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An Artist’s Guide to Reversibly Color Changing Paints and Pigments

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TABLE OF CONTENTS

FOREWORD

Science and art have always gone hand in hand during history, so much that it's impossible to disentangle them and resolve the dilemma about which came first, art or science? Locked in an eternal cycle of supply and demand, art and science have created the need for one another, and allowed each other to evolve further: art asking the questions for science to answer while technological advancements paving the way for new forms of art. This book is concerned with the latest of such translations of technological advancement into the practice of art, its current state of affairs, mechanisms of function and place in contemporary media.

The materials referred to in this book have two properties, they are "paints and pigments" and are "reversibly color changing". Materials that have the latter property, but not the former, have existed for a long time and occasionally made their way into works of art. There are books that survey dynamic materials for architectural purposes and a plethora of scientific literature concerning reversibly color changing properties of materials. However, as Ralph Mayer states in his painter's bible, texts on the technology of paints, pigments and their raw materials have been written mostly from the viewpoint of large-scale industrial production; the information they contain has only occasionally been directly applicable to the artist' practice (683).

The "reversibly color changing" property of certain chemicals, have been known and literature has been published about them over the past decades, however commercial availability of such paints and pigments is a novelty of the past decade. It takes time for new developments to make their way down to the working artist's attention. Historically, only crumbles of data generated through the scientific investigation in the fields of conservation and industrial paint chemistry has been of use to the practicing artist in creative pursuits (Mayer 13). The same is true for the frontiers in material science and engineering, which are responsible for the development of thermochromic, photochromic and hydrochromic materials discussed in this book.

Paints and pigments are the lifeblood of a painter, and this book is perhaps most revolutionary for the artist that practices in some form of painting. Contemporary painting has become a hybridized effort, it encompasses the two, three and four dimensional. The noun *painting* can refer to a surface, be physical or digital, incorporate light and sound, performance and motion, the environment and the audience (Lawrence). Up until the discovery of the technology that could do a better job than it, painting had been concerned with covering surfaces to produce mimetic images. Then it had to keep re-inventing itself, movements and counter-movements redefining what it means to be a painting and what makes a good one. At certain times painting was announced dead, only to be revived again; although it could be argued that it had never died.

The verb *painting*, the act of applying color, or the act of making a picture, can now be used to describe many transmedia acts: painting a volume in sculpture, painting a space through installation, painting a concept with design, painting a readymade with print and painting a motion through performance or video (Lawrence). It is challenging to argue what isn't a painting these days, just like trying to call something "not art" since Duchamp's famous stunt with the fountain. However, at times when many modern approaches have become tried, tired and trite, new dynamic paints offer a redefinition of painting that doesn't require transmedia acts.

Color changing paints and pigments bring a new temporal dimension to the usually spatial materiality of paint, re-defining what it means for a painting to be a painting. The change over time of a prime element of art, such as color, can now be readily synchronized with natural cycles without an algorithmic component to act as a mediator between the artist and the artwork. Because the materials respond to stimuli innately, there is no need for a sensor or an input-to-output translation; the paint and the pigment innately change over time according to the artist's intent. This dynamism can be removed from a digital context and be based purely in the physical world, it can create motion without performers, or it can be integrated with other media to bring a fresh outlook to transmedia definitions of contemporary painting.

This book aims to serve as a guide for the artist, used interchangeably with painter, who is interested in understanding and then manipulating the properties of color changing paints and pigments. The information found in this book is intended to serve as a starting point for the artist who hasn't until now been acquainted with these materials, as a technical guide for the artist that is currently practicing with them, and as an inspiration for the artist that is planning to work with them in the future. It is written with the hope that expanding the methodology of artistic inquiry might further drive scientific curiosity, which will in turn continue the cycle in which the arts and sciences grow together.

ACKNOWLEDGEMENTS

I would like to start by thanking my family for always supporting my decisions with all their heart and sharing their wisdom whenever I needed it.

