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Process Modification in Dye and Dye Intermediates – Acid Dyes

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Abstract—'Process Modification' refers to the development of radical technologies for the miniaturization of process plants while achieving the same production objective as in bulky conventional processes. The goal is to bring down the plant size by 10-1000 times by replacing large, expensive and energy-intensive equipment or processes with ones that are smaller, less costly and more efficient. Hybridization of multiple unit operations and processes into a single compact device is the rule of thumb for process intensification.
The objective of the paper is to Modify, Intensify and Energy Efficient process in dye manufacturing units in Gujarat. The focus of the study is to minimize wastes, to improve energy efficiency and improve the process practices/cycles to optimize resource utilization.

Key words – Process Modification, Intensify, Conventional process, Energy Efficient, Minimize waste.

I. INTRODUCTION

Ever since the beginning of humankind, people have been using colorants for painting and dyeing of their surroundings, their skins and their clothes. Until the middle of the 19th century, all colorants applied were from natural origin. Inorganic pigments such as soot, manganese oxide, hematite and ochre have been utilized within living memory. Palaeolithic rock paintings, such as the 30,000 year old drawings that were recently discovered in the Chauvet caves in France, provide ancient testimony of their application. Organic natural colorants have also a timeless history of application, especially as textile dyes. These dyes are all aromatic compounds, originating usually from plants (e.g. thered dye alizarin from madder and indigo from wood) but also from insects (e.g. the scarlet dye kermes from the shield-louse Kermes vermilio), fungi and lichens. Synthetic dye manufacturing started in 1856, when the English chemist W.H. Perkin, in an attempt to synthesize quinine, obtained instead a bluish substance with excellent dyeing properties that later became known as aniline purple, Tyrian purple or mauveine. Perkin 18 years old patented his invention and set up a production line. This concept of research and development was soon to be followed by others and new dyes began to appear on the market, a process that was strongly stimulated by Kékulé's discovery of the molecular structure of benzene in 1865. In the beginning of the 20th century, synthetic dyestuffs had almost completely supplanted natural dyes.
Economic development is always linked to the quality of the environment since the outset, though its impact could be felt in recent times. The fast paced industrial development in Gujarat in various industrial sectors continues to contribute significantly to the national economy. But indiscriminate use of natural resources has harmed the assimilative capacity of the environment of this state. Today, we are witnessing important new developments that go beyond "traditional" chemical engineering. Engineers at many universities and industrial research centres are working on novel equipment and techniques that potentially could transform our concept of chemical plants and lead to compact, safe, energy-efficient, and environment-friendly sustainable processes. These developments share a common focus on "process intensification" — an approach that has been around for quite some time but has truly emerged only in the past few years as a special and interesting discipline of chemical engineering.
The current paper presents case study of process modification in acid black dye manufacturing unit in order to minimize waste, to improve and to optimize resource utilization.

II. MANUFACTURING PROCESS OF ACID BLACK-10bx

A. Principle

Para Nitro-Aniline is diazotized and coupled with H-Acid in acidic medium. The mono azo dyestuff is dissolved as in turn, coupled with Aniline diazo. The resulting dyestuff is isolated by salting. The isolated dyestuff is filtered, dried, evaluated and finally formulated to the level of the prevailing Sales Standard.

B. Raw Materials

SR. NO.	NAME OF RAW MATERIAL	Quantity Real (kgs.)	Moles
1	H- Acid	182.50	0.5716
2	Soda Ash	36	0.3396
3	HCl for Reprecipitation	21	0.5753
4	p-Nitro-Aniline	87.50	0.6340
5	HCl real	84	2.3014
5	Sodium Nitrite	44.50	0.6449
6	Sulfuric Acid	2	
7	Caustic Soda	72	1.8000
8	Aniline Oil	50	0.2194
9	HCl	48	1.3151
10	Sodium Nitrite	41.50	0.6014
11	Soda Ash	230	2.1698
12	Common Salt	840	

Figure 1. Raw Materials

C. Diazotization of para-nitro Aniline

In a suitable Wooden Coupling Vat, charge 300litre of treated water. Stir and charge enough crushed ice to make up

700litre volume. Then charge 87.5kgs. of real p-Nitro-Aniline (M.Wt. 138.0). Stir for about 1-2 hours to obtain smooth slurry. Then add to it 89litre of as is 50% wt./vol. Sodium Nitrite solution corresponding to 44.5kgs. of real Sodium Nitrite (M Wt. 69.0). Stir further for one hour. Then charge a further quantity of crushed ice to make up the volume to 1500litre at 0-3degrees. Stir for half an hour. Then run continuously, as fast as possible, 280kgs of as is 30% w/w HCl, corresponding to 84kgs of real HCl, maintaining the temperature below 5^0C. Add more ice as required. During the acid addition, frequently test diazotization charge for distinct blue tests on Congo Red KI-Starch papers. Stir the diazo for 1 hour at 0-5^0C. The diazotization is complete by now. The diazo solution is clear. Measure volume of the Diazo and adjust it to 2500litre at 0-5^0C.

