**Self-curable Aqueous Epoxy based Polymeric Dyes**

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**Introduction**

A conventional epoxy resin (NPES-904, epoxy equivalent weight is 815) with the repeating unit, n = 4 is chosen as the polymer backbone of the polymeric dye. The water-reducible epoxy oligomer is prepared from a half-esterification of its secondary hydroxy group with succinic anhydride and then dispersed to aqueous phase after its carboxylic acid neutralized with triethylamine. Amino group of water-based dye reacts with the epoxide of water-reducible epoxy oligomer and producing chemically bonded polymeric dye.

A water-soluble polyaziridine is chosen as a latent curing agent for this aqueous-based polymeric dye solution. The stable self-curable aqueous-based polymeric dye dispersion is resulted when its pH remains above 8.0. This new polymeric dye can be applied for printing, writing, or textile dying purpose, which is self-cured on drying at ambient temperature and becoming water-resistant ink or dye.

**EXPERIMENT**

Preparation of water-reducible epoxy oligomer and its polymeric dye

An epoxy resin (50gm, NPES-904 with 815 eew) and 12 gm succinic anhydride are mixed with methyl isobutyl ketone (MIBK, 50mL) in a 500mL 3-neck flask and add 2 drops T-12 as a catalyst. The esterification reaction is carried out and kept at 120°C for about 18 hr. Cooling the product to room temperature and the un-reacted succinic anhydride is removed by tetrahydrofuran (THF) extraction. The final reaction mixture is neutralized with triethylamine (TEA) and then dispersed with 45mL de-ionized water with agitation. The solution of a water-soluble dye 0.03g (molar ratio, epoxide/dye = 200/1) is added into water-reducible epoxy oligomer dispersion and obtaining an epoxy oligomer based polymeric dye with 25% solid. An amino group containing dyes, such as C. I. Acid blue 62, C. I. Direct orange 39 and C. I. Direct red 2 are used, respectively.

**Single pack self-curable aqueous-based polymeric dye with an aziridine curing agent**

The aqueous-based polymeric dye is mixed with a polyaziridine curing agent (e.g. CX-100, 5phr) and becoming a self-curable aqueous-based polymeric dye. The self-cured polymeric dye is cast dry at ambient temperature and results in a water-insoluble polymeric dye film, which is 80% or above gel content (extracted with THF).

**Appearance Strength (polymer film color fastness)**

The polymer film is prepared from a self-cured polymeric dye sample by air dry. Each polymer film is dipped in water or ethanol for 24 hours and then dried, respectively. The color of treated polymer film is comparing with that of the original sample (without dipping) and the appearance strength in percentage is obtained from the measurements of Sphere Spectrophotometer.

**RESULT AND DISCUSSION**

The conventional hydrophobic epoxy resin is modified to become a water-reducible epoxy oligomer, which is cured and forming a networking epoxy resin with epoxide terminal groups by a polyaziridine curing agent on drying. Water-soluble dye owns the excellent color extension but the poor color water resistance in nature. A dye comprises amino group, such as C. I. Acid blue 62, C. I. Direct orange 39 and C. I. Direct red 2, which reacts with epoxide-terminated water-reducible epoxy oligomer and becoming an aqueous epoxy based chemically bonded polymeric dye. That polymeric dye is treated with a small dosage (~5 phr) polyaziridinyl curing agent (e.g. CX-100), which is formulated as a self-curable aqueous epoxy based polymeric dye and is self-cured on drying. It provides wide potential applications on printing, writing, and textile dying purposes, its self-cured polymeric dye with both excellent on color extension and water-resistance.

**Properties of Self-cured Aqueous Epoxy based Polymeric Dye**

Both the aqueous-based epoxy resin and the amino containing dye are water-soluble and non-film formation material. After drying from the formulation of a self-cured aqueous epoxy polymeric dye, which has the gel content increases to 89.8 (Red 2), 82.1(Blue 62) and 80.4 (Orange 39) respectively to 1/50 of the dye/epoxy ratio and their amount dissolved into water decreases to 8.8, 12.5 and 6.5% (Table I) comparing to the completely soluble aqueous epoxy polymeric dye. These results prove that the latent or self-curing system of polymeric dye works out and forming a water insoluble and organic solvent resistant (both THF and ethanol) polymeric dye or ink.