I would like to thank all the artists and experts who have gone out of their way to supply me with critical information; namely, Andry O’Rourke, Ivo Marinov at Atlanta Chemical Engineering, Yuri Matsunaga at Mitsui Chemicals, Gözde Önder at Istanbul Modern Library, Cara Keyman at Robert College Library, and the representatives at LCR Hallcrest.

I would like to thank all my teachers for instilling in me the passion to learn and share knowledge, they have always been my greatest inspirations. Special thanks to James Butterworth, for allowing me to grow in the laboratory, to Maria Sezer, for showing me how to bring science into my art, to Merril Hope-Brown, for her timeless teachings, to Erin Power, for teaching me to see art in all things, to Alex Downs, for always expecting my best, to Lisa Seed Trujillo, for showing me how to plan ambitiously, and to Francis Levitin, for demonstrating how art can respond to technology.

I am grateful to the University of Chicago community, especially the STAGE Lab at the Pritzker School of Molecular Engineering, for renewing my faith in the value of interdisciplinary research. I am also grateful to the Smart Museum of Art for creating venues where those from all art disciplines can converse and learn from one another.

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LIGHT AND MATTER: AN INTRODUCTION

Until the modern period in history, the practice of art and science had gone hand in hand, often being practiced by the same person. The increase in specializations after the industrial revolution changed that, and the two cultures of science and art became increasingly separate (*The Rede Lecture*). Contemporary times have seen a reversal of that trend, with interdisciplinary work becoming ever more necessary for the advancement and evolution of both fields. The artist and the scientist do many things in common, the prime example being their mutual interest in manipulating matter. There is an innate technicality and systematicity in the practice of art as there is ingrained creativity in the process of science; curiosity, the need to understand how the world works, can be found in ample amounts in both. As such, the fields of science and art should not be thought of as so different from one another.

This is also to say that the artist should not feel intimidated when faced with new scientific concepts that might not seem familiar at first. Having practiced with some physical artmaking medium, the artist should have already developed an understanding of how certain materials interact with each other, light or temperature. Learning more about how the material world functions, especially within an artistic context, should thus come as second nature to the artist. The basic concepts of color, temperature and how light interacts with matter will be developed to ensure the reader has the adequate background for further discussions of these concepts in the context of thermochromic, photochromic and hydrochromic materials.

Color is one of the ways our bodies can interpret electromagnetic radiation, specifically that of visible light. The cells found in the retina of the eyes, when struck by light of different colors, relay different signals to the brain, which allows for colors to be distinguished. The cells in the retina themselves differentiate between different colored light because different colors of light have different wavelengths and therefore carry different amounts of energy. Two simple equations explain this relationship between wavelength and energy. The energy carried by a single photon in a ray of light, E, is equal to the product of the frequency of the light, ν, and a physical quantity called Planck's constant, h. The product of the wavelength of light and its frequency yields the speed of light, with the equation $c = \lambda\nu$, where c is the speed of light, ν is the frequency and λ is the wavelength. A combined equation, $E = \frac{hc}{\lambda}$, allows for a heuristic to be denoted: shorter the wavelength, higher the energy. Due to these relationships that equate the different properties of light, stating the wavelength of light makes a statement about how much energy it carries.

The electromagnetic spectrum orders different kinds of radiation with respect to their wavelength, therefore their energy. From most energetic to least energetic in the electromagnetic spectrum are, gamma rays, X-rays, ultraviolet light, visible light, infrared radiation, microwaves and radio waves. The visible light portion of the spectrum goes from purple to red through the colors of the rainbow. Thus, the cells in the retina can distinguish between two colors of light, blue and green for example, because these colors have fundamentally different energies. But what makes an object reflect a certain colored light to the retina? When light interacts with an object before reaching a person's eyes, it changes. It acquires different properties than before it had interacted with the object. Different matter interacts with light differently, hence the different color of objects.

