Binders for paints and varnishes

Polyisocyanate resins

General methods of test (ISO 11909 : 1996)
English version of DIN EN ISO 11909

DIN
EN ISO 11909

ICS 87.060.20

Supersedes
June 1998 edition.

Descriptors: Binders, paints, varnishes, polyisocyanate resins, testing.

Bindemittel für Beschichtungsstoffe – Polyisocyanate – Allgemeine Prüfverfahren (ISO 11909 : 1996)

European Standard EN ISO 11909 : 1998 has the status of a DIN Standard.

A comma is used as the decimal marker.

National foreword

This standard has been published in accordance with a decision taken by CEN/TC 139 to adopt, without alteration, International Standard ISO 11909 as a European Standard.

The responsible German body involved in its preparation was the *Normenausschuß Anstrichstoffe und ähnliche Beschichtungsstoffe* (Paints and Varnishes Standards Committee), Technical Committee *Lackrohstoffe*.

The DIN Standards corresponding to the International Standards referred to in clause 2 of the EN are as follows:

International Standard	DIN Standard(s)
ISO 385-1	DIN 12700-1
ISO 648	DIN 12690
ISO 842	DIN V 53242-1, DIN 53242-2 and DIN 53242-3
ISO 1523	DIN 53213-1
ISO 2811	DIN 53217-2
ISO 3219	DIN EN ISO 3219
ISO 3251	DIN EN ISO 3251
ISO 3679	DIN EN 456
ISO 3696	DIN ISO 3696
ISO 4630	DIN ISO 4630
ISO 6271	DIN ISO 6271
ISO 10283	DIN 55956

Amendments

DIN 53185, May 1997 edition, has been superseded by the specifications of EN ISO 11909. As compared with the June 1998 edition, some errors in tables NA.1, 1 and 2 and in Annex A have been corrected.

Previous editions

DIN 53187: 1974-12, 1997-05; DIN EN ISO 11909: 1998-06.

Continued overleaf.
EN comprises 6 pages.

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National Annex NA

Data on precision for the determination of isocyanate content

The values specified in Annex A.7 are based on an interlaboratory test in which four laboratories participated.

Table NA.1: Data on precision

	MDI Propylene Desmodur E22	HDI-Biuret Desmodur N75	TDI adduct or urethane modified TDI Desmodur L75	Isocyanate modified IPDI Vestanat T1890L
$\bar{x}$ [1]	7,79	16,15	13,14	11,99
s [1]	0,01	0,04	0,03	0,05
R (95) [1]	0,04	0,11	0,089	0,13
$\bar{x}$ [2]	7,67	15,99	13,02	11,87
s [2]	0,03	0,06	0,03	0,02
r (95) [2]	0,08	0,15	0,07	0,03
$\bar{x}$ [3]	7,4	16,34	13,17	12,18
s [3]	0,39	0,24	0,13	0,05
r (95) [3]	1,08	0,67	0,35	0,13
$\bar{x}$ [4]	7,57	16,22	13,19	12,03
s [4]	0,04	0,05	0,05	0,05
r (95) [4]	0,12	0,13	0,14	0,13
$\bar{\bar{x}}$	7,61	16,18	13,13	12,02
s_r (mean)	0,2	0,13	0,07	0,04
r (95) for s_r	0,55	0,36	0,19	0,11
s_R	0,24	0,18	0,1	0,12
R (95)	0,67	0,49	0,27	0,34