**Thermal Behaviors**

TGA thermogram indicates self-cured aqueous epoxy based polymeric dye has a better thermal stability than the original aqueous-based epoxy resin. And its thermal stability increases with increasing dye dosage to aqueous-based epoxy oligomer (Dye/WEP) (Figure 1). These are due to the presence of higher dosage self-cured polymeric dye with the polyaziridinyl latent curing agent, it helps the interpenetrating polymeric network formation between polymeric dye.

**Appearance Strength**

Each colored polymer film of this aqueous epoxy based polymeric dye before dipping in water or ethanol, its appearance strength is 100%. Most of the dry colored polymer films after dipping in either water or ethanol have the greater value than that of original film. This is due to the water or ethanol soluble fraction is removed and the self-cured film with polymer dye. The color strength of polymer films is more intense than that of standard film (Table II). The higher appearance strength of this self-cured polymer film consists of chemically-bonded dye proves that of good color fastness after water or ethanol extraction.

**CONCLUSION**

A self-curable aqueous epoxy based polymeric dye is stable at pH above 8.0 and it becomes water-resistant on drying. This stable single component self-curing aqueous polymeric dye is convenient for printing, writing or dying applications. It’s self-curing reaction takes place between the latent curing agent and aqueous epoxy based polymeric dye on drying at ambient temperature. This single component self-curable aqueous epoxy based polymeric dye not only meets the requirements of environmental, safety and industrial hygiene and also solves the water-resistance handicap of conventional water soluble dye.

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**REFERENCE**


U. S. Patent 6,291,554

4. Patent of this work is pending

**Table I** Properties of Self-cured Aqueous Epoxy based Polymeric Dyes

<table>
<thead>
<tr>
<th>Properties</th>
<th>Red 2/WEP</th>
<th>Blue 62/WEP</th>
<th>Orange 39/WEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel Content (%)</td>
<td>85.4</td>
<td>87.3</td>
<td>89.8</td>
</tr>
<tr>
<td>Water Uptake (%)</td>
<td>64.8</td>
<td>66.7</td>
<td>70.5</td>
</tr>
<tr>
<td>Polymer wt. dissolved in Water (%)</td>
<td>5.5</td>
<td>6.9</td>
<td>8.8</td>
</tr>
<tr>
<td>Ethanol Uptake (%)</td>
<td>83.9</td>
<td>93.6</td>
<td>117.4</td>
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</table>
Polymer wt. dissolved in Ethanol (%)

<table>
<thead>
<tr>
<th></th>
<th>4.4</th>
<th>5.0</th>
<th>6.5</th>
<th>4.1</th>
<th>5.6</th>
<th>6.8</th>
<th>4.1</th>
<th>4.8</th>
<th>6.6</th>
</tr>
</thead>
</table>

Figure 1  TGA of self-cured aqueous epoxy based polymeric dyes with various dye dosage under nitrogen; Dye/WEP=1/200 (△); 2/200 (□); 4/200 (○) comparing to WEP(─) (Dye use Red2 for example)

Table II  Appearance strength of self-cured aqueous epoxy based polymeric dye

<table>
<thead>
<tr>
<th>Ratio of WEP/dye=100/1</th>
<th>Original</th>
<th>Water</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>WEP/Red2</td>
<td>100</td>
<td>106.6</td>
<td>110.2</td>
</tr>
<tr>
<td>WEP/Red2 +CX-100</td>
<td>100</td>
<td>108.1</td>
<td>112.4</td>
</tr>
<tr>
<td>WEP/Blue62</td>
<td>100</td>
<td>115.3</td>
<td>121.8</td>
</tr>
<tr>
<td>WEP/Orange39 +CX-100</td>
<td>100</td>
<td>129.1</td>
<td>143.2</td>
</tr>
<tr>
<td>WEP/Orange39 +CX-100</td>
<td>100</td>
<td>111.6</td>
<td>137.9</td>
</tr>
</tbody>
</table>

The Structures of Dyes

C.I. Acid Blue 62

C.I. Direct Orange 39

C₃₃H₅₆N₆Na₂O₆S₂

C.I. Direct Red 2