AFD Ep 419 Links and Notes - Synthetic Dyes [Bill/Rachel] - Recording Mar 28, 2022

- Intro: Humans have been changing the colors of things with dye since prehistoric times, but for thousands of years these dyes were all based on things found in the natural world. By the early industrial revolution, some inventors were dabbling with experiments to see if they could come up with artificial colored dyes. But it was not until the mid-19th century that synthetic dyes, based on chemistry and chemical reactions (as opposed to physical reactions), were invented and mass-produced. This story, as we'll get to in a moment, starts in the United Kingdom, but as the first Industrial Revolution transitioned into the second, the story shifts overseas, as it so often did. Almost immediately synthetic dyes became all the rage, launching a massive new industry and enhancing numerous existing industries, including fashion. On this week's episode we'll discuss the emergence of synthetic dye and why it didn't happen until the period that it did, and we'll also talk about the environmental catastrophe of the synthetic dye industry, which is still ongoing.
    - I'm going to go over the history and Rachel will explain the basics of the physics & chemistry that makes certain sub-categories of dyes behave in a desired (or undesirable way) as well as the coloration itself
- General information/history
    - Mauveine and mass production
        - How it was accidentally invented (woops! that's not a malaria drug!)
            - In 1856, British chemistry student William Henry Perkin was just 18 years old when he attempted unsuccessfully to use coal tar to synthesize antimalarial quinine (first synthesized a couple years earlier in Norway by a German chemist). Instead, after purifying coal gas through the various stages of benzene and aniline, Perkin inadvertently found a weird goop that faded to a pale purple. and decided with a friend to figure out if it could be used to color anything. They quickly confirmed that it could be applied to textiles, specifically silk, and remained purple despite sunlight and washing. Perkin patented it and got his father and brothers to assemble capital investment to build a factory and basically by 1857 create a new synthetic dye industry from scratch – or at least to work with existing natural dye producers to get them to branch out. Eventually synthetic dyes basically killed the natural dye industry completely, with the exception of logwood, which is still chugging along in small but valuable volumes, much like it was in the 18th century Golden Age of Piracy and illegal colonial harvesting on the Spanish Main, although now with modern medical usages we'll discuss later.
            https://www.britannica.com/technology/dye/Synthetic-dyes
            https://en.wikipedia.org/wiki/Haematoxylum_campechianum
            (logwood)
            - In theory, Britain was well-positioned after the First Industrial Revolution to take this innovation and run with it, because of the many textile mills and the roaring coal-based heavy industry producing tons of coal tar byproduct that could be used to make dye. And for a few years, things were going well, and Perkin did become a rich man and a very influential chemist, as did his son later. But ironically, in a further demonstration of why Britain started to fall behind in industrial development after the mid-19th century, despite the huge and revolutionary success of the

chemistry research that was creating things like synthetic dye, the government and private industry got bored and disinterested with innovative research and scientific education after the 1861 death of Prince-Consort Albert of Saxe-Coburg & Gotha (who had been pushing it at an official level for decades), and pioneering chemists like August Wilhelm von Hoffman (whose student Perkin had invented Mauveine) simply went home to Germany less than a decade later. German industry remained chemistry-oriented and still is. (Example: BASF.) This kind of trend helps explain why Second Industrial Revolution developments tend to originate in the United States or Germany, propelling them to rising Second-Tier power status with the resulting consequences for the 20th century…

- The rapid takeoff in popularity of the new vibrant synthetic purple
    - All of a sudden, for the first time in thousands of years of fashion history, Europe had a source of purple textile dye that didn't come from mollusc mucus and was no longer like Roman Emperor-level expensive to obtain. But notably, the royals were also quite interested. Queen Victoria and French Empress Eugénie both helped popularize the color.
    - The new synthetic purple dye became a fashion sensation in Britain, France, and elsewhere under names like Mauveine or Mauve, and probably contributed a bit to the emergence of the "off-the-rack" mass-produced clothing industry we've discussed in various past episodes. The actual molecular structure of Mauveine wasn't even understood until 1994, 138 years later, and there are more than a dozen variants known today: https://en.wikipedia.org/wiki/Mauveine
    - I want to bring in some statistics at this point from a fantastic and freely available quantitative study of the early 20th century synthetic dye industry, published in March 2021 in the journal Heritage Science, by Eric Hagan and Jennifer Poulin. From 1856 to 1924, some 1,200 distinct synthetic dyes were invented. The number of new colors being invented peaked around 1890 annually, several decades after the start of the industry, although there were still sudden bursts of new dyes now and then as new chemical categories were explored. Their usage varied based on factors like production cost, how toxic it was, and "fastness" (which is basically how well or durably it sticks in the dyed product, usually textiles). Many of these early synthetic dyes simply did not hold up well to sunlight or washing, and except in cases where the faded color look could be marketed as fashionable, or where a clothing company could specifically sell a garment as being a dazzling one-time event piece, the textile producers wanted something more durable. There was often friction between the companies developing dyes, the companies actually dyeing the textiles, and the companies trying to buy finished textiles to sell to the public because of these challenges. Inventing new dyes and shipping them around the world during that period of globalization was also profitable to manufacturers because both activities helped evade patents on specific colors. In 1916, even with World

