

Technical Requirement for Environmental Products

The Certificable Technical Requirement for Environmental Labelling Products

HBC 18—2003

Adhesive

Replace **HJBZ 28—1998**

1 Scope

This technical requirement specifies definition, basic requirements, technical contents and test method for environmental labelling products of adhesive.

This technical requirement shall apply to structural adhesive, water soluble packing adhesive, adhesive and finishing agent for shoes and cases, adhesive used in wood industry and adhesive used for carpet.

2 Standards cited

Provisions in the following standards are cited in this technical requirement, and therefore form the provisions of the standard. When this technical requirement is published, all of the version of these standards are valid. All of these standards would be revised, and parties use this technical requirement should take into consideration the possibility of using the latest edition of the following standards.

GB/T 14074.13-93 Testing methods for wood adhesives and their resins--Method for determination of free phenol content

GB/T 14074.16-93 Testing methods for wood adhesives and their resins--Method for determination of free formaldehyde content

GB/T 14732-93 Wood adhesives--urea-formaldehyde, phenol-formaldehyde and melamine-formaldehyde resins

GB/T 18446-2001 Using gas chromatography to mensurate carbamate prepolymer and unreacted toluene diisocyanate (TDI) monomer in coatings solution

GB/T 18583-2001 Indoor decorating and refurbishing materials--Limit of harmful substances of adhesives

3 Basic requirements

3.1 Quality of products should meet requirement for each product quality standard;

3.2 Pollutant emission of the company should be obliged to conform with pollutant emission standards nationally or locally.

4 Technical contents

4.1 General requirement

No toxic organic solvent such as benzene, toluene, xylene, ethylbenzene, halohydrocarbon should be used in process of production.

4.2 Requirement for adhesive of wood industry

Free formaldehyde and free phenol concentrations in products should meet relevant requirement in GB/T 14732.

4.3 Requirement for water soluble adhesive of packaging

4.3.1 Total concentration of benzene, toluene, xylene in product should be less than 1000mg/kg, while concentration of benzene should be less than 100mg/kg.

4.3.2 Content of halohydrocarbon in product (in Dichloroethane) should be less than 1000mg/kg.

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4.4 Requirement for adhesive and finishing agent used by packaging of shoes and cases

Limitation of hazardous matters in products should meet requirement in table 1.

Table 1 Limitation of hazardous matters in adhesive and finishing agent for packaging shoes and cases

Items	Indexes
Benzene(mg/kg) ≤	100
Toluene + xylene(mg/kg) ≤	5000
TDI(mg/kg) (It is necessary to test adhesive used by polyurethane shoes) ≤	5000
Halohydrocarbon (in Dichloroethane)(mg/kg) ≤	2000
Total volatile organic compounds(g/L) ≤	700

4.5 Requirement for structural adhesive

4.5.1 Limitation for hazardous matter in water soluble structural adhesive should meet requirement in table 2.

Table 2 Limitation for hazardous matters in water soluble structural adhesive

Items	Indexes					
	ACRYLIC adhesive	Formal adhesive	PVA adhesive	Rubber adhesive	Polyurethanes adhesive	Other adhesive
Free formaldehyde (mg/kg) ≤	100	100	100	100	—	100
Benzene (mg/kg) ≤	100					
Toluene + xylene (mg/kg) ≤	500					
Halohydrocarbon (mg/kg) ≤	500					
TVOC (g/L) ≤	50					

4.5.2 Limitation for hazardous matter in solvent structural adhesive should meet requirement in table 3.

Table 3 Limitation for hazardous matters in solvent structural adhesive

Items	Indexes			
	Lefkoweld	Rubber adhesive	Polyurethanes adhesive	Other adhesive
Free formaldehyde (mg/kg) ≤	—	500	—	500
Benzene (mg/kg) ≤	2000			
Toluene + xylene (mg/kg) ≤	2000			
TDI (mg/kg) ≤	—	—	5000	—
Acetone (mg/kg) ≤	750			
Halohydrocarbon (in dichloromethane)(mg/kg) ≤	2000			
TVOC (g/L) ≤	750			

4.6 Requirement for adhesive used by carpet

4.6.1 Content of volatilizable unsaturated compounds in product should be less than 500mg/kg.

4.6.2 Content of ethylbenzene in product should be less than 100mg/kg.

5 Test

5.1 Provisions in 4.2 of technical contents should be verified by the method of GB/T 14074.13—93, GB/T 14074.16—93.

5.2 Provisions on benzene, toluene, xylene, ethylbenzene, halohydrocarbon in 4.3.1, 4.3.2

of technical contents should be determined according to annex B.