D. HCl Solution for H-acid Precipitation

In a suitable Wooden Vat, Charge 350litre of treated water. Stir and charge 70kgs of as is 30% w/w HCl corresponding to 21 kgs of real HCl. Stir for 5 minutes and stop stirrer.

E. H-acid Solution & Reprecipitation

In a suitable Wooden Solution Vat, charge 850 litre of treated water. Stir and charge 182.5 kgs of real H-Acid (M.Wt. 319.3). Stir for about half an hour to obtain smooth slurry. Then sprinkle slowly on the surface of H-Acid slurry, about 32-40 kgs of real Soda Ash as powder. Stir or 15-20 minutes and check pH of the solution; it should be between 6.8 – 7.2. Correct the pH in the said range with Soda Ash powder. H-Acid dissolves completely to give a clear solution under these conditions. Check a sample for pH and also for completeness of solution.

Stir the H-Acid solution at 60 rpm speed. Add HCl solution prepared above to the H-Acid solution preferably during about 20-30 minutes. Take care of roaming during acid addition. H-Acid precipitates out in a finely divided form. During reprecipitation, the mass tends to become thick which is brought to a stirrable form by diluting the charge to 1900ltre volume with treated water.

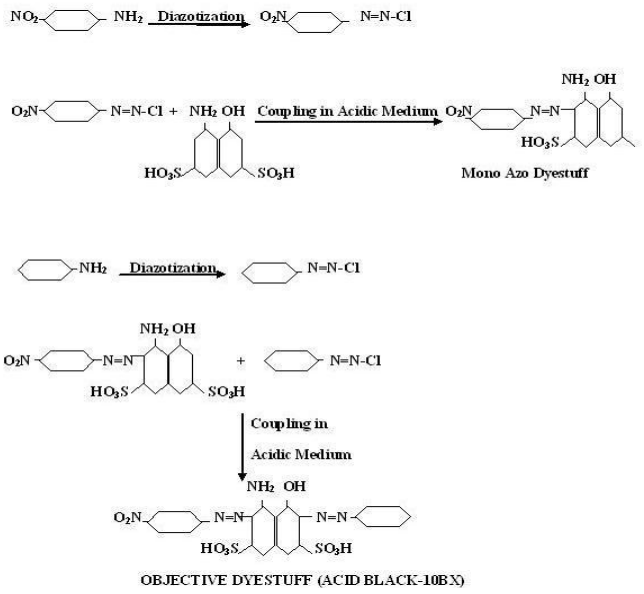

Figure 2. Reaction Mechanism Diagram

First Coupling:-

Check the volume and temperature of the p-NA Diazo solution. Destroys excess Nitrous Acid in the diazo as per the instructions given under preparations. Then run the H-Acid slurry into the p-NA Diazo solution, as fast as possible, allowing the temperature to rise upto 8^0C. Then add more ice as required and stir the coupling for one hour at 8-10^0C. Then further stir the coupling at 8-10^0C for about 8-10 hours or until the test for excess diazo with neutral R-Salt solution just becomes negative. Check a spot of the coupling slurry on the piece of the filter paper. The spot show the red dye almost precipitated. The coupling is now complete. Check the volume of the coupling it will about 5300litre at 8-10^oC.

F. Caustic Soda Solution

In a suitable Wooden Solution Vat, charge 250litre of treated water. Stir and ad 180kgs of as is 40% w/w Caustic Soda lye corresponding to 72kgs of real Caustic Soda. Measure volume and adjust it to 600litre at 20^0C by adding required quantity of ice and water.