War I already under way in Europe, foreign dye importation to the United States was still a big business, and Commerce Department records showed almost 300 different colors being imported in volumes exceeding 10,000 pounds per year, with some of these individual colors being imported by the hundreds of thousands or even millions of pounds annually. Moreover, these colors were often broad classifications with many sub-variant tones from slight tweaks to the chemical processes and ingredients during production. But World War I was proving to be a huge crisis for American companies that had relied upon foreign dye imports from Europe (and especially Germany), which were now increasingly under supply-chain pressure, and this is what spurred a US government emphasis on domestic synthetic dye production in the US. Compared to the nearly 300 dyes being imported in 1916, there were around 100 being produced in the US in 1914 when the war began, and there were arguably around 900 different dyes in use by American industry if you count all the sub-variants, so there was some forced substitution and consolidation down to a narrower number of dyes during the war. In 1914, in just the top 10 imported synthetic dyes, there were 3 blues, 6 blacks, and one yellow. https://heritagesciencejournal.springeropen.com/articles/10.1186/s40494-021-00493-5

- Some other early examples of colors/compounds:
    - *Perkin's accidental discovery of mauve as a product of dichromate oxidation of impure aniline motivated chemists to examine oxidations of aniline with an array of reagents. Sometime between 1858 and 1859, French chemist François-Emmanuel Verguin found that reaction of aniline with stannic chloride gave a fuchsia, or rose-coloured, dye, which he named* ***fuchsine****. It was the first of the triphenylmethane dyes and triggered the second phase of the synthetic dye industry. Other reagents were found to give better yields, leading to vigorous patent activity and several legal disputes. Inadvertent addition of excess aniline in a fuchsine preparation resulted in the discovery of aniline blue, a promising new dye, although it had poor water solubility. From the molecular formulas of these dyes, Hofmann showed that aniline blue was fuchsine with three more phenyl groups (—C6H5), but the chemical structures were still unknown. In a careful study, the British chemist Edward Chambers Nicholson showed that pure aniline produced no dye, a fact also discovered at a Ciba plant in Basel, Switzerland, that was forced to close because the aniline imported from France no longer gave satisfactory yields. Hofmann showed that toluidine (CH3C6H4NH2) must be present to produce these dyes. All these dyes, including mauve, were prepared from aniline containing unknown amounts of toluidine.* https://www.britannica.com/technology/dye/Development-of-synthetic-dyes (https://en.wikipedia.org/wiki/Fuchsine Basically a magenta dye when liquid, but dark green as a crystal. It is a confirmed carcinogen to workers producing it.)
    - Various vibrant synthetic greens and blues soon followed and eventually yellows (which were often based on sulfur)