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5.3 Provisions in 4.4 of technical contents should be tested by method in GB/T 18583—2001.

5.4 Halohydrocarbon specified in 4.4 of technical contents should be determined according to annex C.

5.5 Provisions on free formaldehyde, benzene, toluene, xylene, ethylbenzene, total volatile organic compounds specified in 4.5.1, 4.5.2 of technical contents should be determined by the method in GB/T 18583—2001.

5.6 Halohydrocarbon, acetone specified in 4.5.1, 4.5.2 of technical contents should be determined according to annex A.

5.7 Provisions on TDI in 4.4, 4.5.2 of technical contents should be determined by method in GB/T 18583—2001.

5.8 Determination for volatilizable unsaturated compound, ethylbenzene specified in 4.6.1, 4.6.2 Of the technical contents should accord with annex D.

Annotations:

This technical requirement has been prepared by Department of science and technology, standards of State Environment Protection Administration.

The State Environment Protection Administration keeps the right of interpretation for this technical requirement.

Annex A (annex of the standard)
Determination for halohydrocarbon, acetic in solvent adhesive for building

A.1 Instrument and reagent

A.1.1 Reagent

Carrier gas: high purity nitrogen

Dichloromethane, 1, 1-Dichloroethane, 1, 2-Dichloroethane, 1, 1, 1-trichloroethane, 1, 1, 2-trichloroethane: chromatographically pure

Chloroform, carbon tetrachloride: analytically pure

Methanol: super grade pure

Bromopropane ^{note 1}: analytically pure

Bromopropane solution: weigh ~1g bromopropane (4.9) accurately to 0.2mg; dilute it by methanol in 50ml measuring flask.

A.1.2 Instrument

Gas chromatograph: with electron capture detector;

Chromatographic column: nonpolar adsorption capillary column (such as HP-1, DB-1:30m × 0.25mm × 0.25 μm (membrane thickness)), or whatever chromatographic column which is able to completely separate the substances being tested.

Microinjector, 1 μl.

A.1.3 Chromatographic operation condition

Chromatographic condition ^{note 2}:

Sample mode: split stream sampling;

Velocity of carrier gas flow: 1.0ml/min;

Column temperature: temperature programming, 42 °C, keep for 9min; then raise temperature to 250 °C at 50 °C/min, and keep for 2min;

Injection port temperature: 250 °C;

Detector temperature: 300 °C;

Make-up gas flow: 30ml/min.

Chromatographic column aging: age 16h at 280 °C.

A.2 Measurement procedure:

A.2.1 Determine retention time of substances being tested: inject 0.2 μl standard solution that contains all components being tested after the instrument is stable in the gas chromatograph operational condition; record the peak order and retention time of each standard component.

A.2.2 Quantify the components in the sample: weigh ~1g sample and dilute it in 25 ml measuring flask by methanol; determine it in selected testing condition, and determine what the components are.

A.2.3 Determine the response factor of component: weigh ~1g standard reagent of the component detected in A.2.2 with accuracy of 0.2mg and its corresponding bromopropane solution note 3, dilute it by methanol in 50ml middle according to linear range of the dilution (i.e., the concentration of the agent should be within linear scale, in case of being out of the range, it should increase the dilution rate or dilute it for several times); and shake up. Inject 0.2 μl sample by microinjector, and record its chromatogram.

Calculate the response factor R of component being tested:

$$R = \frac{A_i W_s}{W_i A_s} \quad (1)$$

Where: W_s — Weight of bromopropane, g; W_i — Weight of component being tested, g; A_i — Peak area of component being tested; A_s — Peak area of bromopropane.

Take R value as average of the two results, and its relative deviation should be less than 5%, and round R to 3-digit significant figure.

A.2.4 Sample measurement:

Accurately weigh ~1g sample (with accuracy of 0.0002g), add 1ml bromopropane solution in 50ml measuring flask; and dilute it by methanol to the scale. The added amount of bromopropane solution would be proper if peak area of it in chromatograph is approximately equals to that of component being tested. Start to test after the instrument stabilized.

A.3 Calculation

A.3.1 Calculate content of component being tested

Calculate contents of component being tested in adhesive, C_i , according to the following equation (mg/kg):

$$C_i = \frac{A_i \times W_s}{A_s \times S_{\text{样}} \times R} \times 10^6 \quad (2)$$

Where, A_i —— Peak area of component being tested; A_s —— Peak area of bromopropane;
 W_s —— Weight of bromopropane, g; $W_{\text{样}}$ —— Weight of component being tested, g;

R —— Response factor.