In the table

$\bar{x}$ [1]	is the mean value for laboratory No. 1
s [1]	is the repeatability standard deviation for laboratory No. 1
r (95) [1]	is the repeatability limit for laboratory No. 1 with a confidence level of 95 %
$\bar{x}$ [2]	is the mean value for laboratory No. 2
s [2]	is the repeatability standard deviation for laboratory No. 2
r (95) [2]	is the repeatability limit for laboratory No. 2 with a confidence level of 95 %
$\bar{x}$ [3]	is the mean value for laboratory No. 3
s [3]	is the repeatability standard deviation for laboratory No. 3
r (95) [3]	is the repeatability limit for laboratory No. 3 with a confidence level of 95 %
$\bar{x}$ [4]	is the mean value for laboratory No. 4
s [4]	is the repeatability standard deviation for laboratory No. 4
r (95) [4]	is the repeatability limit for laboratory No. 4 with a confidence level of 95 %
$\bar{\bar{x}}$	is the overall mean
s_r (mean)	is the inter-laboratory standard deviation, averaged for all laboratories
r (95) for s_r	is the inter-laboratory repeatability limit with a confidence level of 95 %, averaged for all laboratories
S_R	is the repeatability deviation
R (95)	is the inter-laboratory repeatability limit with a confidence level of 95 %

National Annex NB

Standards referred to

(and not included in **Normative references**)

DIN 12690	Classes A and B one-mark bulb pipettes for laboratory use
DIN 12700-1	Burettes for laboratory use – General requirements
DIN 53213-1	Determination of the flashpoint of paints and varnishes and similar solvent-borne products by the closed cup method
DIN 53217-1	Determination of density of paints, varnishes and similar coating materials – Survey of test methods
DIN V 53242-1	Sampling of raw materials for paints and varnishes – Concepts and general information
DIN 53242-2	Sampling of liquid raw materials for paints and varnishes
DIN 53242-3	Sampling of highly viscous raw materials for paints and varnishes
DIN 55956	Binders for paints and varnishes – Determination of monomer diisocyanates in polyisocyanates
DIN EN 456	Paints, varnishes and related products – Determination of flashpoint by the rapid equilibrium method (modified version of ISO 3679 : 1983)
DIN EN ISO 3219	Polymers and resins in the liquid state or as emulsions or dispersions – Determination of viscosity using a rotational viscometer with defined shear rate (ISO 3219 : 1993)
DIN EN ISO 3251	Paints and varnishes – Determination of non-volatile matter of paints, varnishes and binders for paints and varnishes (ISO 3251 : 1993)

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN ISO 11909

April 1998

ICS 87.060.20

Descriptors: Binders, paints, varnishes, polyisocyanate resins, testing.

English version

Binders for paints and varnishes

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General methods of test
(ISO 11909 : 1996)

Liants pour peintures et vernis – Résines de polyisocyanate – Méthodes générales d'essai (ISO 11909 : 1996)

Bindemittel für Beschichtungsstoffe – Polyisocyanate – Allgemeine Prüfverfahren (ISO 11909 : 1996)

This European Standard was approved by CEN on 1998-03-26.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

The European Standards exist in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, the Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom.

CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart 36, B-1050 Brussels

Ref. No. EN ISO 11909 : 1998 E

Foreword

International Standard

ISO 11909 : 1996 Binders for paints and varnishes – Polyisocyanate resins – General methods of test,

which was prepared by ISO/TC 35 'Paints and varnishes' of the International Organization for Standardization, has been adopted by Technical Committee CEN/TC 139 'Paints and varnishes', the Secretariat of which is held by DIN, as a European Standard.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, and conflicting national standards withdrawn, by October 1998 at the latest.

In accordance with the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard:

Austria, Belgium, the Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom.

Endorsement notice

The text of the International Standard ISO 11909 : 1996 was approved by CEN as a European Standard without any modification.

NOTE: Normative references to international publications are listed in Annex ZA (normative).

