Colour: History and Advancements

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The article traces briefly the history of dyes and pigments from the prehistoric times to modern times. Till the late 18th century, the colouring substances obtained from natural sources, i.e., earth, plants and animals, were used. From the middle of the 19th century, starting with Perkin's work, synthetic dyes were being made. Much research effort went into developing an increasing number of colouring materials. Today, the range of applications the dyes enjoy is limitless.

History of Dyestuffs

As soon as we open our eyes in the morning we see colour everywhere. It determines our moods as well as emotions. Natural colours are all around us, in the sky, sea, animals, birds, trees and food too. Very often colour of the food is the judging parameter of its quality.

In history, earth pigments were probably first recognized simply because their colour stood out when hard lumps of rock were examined. Such rocks were broken up and the desirable coloured bits were picked out. The coloured pigments were then ground to a fine powder and blown onto the painting surface using a hollow tube, or mixed with fatty materials to form a kind of crude paint that was applied with the fingers or a reed. The prehistoric cave paintings found in parts of Spain and France were made in this way. Examples of such earth pigments are the bright red pigment vermilion (mercury sulphide), the yellow orpiment (arsenic trisulphide), the green malachite (basic copper carbonate) and the blue lapis lazuli (natural ultramarine). There are many natural sources of white pigments such as chalk and kaolin, while black pigments could be obtained as charcoal from incompletely burnt wood and as soot in smoke from burning oils.

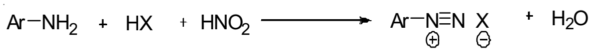
Keywords
Functional colorants, synthetic colorants, high performance pigments.

Synthetic dyes and pigments have been available to the colorant user since the mid-nineteenth century. The important naturally-occurring substrates of pre-industrial societies (cotton, linen, silk, wool, leather, paper, wood) share certain similarities, since they are all essentially saccharidic or peptide polymers. They could thus be coloured using a relatively short range of dyes and pigments, also of natural origin.

Important Breakthroughs

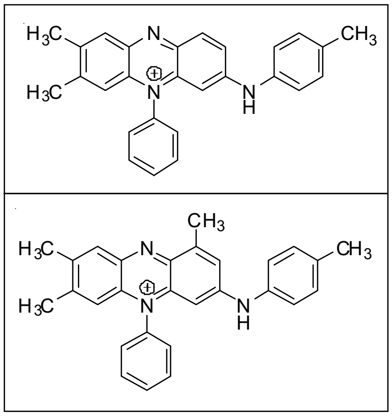
It can be said that the first synthetic dye was picric acid. This was first prepared in laboratory in 1771. It was found to dye silk fabric a greenish-yellow colour; however the fastness properties were very poor, thus it was of no commercial value. The next synthetic dye, Mauveine (*Structures* **1** and **2**), was discovered by Perkin in 1856. In attempts of producing quinine from oxidation of allyl toluene, he observed formation of a low yield of purple dye, which he subsequently patented and launched in the market in 1857.

Shortly after Perkin, a discovery was made which led to what is now the dominant chemical class of dyestuffs, the azo dyes. This development stemmed from the work of Peter Griess, who in 1858 passed 'nitrous fumes' (which correspond to the formula N_2O_3) into a cold alcoholic solution of 2-amino-4,6-dinitrophenol (picramic acid) and isolated a cationic product, the properties of which showed it to be a member of a new class of compounds [1]. Griess extended his investigations to other primary aromatic amines and showed his reaction to be generally applicable. He named the products *diazo* compounds and the reaction came to be known as the *diazotisation* reaction. This reaction can be represented most simply as follows,



$$\mathrm{Ar{-}NH_2} + \mathrm{HX} + \mathrm{HNO_2} \longrightarrow \mathrm{Ar{-}\underset{\oplus}{N}{\equiv}N}\ \underset{\ominus}{\mathrm{X}} + \mathrm{H_2O}$$

In this HX stands for a strong monobasic acid and Ar is any aromatic or heteroaromatic nucleus. This further led to the spectrum of azo dyestuffs.