- Initially, a then-unsophisticated understanding of human perception of color and visible light from a scientific standpoint at the molecular level (so, there were some incorrect hypotheses on color and dye properties at the time, but the rise of synthetic dyes encouraged further research…)
    - See also the “structure and colour” section here: https://www.britannica.com/technology/dye/Synthetic-dyes
    - *Advances in structural theory led to investigations of correlations between chemical constitution and colour. In 1868 German chemists Carl Graebe and Carl Liebermann recognized that dyes contain sequences of conjugated double bonds: X=C—C=C—C=C—…, where X is carbon, oxygen, or nitrogen. In 1876 German chemist Otto Witt proposed that dyes contained conjugated systems of benzene rings bearing simple unsaturated groups (e.g., —NO_2, —N=N—, —C=O), which he called chromophores, and polar groups (e.g., —NH_2, —OH), which he named auxochromes. These ideas remain valid, although they have been broadened by better recognition of the role of specific structural features. He had also claimed that auxochromes impart dyeing properties to these compounds, but it later became clear that colour and dyeing properties are not directly related. Witt suggested the term chromogen for specific chromophore-auxochrome combinations.*
    - *The colours of dyes and pigments are due to the absorption of visible light by the compounds. The electromagnetic spectrum spans a wavelength range of 10^{12} metres, from long radio waves (about 10 km [6.2 miles]) to short X-rays (about 1 nm [1 nm = 10^{-9} metre]), but human eyes detect radiation over only the small visible range of 400–700 nm. Organic compounds absorb electromagnetic energy, but only those with several conjugated double bonds appear coloured by the absorption of visible light. Without substituents, chromophores do not absorb visible light, but the auxochromes shift the absorption of these chromogens into the visible region. In effect, the auxochromes extend the conjugated system. Absorption spectra (plots of absorption intensity versus wavelength) are used to characterize specific compounds. In visible spectra, the absorption patterns tend to be broad bands with maxima at longer wavelengths corresponding to more extended conjugation. The position and shape of the absorption band affect the appearance of the observed colour. Many compounds absorb in the ultraviolet region, with some absorptions extending into the violet (400–430 nm) region. Thus, these compounds appear yellowish to the eye—i.e., the perceived colour is complementary to the absorbed colour. Progressive absorption into the visible region gives orange (430–480 nm), red (480–550 nm), violet (550–600 nm), and blue (600–700 nm); absorption at 400–450 and 580–700 nm gives green. Black objects absorb all visible light; white objects reflect all visible light. The brilliance of a colour increases with decreasing bandwidth. Synthetic dyes tend to give brilliant colours. This undoubtedly led to their rapid rise in popularity because, by comparison, natural dyes give rather drab, diffuse colorations.*
- While the already gigantic textile industry of 1850s Great Britain and France were natural first targets for synthetic dye applications, the wood-pulp paper industry was just about to emerge and ink would be needed for all the new typewriters and newspaper machines, too, so there were plenty of opportunities to branch out in the use of new dyes. Even dyed leather was a future use case. Paints and

then PVC plastics, as we talked about on our episode on that, also used dyes. And we'll circle back in a bit to food coloring (often in the same category as other human consumable dye uses like cosmetics).

- How does modern synthetic dyeing of materials work?
    - *In dyeing operations, the dye must become closely and evenly associated with a specific material to give level (even) colouring with some measure of resistance to moisture, heat, and light—i.e., fastness. These factors involve both chemical and physical interactions between the dye and the fabric. The dyeing process must place dye molecules within the microstructure of the fibre. The dye molecules can be anchored securely through the formation of covalent bonds that result from chemical reactions between substituents on the molecules of the dye and the fibre. These are the reactive dyes, a type introduced in 1956. Many dye-fibre interactions, however, do not involve covalent bond formation. While some dyeing methods have several steps, many dyes can be successfully applied simply by immersing the fabric in an aqueous solution of the dye; these are called direct dyes. In other cases, auxiliary compounds and additional steps are required to obtain the desired fastness. In any event, questions arise as to how and how well the dye is retained within the fibre. The structure of the fibres from which the common fabrics are made provides some guidance for the selection of useful colorants.*
    - Some remedial chemistry here: There are several types of bonds: Covalent, where molecules share electrons; ionic, where negatively charged and positively charged molecules are attracted to each other; hydrogen bonding is an intermolecular force (IMF) that forms a special type of dipole-dipole attraction when a hydrogen atom bonded to a strongly electronegative atom exists in the vicinity of another electronegative atom with a lone pair of electrons; and Van der Waals forces, where molecules that are close together form a weak attraction to each other.
    - Dyeing natural fibers vs synthetic fibers - Natural fibers are made up of chains of polymers. Wool, silk, and leather are made up of protein chains, while cotton is made of cellulose chains. These fibers are then spun into thread or yarn to be made into fabric. Natural fibers are intrinsically porous and these pores provide spaces for the dye molecules to bind to the fiber. Synthetic fibers, the most common being polyester, are made up of chains of synthetic analogs of proteins separated by hydrocarbon chains. The terminal hydroxyl group of these chains do provide a site for polar binding with dyes, but the chains are packed tightly and are less porous than natural fibers. Acrylics are another synthetic fiber with more polar groups along the chain to improve dyeability. There are also the semisynthetic fibers, such as viscose - made from wood pulp - and rayon. These fibers don't allow for hydrogen bonding, and different dyes are needed than for either natural or synthetic fibers.
    - Direct dyeing - The fabric is dyed in a hot aqueous solution of the dye. The dye is then trapped in the fiber structure with hydrogen bonding and Van der Waals forces. Metal salts may be applied to the fabric beforehand to improve dyeability and fastness of the dye; these metal salts are known as mordants. Mordants also help vary the colors of dyes. *For example, treatment with aluminum hydroxide, $Al(OH)_3$, before dyeing with alizarin produces Turkey red, the traditional red of British and French army*