1 Scope

This International Standard details general test methods for polyisocyanate resins and solutions of polyisocyanate resins intended for use as binders in paints, varnishes and related products.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 842:1984, *Raw materials for paints and varnishes — Sampling.*

ISO 1523:1983, *Paints, varnishes, petroleum and related products — Determination of flashpoint — Closed cup equilibrium method.*

ISO 2811:1974, *Paints and varnishes — Determination of density.*

ISO 3219:1993, *Plastics — Polymers/resins in the liquid state or as emulsions or dispersions — Determination of viscosity using a rotational viscometer with defined shear rate.*

ISO 3251:1993, *Paints and varnishes — Determination of non-volatile matter of paints, varnishes and binders for paints and varnishes.*

ISO 3679:1983, *Paints, varnishes, petroleum and related products — Determination of flashpoint — Rapid equilibrium method.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 4630:1981, *Binders for paints and varnishes — Estimation of colour of clear liquids by the Gardner colour scale.*

ISO 6271:1981, *Clear liquids — Estimation of colour by the platinum-cobalt scale.*

ISO 10283:—[1], *Binders for paints and varnishes — Determination of monomeric diisocyanates in polyisocyanate resins.*

3 Definition

For the purposes of this International Standard, the following definition applies.

1) To be published.

3.1 polyisocyanate resin: Synthetic resin containing reactive isocyanate groups and based on aromatic, aliphatic or cycloaliphatic isocyanates.

4 Properties and test methods

Unless otherwise agreed, the properties to be measured and the test methods to be used shall be as given in table 1.

Table 1 — Properties and test methods

Property	Test method
Colour	ISO 6271 (Platinum-cobalt scale) or ISO 4630 (Gardner colour scale)
Viscosity	ISO 3219
Non-volatile matter	ISO 3251, together with table 2 below
Flashpoint	ISO 1523 or ISO 3679
Density	ISO 2811
Isocyanate content	Annex A of this International Standard
Monomeric diisocyanate content	ISO 10283

Table 2 — Test conditions for the determination of non-volatile matter

Resin basis[1)]	Period of heating h	Test temperature[2)] °C
HDI biuret	1	80
HDI cyanurate	1	105
TDI and MDI polyisocyanates, adducts and prepolymers	1	125
IPDI polyisocyanates	1	150

1) HDI = Hexamethylene diisocyanate
TDI = Tolylene diisocyanate
MDI = Diphenyl-4-methane-4,4'-diisocyanate
IPDI = Isophorone diisocyanate

2) For binders dissolved in highly volatile solvents, a lower temperature may be used.

Annex A
(normative)

Determination of isocyanate content (percentage by mass of isocyanate groups)

A.1 Principle

The polyisocyanate resin is reacted with excess dibutylamine. The excess dibutylamine is then titrated with hydrochloric acid, either using bromophenol blue as the indicator or potentiometrically.

A.2 Reagents

During the analysis, use only reagents of recognized analytical grade, and only water of at least grade 3 purity as defined in ISO 3696.

A.2.1 Dibutylamine, solutions containing about 2 mol/l and about 0,2 mol/l, respectively.

To prepare the approximately 2 mol/l solution, dissolve 65 g of water-free distilled dibutylamine (boiling point 157 °C to 162 °C at 1,033 kPa) in toluene (A.2.2) in a 250 ml one-mark volumetric flask, make up to the mark with the same toluene and mix well. Standardize this solution by titrating a 20 ml portion with 1 mol/l hydrochloric acid (see A.2.3).

Prepare the approximately 0,2 mol/l solution in analogous fashion, starting with 6,5 g of dibutylamine. Standardize this solution by titrating a 20 ml portion with 0,1 mol/l hydrochloric acid (see A.2.3).

A.2.2 Toluene, previously dried over calcium chloride and filtered.

A.2.3 Hydrochloric acid, c(HCl) = 1 mol/l or 0,1 mol/l.

A.2.4 Ethanol, water-free.

A.2.5 Bromophenol blue, solution.

Triturate 1 g of bromophenol blue in a mortar with 1,5 ml of sodium hydroxide solution, c(NaOH) = 1 mol/l, and dissolve in a mixture of 20 ml of ethanol (A.2.4) and 10 ml of water.

