The Restriction of Hazardous Materials in Polyvinyl Chloride Artificial Leather

Draft for Approval

Issued on: xx-xx-xxxx To be implemented from: xx-xx-xxxx

Issued by:
General Administration of Quality Supervision, Inspection and Quarantine of the People’s Republic of China
Standardization Administration of the People’s Republic of China
Preamble

Chapter 3 of the present standards is mandatory, others are recommendatory.

From xx-xx-200x, the present standards should be implemented by manufacturers in the production of their products. From xx-xx-200x, marketing of products which do not meet the present standards will not be allowed. Polyvinyl chloride artificial leathers are commonly used in people’s daily life. The present standards are made to protect human health, restrict the contents of hazardous materials and make relevant improvements to the environment.

The standards are proposed by the China National Light Industry Council.

The standards are under the administrative authority of the National Plastics Standardization Technical Committee.

The major entity involved in drafting the present standards is: Shanghai Yanchang Plastics Co., Ltd.

The entities participating the standards’ drafting are:

- China National Inspection Centre of Plastics Products (Beijing)
- Foshan Plastics Group Co., Ltd. – Shuanglong Branch

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1. Scope

The present standards stipulate the restriction of vinyl chloride monomer, soluble lead, soluble cadmium and other volatile substances contained in polyvinyl chloride artificial leather, testing methods, sampling as well as inspection rules.

The present standards apply to polyvinyl chloride artificial leather of foamed or non-foamed form and with base material or without base material (hereinbelow “artificial leather” for short), produced by coating, rolling and compounding processes with the polyvinyl chloride resin used as main raw material and by adding appropriate auxiliary agents.

2. Regulatory Reference Documents

The clauses in the following documents are incorporated herewith by reference into the present standards. For any reference document with an indicated date, all of its subsequent modification notices (not including any errata) or revised versions will not be applicable to the present standards; however, researches by all parties who have entered an agreement based on the present standards are encouraged to consider whether any such latest version of these documents can be used. As to any reference document without indicating a date, its latest version will be applicable to the present standards.


GB/T 4615—1984  Determination Method of Residual vinyl chloride Monomer Contents in Polyvinyl Chloride

3. Requirements
3.1 **Restriction of Vinyl Chloride Monomer**

The vinyl chloride monomer content in polyvinyl chloride layer of artificial leather should be not beyond 5mg/kg.

3.2 **Restriction of Soluble Heavy Metals**

Soluble lead content in artificial leather should be not beyond 90mg/kg.

Soluble cadmium content in artificial leather should be not beyond 75mg/kg.

3.3 **Restriction of Other Volatile Substances**

Contents of other volatile substances in artificial leather should be not beyond 20g/m².

4. **Rules for Sampling**

4.1 Implementation is subject to relevant products standards, and a relevant product does not have sampling stipulation, it is implemented according to 6.1.

4.2 One roll of sample should be taken from each batch of products at random.

4.3 A sample should be extracted after removing outmost 3 layers of the sample roll, and then cutting 1m along the length of the product.

4.4 After taking the sample, it should be sealed with non-polyvinyl chloride plastic bags and put in a cool and shaded place, without any special treatment.

5. **Testing method**

5.1 **Period**

From the date of production, testing should be done after storage for 7 days.

5.2 **Sampling**

All test pieces used for testing should be cut at least 50 mm from the sample edge.

5.3 **Determination of Vinyl Chloride Monomer Contents**

Cut 0.3g ~ 0.5g from the polyvinyl chloride layer of the samples, and the vinyl chloride monomer contents are determined according to GB/T 4615—1984.

5.4 **Determination of the Contents of Soluble Heavy Metals**
5.4.1 **Instrument:**

5.4.1.1 atomic absorption spectrophotometer (flame atomization system);

5.4.1.2 analytical scale (sensitivity 0.0001g);

5.4.1.3 commonly used laboratory instruments.

5.4.2 Reagents and Solutions:

5.4.2.1 hydrochloric acid (analytical pure);

5.4.2.2 lead nitrate (analytical pure);

5.4.2.3 cadmium acetate Cd (CH₃COO)₂·2H₂O (analytical pure);

5.4.2.4 hydrochloric acid (HCl) = 1.0mol/L; taking 83ml of hydrochloric acid (5.4.2.1) and diluting to 1 L with deionized water.

5.4.2.5 hydrochloric acid solution (HCl) = 0.07mol/L;

5.4.2.6 deionized water.

5.4.3 Preparation of Samples: deploy the artificial leather in a flat state and cut 2 pieces of 10mm x 100mm samples uniformly along the width direction, and after taking the weight respectively, cut them separately into 10 pieces of 10mm x 10 mm samples; add 25mL of hydrochloric acid (5.4.2.4) respectively, and after soaking for 24 hours, bring to a constant volume of 50mL by adding the deionized water. Filter the soaking solution for testing. At the same time, prepare a blank solution.

5.4.4 Instrument Conditions:

5.4.4.1 reference wavelength for testing lead is 283.3 nm;

5.4.4.2 reference wavelength for testing cadmium is 228.3 nm.