Structure 1. (top)
Structure 2. (bottom)

The objective of planned research on synthetic dyes was to replace the leading natural extracts (alizarin and indigo) by their synthetic equivalents. Simultaneously, with this diligent and ultimately successful effort, other chemists were discovering totally new chromogens unknown in nature: azine, triarylmethane and others from arylamine oxidation, azo colorants from the diazo reaction, and eventually azo-metal complexes and phthalocyanines. Building on success with indigo and anthraquinone derivatives, the systematic approach led to related but new chromogens with outstanding properties: vat dyes and novel pigments.

The discovery of reactive dyes in 1954 and their commercial launch in 1956 heralded a major breakthrough in the dyeing of cotton.

Commercialization and Growth

The early dyes industry saw the discovery of the principal dye chromogens (the basic arrangement of atoms responsible for the color of a dye). Indeed, apart from one or two notable exceptions, all the dye types used today were discovered in the 1800s [1]. The introduction of the synthetic fibers, nylon, polyester, and polyacrylonitrile during the period 1930–1950, produced the next significant challenge. The discovery of reactive dyes in 1954 and their commercial launch in 1956 heralded a major breakthrough in the dyeing of cotton; intensive research into reactive dyes followed over the next two decades and, indeed, is still continuing today ([1], Section 3.1).

The oil crisis in the early 1970s, which resulted in a steep increase in the prices of raw materials for dyes, created a drive for more cost-effective dyes, both by improving the efficiency of the manufacturing processes and by replacing tinctorially weak chromogens, such as anthraquinone, with tinctorially stronger chromogens, such as (heterocyclic) azo and benzodifuranone. These themes are still important and ongoing, as are the current themes of product safety, quality, and protection of the environment. There is also considerable activity in dyes for high-tech applications, especially in the electronics and nonimpact printing industries.

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The industrial revolution brought about, in the 19th century, the rise of the chemical industry, which is such an important part of the world economy today. The discovery in the 1850s of the first synthetic dye by William Perkin and of the diazo reaction by Peter Griess started the search for other synthetic colorants, leading eventually to their almost complete market dominance. Many of what are now the largest international chemical companies began their activities in this area, later expanding into polymers and pharmaceuticals. For over a hundred years, research aimed at synthesizing new organic colorants was actively pursued. Patents were filed and new products appeared in the market. Thousands of new compounds were prepared and tested so that tens of new colorants, generally dyes, could be introduced commercially. Some of these were also tested for suitability as pigments, but few had all the properties required. Only the organic phthalocyanine and the inorganic titanium dioxide pigments have gone into large-scale production directly as pigments without being first used as dyes.

Functional Applications

Many specialized applications of colorants are related to the way in which they absorb and emit light. The ability of a dye molecule to absorb depends critically on its orientation with respect to the electrical vector of the incident light, i.e., the polarization of absorption.

In recent years this has become of practical significance in the field of liquid crystal displays. Colorants exhibiting high absorption of infrared light have found many diverse applications, ranging from solar energy traps to laser absorbers in electro-optical devices. Dye lasers are based on dyes that fluoresce with high quantum efficiency. They must show good photostability and be marketed in a state of high purity, thus commanding a high unit price. Fluorescent dyes are also used in biochemical and medical analysis where extremely low detection limits are required. Polymeric colorants have been developed as potential food colourings, since chemicals of relative molecular mass greater than about 20,000 cannot be absorbed into the gastro-

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intestinal tract. Such colorants should pose no toxicological problems as food additives. The chemical or photochemical activity of dyes forms the basis of many of their innovative uses. Indicator systems and lactone colour formers exploit reversible colour changes. Thermochromism is applied in novelty inks, temperature sensors and imaging technology. Photosensitising cyanine dyes are used to transfer absorbed light energy to silver halides in photography. Certain dyes are effective sensitisers of free-radical reactions, thereby initiating the crosslinking or photodegradation of polymers on exposure to light. Photochromic colorants have been employed in light monitors, reversible sun screens, optical data recording and novelty surface coatings.

Latest Developments

The last 30 years, and particularly the last decade, has witnessed a phenomenal rise in the growth of dyes for high-technology (hi-tech) applications. The advent and/or consolidation of new imaging technologies, such as electrophotography (photocopying and laser printing), thermal printing, and especially ink-jet printing; invisible imaging by using infrared absorbers in optical data storage, computer-to-plate and security printing; displays, such as liquid crystal displays and the newer emissive displays such as organic light emitting devices; electronic materials, such as organic semiconductors; and biomedical applications, such as fluorescent sensors and probes, and anti-cancer treatments such as photodynamic therapy, created the need for novel dyes to meet new and demanding criteria. Dyes, and related ultraviolet (UV) and particularly infrared (IR) active molecules, which have been specifically designed for these hi-tech applications, are generally called functional dyes.

