The Chemistry of Art

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General Chemistry

Pigments and Dyes: Sources, Types and General Information

Since the dawn of time, various types of pigments and dyes have been used for many different reasons. Pigments and even dyes were used in cave drawings, tribal markings, and even the textile industry, just to name a few. But, how did our ancestor acquire such a large variety of colors to accomplish these tasks? Well, the answer lies in planet earth, quite literally. Many years ago, humans created their own pigments and dyes by using plants and minerals. Sometimes, they even used animals to make certain pigments. They obtained the pigments by crushing plants and minerals or even extracting them from animals. One example is the pigment called tyrian purple or “royal purple,” which came from the tropical murex snail[1]. However, the extraction process was very expensive and so, only the wealthy people would be able to afford this type of pigment. This is how the term was coined to be “royal purple.” Another common substance used for red dye is iron oxide (Fe₂O₃) in a powder form[1]. This was used by the people of ancient civilizations to color their bodies and cloth and to decorate pottery. Furthermore, a plant called the Indigofera plant (see photo to the left), which yields an indigo pigment (see photo below), is yet another example of how pigments were obtained. It is interesting that this plant was used as a pigment because it is insoluble in water; although, the plant was ground and could be converted to a soluble form that could be used for dyeing materials[1].

A dye is a very soluble substance that dissolves quickly. Because of this distinguishing feature, dyes cling to anything they touch. Another property of dyes is that they bleed. Despite this characteristic of dyes being mostly useless for canvas painting, the people of ancient civilizations deemed dyes very useful in the textile industry. For example, they would dye their clothes to give them color[2]. There are many types of dyes, but those used in the textile industry came from compounds like acetic and formic acid. These acids were used because they were effective on thick materials such as wool[3]. On the other hand, pigments were used for a variety of purposes.

A pigment is an colored powder that does not dissolve, insoluble, in the liquid in which it is place. There are two specific types of pigments: organic
and inorganic. Organic pigments consist of carbon compounds. Before being made of carbon, these pigments were made of plants and animals. There is one specific type of organic pigments, which is known as synthetic organic. Some examples are as follows: alizarin, azo-pigments (the yellow, orange and red color range), phthalocyanine (blue and green color range) and quinacridone (a lightfast red-violet pigment, see photo above). Inorganic pigments are made up of metals and oxides, not carbon. Most of the pigments used today are organic ones as there is a greater abundance. Furthermore, there are two types of inorganic pigments: natural and synthetic. Natural inorganic pigment colors include umbers, ochres and siennas. These are called natural pigments because they are excavated from the ground. Synthetic inorganic pigments include cadmium yellow (see photo to the right) and red, cobalt blue and titanium white. These are defined as being synthetic pigments because they are created in the laboratory[4].

**How it’s Made**

Despite their differences, most pigments are made and used in a similar way. First, they are extracted from a plant, mineral, or animal. Next, this substance is crushed until it has a consistency of a fine powder. Then, it is mixed with a dispersing agent solution which allows the pigment to take a consistency that is needed for spread across various medias. After, the pigment is ready to be placed on the media and dried. When the pigment dries, it adheres to the material it was placed on[1].

**Spectroscopy and How We Perceive Light**

Pigments are chemicals that prevent certain wavelengths, this is a measure of the how tall the wave of light is, from being transmitted or reflected. Wavelengths are absorbed and then reflected off of the canvas or media it is on. The amount of light that is absorbed causes the transition of an electron from one of its states to another. When the electron absorbs a certain amount of energy, it becomes “excited” and moves away from the ground state and up to the excited state[5]. This happens because the electron was stimulated by a stimulus, light in this case. This is how we are able to see the different colors. The reflected light is taken in through photoreceptors in our eyes. What we see is actually the light that is reflected. But what is actually going on with the photons, or light particles? This can be explained using spectroscopy. Spectroscopy is the process by which a spectrophotometer can be used to measure the intensity of light, which is determined by the number of photons, absorbed after it is passed through a substance. Because light has wave-like properties, the spectrophotometer also measures the wavelength of the light in nanometers[6].
One factor that influences wavelength is a term called delocalization. Delocalization is the free movement of electrons within a molecule. The more or less delocalized a molecule is, the different wavelengths it can absorb and emit. If a molecule has a lot of delocalized electrons, then the electrons will be promoted to a higher energy level. Therefore, the light will be absorbed at a higher wavelength and, thus, the light reflected will be stronger[7].

