

Global Anodizing Dye Perspective - Navigating the Dynamic Supply

Randy Yorston

Organic Dyes and Pigments LLC

Lincoln, Rhode Island, USA

www.organicdye.com



Abstract

Introduction

The use of dyes for anodizing has a long and varied history and there is no doubt that dyeing aluminum (and some other metals) through the anodizing process yields a variety of rich, stunning colors. Anodizing Dyes can turn a simple aluminum part in to a premium object, often mimicking other more expensive metals or metal finishes.

Anodizing Dyes are not created solely for the anodization process – instead, they are derived from dyes commonly used around the world for everything from Textile Dyeing and Printing, to Water Tracing, Printing Inks, Agricultural Products, Detergents, and Paper Manufacturing’

Anodizing Dyes represent a worldwide use of dyes, and they are subject to the global demand, availability and market pricing that effects all dyes. Since almost all dyes are manufactured in China, India, and to a smaller extent, Europe, any disruption of supply from these countries has a ripple effect across all industries that use dyes.

This paper will explore the world wide dye market and detail how recent environmental and production changes in dye manufacture in China has set the world wide dye market in turmoil.

Anodizing Dyes – What are they?

Anodizing Dyes are derived from two different dye classes – Acid Dyes and Mordants. Acid Dyes are typically applied and fixed at a low pH, hence the name. Acid dyes are very versatile and are used in a variety of industries, including Textiles (Wool and Silk), Agriculture (Water Coloring, Seed Coatings), Anodizing, and Detergent Coloring (Windex Blue), along with a variety of other niche uses. Acid Dyes typically run the entire shade spectrum from blues and greens, to reds, yellows and mixtures of those shades.

Mordant Dyes are not specifically dyes at all, but rather describe the use of mordant as a dye fixative for difficult to fix metal complex dyes. Mordant dyes typically feature earth tones and metallic shades, such as blacks, browns and muddy bronze. Since Mordant Dyes feature chromium complexes, environmental regulations have largely curtailed their use in industries other than anodizing, though you can still see them featured when dye users have extensive environmental controls in place.

Anodizing Dyes – Chemistry

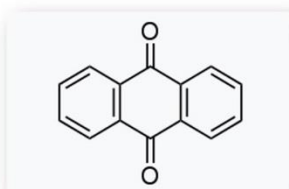
Acid Dyes come in a variety of chemical forms, each which pertain to different shade groups, depending on the chemical structure or chromophore.

Anthraquinone – Blues, Greens (Fig. 1)

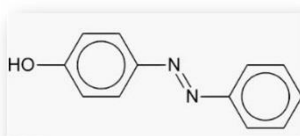
Metalized Azo – Reds, Browns, Yellows, Oranges (Fig 2)

Metal Free Azo – Violets, Bright Reds

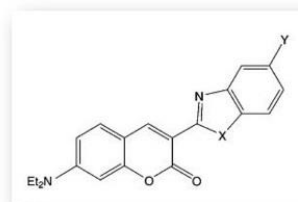
Sulphonated Coumarin – Bright Yellows (Fig. 3)



(fig 1) Anthraquinone



(fig 2) Azo Structure



(fig 3) Coumarin

Anthraquinone and Azo type Acid Dyes make up the majority of Anodizing Dyes and their manufacture, and as stated, is done primarily in China and India. Typically, Anthraquinone Dyes have good lightfastness and feature bright shades in the violet, blue and green spectrum. Azo type Acid Dyes feature shades in the orange and red spectrum and typically do not have as good a lightfastness as anthraquinone dyes; however, the Azo type dyes are more popular than anthraquinone based dyes based on the variety of shades that can be obtained.

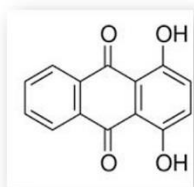
Metal complexed Azo Acid Dyes use metals such as copper, cobalt, nickel and chromium in their structure to produce specific solubility properties, improved lightfastness, improved wash fastness and enhanced bonding with specific fibers or substrates. This increased performance of Metalized Azo Dyes is often offset by the need to keep the actual metal portion (for example Chromium III) out of the manufacturing waste stream.

Anodizing Dyes – Manufacture

The first synthetic dyes were discovered and synthesized in 1856 by William Henry Perkin. His attempt to create the anti-malaria drug quinine in the laboratory (at that time in history, the vast British Empire included many areas of the world where malaria was a significant detriment to health) resulted in creating the coal-tar derived dye called Aniline Purple. From that point on, the synthetic dye industry, as well as its close cousin the pharmaceutical industry, was born.