Measurement outcome should be the mean of the two measurements, and the relative deviation should be less than 5%.

A.3.2 Calculation of halohydrocarbon content $W_{\text{卤代烃}}$ in sample (in dichloromethane, mg/kg)

$$W_{\text{卤代烃}} = W_{\text{二氯甲烷}} + 0.858 \times (W_{1,1\text{-二氯乙烷}} + W_{1,2\text{-二氯乙烷}}) + 0.637 \times (W_{1,1,1\text{-三氯乙烷}} + W_{1,1,2\text{-三氯乙烷}}) + 0.552 \times W_{\text{四氯甲烷}}$$

0.858—Ratio of relative molecular weights of dichloromethane to Dichloroethane

0.711—Ratio of relative molecular weights of dichloromethane to chloroform

0.637—Ratio of relative molecular weights of dichloromethane to trichloroethane

0.552—Ratio of relative molecular weights of dichloromethane to carbon tetrachloride
 Calculation results round to ten's place.

Note1: No internal standard bromopropane should be contained in the sample. In case of quantitatively measuring components in the sample, if the sample does not contain a certain component being tested, this component could be also used as internal standard.

Note2: Because the chromatographic condition varies in different experiment conditions, the optimum condition should be established according to the model of gas chromatograph and its performance.

Note3: The response value in chromatograph of the added bromopropane internal standard solution should be equivalent to that of components being tested; moreover, they should be within the linear range.

Annex B (Annex of the standard)

Test method of benzene, toluene, xylene, ethylbenzene, halohydrocarbon in water soluble adhesive for packaging

B.1 Material

B.1.1 Reagent

Carrier gas: high purity nitrogen

Combustion gas: hydrogen gas, degree of purity > 99.8%

Combustion-supporting gas: air

Dichloromethane, 1, 1- Dichloroethane, 1, 2- Dichloroethane, 1, 1, 1 - trichloroethane, 1, 1, 2 - trichloroethane: analytically pure

Carbon tetrachloride, benzene, toluene, xylene (mixture of o-xylene, m-xylene, p-xylene): analytically pure

Ethylbenzene, methanol: analytically pure

B.1.2 Instrument

Gas chromatograph: any chromatograph with hydrogen flame ionization detector that could meet the the analysis condition 6; benzene detection limit $D \leq 1 \times 10^{-9}$ g/s

Chromatographic column: nonpolar adsorption capillary column, 30m × 0.25mm × 0.25 μm

(membrane thickness) (such as HP -1, DB -1);

Sample injector: head-space sampling postulationalvice which could meet the requirement of analysis condition.

Head-space sample bottle: 20ml

Disposable syringe, 5ml

Chromatographic operational condition: head-space sample injector, Temperature of water bath: 80°C; equilibration period: 90min; volume of quantified tube: 10 μ l, temperature 85°C;

Temperature of gas transfer lines: 85°C.

Gas chromatograph condition: split stream sampling; split ratio 80:1 (the flow ratio could be 20:1 if it's without head-space sample injector; 80:1 for with head-space sample injector); velocity of carrier gas flow: 1.0ml/min; hydrogen flow rate: 30ml/min; air-flow rate: 380ml/min.

Column temperature: temperature programming, 40 °C, keep for 4min; then raise temperature to 150°C at 10°C/min, and keep for 5 min; injection port temperature: 150 °C;

Detector temperature: 280°C;

Make-up gas flow rate: 10ml/min.

Chromatographic column aging: age 16h at 280°C.

B. 2 Measurement procedure

B. 2.1 Determination for retention time of component being tested

Inject 1 μ l standard solution which contains all the components being tested after the instrument is stabilized in the gas chromatograph operational condition; record the peak order and retention time of standard component being tested.

B. 2.2 Quantify the components in sample

Add ~5ml sample into the sample bottle; test it according to the selected condition in B. 2.1; determine the components being tested.

B. 2.3 Preparing mixed standard solution

Prepare mixed standard solution of tested components by procedure of B. 2.2 by using methanol as solvent.

B. 2.4 Test the sample

Inject ~5ml sample separately into four sample bottles with syringe, weigh it accurately to 0.0002g; sample difference in each sample bottle should be less than 1%; inject 10 μ l, 20 μ l, 30 μ l mixed standard solution by microinjector into three of the sample bottles, and seal the sample bottles as soon as possible; the standard solution of amount added should be approximately equivalent as for the peak area in chromatograph to that of components being tested.