Light is electromagnetic radiation, a form of energy that has radiated from a source, that travels through space and interacts with matter. It can be thought of as existing in a wave or particle form, a phenomenon called the wave-particle duality, which helps explain how light behaves under different circumstances. One can imagine waves of light radiating outward from a lightbulb that get reflected from the surface of a mirror, like ripples on the surface of a pool that bounce back from the edge. One can also imagine light particles, photons, repeatedly interacting with a single molecule to give its electrons more energy, which can be likened to a billiard ball hitting another one to get it moving. Both visualizations are valid, and light can behave both as a wave and as a particle.

We see the macroscopic visual effects of something being shiny, matte, transparent or opaque, which are manifestations of microscopic interactions between light and matter. When electromagnetic radiation traveling through space encounters matter, some portion of it can pass through unaffected, the rest is either absorbed or reflected. The amount that is transmitted determines the opacity of the matter. The color on the other hand, depends on absorption and reflectivity. If some infrared, ultraviolet and visible radiation shines on a hypothetical piece of matter for example, and all but the green and yellow portion of the visible spectrum gets absorbed, then the reflected light is green and yellow. Thus, the wavelength of light that is absorbed by matter corresponds to the color that is complementary to the color of the light that is reflected. UV and infrared radiation don't have corresponding colors for human color sensation, so they are don't contribute to complementary color considerations.

What is happening on the subatomic level when light interacts with an atom, or molecule, can be thought of as a collision. The electrons that move around nuclei get hit by a light particle, which energizes them. The photon is thus absorbed by the atom or molecule and the electrons can transition to an excited state. They eventually return to their ground state, but that process will be touched upon later. The photon that was absorbed carries some amount of energy that depends on its wavelength as discussed earlier. If the energy carried by that photon is equal to the energy required to excite an electron from its current state to an excited state, then the atom or molecule at hand exhibits high absorption at the wavelength that corresponds to the energy that the photon was carrying. Electrons have many energy levels they can exist in and be excited to; if light with enough energy hits an electron, it could even give it enough energy to escape the pull of a nearby nucleus, whereby abstracting the electron and ionizing the nucleus.

The amount of energy required to excite an electron to an excited state depends on the environment of the electron. Electrons move around nuclei in atoms, but its not a simple moonaround-the-earth kind of rotation. In fact, when many atoms are bonded together to form a molecule, the electrons revolve around all of them, spending more time around some than the others. It is better to think of an electron cloud wrapping around the nuclei found in the molecule than individual electrons flying around. This is because electrons move very fast and its better to think of where they spend more time statistically then try to pin down their locations. The energy required to excite an electron to a higher level then depends on how close to the nucleus it is, which correlates with how strong of a pull is exerted on it by the nucleus. The outermost electrons will experience the least amount of force, and they are more readily excited.

The outermost electrons are also the ones involved in bonding between atoms. Metals, plastics, wood, paint and glass all have their atoms arranged in different structures, with different kinds of bonds, which is why the electrons that are involved in bonding form different clouds around in each one of them. The nature of the cloud dictates the experience of the electrons and the energy required to excite them. Hence, the arrangement of atoms in a material determines its color and other optical properties. Thermochromic and photochromic materials employ organic molecules, which is why their clouds will be discussed in detail.

Organic molecules are comprised mostly of carbon atoms that bond to form chains and rings, with atoms of different elements attached to these structures or replacing the carbon in portions of the structure. Electrons form clouds around these structures, being more concentrated around atoms that exert a stronger pull on them. The catch is that a larger, more spread out electron cloud means that the electrons experience less pull, therefore need less energy to be excited. Normally, UV light or more energetic radiation can excite electrons in organic molecules, but if an electron cloud is diffuse enough, light in the visible portion of the electromagnetic spectrum can also excite the electrons in it. If such a cloud is formed, then the organic molecule can absorb light in the visible part of the spectrum, hence reflect only portion of the visible spectrum. If the entire visible spectrum were to be reflected, our eyes would see that as white light, but if only a portion is reflected then we see a certain color.