Take a look around you, and look at all the things that feature color to one degree or another. Most of the color you see is derived from synthetic dyes. Through the very complex chemistry of manipulating dye molecules - adding, subtracting, combining additional chemical moieties - dyes can be made to color a vast variety of substrates (fiber, paper, solutions, yes even aluminum) and impart specific shades, fastness and activity.

An important key intermediate in the manufacture of Anthraquinone based dyes is 1, 4-



(fig 4) 1,4-Dihydroxyanthraquinone
(Quinizarin)

Dihydroxyanthraquinone, commonly known as Quinizarin (Fig 4). This intermediate is integral to the production of Anthraquinone based Dyes, and its interaction with other chemicals produces a large number of shades and dyes with particular properties (better light fastness, ability to react with different substrates, etc). The majority of the world's production of Quinizarin is in China, to support Chinese dye manufacturing.

Quinizarin is but one of many important feed stocks or intermediates necessary for dye manufacture. What happens, then, when this supply is disrupted?

World Wide Dye Manufacturing

As the dye industry grew in manufacture and use, so also did the chemical industry to support it. In many areas of the world, chemical manufacturing – specific intermediates and raw materials used in dye manufacturing – was located in the same region and geographical areas as the dye manufacture. This was done for a variety of reasons including logistics (no need to transport potentially hazardous chemicals long distances), expertise (many chemists and experts gathered in the same area) infrastructure (transportation, facilities, and favorable regulations), and experienced, low cost labor.

Through the end of the 19th century, and well into the 20th century, dye manufacturing (and related chemical manufacturing) was prevalent throughout the developed world. A snapshot of early 20th century dye manufacturing shows that the leading powers in the world were also leading dye manufactures:

Capacities of leading producer nations, in millions of pounds:

Germany (1913)	280
United States (1923)	94
Britain (1920)	43
France (1923)	24
Switzerland (1920)	24

Italy (1922) 10

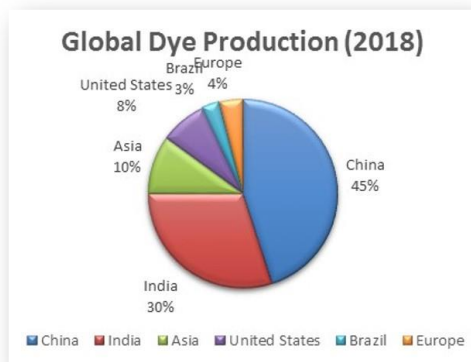
Japan (1919) 10

[*“The American Dye Industry.”* Journal of the Society of Dyers and Colorists, 40 (December 1924); 428-429]

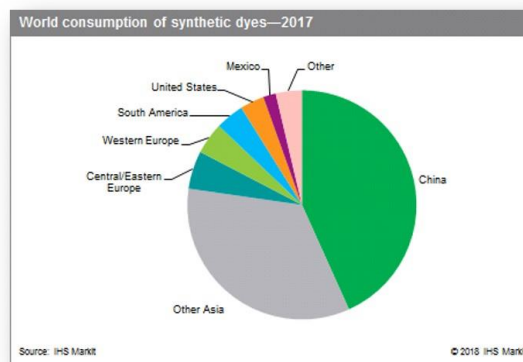
At this point in time, the new millennium, China and India are where the large majority of dyes are manufactured worldwide. China is also the largest consumer of dyes. How did this all occur?

It’s no secret that dye manufacturing can be a messy business. Not only is it technically intensive and demanding of many supporting chemical manufacturing (reaction chemicals, intermediates etc) sites, it also results in extensive chemical waste - much of it colored and perhaps difficult to hide. In our lifetime (last 40 years) environmental regulations and pressures on dye manufacturers in North America and Europe resulted in much of the dye manufacturing moving to China, and to a smaller extent, India. At the same time, much of the large scale Textile manufacturing – dyeing and printing – that was in North America and Europe also moved off-shore to China and other nations with less strict environmental laws.

Along with the environmentally driven move of dye manufacture and use to China and India, labor costs also factored into this exodus. Wages in China and India – whether at dye manufacturers or dye users – were much less than in the United States or Europe. China again came to the forefront as they now had a large part of the world wide dye manufacture industry and a significant proportion of the dye use industry through the growth of Chinese textile manufacturing.



Source AATCC December 2018 Issue



Source: IHS Markit

© 2018 IHS Markit

To a lesser degree, India also started producing more dyes and the intermediates needed for their manufacture, and as well their dye consumption rose as more textile production moved there. Though India’s environmental laws were not as strong as those in the United States and Europe, they did have stronger laws than China. Indian wages also have been historically higher than in China, but China always had better infrastructure and market presence to get their dyes distributed around the world. India was slow to catch up as far as worldwide distribution is concerned.

