Special water-based ink for printing polyvinyl chloride (PVC) foam wallpaper and preparation method thereof
CN 103146257 A

ABSTRACT
The invention discloses special water-based ink for printing polyvinyl chloride (PVC) foam wallpaper. The special water-based ink comprises thermosetting acrylic resin, thermoplastic acrylic resin, pigment, defoamer, surfactant, cosolvent, water-based wax emulsion, wetting dispersant, a water-based thickener, and water. A method for preparing the special water-based ink for printing the PVC foam wallpaper is also provided by the invention. According to the special water-based ink for printing the PVC foam wallpaper, the heavy metal content test indicator and volatile organic compounds (VOC) technical standard completely accord with the national standard; the special water-based ink is wonderful in printing effect; and the heat resistance, the weather fastness, the water tolerance and the oil resistivity are equivalent to those of solvent ink. The water-based ink disclosed by the invention is simple in formula, low in price, good in printed adhesive force, strong in water resistance, and fast to dry. Thus, the water-based ink is especially suitable for package printed matters such as foods, beverage and medicaments.

DESCRIPTION translated from Chinese
- Kind of PVC foam wallpaper for printing special water-based ink and method

BACKGROUND
[0002] As people's living standards improve, decoration materials have gone up, wallpaper decorating decorating market share in the increasingly high, and PVC foam wallpaper with its colors, rich patterns, affordable, short construction period, resistance dirty, scrub. High strength, impact-resistant, easy to clean, not Alice, not grilled seam. Replacement, can peel a whole, do not damage the wall, saving a lot of re-decoration costs and occupies nearly half of the market share of traditional PVC foam wallpaper printed using solvent-based inks, there is a low level of security printing, transport security is low, do not comply with environmental requirements, the need to install the printer recycling system, greatly increasing the cost of printing and so on shortcomings. Therefore, he proposed further improvements on wallpaper ink is non-toxic non-flammable water-based inks.

CLAIMS (10) translated from Chinese
A method for PVC foam wallpaper printing special water-based ink, characterized in that it comprises the following components in percentage by weight: a thermoplastic acrylic resin, 5 to 45%, thermosetting resin acid C Xi, IO ~ 45%, pigments, 5 to 40%, an antifoaming agent, 0.05 to 0.5%, surface active agent, 0.1 to 0.5%, solvent, 5 to 30%, aqueous wax emulsion, 0.5 to 4%, wetting and dispersing agents, 0.2 to 3% water thickener, 0.2 to 10% water, 5 to 30%.

(2) as claimed in claim 1, wherein the aqueous ink, characterized in that the molecular weight of the thermoplastic acrylic resin is 5000 ~ 6000, pH 6.9 to 7.5, a solids content of 35% to 45%; wherein the molecular weight of thermosetting acrylic resin of 8000 ~ 8500, pH 6.9 to 7.5, a solids content of 35% to 45%.

3 according to claim 1, wherein the aqueous ink, wherein the heat resistance of the pigment in the above 200 °C, weather resistance of the pigment in the above 7, which has a range of 10 ~ 100nm an average particle diameter.

As claimed in claim 3, wherein the aqueous ink, wherein said range of 10 ~ 40nm pigment has an average particle diameter.

5 according to claim 1, wherein the aqueous ink, wherein said defoaming agent is a polysiloxane - polyether copolymer emulsion.

As claimed in claim 1, wherein the aqueous ink, wherein said non-ionic surfactant is a fatty acid derivative modified.

As claimed in claim 1, wherein the aqueous ink, wherein said solvent wetting and dispersing agent is an amine and ethoxylated nonylphenol dispersing agent.

As claimed in claim 1, wherein the aqueous ink, wherein the aqueous acrylic thickener is an aqueous associative thickener.
SUMMARY OF THE INVENTION

[0004] Heat resistance of existing water-based inks are often, but off during foaming (foaming need 150 ~ 200 °C) tend to produce color, resin crust, yellow and so on.

[0005] In order to solve the above problems, a first object of the present invention is to provide a PVC foam wallpaper printing special water-based ink.

[0006] A second object of the present invention is to provide a method for preparing said water-based ink.