The nature of chemicals can be influenced and changed by the addition of heat. Heating a pigment or dye can have varying effects depending on the chemical’s characteristics. Sometimes it will completely degrade and destroy the compound; however, other times, it will simply change its color. Surprisingly, the changed pigment might even return to its original color after it has cooled. The use of heat, however, is very common in the textile industry for clothing or different fabrics[8].
Body Art

Walking down the street is a lot like walking through a museum. Many of the people passing by are displaying artwork on their bodies through piercings, tattoos, henna and hair dyes. Cultures all around the world use body art, many just for aesthetic reasons but others to symbolize status or wealth, to remember loved ones or significant moments, to celebrate major events, or mark a rite of passage. Whether it’s permanent or temporary, displaying art on our bodies is an intrinsically human trait that more often than not uses some variety of pigments or dyes.

Tattoos

Tattoos are one of the most common forms of permanent body art found in America with a 2012 study finding that 21% of adults have a tattoo and an earlier study found that percentage doubled when examining those between the ages of 18-29\[9\]. Interestingly, very few know the chemistry of what they’re putting on their bodies...even the tattoo artists themselves.

Although we often refer to tattoos as “inks” most tattoo “ink” is actually colored carbon pigment or dye in a carrier like water or glycerin. Most tattoos today are done with highly reflective pigments because they are an easy medium for tattoos because they don’t require a chemical reaction with the skin in order to maintain permanence. Instead, they are held in the skin by intermolecular forces and physical forces-like the skin barrier. Intermolecular forces are forces of attraction or repulsion between a molecule and its surrounding molecules. The slight charge on the skin and the charge of the pigment molecules help anchor the color in the skin without changing the molecule or the skin in any way. Dyes, on the other hand, require a physical or chemical reaction to be anchored and must react with the surface it’s applied to in order to show up. See the section on henna below to learn more about dyes.

Over the last couple of decades, the tattoo community has been developing new, safer inks, deviating from mineral-based inks from centuries past. Today, most tattoo colors, up to 80%, come from organic carbon-based molecules. Of those organic dyes, nearly 60% are azo pigments and of all the colorants used only 30% are officially approved for cosmetic use despite their continued use for that purpose\[10\]. Most of the tattoo inks found in reputable tattoo parlors are azo pigments.
Azo pigments are derivatives of a molecule called diimide. Diimide is a fairly simple molecule with the chemical formula N2H2 (See figure on right). Organic diimides, meaning diimide molecules which are attached to carbon molecules, (like azo pigments) are commonly referred to a diazene[10]. Di meaning two, for the two areas where carbon radicals can bind and azene which denotes organic molecules with hydrogen and double bonded nitrogen –N=N-. Figure 2 and 3 demonstrates where carbon radicals would attach to the diazene molecule as designated by the letter R. It is worth noting that the position of the R groups in relation to the nitrogen frequently affects what wavelength the molecule emits.

![Figure 2](image1.png) ![Figure 3](image2.png)

One of the simplest examples of an azo diazene molecule is azobenzene[11] which has two benzene rings on either end. This molecule demonstrates the colorant properties of azo molecules as it has a red-orange color. However, this molecule is not used in tattoos, as the molecules are usually much larger and more vibrant. There are several examples of actual azo molecules in the pigments from the company Intenze tattoo inks in figures below[12]. The pigments used in tattoo inks vary widely and it’s important to realize these are only examples from one company to demonstrate how azo pigments are used in tattoo dyes.

![Red Pigment Molecule](image3.png) ![Yellow Pigment Molecule](image4.png)

As the figures show, the pigment molecules are large with many electrons and a high delocalization allowing for vibrant colors as the electrons jump energy levels.
These tattoo molecules are usually fairly large which is responsible for their permanence in the skin. The pigment molecule is too large for the body to break down particularly at the nitrogen double bond and so the color remains. Laser removal targets the bonds in the pigment molecules exciting them until they break apart allowing the body to attack and remove the smaller molecules. A similar process occurs with the UV radiation from the sun which is why tattoos start to fade[10]. The different bonds and sizes of each molecule change the permanence of the color in the skin which is why colored tattoo inks often have to be touched up.