Turmoil in China

China's growth as the largest producer of dyes in the world, and one of the largest consumers of dyes, mirrors its rise to worldwide dominance in a lot of industrial and chemical manufacturing (for many of the same environmental and wage reasons).

As a result of China's dominance as a producer of raw materials AND a consumer of finished products, the explosive growth in the Chinese middle class became an important force. We've all seen the pictures of Beijing and other major Chinese cities shrouded for months on end in smog. We've heard horror stories of rivers and lakes turning in to toxic waste dumps. Entire cities and towns were moved to make way for rampant chemical manufacturing "provinces" – entire areas of hundreds of square miles given over to chemical manufacturing.

Environmental Laws

The Chinese middle class finally had enough, and Beijing listened.



In 2013, China began the Revised Environmental Protection Law of the People's Republic of China, which along with new sweeping environmental regulations, was to be implemented IMMEDIATELY. The law also included a crackdown on the corruption rampant in provincial pollution control bureaucracy.

Enforcement of the new environmental laws fell on local politicians and governments, who had a new set of air, water and ground environment laws to interpret and implement in their jurisdictions – IMMEDIATELY. No more five or ten year plans to get in compliance. It had to happen NOW.

And if compliance isn't met? Environmental fines of up to 200K RMB were imposed on violators. Business owners could be, and were, jailed if they failed to meet a compliance schedule. Provincial government regulators were jailed if their provinces were not meeting a compliance schedule. Manufacturing plants and entire manufacturing regions were closed instantly as government officials tried to figure out ways to get in compliance – without risking huge fines and jail time. Suddenly, to the rest of the world, there started to be unforeseen shortages of all kinds of chemicals and dye raw materials as plants were suddenly taken off-line. Availability of certain items - and there was no forecasting available of which items would be affected and when - became scarce and the worldwide supply tight, or non-available. And of course, with tight availability, prices rose quickly.

Safety & Health

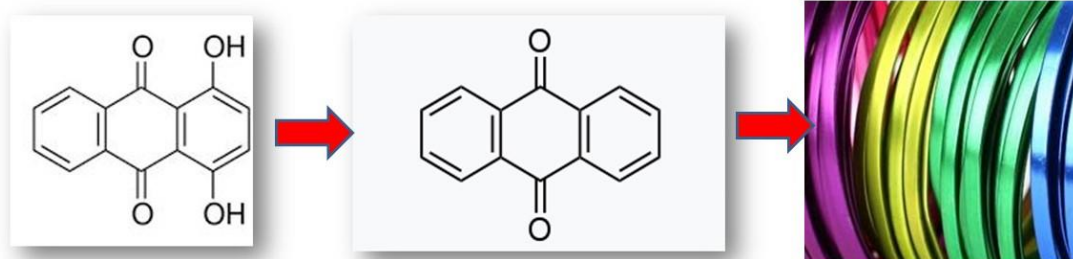
Since early 2018, there have been a number of safety incidents that also contributed to the dye turmoil in China. A series of plant explosions across China have killed and injured hundreds

of workers. These “plants” also included large industrial complexes that even though they were not affected by an explosion, were shut down for safety review. Depending on the cause(s) of the recent explosions, many producers of similar chemicals/dyes/products were also shut down until a cause could be identified, and then rectified at other similar producers. In scope, it is similar to an explosion at a small oil refinery in West Texas causing the shutdown – indefinitely – of all chemical manufacturing and oil refining in Houston!

“The March 21 explosion occurred at the Tianjiayi chemical plant in Xiangshui, Jiangsu province. The blast broke windows up to five kilometers away and destroyed a significant portion of the surrounding industrial park, killing 78 people and injuring hundreds more. This is not the first such incident in China—the same industrial park experienced an explosion in 2007 that killed eight people, and an even larger explosion occurred at a chemical warehouse in Tianjin in 2015. Chinese environmental conditions remain a significant concern beyond headline-grabbing explosions, with more than 110 fatalities resulting from industrial accidents in the first four months of 2019” [China Business Review, July 2019]

Date	Industrial Zone	Key Supplier	Category	Impact
May 2018	Shandong Hongwei blast	Reactive Blue 19	Reactive Dye Acid Dyes	supply
July 2018	Sichuan province explosion, kills 19 and injures 12	Chongqin Kuayue	Disperse intermediates	supply
August 2018	Jihua Blue 56 plant explosion with 1 dead	Jihua	Disperse intermediates	supply
March 2019	Yanchen plant explosion with 78 dead	Tianjiayi	Disperse/Reactive intermediates Acid Dyes	supply

Let’s go back to that raw material used in Anthraquinone Acid Dyes – **Quinizarin**. Jiangsu Province was one of a few places worldwide that manufactured Quinizarin, and that shutdown has drastically effected Anthraquinone Dye availability and pricing. Due to this shutdown, some dyes have risen 30-70% in price over a 6 month period, if you can get them at all. This has affected not only Acid Dyes (and Anodizing Dyes) but also a wide variety of other dyes used in a variety of industries. Furthermore, when a dye or chemical plant is brought back on-line, they have to fulfill domestic (Chinese) needs first before exporting to the rest of the world.