G. Diazotization of Aniline

In suitable wooden solution vat, charge 160kgs of as is 30% w/w HCl corresponding to 48kgs of real HCl. Then charge necessary quantity of crushed ice to make up the volume to 600litre at 0-(-8)^{o}C. Now charge slowly, controlling fuming, 55kgs of real Aniline Oil (M.Wt. 93.0) and stir to form the hydrochloride. Check temperature and add enough surplus ice to keep floating on the surface. Then add as fast as consumed and controlling the temperature below 3^0C. 83litre of as is 50% w/vol. Sodium Nitrite Solution corresponding to 41.5kgs of real Sodium Nirite. During the nitrite addition, continuously test for blue on KI- Starch paper and also maintain the diazotization temperature strictly below 3^0C with the addition of mere ice as necessary. A distinct blue test for excess acidity on Congo Red papers must be shown throughout the diazotization. Stir the Diazo below 3^0C for 15-20 minutes. Confirm positive blue tests on Congo Red and KI-Starch papers. The diazotization is now complete. Measure volume of the diazo; it will be about 925litre at 0-2^oC.

Second Coupling:-

Check the temperature of First coupling. Add sufficient quantity of crushed ice to adjust its temperature to 0^0C. Then run into it the Caustic Soda solution prepared above to adjust the pH of coupling in the range of 2.7 – 3. The Mono azo dyestuff now goes into solution. Stir for 10 minutes and confirm the pH in the said range.

Then run into it the Aniline Diazo as fast as possible, maintaining the Coupling temperature below 3^0C. Stir the coupling for 10 minutes at 0-2^0C. Then add to it as fast as possible, preferably during about 10-15 minutes 230kgs of real Soda Ash as powder, repeatedly testing the coupling on B.Y. paper for a red test. Stir the coupling for 10-15 minutes at 0-2^0C to dissolve the Soda Ash and confirm a positive red test on B.Y. papers.

Stir the coupling for 2 hours at 0-2^0C throughout during stirring. Finally, stir the coupling for an hour and half without temperature control. The coupling is positively complete by now. Measure volume of the coupling; it will be about 7000litre at 5-8^0C.

H. Isolation & Filtration

Steam the bath slowly during 1 hour to 30^0C. Then during second hour, heat the batch to 50^0C. Finally, heat the batch to 85^0C during 3 hours. Measure volume and record; it will be about 8400litre at 85^0C. Then charge in the coupling, common salt at a rate of 1060litre by volume. This will account to 840kgs of Common Salt. Stir for half an hour at 85^0C. Finally, cool the batch indirectly through cooling coils to 40^0C. Check spot of isolation slurry on a piece of filter paper; it should show only a slight bluish run out. The isolation is complete.
The batch is now ready for filtration. Filter the batch through Filter Press at 40^0C. Discard M.L to drains. Air the press to no drip and dump the press. Weigh the wet cake and record weight. Dry cake wet dyestuff at 90^0C in air dryers. Weigh the dry, crude dyestuff and record weight. Pulverize the dried dyestuff and evaluate the ground sample for Strength and Shade against the Standard Sales Type. Formulate the blend to the level of the corresponding Sales Standard.

III. PROCESS MODIFICATION STEPS

- Increasing the process throughputs
- Increasing the transfer coefficients
- Increasing the interfacial area
- Increasing the driving force for mass transfer
- Hybridization of different unit operations

A. Components of process modification in manufacturing process.

- Efficient use of raw materials according to the reaction mechanism.
- Maintaining the reaction temperature by effective heat transfer mechanism.
- Efficient use of ice to maintain the required temperature. Use of proper ice cubes of definite size.
- Efficient drying system should be adopted so as to provide a good yield product.
- Isolation and filtration of product should be done cautiously so as to assure that there contains no impurities.
- Minimum waste should be generated by using alternate and efficient raw materials.

B. Cleaner Production Concept

- Cleaner Production can be defined as: A new and creative way of thinking about products and the processes that makes them. It is achieved by the continuous application of strategies to minimize the generation of wastes and emissions.
- For processes, Cleaner Production involves conserving raw materials and energy, eliminating as much as possible the use of toxic substances, reducing quantity and toxicity of emissions and wastes before they leave the process.
- For products, it means reducing their environmental impacts during entire life cycle from raw material extraction till ultimate disposal.
- Input material change includes the use of less hazardous materials or raw materials of higher quality, both of which may reduce the generation of waste in the process. Existing raw materials could be substituted with less polluting ones.
- Modifications of the working procedures, machine-operating instructions and process record keeping in order to run the processes at higher efficiency and with lower waste generation and emissions.
- Modification of existing production equipment and utilities, for instance by the addition of measuring and controlling devices, in order to run the processes at higher efficiency and lower waste and emission generation rates. Many a time, simple and inexpensive modifications can help to ensure that materials are not wasted.
- Replacement of the technology, processing sequence and/or synthesis pathway in order to minimize waste and emission generation during production is the CP interventions under the Technology Change technique.

