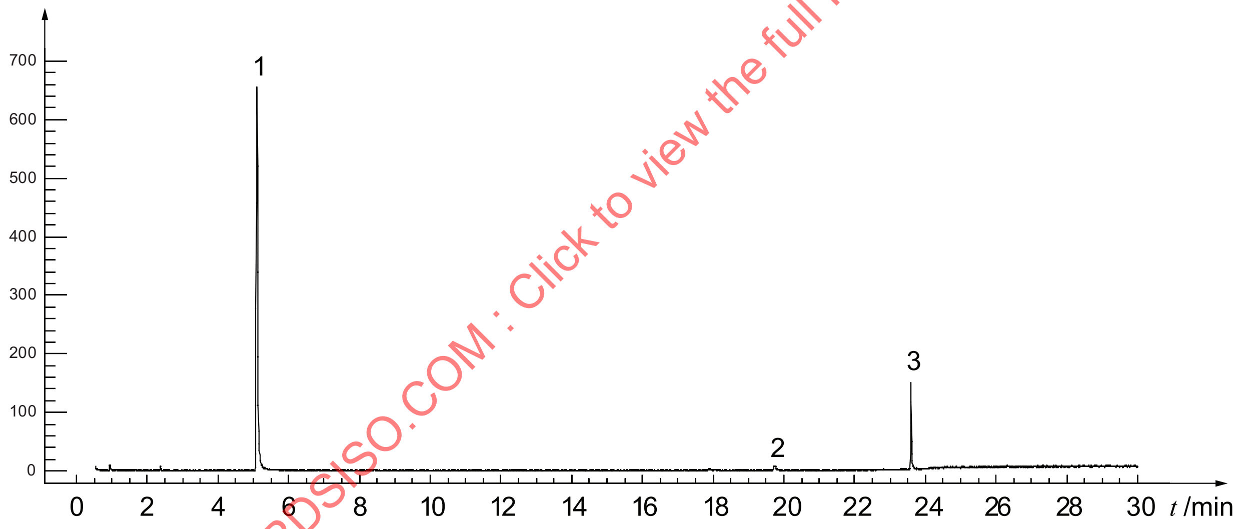
Quality assurance materials should be prepared and analysed in the same way as the test samples, using the appropriate procedures specified in Annex A.



Key

C2 to C34	carbon numbers
t	time

Figure D.1 — Pyrogram of high-density polyethylene (HDPE) at 800 °C



Key

1	styrene
2	styrene dimer
3	styrene trimer
t	time

Figure D.2 — Pyrogram of polystyrene (1 µg) at 600 °C

Annex E
(informative)

Example of a test report

ISO 15011-5	**Date test report issued: 2009-01-01**
Manufacturer: Perfect Primer Manufacturers **Address**: Paint Street, Coatingstown	**Sample preparation**: The shop primer was applied to a metal plate as a coating, with a roller, to a thickness of 20 µm. The coating was allowed to dry for 24 h, a test sample was removed for analysis by light scraping and placed directly on to the pyrolyser filament
Test laboratory: The Best Test House **Address**: Quality Street, Coatingstown	
Trade name: Primer Max	
Generic product type: Alkyd shop primer	**Test method**: AB-123
Lot no.: ABC00123	**Pyrolysis temperatures**: 600 °C; 800 °C
Pyrolyser model/type: P1/filament type	**GC–MS model**: XS1000
Chromatographic details: 30 m × 0,22 mm XP-5 column (0,5 µm); helium carrier gas (1 ml/min); oven programme as per Method AB-123	
Remarks:	

Component	**Test 1** (600 °C)		**Limit value/remarks**
	TIC data		
	Peak area[a]	%	
Phthalic anhydride	27 000	26,5	4 mg/m^3
Aromatic esters	10 600	10,4	5 mg/m^3 [b]
Benzoic acid	9 700	9,5	5 mg/m^3 [b]
Ethylacrolein	6 800	6,7	0,34 mg/m^3 [b]
Methylacrolein	1 400	1,4	0,23 mg/m^3 [b]
Benzene	500	0,5	2,3 mg/m^3
Others	46 000	45,0	—
Total	102 000	100	—

[a] A standard containing 1 µg of polystyrene gave a peak area of 50 000.

[b] Limit value for related compound.