(fig 4) 1,4-Dihydroxyanthraquinone (Quinizarin)

(fig 1) Anthraquinone

India – Where are You?

As detailed earlier, India has a robust dye manufacturing industry, but is subject to tightening environmental controls. They are working to bring more chemical intermediate manufacturing online to lessen Chinese control over the dye manufacturing process, and smooth out availability issues. Indian dye manufacturers are working hard to take advantage of supply problems in China (when they can manufacture without Chinese intermediates or raw materials) and grow their industry accordingly. They are also working hard on building up the chemical and dye distribution networks around the world, partnering with many North American and European dye sellers and distribution companies.

New information received since publication (Info received early September) shows that the movement of dye manufacturing is already moving from China to India – or at least the fear is there that it is moving:

- "Indian dyestuff and intermediates enterprises are actively seeking technical cooperation with Chinese dyestuff and intermediates enterprises, and it is proposed to set up factories in India in the form of technical equity participation. (Aug, 2019, *Jiansu YaBang Dyestuff Corporation*)
- "It is not just individual companies that are worried. "The international competitiveness of our dyestuff products is also gradually declining, and we are facing a strong impact from Indian products..." (Aug, 2019, *Jiansu YaBang Dyestuff Corporation*)

Another view of WHY manufacturing of dyes (and Pharmaceuticals are moving from China to India:

- "First, India's labor costs are relatively low.
 - Second, India has 2.8% export tax rebate for dyestuff products. China has reduced the export tax rebate rate for dyestuff products from 13% to 0 since January 1, 2006. As for dye intermediates, China has an export tax rebate of 9 to 13 percent, while India has a 1.5 percent tax rebate.
 - Third, India's environmental policy is relatively loose...for now.
 - Fourth, local water, coal, electricity, and land have many concessions.
 - Fifth, the country's climatic factors are conducive to dye production."
- (Aug, 2019, *Sun Yang, director of Zhejiang Hisoar Pharmaceutical Co.*)

China – Tariffs?

As of January, Anodizing Dyes are subject to the full 25% Tariff imposed by the US Government, previous to that it was 10% imposed since last fall. These additional costs have not helped the supply stability issues.



Your Anodizing Dye Supplier – the Right Choice

To date, even with (or in spite of?) dynamic Chinese dye availability and pricing, there has not been the significant upward pressure on Anodizing Dye pricing that has been seen in many other industries. This could be due in part to the smaller niche Anodizing Dyes represent, or to dye supplies already in inventory away from China. Part of this stability is also due to the fact that some international dye manufacturers have formed joint ventures with Chinese companies to at least assure they are in line to get supplied...eventually.

It is also a fact that many Anodizing Dye suppliers are absorbing some of these large price swings in hope of “riding out the storm”. But as we have seen, the storm is far from being over.

Today’s premium Anodizing Dye supplier not only provides technical and application expertise, they also have to be experts at Global Supply Chain Management. They must have the quality expertise and knowledge to standardize these dyes from different manufacturers and different countries so that today’s Metal Finisher and Anodizer are assured of a consistent product to work with. Global Supply Chain Management also necessitates qualifying multiple suppliers of the same dye to smooth over availability issues.

Today’s Anodizer must work with their supplier to forecast usage and shade trends so that dye logistic pipelines – which can stretch up to three months for ocean deliveries to the United States – are filled with the right dye shade for the upcoming needs.

Your Anodizing Dye supplier should also keep significant inventory which can smooth out “some” short term availability and pricing issues – as long as they didn’t have to buy when the pricing was at the top of an upward swing.

There is doubt that the dynamic dye supply and pricing situation in China will ever return to earlier reasonable levels. Some Chinese supply voids will be filled by Indian suppliers, but China, and all the good and bad that comes with it being the center of dye manufacture world, will still move the markets with any move they make. Your supplier should have a good understanding of the Global Dye Industry, what is going on NOW in China (and the rest of the world), strong interest in what may happen in the coming years, and the foresight to plan accordingly.

<end>