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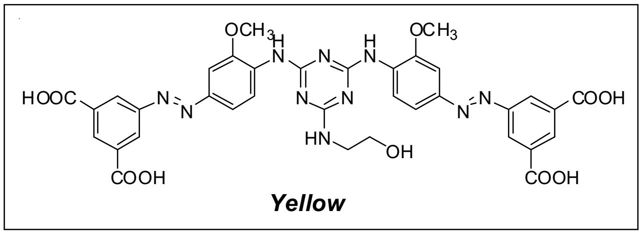
Functional dyes may be classified in several ways. To cover each class is not in the scope of this article; thus we have made an attempt to address the same based on their interactions.

Interactions of Functional Dyes

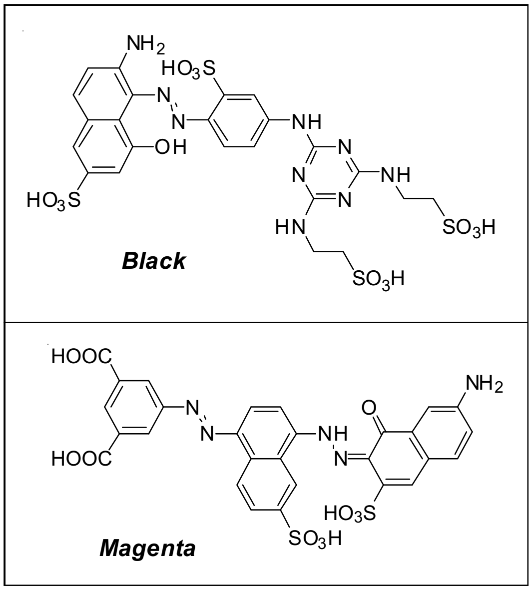
Functional dyes are designed to interact with electromagnetic radiation, pH, electricity, heat, pressure and even frictional forces. Each of these interactions is discussed, beginning with the most important interaction, that with electromagnetic radiation.



Structure 3 .

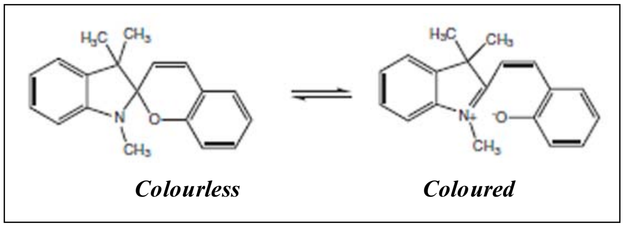
Electromagnetic Radiation: Functional dyes interact with electromagnetic radiation in the near-UV (300–400 nm), visible (400–700 nm), and near-IR (700–1500 nm) to produce a variety of effects required for hi-tech applications. The more important effects are described briefly, including their main applications. Selective absorption of visible radiation produces *colour* (hue). The important colors for hi-tech applications are black and the three subtractive primary colors yellow, magenta, and cyan. The use of subtractive colors in inkjet printing is well demonstrated. The general structures of second generation inkjet primaries are represented by *Structures* **3–5**. For displays, the three additive primary colors red, green, and blue are used. The main applications for colored dyes (and pigments) are ink-jet printing, photocopying, laser printing, thermal printing, liquid crystal displays, and organic light-emitting devices. Selective absorption of nonvisible radiation, such as UV and particularly IR, is also important in applications such as optical data storage, computer-to-plate, security, and printing.

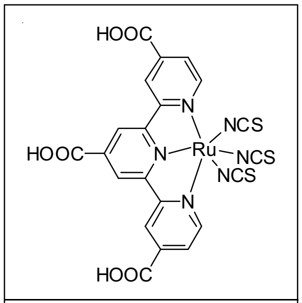
Structure 4 (top).
Structure 5 (bottom) .