5.4.5 Drawing a Lead Standard Curve:

5.4.5.1 Lead standard stock solution: 0.1mg/mL

Weigh out 0.1600g of lead nitrate (5.4.2.2), after being dissolved in hydrochloric acid (5.4.2.5) put it into a flask of 1L volume and dilute it to the scale; thoroughly shake it and the solution contains 0.1mg/mL of lead in 1 ml of solution;

5.4.5.2 standard lead solutions: put standard stock solution (5.4.5.1) of 0ml, 0.5ml, 1.0ml, 2.0ml, 5.0ml into 100ml volumetric flasks respectively, dilute each with hydrochloric acid (5.4.2.5) to the scale, so to prepare standard solutions with lead contents of 0mg/ L, 0.5mg/ L, 1.0mg/ L, 2.0mg/ L, and 5.0mg/ L.
5.4.5.3 Drawing a Lead Standard Curve

Adjust the atomic absorption spectrophotometer to an optimal state, determine the absorbance values of the lead standard solutions (5.4.5.2) in turn, and draw the lead standard curve with the lead contents of the standard solutions as the abscissa and with the relevant absorbance values minus the absorbance values of blank test solution as the ordinate.

5.4.6 Drawing a Cadmium Standard Curve

5.4.6.1 Cadmium Standard Stock Solution: 0.1mg/mL

Weigh out 0.2371g of cadmium acetates (5.4.2.3), dissolve it in a flask of 1L volume by hydrochloric acid (5.4.2.5) and dilute it to the scale; thoroughly shake it up (1 mL of this standard solution contains 0.1 mg of cadmium).

5.4.6.2 Cadmium Standard Solutions: put cadmium standard stock solution (5.4.6.1) of 0 mL, 0.5 mL, 1.0 mL, 2.0 mL, 5 mL into flasks of 100mL volume respectively, dilute then with hydrochloric acid (5.4.2.5) to the scale. Standard solutions of cadmium contents of 0mg/L, 0.5mg/L, 1.0mg/L, 2.0mg/L, and 5.0mg/L are prepared.

5.4.6.3 Drawing a Cadmium Standard Curve

Adjust the atomic absorption spectrophotometer to an optimal state, determine the absorbance values of the cadmium standard solutions (5.4.6.2) in turn, draw the cadmium standard curve with the lead contents of the standard solutions as the abscissa and with the relevant absorbance values minus the absorbance values of blank test solution as the ordinate.

5.4.7 Testing the samples: according to the standard curves, draw the operating conditions and steps, test the absorbance of sample’s soaking solutions, and enter the same into the standard curves so as to get the contents of the soluble lead, and the soluble cadmium in the sample’s soaking solutions.

5.4.8 Calculation:

\[ X_1 = \frac{(a_1 - a_o) \times V}{M} \]  

\[ \cdots (1) \]
where:

\( X_1 \) — heavy metal contents in the samples, in milligram per kilogram (mg/kg);
\( a_1 \) — heavy metal contents in the sample’s soaking solutions checked from the standard curves, in milligram per millilitre (mg/mL);
\( a_0 \) — heavy metal contents in the blank solution, in milligram per millilitre (mg/mL);
\( V \) — total volume of the sample’s soaking solutions, in millilitre (mL);
\( M \) — mass of the sample, in kilogram (kg).

5.4.9 Presentation of Results:

It should be presented by the arithmetic mean value of the tested results of 2 samples with the reservation of 2 significant digits.

5.5 **Determination of the contents of other volatile substances**

5.5.1 Instrument and Equipment:

5.5.1.1 electric heated blast drying box;
5.5.1.2 analytical scale (sensitivity 0.0001g).

5.5.2 Preparation of Samples: deploy the artificial leather in a flat state and cut 3 pieces of 100mm x 100mm samples uniformly along the width direction, and the samples are conditioned for 24h according to environmental conditions of 23/50 ±2 in GB/T 2918-1998.

5.5.3 The sample is weighed to the accuracy of 0.0001g.

5.5.4 Set the electric heated blast drying box to 100°C±2°C, lay the samples horizontally on a wire netting or a perforated plate. The samples should be separated by at least 25mm with blasting to keep air circulation. The samples should not be radiated directly by the heating elements.

5.5.5 Take out the samples after 6h±10min, and weigh the samples after putting them in environmental condition 23/50 ±2 of GB/T 2918-1998 for 24h (accuracy to 0.0001g).

5.5.6 The contents of volatile substances are calculated with the following formula:
\[ X_2 = \frac{m_1 - m_2}{S} \] \hspace{1cm} (2)

where:

- \( X_2 \) — contents of other volatile substances, in gram per square meter (g/m²);
- \( m_1 \) — mass of the samples before testing, in gram (g);
- \( m_2 \) — mass of the samples after testing, in gram (g);
- \( S \) — area of sample, in square meter (m²).

5.5.7 Presentation of Results:

It is presented by the arithmetic mean value of the test results of 3 samples, with the reservation of 2 significant digits.

6. Inspection Rules

6.1 Items in the present standards are all type inspection items.

6.2 Under normal production conditions, type inspection is performed at least once each year.

6.3 With one of the following conditions, type inspection should be implemented:

- When trial-manufacturing of a new product is finalized;
- When there is a significant change in a manufacturing process and its raw materials;
- When the production is re-started after it has been stopped for a long period.

6.4 When inspection results of all items meet the requirements stipulated in the present standards, the products should be judged as qualified; if one of the test results doesn’t meet the requirements stipulated in the present standards, the products are judged to be unqualified.