A.3 Apparatus

Ordinary laboratory apparatus and glassware, complying with the requirements of ISO 385-1 and ISO 648, together with the following:

A.3.1 Conical flasks, capacity 250 ml and 500 ml, with ground-glass stoppers.

A.3.2 Potentiometric titration apparatus, fitted with a glass electrode and a reference electrode (for use with highly coloured resins — see A.5).

A.4 Sampling

Take a representative sample of the product to be tested, as described in ISO 842.

A.5 Procedure

Carry out the determination in duplicate.

By reference to table A.1, select the appropriate mass of test portion. If the approximate isocyanate content is not known, carry out a preliminary determination using a test portion of 3,5 g.

Weigh, to the nearest 1 mg (or 0,1 mg — see below), the appropriate mass of test portion into a 500 ml conical flask and dissolve it in 25 ml of toluene (A.2.2), if necessary with slight heating. After cooling to room temperature, pipette 20 ml of the appropriate dibutylamine solution (A.2.1) into the flask. Close the flask and allow to stand for 15 min, swirling occasionally. Dilute with 150 ml of ethanol (A.2.4), add a few drops of bromophenol blue solution (A.2.5) and titrate with the appropriate hydrochloric acid (A.2.3) until the colour changes to yellow. If separation occurs during the titration, add further ethanol.

Table A.1 — Mass of test portion and permitted difference between results

Isocyanate content % (*m/m*)	Maximum mass of test portion g	Permitted difference between individual values and mean value % (absolute)
below 1	25	0,15
1 to 10	12	
above 10 to 20	6	
above 20 to 25	5	
above 25 to 30	4	0,2
above 30 to 40	3,5	
above 40 to 50	3	

If 0,1 mol/l hydrochloric acid is used, the test portion shall be weighed to the nearest 0,1 mg, its mass shall be about one-tenth that in table A.1 and the 0,2 mol/l dibutylamine solution shall be used.

In the case of highly coloured resins, titrate potentiometrically.

A.6 Expression of results

Calculate the isocyanate content IC, expressed as a percentage by mass, using the following equation:

$$IC = \frac{(V_1 - V_2) \times c}{m} \times 4{,}2$$

where

V_1 is the volume, in millilitres, of hydrochloric acid required for the standardization of the dibutylamine solution;

V_2 is the volume, in millilitres, of hydrochloric acid required for the determination;

c is the actual concentration, in moles per litre, of the hydrochloric acid used;

m is the mass, in grams, of the test portion.

A.7 Precision

NOTE 1 The precision data were obtained with methanol as solvent.

The repeatability r and the reproducibility R depend on the product tested.

	Repeatability (*r*)	Reproducibility (*R*)
IPDI trimer NCO content about 12 % (*m/m*)	0,11	0,34
HDI biuret NCO content about 16 % (*m/m*)	0,36	0,50
TDI adduct NCO content about 13 % (*m/m*)	0,19	0,27
MDI prepolymer NCO content about 7 % (*m/m*)	0,55	0,67

A.8 Test report

The test report shall contain at least the following information:

a) all details necessary to identify the product tested;

b) a reference to this International Standard (ISO 11909);

c) the result of the test, as indicated in clause A.6;

d) any deviation from the test method specified;

e) the date of the test.

Annex ZA (normative)
Normative references to international publications with their relevant European publications

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

Publication	Year	Title	EN	Year
ISO 3219	1993	Plastics - Polymers/resins in the liquid state or as emulsions or dispersions - Determination of viscosity using a rotational viscometer with defined shear rate	EN ISO 3219	1994
ISO 3251	1993	Paints and varnishes - Determination of non-volatile matter of paints, varnishes and binders for paints and varnishes	EN ISO 3251	1995
ISO 3679	1983	Paints, varnishes, petroleum and related products - Determination of flashpoint - Rapid equilibrium method	EN 456	1991
ISO 3696	1987	Water for analytical laboratory use - Specification and test methods	EN ISO 3696	1995