Some organic molecules have their outermost electrons fully dispersed around the molecule to form a large cloud, which is made possible by a special kind of bonding arrangement between the atoms. This is called conjugation, the alternating arrangement of single and double bonds between the atoms of the molecule that allows the outermost electrons to be shared by all the atoms, hence forming a spread-out electron system. If the pattern is broken at some point in the carbon chain or ring however, then the conjugation doesn’t continue.

Let’s imagine a conjugated chain that connects two conjugated rings to form a large conjugated system. If by some chemical reaction the alternation of single and double bonds is broken at the middle of the chain to give two consecutive single bonds for example, then the molecule would have smaller conjugated systems that are separate. This means that instead of having one large electron cloud, it would have two half-sized electron clouds. Since the conjugated systems are smaller, the electron clouds would require more energy to be excited and the molecule would absorb light with shorter wavelengths. If the molecule was able to absorb yellow light for example, it would now require something more energetic, like purple light. The color of light absorbed is complementary to the color of light that is reflected; thus, the molecule would transition from a bluish color to a yellowish color.

Now that it is established how an electron becomes excited, let’s consider what happens when it comes down to its ground level. Since energy can’t be created or destroyed, only transformed, the energy that electron absorbed must go somewhere. There are many ways this can happen, the most relevant example being the emission of some form of electromagnetic radiation. The emission can occur all at once or more often than not, in steps. This leads to less energetic radiation being emitted than the one that was absorbed. For a molecule absorbing in the visible light region, infrared radiation could be emitted. Radiation beyond the infrared region of the spectrum doesn’t have energy to abstract electrons from molecules, but it can give them energy to vibrate, jiggle and rotate. That is what happens in a microwave when water molecules get heated for example. As such, when a molecule absorbs infrared radiation it gains kinetic energy. This is the energy of motion and the kinetic energy of a group of molecules or atoms is important for the definition of temperature.

Temperature is defined as the average kinetic energy of the particles found in a system, which could be a bowl of water in the microwave or paint on a canvas. In both cases, the molecules found in the system demonstrate some mode of movement on the atomic level as does all other matter in the universe. This movement can be that of atoms vibrating in molecules, molecules rotating around themselves or colliding with one another. The gentle bumping of molecules can transfer energy, which is how heat gets conducted. More energetic collisions can even trigger reactions, as such, there is an innate connection between temperature and reactivity. The higher the temperature of the system, the more energetic the collisions, and the more likely that a collision will result in a successful reaction.

The conversion of radiant energy to thermal energy, the conduction of heat, the destructive power of UV light, how light behaves when travelling through media and how temperature can speed up reactions will all be important concepts to consider when working with reversibly color changing materials. Although the macroscopic color change might be the most striking visual element in artworks that utilize these dynamic materials, the microscopic processes that are ingrained in the atomic world allow deeper layers of meaning to be incorporated into artwork. At times when visual tropes carry quite a lot of baggage with them, the allegories made possible by the dynamic materiality of paint offer fresh modes of communication.

There are a few companies that currently sell thermochromic paints, pigments, inks and other supplementary chemicals both in bulk and in trial quantities (*Thermochromic Pigment for Colour Changing Paint – SFXC | Special Effects and Coatings*; *Thermochromic Technology | TMC Hallcrest*; *Frequenly Asked Questions | Atlanta Chemical Engineering*). One can order their products online, although for some of them shipping outside Europe and North America can incur high costs. Their product lines can be discontinued depending on demand, as the manufacturers of color changing materials are standalone commercial enterprises. No national or universal standard of quality exists as it does in other commercial paints either, each batch of material might have different properties. Therefore, the artist must be aware of the rather volatile temperament of supply when it comes to color changing materials and should contact the manufacturer directly if a certain product is going to be desired for extended periods of time.