**Henna**

*Interesting fact: Despite its marketing as a temporary skin ornament, the dye, henna, is far more permanent than a tattoo.*

Henna has been used by women all around the globe for thousands of years to signify special events like weddings, to dye their hair and for fun[13]. Historically, henna has been a women’s art form and remains so in many cultures but in the modern American culture, where henna is increasingly being used for fun, people of all genders are trying out the dye.

Henna is an organic molecule from the leaves of the *Lawsonia inermis* plant, commonly known as the henna tree[13]. The leaves themselves will not dye the skin as it’s the molecule lawsone found in the leaves which results in coloration. This molecule is commonly extracted by drying and crushing the leaves. As a molecule, Lawsone is originally translucent. However, the molecule becomes a dark red-brown through a series of chemical reactions. Dye molecules, like lawsone, must react chemically with a surface in order to show up and remain adhered. These chemical reactions are responsible for the permanence of dyes.
Henna undergoes two chemical processes through three unique chemical stages to arrive at its desired pigmentation on the skin (see figures in text). The first stage is the pure extracted Lawson molecule. The molecule itself is and this translucence allows henna to work on all skin tones as it doesn’t originally have a color that darkens instead it will react with someone’s natural skin tone, resulting in darker coloration[14].

During the second stage, the lawsone molecule undergoes oxidation and has a yellow-green color. Oxidation is when a molecule loses an electron or hydrogen atom. This often results in the original molecule having a new structure and charge. In the case of the lawsone molecule, during stage two the molecule undergoes partial oxidation losing two hydrogens from its three hydroxyl groups (R-OH). This oxidation occurs rapidly so when henna is packaged and stored it is often kept in a slightly acidic solution which can donate electrons to the Lawson molecule, thus acting as a reducing agent. It is during this stage that the henna is applied to the skin through a paste. Once applied the lawsone molecules in the paste form bonds with the protein keratin. (Keratin is an incredibly important protein in our hair, fingernails, and skin.) The bond formed with keratin is permanent and the longer one leaves the henna on their hand, the more bonds lawsone molecules can make with keratin. The more lawsone bonds result in more dye molecules in the skin and a thus a darker and more vibrant color[14].

The third stage of henna is a fully oxidized molecule, where the original molecule has lost all three oxygens bonded to hydroxyl groups. After several hours when the paste is removed the bonded dye is exposed to the air fully oxidizing the molecules from stage two. As oxidation occurs the henna darkens from a pale brown to a dark rust red on the skin.

Interestingly, this pigmentation change of the skin cells is permanent—far more permanent that tattoo’s in fact which can fade with sun and UV exposure. However, because the dye only penetrated a few layers of skin and the body regularly sheds and replaces old skins cells the color will “fade” in about two weeks [14].
Chemistry in Art Through History

Ever since humans began creating, the identity of the substances that give color to what we make has defined our art. Long before chemistry was a science as we know it today, an understanding of the behavior of colored chemicals has allowed artists to make a wide variety of creations.

For example, the famous cave paintings like that on the left[15], of the Paleolithic era, from tens and even hundreds of thousands of years ago, relied on chemicals and even chemical reactions for the range of colors they employed. Commonly found today in these paintings are ocher pigments, which owe a great deal of their yellowish and sometimes ruddy color to iron(III) oxide, a compound similar to iron rust. Other reds were derived from aluminum oxide (bauxite) and a type of iron(II) oxide (maghemite)[16]. The Paleolithic artists responsible for these paintings employed chemical reactions to alter the colors of their materials, heating the yellow hematite ocher (right[17]) with fire and forming a reddish pigment (far right[18]). The iron(III) oxide provides the yellow color as a hydrate salt, a type of material in which the atoms of the compound, those being iron and oxygen in this case, are loosely attached to molecules of water. With heat from fire, these water molecules evaporate and leave the ocher in its anhydrous form, which is redder in color[16].

Manufacturing of pigments was also important in ancient Egypt. ‘Egyptian blue’, the first synthetic pigment, was made with calcium copper silicate; a yellowish pigment could also be made from lead and antimony oxides. Perhaps more impressive was the use of corrosive vinegar
vapor to transform copper into green copper(II) acetate (verdigris) and lead into a white type of lead carbonate, $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$.[20]

The union of chemistry and art is also evident in the history of the color vermilion, which includes the compound mercury sulfide, used for its red color since at least the era of ancient Rome. A twelfth-century Benedictine monk under the name Theophilus wrote on the artificial synthesis of this colorful compound from its component elements, mercury and sulfur, by heating these elements together in a sealed pot. “[A]s the mercury unites with the blazing sulfur” a crashing sound indicates the formation of the new red, says Theophilus, intent on encouraging artists to create their own materials[20]. Below is an example of vermilion in Roman art[19].