B. 2.5 Put the weighed sample bottle into head-space sample injector. Test according to the condition of B. 2.1, and calculate the test result.

B. 3 Calculation

B. 3.1 Calculate equation of linear regression

Calculate regression equations according to the concentration, W_i , of standard components in sample and its corresponding peak area, A_i .

$$A_i = a \times W_i + b \quad (4)$$

A_i — Peak area of component i being tested; ; W_i — Concentration of standard component i in the sample, mg/kg;

a — Slope of regression equation; b — Intercept of regression equation.

B. 3.2 Calculation on concentration of substances being tested

When $A_i = 0$, $W_{si} = -b/a$ is the concentration of component being tested in the sample (mg/kg)

W_{si} — Concentration of substance i in water soluble adhesive, mg/kg.

B. 3.3 Calculation of halohydrocarbon content in sample (in dichloromethane, mg/kg)

$$W_{\text{卤代烃}} = W_{\text{二氯甲烷}} + 0.858 \times (W_{1.1.1\text{-二氯乙烷}} + W_{1.2\text{-二氯乙烷}}) + 0.637 \times (W_{1.1.1\text{-三氯乙烷}} + W_{1.1.2\text{-三氯乙烷}}) + 0.552 \times W_{\text{四氯甲烷}}$$

0.858—Ratio of relative molecular weights of dichloromethane to Dichloroethane

0.711—Ratio of relative molecular weights of dichloromethane to chloroform

0.637—Ratio of relative molecular weights of dichloromethane to trichloroethane

0.552—Ratio of relative molecular weights of dichloromethane to carbon tetrachloride
Calculation outputs for benzene series matters should round to unit's order, and for halohydrocarbon, it should round to ten's place.

Annex C (Annex of the standard)

Test method of halohydrocarbon in adhesive and finishing agent for packaging shoes and cases

C.1 Instrument and reagent

C.1.1 Reagent

Carrier gas: high purity nitrogen

Dichloromethane, 1, 1-Dichloroethane, 1, 2-Dichloroethane, 1, 1, 1-trichloroethane, 1, 1, 2-trichloroethane: chromatographically pure

Chloroform, carbon tetrachloride: analytically pure

Methanol: super grade pure

Bromopropane^{note 1}: analytically pure

Bromopropane solution: weigh ~1g bromopropane accurately to 0.2mg; dilute it by methanol in 50ml measuring flask.

C.1.2 Instrument

Gas chromatograph: with electron capture detector;

Chromatographic column: nonpolar adsorption capillary column (such as HP-1, 30m×0.25mm×0.25μm (membrane thickness), or other whatever chromatographic column which could completely separate the substances being tested.

Microinjector, 1μl.

C.1.3 Chromatographic operation condition

Chromatographic condition^{note 2}:

Sample mode: split stream sampling;

Velocity of carrier gas flow: 1.0ml/min;

Column temperature: temperature programming, 42°C, keep for 9min; then raise temperature to 250°C at 50°C/min, and keep for 2min;

Injection port temperature: 250°C; detector temperature: 300°C

Make-up gas flow rate: 30ml/min.

Chromatographic column aging: age 16h at 280°C.

C.2 Measurement procedure:

C.2.1 Determination for retention time of substances being tested: inject 0.2μl standard solution that contains all of the substances being tested, record the peak order and retention time of each standard component being tested.

C.2.2 Quantify the components in the sample: weigh ~1g sample and dilute it in 25 ml measuring flask by methanol; determine it in selected testing condition, and determine what the components are.

C.2.3 Determination for response factor of the substances being tested

C.2.3 Determine the response factor of component: weigh ~1g standard reagent of the component detected in C.2.2 with accuracy of 0.2mg and its corresponding bromopropane solution^{note 3}, dilute it by methanol in 50ml middle according to linear range of the dilution (i.e., the concentration of the agent should be within linear scale, in case of being out of the range, it should increase the dilution rate or dilute it for several times); and shake up. Inject 0.2μl sample with microinjector, and record the chromatogram.

Calculate the response factor R of component being tested:

$$R = \frac{A_i W_s}{W_i A_s} \quad (6)$$

Where, W_s — Weight of bromopropane, g; W_i — Weight of component being tested, g;

A_i —Peak area of component being tested; ; A_s —Peak area of bromopropane.

Take R value as average of the two results, and its relative deviation should be less than 5%, round to 3-digit significant figure.

C.2.4 Sample measurement:

Accurately weigh ~1g sample (with accuracy of 0.0002g), add 1ml bromopropane solution in 50ml measuring flask; and dilute it by methanol to the scale. The added amount of bromopropane solution would be proper if peak area of it in chromatograph is approximately equals to that of component being tested. Start to test after the instrument stabilized.

