Abstract

Organic pigments are cost-effective, non-toxic, and possess good color strength, which makes them good choice for their use across various end-use sectors. Copper phthalocyanine (CPC) blue is the copper (II) complex of tetra aza tetra benzoporphine (CPC) whereas phthalocyanine green is its chlorinated derivative. The brominated derivatives of CPC provide a yellowish green shade. The specific crystal modification decides the hue of the product as in Alpha Blue-red shade copper phthalocyanine (Pigment Blue 15) and in Beta Blue-green shade blue (Pigment Blue 15:3). CPC Blue is an upstream product and is a raw material used for the manufacture of our Pigment Blue and Pigment Green products. CPC Blue is also sold to other manufacturers of pigments including a related party for the manufacture of textile dyestuffs. Here we have presented the manufacturing process of two organic pigments – CPC Green and Blue.

Keywords: CPC Green, Beta Blue, Ink, Manufacturing, Textile, Tint

Introduction

Manufacture of organic pigments with good light fastness property is gaining traction among global manufacturers. Besides, developing countries such as China and India are shifting towards becoming the center of global organic pigments market, both from the demand and supply side. The manufacturing of organic pigment is in a cautious phase as API bulk drug. The information sheet for organic pigments is listed in Table 1.

Copper Phthalocyanine (CPC) Blue is the copper (II) complex of tetra aza tetra benzoporphine (CPC) whereas Phthalocyanine Green is its chlorinated derivative. The brominated derivatives of CPC provide a yellowish green shade. The specific crystal modification decides the hue of the product as in Alpha Blue – red shade copper phthalocyanine (Pigment Blue 15), and in Beta Blue – green shade blue (Pigment Blue 15:3). The alpha modification is phase stabilized by partial chlorination called solvent stable Alpha Blue or Pigment Blue 15:1. The alpha modification which is stabilized towards flocculation and the phase change is registered as Pigment Blue 15:2. These pigments find use in paints. Pigment Blue is a cyclic product of copper and reaction between phthalic anhydride and urea. Alpha Blue and Beta Blue are variations of Phthlocyanine Blues. Alpha Blue is redder in shade and of smaller particle size and is available as crystallizing type and non-crystallizing non-flocculating type. Beta Blue yields bright greenish blue shades with slightly lower tintorial strength. Beta Blue is of a more stable crystal formulation than Alpha Blue and is available as the non-crystallizing type and the non-crystallizing non-flocculating type.
Table 1. Information Sheet for Organic Pigments

<table>
<thead>
<tr>
<th>Particular</th>
<th>Copper Phthalocyanine (CPC) Green</th>
<th>CPC Beta Blue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical state</td>
<td>Solid</td>
<td>Solid</td>
</tr>
<tr>
<td>CAS No.</td>
<td>1328-53-6</td>
<td>147-14-8</td>
</tr>
<tr>
<td>Formula</td>
<td>$\text{C}<em>{32}\text{Cl}</em>{16}\text{CuN}_8$</td>
<td>$\text{CuC}<em>{32}\text{H}</em>{16}\text{N}_8$</td>
</tr>
<tr>
<td>MW (g/mol)</td>
<td>1127.154</td>
<td>576.0690</td>
</tr>
<tr>
<td>Uses</td>
<td>Inks, coatings and many plastics, in manufacturing of other pigments in the category</td>
<td></td>
</tr>
<tr>
<td>Toxicity</td>
<td>Serious birth defects in developing embryos; non-biodegradable</td>
<td></td>
</tr>
<tr>
<td>LD50</td>
<td>$&gt;3 \text{ g per kg body weight}$</td>
<td>$&gt;5 \text{ g per kg body weight}$</td>
</tr>
<tr>
<td>LC50</td>
<td>$&gt;250 \text{ mg/L for 48 h}$</td>
<td>$&gt;100 \text{ mg/L for 48 h}$</td>
</tr>
<tr>
<td>Reference</td>
<td>Sandor et al.¹</td>
<td>OECD SIDS, 1990</td>
</tr>
</tbody>
</table>

Raw Material

The list of raw material required for the manufacturing of two organic pigments is shown in Table 2.