Some scholars suggest that vermilion was a byproduct of the alchemical search for gold. According to Arabic alchemist Jabir Ibn Hayyan, influential in the 8th century, mercury and sulfur were ‘principles’ of all known metals, and combining them in the correct ratio could create gold. Of course, elemental gold is not the same as mercury sulfide. However, mercury sulfide was bright red, like the alchemical ‘red king’, the philosopher’s stone, thought to be capable of forming gold from any other metal. Therefore, it was likely considered a step in the right direction by alchemists at the time[20].

By the 1700s, chemistry had begun to emerge as a full academic discipline, and artists were less likely to, for example, synthesize their own vermillion pigments. However, the link between chemistry and art held fast. As chemistry developed, processes were available for manipulating materials into an even wider range of hues, like the yellow of lead(II) chromate, the the purple of cobalt(II) phosphate, and ultramarine blue, consisting largely of a sodium-aluminum-silicon compound that incorporates sulfur and oxygen. This explosion of new colors allowed artists to create works more brilliant than ever before, influencing movements like Impressionism that challenged popular notions of what art could be[20].
**Analysis and Preservation**

Because the chemistry of materials used is often characteristic to an era or artist, chemical laboratory analysis of samples is helpful in learning about a work of art. Techniques include mass spectrometry, which separates and helps identify substances based on their mass, and various types of spectroscopy, involving the study of how a sample interacts with different wavelengths of electromagnetic radiation. Information can be determined about the structure of atoms, molecules, and small crystals in paints and pigments; a particularly interesting technique involves inspecting cross sections of layers of paint to discover the composition[21, including right image].

Analytical information about a piece can be compared with what we assume about the creator and the painting or other work itself. For example, painter Orazio Gentileschi was once solely credited for “St. Cecilia and an Angel”, pictured left[24]. He was known for using a yellow paint made of lead and tin, while his peer Giovanni Lanfranco used a yellow made of lead, tin, and antimony. Upon creation of an ‘elemental dot map’, sections of the painting showed both paints were present, proving that Lanfranco had painted over some of Gentileschi’s work[22].

Approximate dates for works of art can also be found. Lead white was a common paint color in the Middle Ages, and it often contained traces of a slightly radioactive carbon isotope, carbon-14. Just like a fossil or ancient artefact, samples from artwork that contain this carbon form can be dated by analyzing how much of the isotope has decayed[23].

Beyond simple analysis, actual restoration and conservation of historical art is made possible by an understanding of both of how the fields of art and chemistry have changed over time and of how chemicals in modern times can be used.
Often, the materials of old fail to stand the test of time. Much varnish, used originally by artists to preserve the shine and deep colors of their work, actually degrades over time thanks to chemical reactions like oxidation, giving paintings a dull yellowish appearance. The exact makeup of a varnish used can be analyzed with the techniques mentioned earlier in this section. Discolored varnish is usually removed by art conservators, sometimes by a process as simple as swabbing the surface with appropriate liquid solvents[23]. An example [25] is below.

![Christ’s Gift to St. Francis](image1.png)

*Christ’s Gift to St. Francis*, by 16th century oil painter Masaccio. On the left is the varnished and aged painting, with a cleaning test evident on the clothing of the leftmost figure. On the right is the piece after a full cleaning.

Often, after undoing this damage, conservators add a new varnish, chosen with the characteristic style of the painting’s era in mind. It is important that any alterations made by conservators is reversible, so the artwork can be preserved in the future should any new and improved chemical techniques arise for restoration.

In any field involving objects from the past, issues of ethics arise. Conservators aim to maintain a truthful vision of the artwork, and this involves a full understanding of artistic and chemical principles[26]. Art preservation done without care for the work or its chemistry can have unfortunate consequences, exemplified by the somewhat infamous restoration of *Ecce Homo*, a Spanish fresco of Jesus, pictured right[27].