THERMOCHROMIC PAINTS AND PIGMENTS

Thermochromic paints and pigments change color depending on temperature. They can have an activation temperature, below which they are one color and above which they are a different color (*Thermochromic Technology | TMC Hallcrest*). Heating or cooling through this activation temperature visibly changes the color exhibited by the material. They can also have a range of temperatures through which they go through a spectrum of colors. The material is indifferent to the method by which its temperature is changed; its color changes regardless of whether it absorbs heat energy from its ambient atmosphere, the body of a living being, a light source shining on it or any other method of heating.

The activation temperature for commercially available thermochromic paints and pigments usually lie within the range of temperature where water exists as a liquid. It is especially easy to find an extensive selection of colors with activation temperatures around room temperature and body temperature, as changing color due to contact with a human body is a desirable trait for manufacturers. The efficiency of such thermochromic materials decreases near boiling or much below freezing temperature, as the molecular structure of the pigments change, irreversibly damaging them. If the artist desires a color change at much below freezing (less than -30 °C) or above boiling temperatures, this is possible through temperature sensitive paints utilized in the aerodynamics industry to conduct experiments (*Pressure and Temperature Sensitive Paints*). Those paints utilize physical mechanisms beyond the scope of this book and must be sought after in aerodynamic specific literature.

Thermochromic paints and pigments come in a wide variety of colors for any given activation temperature. There are two types of transitions possible at a given activation temperature: color-to-transparent and color-to-color. Color-to-transparent materials have a pronounced color that fades as the temperature increases. The sharpness of the color change varies, some materials going from intensely colored to fully transparent within a degree of their activation temperature, others turning a pale version of their actual color over a few degrees around their activation temperature. In literature this phenomenon is referred to as hysteresis, which is defined as the lag of the observed physical property of a material behind the environmental stimulus that drives it (Bašnec et al.).

The same color might be available at various activation temperatures within a range of temperatures, the most variety existing in 0 °C to 70 °C. The artist can easily find red-to-colorless paint or pigment with an activation temperature of 21 °C, 24 °C and again at 28 °C (*Thermochromic Paint For Sale | Color Changing Leuco Dyes*). It is possible to find any desired color for a color-to-transparent transition, although the exact hue might not exist. For example, one is sure to find red-to-colorless material, however whether it's carmine, scarlet, ruby, venetian or Indian won't be on the label and will have to be tested once the artist acquires the color. Since the primary concern for manufacturers of dynamic paints, unlike producers of classic paints, isn't to offer a wide selection of hues for a given color, if the artist desires different hues of a given color, then ordering from various producers would be the best bet to create variety.

Although the activation temperature range and availability are just as wide for color-to-color materials, the combination of colors is much more limited. This is reasonable, considering the sheer amount of materials or combination of pigments a manufacturer must produce to cover every combination possible. Some transitions might be directly available from manufacturers, such as color-to-black or color-to-yellow, however if the exact two colors the artist desires can't be found, other methods must be used to achieve a specific color-to-color transition. Different paints can be painted in layers to achieve the same visual effect as a color-to-color transition. For example, if a blue-to-red paint can't be found, then a blue-to-colorless layer can be painted on top of a colorless-to-red layer, making sure that the activation temperature of the two are the same. Mixing paints is an experimental endeavor and is advised against by some manufacturers, so it is up to the artist to try out combinations. Two paints can certainly be mixed, many of the color-to-color transitions concocted by manufacturers feature more than one pigment anyway.

There are two very different classes of chemicals that give thermochromic paints and pigments their color changing properties. Liquid crystal systems are utilized for color-to-color transitions and go through a spectrum of colors as they transition. They are generally used for higher precision applications in the medical and scientific industries since the temperature response point can be tightly engineered (*Liquid Crystal Formulations (LCs)*). Leuco dyes are used for both color-to-colorless and color-to-color transitions. Their temperature dependence is less precise but as a material they are easier to work with (*Thermochromic Paint For Sale | Color Changing Leuco Dyes*). They are commonly used for packaging, labels, graphics, toys, and quality control applications.