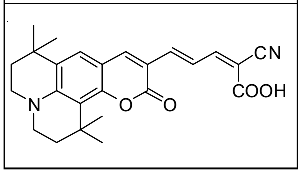


Luminescence occurs when a molecule in an excited state, normally achieved by absorption of a photon, loses some or all of the excess energy as light rather than the normal relaxation mode of heat loss. Luminescence from the first excited singlet state to the ground singlet state is known as fluorescence. *Phosphorescence* is a much rarer spin-forbidden luminescence which occurs from the first excited triplet state of the molecule to the ground singlet state. Phosphorescence is normally only

Structure 6.





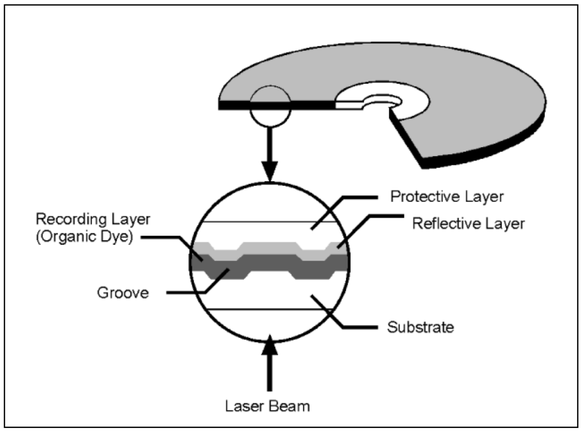


Structure 7. (top)
Structure 8. (bottom)

observed at low temperatures and/or when a dye is in a rigid matrix. Fluorescence and phosphorescence both occur at a longer wavelength than the absorption maximum, the difference being known as the Stokes shift. Fluorescence is important in biological applications, laser dyes, emissive displays, and in providing vivid, bright dyes, particularly for ink-jet printing. A *color change* caused by electromagnetic radiation is called photochromism. The change in color may be from colorless to colored (or vice versa) or from one color to another. Photochromism is undesirable in traditional textile dyes, but is used in eyeglasses and optical data storage (*Structure* **6**). Indicator dyes are probably the most familiar example of a color-change effect. In this case, a change in pH causes the color change.

One of the recent applications of dyes are in energy harvesting by means of Dye-Sensitized Solar Cells (DSSC), where dyes act as sensitizers for solar cells which convert solar energy to electrical energy. Some of the structures (*Structures* **7** and **8**) of the dyes used in solar cells are given for reference.

Figure 1. Mechanism of data storage on disc.



Heat: As mentioned above most molecules lose energy from the excited state as heat. The most efficient molecules for converting electromagnetic radiation into heat are those that absorb in the near-IR region, i.e., infrared absorbers (IRAs). There has been much interest in IRAs because of their use in laser thermal transfer, optical data storage (the older write-once read-many (WORM) and the newer compact disc recordable (CD-R) and digital versatile disc recordable (DVD-R) systems, computer-to-plate printing, and as solar screens for car windscreens and windows. *Thermochromic dyes* change color with temperature (heat). The effect may be due to a single dye or a composite system, and the color change may be reversible or irreversible. Thermochromic dyes find use in direct thermal printing and as temperature sensors, as well as in clothing and novelties.

Absorption of a photon to produce a triplet excited state (via intersystem crossing from the first excited singlet state) can lead to energy transfer to another molecule. The phenomenon is used in photography for *sensitization* of the red end of the visible spectrum. More recent uses are in photodynamic therapy, an anticancer treatment, and in photobleaching. In both these applications, a triplet state dye molecule converts triplet oxygen to highly reactive singlet oxygen. In the photoelectrical effect a photon removes an electron from a molecule to produce a radical cation or hole. This effect is utilized in the key imaging step in photocopiers and laser printers, and in solar cells.