C. Good Housekeeping

Poor maintenance can increase energy consumption by as much as 10 percent. A few easy housekeeping measures can help to minimize wastefulness:

- Check burner efficiency in heaters.
- Check heat exchangers for fouling and leaks.
- Check filters for fouling and increases in pressure drop.
- Look for water leaks; inspect steam traps regularly.
- Check for air leaks; make sure that doors fit well and seals work.
- Have instruments serviced regularly according to the manufacturer's recommendations.
- Check thermocouples and humidity sensors for fouling.

IV. STEPS FOR INTENSIFIED ENERGY EFFICIENT DRYING SYSTEM

When considering opportunities for saving energy, it is necessary to view the system holistically, from energy source to exhaust gas recirculation. Potential energy savings must be weighed against other factors including capital expenditure, safety, emissions, and product quality.

A. Mechanical Dewatering

One effective way to reduce the energy required for the drying process is to use mechanical means whenever possible to reduce

the water content prior to any thermal drying. Methods of mechanical dewatering include filtration, centrifugal force, gravity, high velocity air, or compression to force water from the material. Means of compression include presses, rollers, and belts that squeeze water out of the material.
The effectiveness of these methods is limited, and additional thermal drying is usually required. However, the energy used in mechanical dewatering is only 1% of the energy used to evaporate the same quantity of water

B. Control

Dryers have a number of inputs that, if properly controlled, will result in a cost-effective product that is of acceptable quality. Poorly controlled dryers waste energy both directly by consuming more energy than necessary and indirectly by yielding a product that doesn't meet specifications and must be discarded.
Dryer inputs fit in two categories: those that can be manipulated (e.g., valve, damper, and burner settings, fan speeds, and belt feed rates) and those that are not easily manipulated but that can greatly disturb components of the process (e.g., ambient air temperature and humidity, feedstock composition, and moisture content).
"The aim of a control system is to maintain the values of the outputs, i.e., quality and cost, at as near to their desired values as possible by changing the manipulable inputs so as to compensate for fluctuations in the values of the non-manipulable inputs."

Feedback controllers monitor the output, often outlet air temperature and humidity, and adjust manipulatable inputs like fan speed and/or feed rate. The limitation of such a system is that, in many cases, there is a significant lag between when the manipulatable inputs are adjusted and the corresponding changes affect the outputs. During the lag time, significant amounts of out-of-specification product can be produced.
Feed forward controllers monitor "disturbance" inputs like ambient air temperature and humidity and/or product moisture content and adjust the manipulatable inputs accordingly. The challenge with these systems is the need for a mathematical model that accurately predicts the effects of changes to the inputs on the final outputs. Since an accurate model does not always exist, a combination of feedback and feed forward control is used in some cases.

C. Insulation

Many dryers have hot surfaces that are exposed to air. Any loss of heat through these surfaces reduces energy efficiency. Insulating exposed surfaces and repairing damaged insulation can minimize heat loss. Properly insulating flanges and valves can help, as well.
The importance of good insulation cannot be overestimated. Poor insulation may reduce the effectiveness of other system changes like increasing the temperature differential in order to improve the productivity of the dryer. Higher temperatures and inadequate insulation means more radiant heat loss and wasted energy.

V. CONCLUSIONS

Intensified process and modification is been in studies for past decades but still these technologies are not adapted to its full scale. Process modification in dye industry can change the scenario and could lead to effective and more energy efficient production of useful dyes and its intermediates.
Waste and other polluting ingredients are big concern for the environment and many steps are being employed for to minimize the waste or recycle it, or to have useful ingredients that can be reused again, modifying the process can help eventually to reduce waste, improve raw material consumption, more energy saving, good and healthy environment for manufacturing purpose.
Implementing the cleaner production concept inside the manufacturing premise could ultimately lead to a good and efficient production of desired products with high yield and purity.
Manufacturing of dyes and its intermediates practices in Gujarat is very old and thus have an influential effect on the market, national as well as international. Thus, it is required to have modified/intensified production facility with eventual and efficient energy savings so as to sustain in the market both in terms of quality and environmental clarity.
Use hybrid technology to intensify the process can also eventually give a good manufacturing facility and highly energy efficient productivity.

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