    uniforms. Alizarin gives violet colours with magnesium mordants, purple-red with calcium mordants, blue with barium mordants, and black-violet with ferrous salts.
    https://www.britannica.com/technology/dye#ref277819
        - *Side note: Historically [Alizarin] was derived from the roots of plants of the madder genus. In 1869, it became the first natural dye to be produced synthetically.*
          https://en.wikipedia.org/wiki/Alizarin
    - Disperse dyeing - This technique is used for polyester and other synthetics. The fabric is immersed in a boiling aqueous dispersion of insoluble dyes. The dyes then transfer to the fabric and react with the fabric to form a solid solution. The exact mechanism isn't known, but it's believed the chains relax from their tightly formed bonds to allow the dye in, then revert back to their tightly chained state.
    - Vat dyeing - This is an ancient dyeing technique. A dye is converted from a soluble to insoluble state. For example, indigo is reduced to leucoindigo, a soluble colorless form, then cotton is immersed in the leucoindigo bath. After the cotton is removed from the bath, the leucoindigo is oxidized back into indigo. The indigo molecules form complexes that are too big to leave the fiber structure, and indigo is insoluble, so the indigo is trapped in the fabric.
    - Azo dyeing - This technique was developed in the late 19th century. A diazonium salt reacts with a coupling component to form a dye. A fabric can be immersed in a solution of coupling component then a solution of diazonium salt to form the dye right on the fabric. Alternatively, the fabric can be treated with diazonium salt before immersion into the coupling component solution. Because the dye is formed in the fiber, it has excellent fastness.
    - Reactive dyeing - This technique directly links the dye to the fiber using covalent bonds. This technique was developed in the 1920s, but the bonding process led to degradation to the fiber itself. It wasn't until the 1950s that the process was perfected. This process is very effective for dyeing cotton and cotton-poly blends.
    - https://www.britannica.com/technology/dye/Synthetic-dyes
    - https://fashion-history.lovetoknow.com/fashion-clothing-industry/chemical-synthetic-dyes
    - In 2021, the global synthetic dye industry was meeting a market demand for dye worth over $18 billion and still growing by nearly double-digit percentages in value annually. Apparently a pretty obscene amount of this market growth is literally just packaging materials for other products. Another rapidly growing sub-market is dyes suited to the specific stretchy component materials of sportswear and athleisure garments
      https://www.thebusinessresearchcompany.com/report/synthetic-dyes-global-market-report
- Food coloring
    - Various types of superficial or embedded coloring in foodstuffs
        - *Technically, color additives are any dye, pigment or substance that can impart color when added or applied to a food, drug, cosmetic or to the human body.*

        A color additive is often considered to belong to one of two classes: "natural" color additives, or "synthetic" color additives. The distinction is not always meaningful because there are some color additives that are considered natural that are produced through chemical synthesis.

        Whether a color additive is synthetic or natural has no bearing on its overall safety. Both types of color additives are subject to rigorous standards of safety prior to their approval for use in food.

        There are three types of color additives:

        Straight colors - dye (soluble) or pigment (insoluble) that aren't mixed or used in a chemical reaction with another substance;

        Lakes - formed by chemically mixing straight colors with precipitants or substrata. Lakes must be made from certified batches of straight colors with the exception of carmine made from cochineal extract. Lakes are used in applications where color bleeding is undesirable such as frostings;

        Mixtures - As the name implies, mixtures are formed by mixing one color additive with one or more other color additives, or one or more straight colors and one or more diluents