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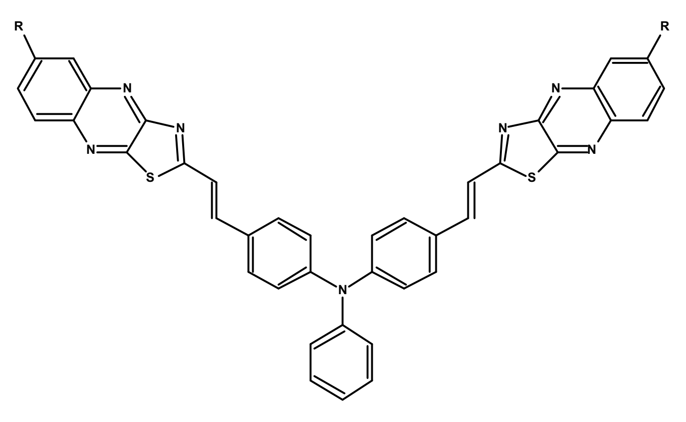
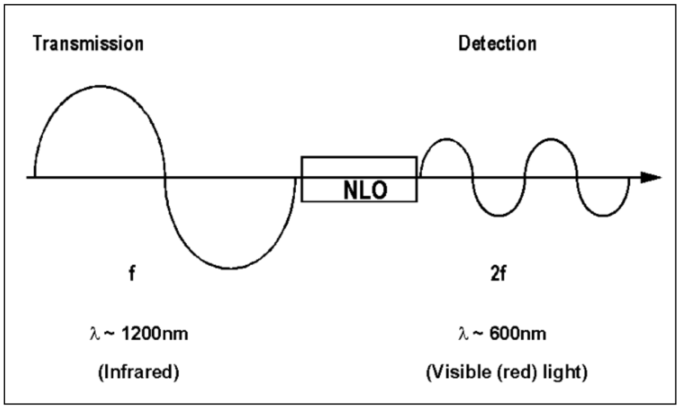
***Electricity*:** Functional dyes have been designed to interact with electricity to produce a color change or to fluoresce. Electrochromic dyes change color, normally from colorless to colored, when an electrical voltage is applied. This phenomenon is used to provide electrochromic mirrors on luxury cars. The electrical injection of electrons and holes in organic semiconductors to produce fluorescence emission (red, green, and blue) is used in emissive displays such as organic light emitting devices (OLEDs) (*Structure* **9**). The process is essentially the reverse of that used in electrophotography, where light produces a hole and an electron.

Structure 9.



***Frictional Forces*:** Dyes have been designed to produce an elec-

Figure 2.



trostatic charge when frictional forces are applied. Such dyes, known as charge-control agents, are used in the toners for photocopiers and laser printers to both produce and regulate the triboelectric charge on the toner particles.

***Pressure*:** Barochromic (pressure-sensitive) dyes change color with pressure. As with thermochromic dyes, the effect may be due to a single dye or a composite system. Barochromic dyes find use in imaging (carbonless paper) and for testing pressure points in, for example, aeroplanes and cars.

***Optical Effects*:** Some dyes have a tendency to absorb multiple photons and reach higher excited states. While coming to the ground state they emit light of higher frequency than that of absorbed. This concept is used in non-linear optics, upconverted lasing, and communication technology where the wavelength of the light needs to be altered (*Figure* 2).

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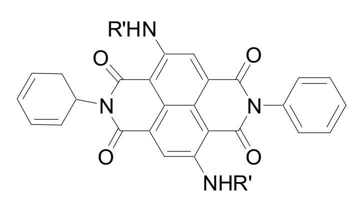
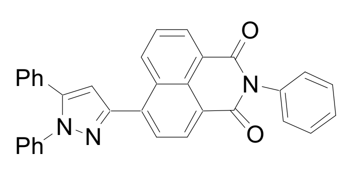
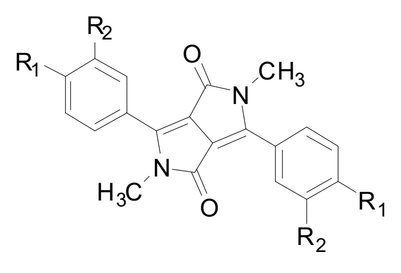
***High Performance Pigments*:** These pigments demonstrate high performance properties in their end-use applications. High performance pigments should give excellence of performance, application permanence, compatibility with health, safety and environmental issues, good profitability in value-in-use to the consumer and return of investment to the producer. The typical examples of the HPPs (*Structures* **10–12**) involve Quinacridone pigments, Perylene pigments, Diketopyrrolo-pyrrole (DPP) pigments, Dioxazine pigments, Phthalocyanine pigments,







$R_1 = H, Br; R_2 = H, OCH_3, CH_3$

Structure 10 . (left)
Structure 11. (right)
Structure 12. (center)

Quinophthalone pigments, etc.

In conclusion, it is surely not in the scope of this article to cover the entire spectrum of the colorants; however, one can definitely be witness to the fact that colour plays a crucial role in our everyday lives.

Acknowledgement

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Suggested Reading

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