[0007] To achieve the object of the present invention, the technical solution of the present invention are as follows:

[0008] A method for PVC foam wallpaper print specific aqueous ink, which comprises the following components in percentage by weight:

- Thermoplastic acrylic resin, 5-45%,
- Thermosetting acrylic resins, 10-45%,
- Pigments, 5-40%,
- Defoamers, 0.05 to 0.5%,
- Surfactant, 0.01 to 0.5%,
- Cosolvent, 5-30%,
- An aqueous wax emulsion, 0.5 to 4%,
- Wetting and dispersing agent, 0.2-3%,
- Aqueous thickener, 0.2-10%,
- 5 to 30% water.

[0009] Preferably, the molecular weight of the thermoplastic acrylic resin is 5000 ~ 6000, pH 6.9 to 7.5, a solids content of 35% to 45%; the molecular weight of thermosetting acrylic resin 8000 ~ 8500, pH 6.9 to 7.5 solid content of 35% ~ 45%.

[0010] Preferably, the heat resistance of the pigment in the above 200 °C, weather resistance of the pigment in the above 7, which has a range of 10 ~ 100 nm an average particle diameter. The pigment is generally red, yellow, blue, white pigments.

- For the Fast Red Lily chemical, light yellow, phthalocyanine blue, white titanium dioxide as Yue Jiang Chemical.

- Preferably, the range of 10 ~ 40 nm pigment having an average particle diameter.

- Preferably, the defoaming agent is polysiloxane - polyether copolymer emulsion.

- Preferably, the surfactant is non-ionic fatty acid modified derivatives.

- Preferably, the wetting and dispersing agent is free of solvents, amines and ethoxylated nonylphenol dispersing agent.

- Preferably, the aqueous thickener is water-based acrylic associative thickener.

- Preferably, the co-solvent is ethanol, ethylene glycol, ethylene glycol monobutyl ether.

[0018] Further, the present invention provides a method for the preparation of the aqueous ink, which comprises the steps of:

[0019] (I) preparation and weighing: thermosetting acrylic resin, thermoplastic acrylic resin, pigments, defoamers, surfactants, solubilizers, water-based wax emulsions, wetting and dispersing agent, aqueous thickener, according to the proportion of water each weighing spare;

[0020] (2) mixing and stirring: the weighing the prepared materials thermosetting acrylic resins, pigments, defoamers, wetting and dispersing Qi IJ, mixed sequentially feeding, to join the total water 2/3 of the water, speed 300 to 400 r / min with stirring successively feeding, stirring for 10 to 15 minutes;

[0021] (3) sand scattered: the step (2) Stir the mixture into the sanding machine sanding dispersed, the total water consumption of 1/3 of the water cleaning mixing container, add water sander joint, in a sand mill to 3 to 4 times, until the...
mixture particle size of 150 ~ 260nm, the grinding and dispersion is complete;

(4) post-processing: After the grinding material in the mixing vessel 300 to 500 rev / min stirring, mixing process of adding a thermoplastic acrylic resin, aqueous wax emulsion, surfactants, aqueous thickener help solvent to a suitable viscosity (Tu 4 # cup 15 to 30 seconds), stirred for 50 ~ 70 minutes;

(5) filtering and packaging.

Preferably, the step (5) further comprises testing the product hue, solid content, fineness, viscosity, after passing the filtration and packaging. The beneficial effects of the present invention are as follows:

The present invention prepared for PVC foam wallpaper printing special water-based ink, and its heavy metal content and VOC test indicators technical standards in full compliance with national standards; their excellent printing effect, heat resistance, weather resistance, water resistance and oil resistance and solvent-based inks fairly. Water-based ink formulations of the present invention is simple, cheap, printed, good adhesion, water resistance, fast drying, it is especially suitable for food, beverage, pharmaceutical and other packaging printing.

Specific embodiments

The following specific embodiments with the accompanying drawings and described in detail the present invention. Protection of the present invention is not limited to the following examples orientation, should include the entire contents of the claims.

The present invention provides a PVC foam for wallpaper printing special water-based ink, wherein the thermoplastic acrylic resin (binder play a role), which means a molecular weight of 5000 to 6000, having a pH of 6.9 to 7.5 range, the solids content of 35% to 45%. The thermosetting acrylic resin (to play the role of binder and water), a molecular weight of 8000 to 8500, having a pH of 6.9 to 7.5 range, the solids content of 35% to 45%.