        - Here's the trade association site (their role seems to be to lobby regulators to say "no you can eat that, it's fine, have a treat": https://iacmcolor.org/
    - Safety regulation for consumable dyes? Food coloring laws use a positive listing of permitted dyes, rather than a negative listing of banned dyes. In the US, the Pure Food and Drug Act of 1906 reduced the list of permitted synthetic colors from 700 to 7. As of 2016, there are 7 dyes permitted in food, though not the same 7 as were permitted in 1906. There is also a dye permitted to color orange peels, and a dye used to color sausage casings that hasn't been produced since 1978, but it hasn't been officially delisted. There are also several permitted natural food dyes such as elderberry juice, annatto, turmeric, and caramel coloring. https://en.wikipedia.org/wiki/Food_coloring#History_of_artificial_food_colorants
- Research/medical dye
    - Dye used in studying samples
        - https://en.wikipedia.org/wiki/H%26E_stain Haematoxylin and Eosin stain, used in pathology. Haematoxylin stains cell nuclei blue and eosin stains extracellular material pink. It's considered the gold standard in pathology.
        - https://en.wikipedia.org/wiki/Gram_stain Used in bacteriology to differentiate bacteria based on the composition of their cell walls. Crystal violet is used to stain bacteria. Gram-positive bacteria have a thick layer of peptidoglycan in the cell wall that retains the stain, while gram-negative bacteria have a thinner cell wall that doesn't retain the stain. Iodine is used to strengthen the cell wall-crystal violet bond. Ethanol is used to wash the slide; gram-positive cells will still retain the violet stain, while gram-negative cells will have the stain washed away. A counterstain of

safranin or fuchsine will then be applied to stain gram-negative cells pink, making it easy to differentiate gram-positive and gram-negative cells.

        - Uh oh – the Logwood used for this might experience shortages soon and need to be replaced but no one can agree on a substitute and everyone would probably need to be retrained on a new dye: https://en.wikipedia.org/wiki/Haematoxylin#Shortages_and_possible_alternatives
    - Dye used in the human body for condition treatment (19th century):
        - *In 1891 Paul Ehrlich discovered that certain cells or organisms took up certain dyes selectively. He then reasoned that a sufficiently large dose could be injected to kill pathogenic microorganisms, if the dye did not affect other cells. Ehrlich went on to use a compound to target syphilis, the first time a chemical was used in order to selectively kill bacteria in the body, he also used methylene blue to target the plasmodium responsible for malaria.*[15]
    - Dye used in the human body for diagnostics (present-day) - Contrast dyes are used to improve imaging for CTs or X-rays. Typically made from iodine or barium sulfate. They can be injected or swallowed. MRI contrast agents are used to change the magnetic properties of nearby hydrogen nuclei to change how they appear on the MRI, and as such aren’t classified as dyes.
- Pollution consequences
    - There is a horrifying history of synthetic dye pollution over the past 166 years because the nature of applying most dye involves mixing it into water-based solutions and dunking an object or component ingredient into that solution until the dye takes, which still leaves a lot of colored wastewater at the end of the process. And when an industrial process finishes with wastewater, traditionally this has simply been dumped right back into the local environment, such as a stream, river, pond, or ocean. And unless it’s food coloring type dye, it’s probably not good for local wildlife or the aquatic ecology, especially when it blocks sunlight. A lot of these dyes are pretty harsh, toxic, or cancerous products derived from sulfur, acid, benzene, etc.
        - Astonishingly, some developing economies still use one of the toxic or carcinogenic mid-19th century synthetic dyes, Malachite Green, as an antimicrobial solution in aquaculture, even though eating fish that have consumed Malachite Green has been a known serious risk to humans for decades. https://en.wikipedia.org/wiki/Malachite_green
    - Shocking present-day volumes of dumping still continue, with the better case scenarios often still involving using carbon-filtering on the wastewater to somewhat reduce the pollution content before its release but then still leaving masses of toxic carbon filters to be dumped into landfills. In 2009, to give a sense of the scale of the dye wastewater problem, which has only really grown since then, China alone was generating 1.6 billion tons of dyed wastewater yearly. Chinese and American researchers at the time were working together on trying to invent various filtration and sort of sponge-like technologies that could clean up the wastewater. https://www.chemistryworld.com/news/new-solution-for-dye-wastewater-pollution/3002870.article
    - Some articles suggest possible hope for eco friendly but still artificial dyes, part of so-called “green chemistry,” but that sector has yet to really prove itself: https://www.sciencedirect.com/book/9780081024911/the-impact-and-prospects-of-green-chemistry-for-textile-technology#book-description

- Some emerging market countries like India have banned certain kinds of synthetic dyes in favor of all-natural dyes because the synthetic substitutes are simply too ruinous to the environment and public health to tolerate importation or local production: https://www.thebusinessresearchcompany.com/report/synthetic-dyes-global-market-report