CLEANER PRODUCTION OPPORTUNITIES

IN

DYSES AND DYE INTERMEDIATE INDUSTRIES
Introduction to Dyes & Dye intermediates Industry

The Indian dyestuff industry is only about 40 years old though a few MNCs set up dyestuff units in the pre independence era. Like the rest of the chemical industry, the dyestuff industry is also highly fragmented. A remarkable feature of the Indian dyestuff industry is the co-existence of units in the small, medium and large sectors, actively involved in the manufacture of dyestuffs and their intermediates. The actual Production during the 2006-07 to up to September 2012 is shown in table:

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<td>Dyes &amp; Dye Intermediate Production</td>
<td>90</td>
<td>117</td>
<td>110</td>
<td>149</td>
<td>164</td>
<td>171</td>
<td>86</td>
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<td>Growth rate(%)</td>
<td>29.5</td>
<td>30.5</td>
<td>-6.5</td>
<td>35.8</td>
<td>10.5</td>
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Note: Figures in Thousand Metric Tonne. Production is aggregated based on Monthly Production Returns from manufacturers under large and medium scale.

At present, India contributes about 6% of the share in the global market with a CAGR of more than 15% in the last decade. The organized sector dominates, with 65% share of the total market, while the unorganized sector controls the remaining 35% of the market. The demand for dyes and dye intermediates is expected to grow at around 6%, backed by strong demand from the textiles, leather, and inks industries. Dyestuff sector is one of the core chemical industries in India. It is also the second highest export segment in chemical industry. The major users of dyes in India are textiles, paper, plastics, printing ink and foodstuffs. The textiles sector consumes around 80% of the total production due to high demand for polyester and cotton, globally. Globally the dyestuffs industry has seen an impressive growth.

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Dyes are any substance, natural or synthetic, used to colour various materials, and have wide industry applications ranging textiles, leather, and food, paper etc.
Dye Classification for Application

Highlights of processes for Dyes & Dye intermediates Industry

Dyes and Dye Intermediates are synthesized in a reactor, filtered, dried, and blended with other additives to produce the final product. In case of Dyes, the synthesis step involves reaction such as Sulphonation, Oxidation, Reduction, Isolation, Halogenations, Amination, Diazotization, and coupling followed by separation processes, which may include distillation, precipitation, and crystallization. The dye is then separated from the mixture and purified. On completion of the manufacture of actual color, finishing operation including drying, grinding, and standardization are performed and these are important for maintaining consistent product quality. In case of Dye
Intermediates, the process steps cover sulphonation, oxidation, reduction, isolation, filtrations and drying.

**Operation Sequence in Dye manufacture**
Operation Sequence in Dye Intermediate manufacture:

Filtration: Filtration is most widely used separation process. Equipments used to carry out filtration are Filter press, centrifuge, and cake filters. At present, Filter press and Nutsche Filter are most common equipments used by the industries.

Drying: Drying is the process of removing liquid from solids by evaporation. Different types of dryers used in the industry are Hot air Dryers – bin dryers, Cabinet Dryers – tray dryers, Continuous Conveyor Dryers – belt dryers, Pneumatic Dryer, Fluidized bed dryer, Spray Dryer.
To improve drying efficiency with energy conservation, following options are given like Improving Existing Method of Tray Drying, Flash Drying, Spray Dryer, Solar Drying Techniques.

Sulfonation: The introduction of sulfonic group in an aromatic nucleus is known as "Sulfonation". This group is introduced to render intermediates soluble in water or to provide a route to other substituents, such as the hydroxyl group, which is obtained by subsequent alkaline fusion.

Sulfonation of the aromatic compounds is carried out by heating the compounds with the sulfonating reagent during which water is eliminated.

The current technology uses following sulfonating agents because of their low cost, ease of availability and handling:

- Sulfuric acid
- Oleum
- Sodium bisulfate

Reduction: The most common reduction method in the manufacture of dye intermediates is the conversion of a nitro compound to the corresponding amines. The only reducing agent used in this sector is iron powder with acid. This technology is employed on a large scale because of its simplicity. The effective reducing agent is nascent hydrogen, which produced by the reaction of iron and water having a small of HCl acid to promote a reaction. Using iron powder as reducing agent generates large amount of iron oxide sludge, which is hazardous and therefore required to be send to the landfill sites.

Emissions in Dyes & Dye intermediates Industry

- **Air Emission**

  Mostly, in dye manufacturing volatile organic compounds (VOCs), nitrogen oxides (NOx), hydrogen chloride (HCl), and sulfur oxides (SOx) are emitted. Moreover, air pollution was caused by emission of particulate for example dust during material transport, grinding or as a result from open dumping while drying material such as spray dryer.