Preferably, the heat resistance of the pigment in the above 200 ° C, weather resistance of the pigment in the above 7, which has a range of 10 ~ 100nm average particle diameter; More preferably, the average particle diameter of the pigment 10 ~ 40nm. The pigment is usually red, yellow, blue, white pigment or carbon black. For the Fast Red Lily chemical, light yellow, phthalocyanine blue, white titanium dioxide as Yue Jiang Chemical.

Preferably, the defoaming agent is polyethylene oxide sand burn - polyether copolymer emulsion of the present invention used Tego foamex842.

Preferably, the surfactant is non-ionic modified fatty acid derivatives, the present invention selects Tego twin4000.

Preferably, the solvent-free wetting and dispersing agent, amines and ethoxylated nonylphenol dispersant of the present invention used Tego wet505. .

Preferably, the aqueous thickener is water-based acrylic associative thickener of the present invention used Tego Viscoplus3000o.

Preferably, the co-solvent is ethanol, ethylene glycol, ethylene glycol monobutyl ether.

The preparation of the performance of water-based inks and their effects are as follows:

1. Environmental Labeling Product Certification Technical Requirements wallpaper HBC23-2004 for wallpaper ink heavy requirements as shown in Table I below:

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Index</th>
<th>Index Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (as Pb)</td>
<td>mg / kg</td>
<td>&lt;90 A</td>
<td></td>
</tr>
<tr>
<td>Mining (as Hg)</td>
<td>mg / kg</td>
<td>&lt;60 A</td>
<td></td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>mg / kg</td>
<td>&lt;75 A</td>
<td></td>
</tr>
<tr>
<td>Chromium (Cr meter in)</td>
<td>mg / kg</td>
<td>&lt;60 A</td>
<td></td>
</tr>
</tbody>
</table>

This standard requires wallpaper ink itself heavy metals must be less than this standard, therefore, the present water wallpaper dedicated SAR selected pigments and additives used without heavy metals, Resin; heavy metals present invention is water-based ink test indicators examined according to GB GB/T8449-1987, GB/T8450-1987 testing methods. As shown in Table 2, it is fully in line with national standards.
Table 2 invented heavy metal water-based ink technical standards:

<table>
<thead>
<tr>
<th>Inspection Item</th>
<th>Unit</th>
<th>Value</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (as Pb)</td>
<td>mg / kg</td>
<td>^ 90</td>
<td>0.9</td>
</tr>
<tr>
<td>Mountain Mercury (as Hg)</td>
<td>mg / kg</td>
<td>&lt;60</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Inorganic elements

| Cadmium (Cd) | mg / kg | ^ 75 | 0.13 |
| Chromium (Cr) | mg / kg | <60 | 4.1  |

2, the water-based ink VOC problem of wallpaper.

Environmental Labeling Product Certification Technical Requirements wallpaper HBC23-2004 require wallpaper ink VOC requirements shown in Table 3:

Table 3 HBC23-2004 wallpaper ink VOC requirements shown in Table 3:

<table>
<thead>
<tr>
<th>Project</th>
<th>Unit</th>
<th>Index</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zen worry organic compound</td>
<td>g / L</td>
<td>^ 250</td>
<td>A</td>
</tr>
<tr>
<td>Halogenated hydrocarbons (methylene burn to count)</td>
<td>mg / kg</td>
<td>Pie 500</td>
<td>A</td>
</tr>
<tr>
<td>Benzene, toluene, xylene, ethylbenzene total</td>
<td>mg / kg</td>
<td>^ 500</td>
<td>A</td>
</tr>
<tr>
<td>Methanol</td>
<td>mg / kg</td>
<td>^ 300</td>
<td>A</td>
</tr>
<tr>
<td>Ammonia and its compounds</td>
<td>g / kg</td>
<td>^ 30</td>
<td>A</td>
</tr>
</tbody>
</table>

This standard wallpaper VOC content of the ink itself to be smaller than the standard, the present invention does not use any organic solvent, an organic solvent and mixed resin additives. The present invention is an aqueous ink VOC standard method by YC/T207 test method, as shown in Table 4, which is far below the national standard.