C.3 Calculation

C.3.1 Calculate content of component being tested

Calculate contents of component being tested, C_i (mg/kg), in coating according to the following equation:

$$C_i = \frac{A_i \times W_s}{A_s \times S_{\text{样}} \times R} \times 10^6 \quad (7)$$

Where, A_i — Peak area of component being tested;

A_s — Peak area of bromopropane;

W_s — Weight of bromopropane, g;

$W_{\text{样}}$ — Weight of component being tested, g;

R — Response factor.

Measurement outcome should be the mean of the two measurements, and the relative deviation should be less than 5%.

C.3.2 Calculation of halohydrocarbon content $W_{\text{卤代烃}}$ in sample (in dichloromethane, mg/kg)

$$W_{\text{卤代烃}} = W_{\text{二氯甲烷}} + 0.858 \times (W_{1,1\text{-二氯乙烷}} + W_{1,2\text{-二氯乙烷}}) + 0.637 \times (W_{1,1,1\text{-三氯乙烷}} + W_{1,1,2\text{-三氯乙烷}}) + 0.552 \times W_{\text{四氯甲烷}}$$

0.858—Ratio of relative molecular weights of dichloromethane to Dichloroethane

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0.637—Ratio of relative molecular weights of dichloromethane to trichloroethane

0.552—Ratio of relative molecular weights of dichloromethane to carbon tetrachloride

Calculation results round to ten's place.

Note1: No internal standard bromopropane should be contained in the sample. In case of quantitatively measuring components in the sample, if the sample does not contain a certain component being tested, this component could be also used as internal standard.

Note2: Because the chromatographic condition varies in different experiment conditions, the optimum condition should be established according to the model of gas chromatograph and its performance.

Note3: The response value in chromatograph of the added bromopropane internal standard solution should be equivalent to that of components being tested; moreover, they should be within the linear range.

Annex D (Annex of the standard)

Analytic method of volatile unsaturates and ethylbenzene in adhesive for carpet

D.1 Experiment condition

D.1.1 Instrument equipment

Instrument: gas chromatograph with FID

Fused quartz capillary column: 30m long, 0.53mm in diameter, inner-column is coated with 1-5 μ m dimethyl polysiloxane

Microinjector: 10 or 50 μ L

Analytical balance: with 0.0001g accuracy

D.1.2 Reagent

De-ionized water, ethyl cyanide (analytically pure), standard sample containing component to be tested (analytically pure).

D.2 Experimental procedure

D.2.1 Internal standard sample and preparation of sample to be tested

Preparation of ethyl cyanide standard solution: transfer about 800mL de-ionized water into

1L measuring flask, add in 0.3000g ethyl cyanide; add in water to the scale, and shake up; store it after sealing it.

Preparation of sample to be tested: weigh 10.0g sample to be tested; add in 30mL ethyl cyanide standard solution, stir completely after sealing.

D.2.2 Determination for relative response factor

Transfer a given mass of standard sample containing component to be tested into a sample to be background; quantify ethyl cyanide standard solution added; seal it and stir; test it by chromatography.

Calculate relative response factor from peak area of each component according to the following equation:

$$R_f = \frac{A_s \times W_v}{A_v \times W_s} \quad (9)$$

Where, R_f —Relative response factor relative to internal standard of the volatile component to be tested; A_s —Area of internal standard (ethyl cyanide);

A_v —Peak area of volatile component to be tested; W_v —Mass of internal standard (ethyl cyanide); W_s —Mass of volatile component to be tested

D.2.3 Determination for concentration of component to be tested

Add 30.0g internal standard (ethyl cyanide) solution into 10.0g sample; seal it and stir completely; inject 1 μ L; measure their peak areas under the preset chromatographic conditions; measure it in specified condition, and get the peak areas of internal standard and each component in sample.

Calculate concentration of component according to the following equation:

$$C_v = \frac{A_v \times R_f \times C_s \times W_v}{A_s \times W_d} \quad (10)$$

Where, C_v —Concentration of component to be tested (mg/kg); C_s —Internal standard concentration of internal standard solution (mg/kg);

A_v —Peak area of related volatile substances; A_s —Peak area of internal standard;

W_v —Mass of internal standard solution in diluted sample, g (about 30g);

W_d —Mass of original polymer dispersion/ latexes, g (about 10g),

R_f —Relative response factor relative to internal standard of the component to be tested;

Repeat the determination at least two times; and get the mean concentration of component to be tested.