![Ecce Homo](image2.png)

*Ecce Homo*, “Behold the Man”, before (left) and after (right) its 2013 “restoration”. The original piece was the work of 20th century painter Elías García Martínez.
The Future of Pigments in Art

Over the ages, art has shown its ability to adapt and evolve due to the technological advances of the times. Whether it be brought on by the creation of more effective tools or the industrialization of the entirety of western culture, advancements in technology will in turn shape advancements in art. Over the past fifty years, western culture has seen the integration of film, television, and social media platforms into the realm of prominence, greatly influencing how the public consumes popular culture and, with that, popular art. The rising prominence of these new mediums, tied to the creations of applications such as Photoshop or Microsoft Paint, are allowing for the younger generations of artists to mass produce works of this relatively new medium to the art community with its demanding prevalence that is bound to influence the future of respected art. The process in which our eyes perceive colors from digital is a little different than the way our eyes perceive colors of traditional paints and dyes. Any art that is shared online, whether it originated digitally or on paper or film, is perceived by the eyes in this new way. This is done through the microscopic simulation of different wavelengths of light in order to stimulate the same experience of traditional pigments in the eyes of the viewer on a nontraditional medium.

What Is the Difference?

While it may seem that traditional art and modern digital art seem incredibly similar to the naked eye when it comes to shapes, colors, and designs, the ways our eyes are able to perceive those aspects of art and the chemistry behind them differ greatly between the two art forms. When looking at traditional art, the cells in our eyes absorb the visible radiation that originates from external light sources like the sun and fluorescent lights that allow surfaces to
reflect the light that is not absorbed by the pigments existing in a medium and creates what we perceive as color [see Spectroscopy and How We Perceive Light]. Digital art differs in the sense that it does not reflect light, but rather it is the light source itself [28]. While light that comes from screens that portrays digital art create and project their own light through specialized subpixels that create color through differing electromagnetic (relating to electricity and magnetic fields) signals that appear in one of three colors: red, green or blue [29]. Out of all of the colors that you think you are seeing on this screen right now, the only ones that are actually there are these three colors. When examining a screen up close, one may begin to see glimmers of red, green, and blue, but as technology advances, and more of these subpixels can be fit into smaller areas, the more efficiently LCDs can trick our minds into seeing colors that exist as pigments in the real world [30].

Why Red Green and Blue?

Digital screens such as liquid crystal displays (LCDs) often use the RGB color model (near microscopic red, blue and green pixels) to trick the human eye into seeing an array of solid color that does not actually exist on the screen. The reasoning behind this is due to the additive properties of these colors. Since red, green and blue are all primary colors, the light of the corresponding wavelengths to these colors interact and they create new wavelengths that correspond with the color our eyes see from a distance. Each of these three types of subpixels can be shone at 256 intensities in LCD screens, ultimately resulting in 16.8 million color possibilities (256 red x 256 blue x 256 green) [31]. The evolution of screen technology has allowed for the closer mimicking of digital art to physical art as more colors are being able to be achieved at a much easier and more cost effective methods than often times in traditional art.
How Do Screens Show RGB?

Within each of the aforementioned subpixels lies different molecules that scatter light to form the red, green and blue colors created by LCD displays. These colors arise due to an electric field being passed through these molecules existing in a phase known as liquid crystals (a molecular state where the molecules flow like a liquid but contain a repeating structure similar to a crystal). This is the origination for the naming of the Liquid crystal displays (LCDs) [31]. This is due to the intermolecular forces (attractions between molecules that are influenced by their structures and charges) each molecules exhibits on the ones around it. The long chain structure of these molecules aids in the closer association and achievement of crystalline structure. These light scattering properties were discovered when it was found that these molecules have multiple melting points (the temperature where a molecule changes phase from solid to liquid), the cooler of which creates a cloudy liquid with a certain degree of order. The changing degree of order is what allows for light to scatter when stimulated by radiation. The molecules that make up these liquid crystals typically have two benzoid rings (a ring of 6 carbon atoms). They also usually consist of hydrocarbon chains (chains of carbon atoms each bound to hydrogen atoms) that elongate the structure and commonly contain polar (partially charged) ends in order to increase intermolecular forces that allow for the more structured form that characterizes a liquid crystal [32].


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\text{C}_{10}\text{H}_{21}\text{O} & \text{CH=N} & \text{CH=CH-CO}_2\text{CH}_2 & \text{CHC}_2\text{H}_5 \\
\text{CH}_3
\end{array}
\]
References


[14] The Chemistry of Henna for Body Art