Table 4 of the present invention the VOC content of water-based ink technical standards:

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Index</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC</td>
<td>g / L</td>
<td>Sg 250</td>
<td>1.1</td>
</tr>
<tr>
<td>Halogenated hydrocarbons (methylene burn to count)</td>
<td>mg / kg</td>
<td>Pie 500</td>
<td>Not Detected</td>
</tr>
<tr>
<td>Benzene, toluene, xylene, ethylbenzene total</td>
<td>mg / kg</td>
<td>^ 500</td>
<td>0.13</td>
</tr>
<tr>
<td>Methanol</td>
<td>mg / kg</td>
<td>^ 300</td>
<td>5.6</td>
</tr>
</tbody>
</table>

The effect of water-based ink printing problems

All along, there is a water-based ink printing effects than solvent-based inks issue that is restricting the development of water-based ink of the main factors, the present invention highly selected matching ink system, dedicated wetting and dispersing agent, printing very effective, and the effect is quite solvent-based inks, leveling, excellent color development. To solve the water problem of poor ink printing effect, accelerate the development of water-based ink.

4, the surface tension of water-based ink problems

Water-based ink is mainly solvent is water, an organic solvent, the surface tension ratio large, so the surface tension of water-based ink is large (typically around 38dyn), to make the water-based ink on the paper surface with good adhesion, to the printing material has a large surface tension (38dyn above), the surface tension of wallpapers of about 7 to 10; therefore, necessary to reduce the surface tension of water wallpaper to fit the ink printed, the present invention is modified using nonionic surfactant is a fatty acid derivative without decreasing the printing effect, while greatly reducing the surface tension of the ink to improve the printability, thereby solving the problem of the surface tension of water-based ink.
4, pH, \textit{water-based ink} and the complex problem of poor solubility.

- consistent since, Common \textit{water-based ink} the pH of between 8.5 and 9.5, the pH of aqueous ink amine compounds rely mainly maintained, the printing process of the volatile amines, the PH value decreased, causing the ink increase in viscosity, poor transferability, drying speed, blocking roller, malfunction occurs paste version. Therefore, to maintain the stability of \textit{water-based ink} PH value, on the one hand to try to avoid leakage of amines, for example, cover the ink tank cover. The other hand, the addition of a stabilizer regular meals. Typically \textit{water-based ink} should be maintained at a pH between 8.0 and 9.5, pH, low high print quality are affected, pH value is too low, the impact properties of the acrylic resin printing play; PH value is too high, the slow-drying ink, prone dirty and sticky back printing problem of poor water resistance. In the printing process need to constantly adjust the PH value of the printing ink, greatly increasing the difficulty of printing and increased difficulty of promoting \textit{water-based ink}. The present invention is thermoplastic and thermosetting acrylic resin acrylic resin acrylic resin mixed in the ink PH stable about 7 ± 0.5, excellent ink-soluble complex, stable viscosity. Metastatic eliminate poor printing process, drying speed, blocking roller, scumming failure occurs, reducing the labor intensity of the printing process. To solve the \textit{water-based ink} PH value and the complex problem of poor solubility.

5, the problem of heat resistance of the \textit{ink wallpaper}

As PVC foam \textit{wallpaper ink} printing process is foaming after printing after printing after 180 ° C ~ 220 ° C after drying tunnel foam hue change, \textit{water-based wallpaper ink} has high heat resistance requirements, the present invention is used as a high temperature paint, pigment, heat resistance above 200 ° C were. \textit{Water-based} inks to solve the heat problems \textit{wallpaper}.

6, \textit{wallpaper} inks weather resistance, water resistance, oil resistance problem

As \textit{wallpaper} in the decor, the service life of 10 years, during which need to scrub them, so \textit{water-based ink wallpaper} weather resistance, water resistance, oil resistance, demanding. The pigment used in the present invention, high-temperature paint, acrylic resin is a mixture of high molecular weight resin, to solve the \textit{wallpaper ink} weather resistance, water resistance, oil resistance problem.