Although the two chemicals differ in their properties, mechanisms and limitations, a technique employed by many manufacturers to increase the stability and workability of the thermochromic paints and pigments allow the two to be handled as practically the same for most general intents and purposes concerning dispersal of a pigment through a medium. This technique is called microencapsulation, and it forms an outer wall around the sensitive thermochromic chemicals to protect it from environmental stresses (*Microencapsulation | Liquid Crystal & Leuco Dye*). Therefore, the microcapsule itself is treated as the pigment particle for determination of paint properties, not the leuco dye or the liquid crystal molecules themselves.

Various methods exist for microencapsulation, including coacervation, spray drying, interfacial polymerization, and situ polymerization. Coacervation is the most frequently used method for industrial applications (Durasevic; Bašnec et al.). Whatever molecules are desired to be bound in a microcapsule are dispersed in a mixture of polymers, such as gum Arabic and gelatin, then the molecules are encapsulated by taking advantage of the different surface charges of the chemicals. As a result, regardless of the material on the inside, the microcapsule can be engineered to offer particles compatible with aqueous or non-aqueous dispersions.

MECHANISM: LIQUID CRYSTALS

Liquid crystals are optically active mixtures of organic molecules that can be thought of as existing between a traditional solid and liquid phase: they are more ordered than a liquid but less ordered than a solid in the way their molecules are arranged in space ("Liquid Crystals"). As the temperature changes, the way individual molecules are oriented and organized changes, similar to how solids melt when they get warm. This is because one phase is thermodynamically more favored at higher temperatures than the other. The phase change alters the way light interacts with the liquid crystal, which is observed as a color change.

Liquid crystal based thermochromic materials have a temperature range rather than a single activation temperature. They appear black below and above their temperature range. In their temperature range, they can exhibit one of two behaviors: they either exhibit a single color or smoothly transition through many colors. For example, as they are heated, they can go from black to green at the beginning of the temperature range, stay green throughout, then go back to black once the temperature is higher than the range. Or they can start black, turn red at the cold end of the temperature range, then go through the colors of the rainbow in order through the range, ending with blue violet at the hot end of the temperature range. The red to blue transition is the most common commercially available type of transition, however it is possible to formulate mixtures where the color change is from blue to red as the temperature goes from cold to hot.

Because only a very small percentage of incident light is reflected by the liquid crystal, the materials must be viewed against an absorbing background for optimum visualization of their color change properties. For this reason, liquid crystal containing media is usually applied over a black surface. They are commercially available as adhesive sheets, ready-to-spray slurries, and microcapsulated pigments (*Liquid Crystal Formulations (LCs)*).

MECHANISM: ACID-ACTIVATED LEUCO DYES

Leuco dyes are organic molecules with two chemically different forms, which absorb light at different wavelengths and therefore have different color (*Chemistry and Application of Leuco Dyes*). When a chemical reaction transforms the molecule from one form to the other, a visible color change occurs. Because they all exhibit two forms, the colorless leuco form (from Greek, meaning white) and the colored form, they can be generally referred to as leuco dyes. However, leuco dye is a generic term, it could be applied to all sorts of molecules with drastically different mechanisms of transition. The thermochromic mechanism of most commercially available thermochromic pigments employs an acid-activated leuco dye, usually a spirolactone like a diarylphthalide or fluorane, that exhibits a color-to-colorless transition (Ritter, "Energy-Exchanging Smart Materials"). The color transition is due to the change in the structure of the leuco dye, which causes a shift in its absorption spectrum. Chemically, the conjugated system of the leuco dye is expanded by protonating an oxygen moiety; most commonly a heterocyclic ring is opened, connecting the isolated polycyclic systems into a single expanded conjugated system (Nakazumi).