Table 2. Raw Material Consumption (per ton of product)

<table>
<thead>
<tr>
<th>Organic Pigments</th>
<th>Raw Material</th>
<th>Physical State</th>
<th>Raw Material Consumption (per ton of product)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPC Green</td>
<td>Aluminum Chloride</td>
<td>Solid</td>
<td>1.928</td>
</tr>
<tr>
<td></td>
<td>Salt</td>
<td>Solid</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>CPC Blue</td>
<td>Solid</td>
<td>0.571</td>
</tr>
<tr>
<td></td>
<td>Cupric Chloride</td>
<td>Solid</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>Chlorine Gas</td>
<td>Liquid/Gas</td>
<td>1.265</td>
</tr>
<tr>
<td></td>
<td>MCB (Recovered)</td>
<td>Liquid</td>
<td>2.97</td>
</tr>
<tr>
<td></td>
<td>MCB (Fresh)</td>
<td>Liquid</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Caustic lye</td>
<td>Liquid</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>Emulsifier</td>
<td>Liquid</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Oleic Acid</td>
<td>Liquid</td>
<td>0.02</td>
</tr>
<tr>
<td>Beta Blue</td>
<td>CPC Blue</td>
<td>Solid</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Salt</td>
<td>Solid</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Xylene (Recovered)</td>
<td>Liquid</td>
<td>2.940</td>
</tr>
<tr>
<td></td>
<td>Xylene (Fresh)</td>
<td>Liquid</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Emulsifier</td>
<td>Liquid</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>Caustic</td>
<td>Liquid</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Manufacturing Process for Copper Phthalocyanine Green

- **Chlorination:** In a glass-lined reactor, eutectic mixture of aluminum chloride and sodium chloride is prepared and is melted. Now CPC AD blue and cupric chloride are charged. The chlorine gas is purged till the drawdown is found O.K. The mass is then drowned.
- **Drowning:** In a vessel, water is taken. The chlorinated mass is then received slowly. The mass is stirred and filtered.
- **Filtration:** Drowned mass is filtered and is then washed to make it free of chloride or aluminum. This gives CPC green crude wet cake.
- **Pigmentation:** In a reactor, monochlorobenzene, water and caustic soda lye are mixed. Now dispersing agents are added to it and an emulsion is prepared. The wet cake from above stage is taken to it and stirring is continued. The mass is then refluxed. Solvent monochlorobenzene is then recovered by distillation and the mass is filtered.
- **Filtration:** The suspended slurry is then filtered and is washed to make it free of alkali.
- **Drying:** The wet cake from above filtration is dried in a spin flash dryer.
Figure 1. Structure of CPC Green

Figure 2. Chemical Reaction CPC Green
MASS BALANCE OF CPC GREEN

**Chlorination**
- $\text{AlCl}_3$: 1928 kgs
- Salt: 300 kgs
- CPC Blue: 571 kgs
- CuCl$_2$: 85 kgs
- Cl$_2$ gas: 1265 kgs
- Unreacted Chlorine gas: 250 kgs
- Three stage Scrubber
- HCl (30%): 833 kgs

**Drowning**
- Water: 583 kgs

**Filteration & Washing**
- Water: 12000 kgs
- AlCl$_3$ Soln. (10-12%): 12000 kgs
- Effluent to ETP: 22000 Kgs

**Pigmentation**
- MCB: 3000 kgs
- Water: 1200 kgs
- Caustic: 160 kgs
- Oleic Acid: 20 kgs
- Emulsifer: 20 kgs
- MCB recovered: 2970 kgs
- MCB loss: 30 kgs
- Effluent to ETP: 23299 kgs

**Filteration & Washing**
- Water: 20000 kgs
- Evaporation loss: 1500 kgs

**Spin Flash Dryer**

**CPC Green: 1000 kgs**

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Figure 3. Mass Balance of CPC Green

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**CPC Green Manufacturing**

**Aluminum Chloride Solution**

**Copper Removal & Purification**

**Copper (For Sale)**

**Purified Aluminum Chloride Solution**

**Aluminum Hydroxide Plant**

**Pharma Grade Aluminum Hydroxide**

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Figure 4. Hazardous Waste Management during Manufacturing of CPC Green
Manufacturing of CPC Beta Blue

- **Ball Milling**: Copper Phthalocyanine Blue is milled along with vacuum salt below 70°C. It is unloaded and transferred for pigmentation.
- **Solvent Pigmentation**: The milled powder is treated with solvent at 90°C.
- **Filtration and Washing**: The mass is filtered off in filter press, and washed up to neutral pH.
- **Drying**: The wet cake is dried in a spin flash drier and finally packed.

There is no chemical reaction taking place, only rearrangement of molecules of Phthalocyanine Blue and Beta Blue are formed which is stable and has greener blue tone.
Conclusion

The CPC green and blue pigments are used widely in textile units to color the yarn and used in printing. The CPC pigments are broad-spectrum organic pigments. Beta Blue is of a more stable crystal formulation than Alpha Blue and is available as the non-crystallizing type and the non-crystallizing non-flocculating type. During manufacturing of organic pigments, major issue is hazardous water; it should be properly handled. The life cycle analysis should be done before use of organic pigments.

Conflict of Interest: None

References


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