Example 1 Preparation of yellow \textit{ink}

The following ingredients were made with \textit{water-based ink}

\textbf{Water-based wallpaper} dedicated Yellow (Light Yellow) 15%

5% thermoplastic acrylic resin
Thermosetting acrylic resin 40%
Tego foamex 842 0.2%
Tego twin 4000 0.02%
Tego wet505 2%
842N 3% aqueous wax emulsion
Tego Viscoplus 3000 1%
Deionized \textit{water} 15%
Alcohol 18.78%.

I) preparation and weighing: weight ratio of each weighed in accordance with the alternate;

(2) mixing and stirring: the prepared materials will be weighed thermosetting acrylic resins, pigments, Tego foamex842, Tego wet505, sequentially feeding mix, to join the total \textit{water} 2/3 of the \textit{water}, at low speed 300 400 r / min with stirring successively feeding, stirring for 10 to 15 minutes;

(3) sand scattered: the step (2) Stir the mixture into the sanding machine sanding dispersed, the total \textit{water} consumption of 1/3 of the \textit{water} cleaning mixing vessel, and it gets into the \textit{water} with sand ` mill, in a sand mill to 3 times, until a particle size of mixture 150 ~ 260nm, the grinding and dispersion is complete;

(4) Follow-up treatment: polishing finished mixes in containers of 300 to 500 rev / min stirring, stirring, adding thermoplastic acrylic resin, 842N, Tego twin4000, Tego Viscoplus3000, cosolvent transferred appropriate viscosity (Tu 4 # cup 15 to 30 seconds), stirred 50 minutes;
(5) Inspection of products hue, solid content, fineness, viscosity, after passing the filtration and packaging.

Product testing standards are as follows:

1. Determination of fineness

   a) by GBT13217.3-2008 "liquid ink fineness test methods" methods.

2. Viscosity

   a) by GBT13217.4-2008 "liquid ink viscosity test methods" methods.

3. Determination of solid content

   3.1 Test Summary

   Solid content is a certain amount of ink is completely dry mass of solid content of the ink and the quality of the original ratio, in percent (%) total.

   3.2 The main test instrument

   a) the balance (weighed to 0.001g).
   b) electric oven thermostat blast.
   c) clean aluminum foil.

   3.3 Test Methods

   a) electric heated drying oven set temperature of the required temperature, open the blast.

   b) Weigh accurately about 1g test ink around in aluminum foil, placed in electric heated blast drying oven, heated drying 6hr, remove the weighing.

   3.4 Calculation method:

   Solid content (%) = (W2-W) / (W1-W) X 100%

   where: W ----- foil Weight
   W1 - test inks and foil weight
   W2 weight after drying ink and foil

   3.5 Two parallel do averaged.

   3.6 Test conditions:

   a) The test conditions for water-based ink 150 ± 2 ° C.
   b) All inks must be shaking even before the test to ensure accurate sampling.

4. Determination of color

   4.1 Test Summary

   The sample subjects ink ink samples in parallel with the standard method of scraping samples were compared to view ink color ink sample meets the standards of quality standards.

   3.4.2 The main test equipment and materials:

   a) RK.12 X 22cm imprint bed.
   b) RDS06 wire rods.
   c) clean and tipping paper.
   d) Mexican knife.

   4.3 Test Methods

   a) would have cut a good scraping samples of paper fixed to the imprint on the bed.

   b) transfer ink knife with a standard sample and the sample (with connecting material mixed into the ink), stir, respectively, scratch-like drops in a small amount of paper upper left and right, and not connected to the two adjacent.
c) evenly from top to bottom with a wire rod forced to scrape into the ink on the paper sheet. d) to view the sample and standard sample complexion.

4.4 test results to view the sample and the standard samples are the same complexion.

4.5 Test conditions

a) inspection shall be at a temperature of 25 ± 1 ° C, humidity of 65 ± 5% conditions.

b) view complexion should be at an incident angle of 45 ° ± 5 ° under standard illuminant D65.

5 Determination of surface tension

According to GB/T18396-2008 "Natural rubber latex - Determination of surface tension ring" approach.

Product test results see Table 5, Table 6 and Table 7.