- **Water Emission**

  The main liquid effluent generated, is from equipment washing after batch operation. Mostly, wastewater from dye manufacturing is highly variable in composition and contains a large number of different compounds such as raw materials (e.g. anilines, solutes, etc.), intermediate products, and even the dyes themselves. They are considered as a more dangerous source of environmental problem. High chemical oxygen demands (COD), biochemical oxygen demands (BOD), suspended solids and intense color due to dye
intermediates or residues and auxiliary chemicals characterize from the dye production process.

- **Solid Emission**

  Major solid wastes such as sludge that are generated from effluent treatment process and container residues. In conventional wastewater effluent treatment process sludge produced after it is treated, it becomes sludge cake that is mainly contains gypsum. Some industries sell it to cement manufacturers or dispose at landfill.

**Environmental Issues in Dyes & Dye intermediates Industry and CP options**

- Gaseous emission such as SO$_x$,NO$_x$, HCl and NH$_3$ are generally scrubbed. So, properly designed scrubber with recovery reuse of scrubbed liquid is required.

- Centrifuge is a highly energy intensive operation, which requires running time of around 12 hours a day. Optimum time required for removal of moisture is around 30-35 minutes. But because of the negligence of the worker, almost it runs for around 40-45 minutes or 1 hour consuming more energy. To overcome this, a simple timer can be installed on centrifuge. The digital timer will be connected to the centrifuge motor. Now after installing the timer one can set definite time for which they want to operate the centrifuge. As soon as the set time will be over, the motor will automatically stop running and thus saving the electrical energy.

- The most commonly filtration system used are filter press and Nutsche Filter. Because the all products in dyes and dye intermediates are highly water soluble, there is high filtration loss.  
  1. The End product of filter press contains higher moisture content which increases the load on the dryer.  
  2. The technology may be suggested which either can reduce the moisture content of end product of filter press or some methods which can recover the filter loss which is otherwise inevitable.  
    Use Agitated Nutsche filter which is a closed vessel designed to separate solid & liquid by filtration under pressure & vacuum, it offers an economical operation where maximum percentage of liquid in slurry is separated through mechanical means.

- Use a) Improving Existing Management Practice – Efficient Energy Utilization in Drying,  
  b)Flash Dryer , c)Spray Dryer , d)Solar Dryer as a Technology up gradation Option for Drying

- Use Sun drying :Use solar system for heating thermic fluid up to 180$^\circ$ C. One chamber with trays for solar drying of dye material can be used. Material may be kept in trays and hot air is blown in the chamber. Using solar energy, hot air is generated and that can be blown by two blowers with sensor to control temperature. Benefit of the system could be: a)Reduction in
time for drying, b) Elimination of dust contamination (Value addition to the material) and c) Reduction in labor cost.

- Possibilities for adoption of cleaner process option for reducing the water consumption and effluent generation; better management practices for segregation and reuse/recycle of the treated effluent; effective utilization of raw materials; improvement in efficiency of process. The effluent generated from manufacturing of some of the dyes and intermediates such as H-acid is not biodegradable, which requires process change.
- Sulphonation with SO₃, Chloro sulphonic acid and sulphamic acid can reduce effluent generation.
- For Reduction process by product from Iron sludge can be produced. Cleaner process technologies e.g. catalytic hydrogenation, use of spent acid after nitration for acidification of fusion mass, which can eliminate generation of iron and Gypsum sludge.
- Areas which can be addressed with Common Facility: There are certain areas wherein technology upgradation is possible with collective approach i.e. common facility can be created like CETP and secured land fill site.

The areas are as under:
- Common drying facility
- Gypsum recovery
- Spent sulfuric acid concentration and reuse

- **On – Site Reuse and Recovery**
  It is recycling or reuses a waste material each of originating process that is substituted input material or another process within the same production site.

1. **Gaseous:**
   - Separation of entrained liquid from reactors.
   - Separation of Dust from dryers, pulverizes.
   - Condensation of organic vapours.
   - Adsorption of uncondensed organic.
   - Scrubbing of HCl by multiple scrubbers to get concentration HCl from 1st Scrubber.
   - Scrubbing of lean HCl,Cl₂ with alkali.
   - Recovery of NaSH, Na₂SO₃ by scrubbing H₂S, SO₂ by NaOH.
   - Treatment of scrubber solution.
   - Incineration of Toxic gases.

2. **Liquid:**
   - Segregation of effluent streams and Recycling wherever possible.
   - Recovery of sodium sulphate from aqueous effluent.
   - Recovery/Reuse of H₂SO₄.
   - Removal of non-Biodegradable sulphonic acids by extraction.
   - Removal of Heavy metals by precipitation.
• Biodegradable of Biodegradable impurities.
• Removal of colour by Adsorption/Oxidation /Bleaching.

3. Solid:
• Recovery of salts such as sodium sulphite, sodium sulphate.
• Effective washing of Gypsum sludge and use in cement manufacture.
• Recovery of Mercury naphthalene from their sludge.
• Manufacture of pigment from iron sludge.
• Regeneration of spent carbon.
• Incineration of organic residue.
• Secured land filling of Ash, ETP sludge.