Example 2 Preparation of magenta ink

The following ingredients were made with water-based ink

- anti-reddening 15%
- C Women thermoplastic resin acid 5%
- Thermosetting acrylic resin 42%
- Tego foamex 842 0.2%
- Tego twin 4000 0.02%
- Tego wet505 2%
- 842N 3% aqueous wax emulsion
- Tego Viscophis 3000 1%
- Deionized water 16%
- Alcohol 15.78%

Preparation and testing methods described in Example 1, the product test results, see Table 5, Table 6 and Table 7.

Example 3 Preparation of Black Ink

The following ingredients were made with water-based ink

- 13% carbon black
- Thermoplastic resin 5% C Xi sour
- Thermosetting resin 32% propylene broom acid
- Tego foamex 842 0.2%
- Tego twin 4000 0.02%
- Tego wet505 2%
- 842N 3%
- Tego Viscoplus 3000 1%
- Deionized water 20%
- Alcohol 21.78%

Preparation and testing methods described in Example 1, the product test results, see Table 5, Table 6 and Table 7.

Example 4 Preparation of white ink

The following ingredients were made with water-based ink

Preparation and testing methods described in Example 1, the product test results, see Table 5, Table 6 and Table 7.
Qin white 35%
Thermoplastic resin 5% C Xi sour
Thermosetting acrylic resin 25%
Tego foamex 842 0.2%
Tego twin 4000 0.02%
Tego wet505 2%
842N 3%
Tego Viscoplus 3000. 1%
Deionized water 15%
Alcohol 15.78%

Preparation and testing methods described in Example 1, the product test results, see Table 5, Table 6 and Table 7.

Example 5 Preparation of golden ink
The following ingredients were made with water-based ink
Copper powder 15%
20% thermoplastic acrylic resin
Thermosetting acrylic resin 20%
Tego foamex 842 0.2%
Tego twin 4000 0.02%
Tego wet505 2%
842N 3%
Tego Viscoplus 3000. 1%
Deionized water 20%
Alcohol 18 78%

Preparation and testing methods described in Example 1, the product test results, see Table 5, Table 6 and Table 7.

The present invention provides for PVC foam wallpaper printing special water-based ink, and its heavy metal content and VOC test indicators technical standards in full compliance with national standards; their excellent printing effect, heat resistance, weather resistance, water resistance and oil resistance and solvent-based inks fairly.

Table 5 invented heavy metal various inks technical result 1:

<table>
<thead>
<tr>
<th></th>
<th>紫色油墨</th>
<th>红色油墨</th>
<th>黄色油墨</th>
<th>水洗剂</th>
<th>全部溶剂</th>
</tr>
</thead>
<tbody>
<tr>
<td>含量</td>
<td>92%</td>
<td>91%</td>
<td>95%</td>
<td>/</td>
<td>92%</td>
</tr>
<tr>
<td>认定</td>
<td>≤15μm</td>
<td>≤15μm</td>
<td>≤15μm</td>
<td>/</td>
<td>≤15μm</td>
</tr>
<tr>
<td>干透（温度40℃，湿度55%）</td>
<td>1/3分</td>
<td>1/3分</td>
<td>1/3分</td>
<td>1/3分</td>
<td>1/3分</td>
</tr>
<tr>
<td>固体（温度40℃，湿度55%）</td>
<td>40%</td>
<td>41%</td>
<td>43%</td>
<td>25%</td>
<td>50%</td>
</tr>
</tbody>
</table>

Table 6 invented heavy metal various inks technical result 2:
The above description is only preferred embodiments of the present invention, it should be noted that for the technical field of ordinary skill in the technique of the present invention without departing from the principles of the premise, but also a number of improvements and modifications can be made, these improvements and modifications should also be regarded as the protection scope of the present invention.

### CLASSIFICATIONS

| International Classification | C09D11/10 |

### LEGAL EVENTS

<table>
<thead>
<tr>
<th>Date</th>
<th>Code</th>
<th>Event</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jul 17, 2013</td>
<td>C10</td>
<td>Request of examination as to substance</td>
<td></td>
</tr>
<tr>
<td>Jun 12, 2013</td>
<td>C06</td>
<td>Publication</td>
<td></td>
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