This interaction between an acid and the acid-activated leuco dye is mediated by a change in temperature with a cleverly engineered three component system. The thermochromic pigment at its most basic form is a microcapsule that includes the leuco dye, an acid and a solvent (*EP1084860B1 - Thermochromic Microencapsulated Pigments - Google Patents*; *Thermochromic Technology | TMC Hallcrest*; Fujita and Senga). When the solvent is in its solid state, below the activation temperature, the acid and the dye are bound, which gives the pigment its color. When the pigment goes above the activation temperature, the solvent transitions into its liquid state, causing the dye and the acid to dissociate, resulting in a loss of color. The "melting and freezing" of the solvent therefore facilitates the chemical reaction that causes the color change. The activation temperature of the pigment is can simply be thought of as the melting point of the solvent, which is easily adjustable, allowing for a wide selection of activation temperatures for any given color transition.

Some products have a colorless-to-color transition, which employs the same microcapsule system and mechanism (Fujita and Senga). Only now, when the solvent is in its solid state, below activation temperature, the acid precipitates and is not bound to the dye. Thus, at colder temperatures, the pigment is colorless. When the pigment is above activation temperature, the solvent is in its liquid state, the dye reacts with the acid and turns it into its colored form. Thus, at increased temperatures, the pigment is colored.

The most common transition is color-to-colorless; however, careful selection of the acid-activated leuco dye can enable a color-to-color transition (Durasevic). It is also possible to use a mixture of thermochromic pigments with different activation temperatures: at the colder one of the two activation temperatures, one component of the mixture becomes colorless, while the second component of the mixture remains colored (Durasevic). In such mixtures, the color originates from the pigments that remain colored, depending on the relationship between the temperature of the pigment and the melting point of the solvents. Some of the color-to-color transitioning thermochromics available employ a mixture of two or more pigments to achieve the desired visual effect. An artist can often not tell whether the color-to-color transition pigment is pure or a mixture without testing it. When heated, the pure pigment will transition smoothly from one color to the next, but a mixture of pigments could develop an off-color right at the activation temperature due to hysteresis. Neither is superior to the other, the choice depends on the artist's needs.

Research on thermochromics is ongoing and patents are being issued even today (Senga et al.; Fujita and Senga). There is still much discover and improve upon when it comes to thermochromic pigments, even though paints and pigments are commercially available for artists to use. The three-component system is well known, the first related patent in the US dates to 1993 and it has gone through many renditions before being used in artists' materials (Novinson). Other mechanisms of thermochromism have been developed in a variety of media, however they aren't commercially available yet (*Thermochromism - an Overview | ScienceDirect Topics*).

EXAMPLE: SNOW DOG UNDER THE SUN

In 2017, Andy O'Rourke built a man-sized dog sculpture for the Snow Dog Project, and he embellished it with adhesive liquid crystal sheets. He cut vinyl sheets into pieces and arranged them in compass-like patterns on the dog (fig. 1 and 2). He used super glue to supplement the adhesive, and to seal the cut edges of the vinyl sheets, he covered them with three layers of two-component lacquer (O'Rourke). The base color of the sculpture was black, so the sheets displayed vibrant colors when heated up or cooled down through their temperature range.

The Snow Dog Project aimed for each dog-shaped installation to be positioned around different cities to encourage locals and tourists to exercise by making it enticing to find and take a picture with each sculpture ("The Snowdog Art Trails - Find a Snowdog Art Trail near You"). The Snow Dog sculpture stayed up under the sun, exhibiting oscillating patterns of color as it heated up and cooled down in sync with the day night cycle. It is well known that UV light and organic chemicals don't play well, and sunlight has a hefty UV component. Because UV light carries much more energy than light from the visible color spectrum, it can excite electrons bound in stable organic bonds, break them, activate chemicals and catalyze the formation of new bonds. Over time this has a devastating and unpredictable cumulative effect on chemical mixtures composed of organic molecules like liquid crystals.

That's why manufacturers recommend against using thermochromic material outdoors, even indoors their shelf life is just a couple of years at best (L.). According to the artist, for the months that the sculpture was out in the sun for public display, the color changing property of the sheets didn't deteriorate (fig. 3 and 4). The sculpture was then sold on an anonymous auction and

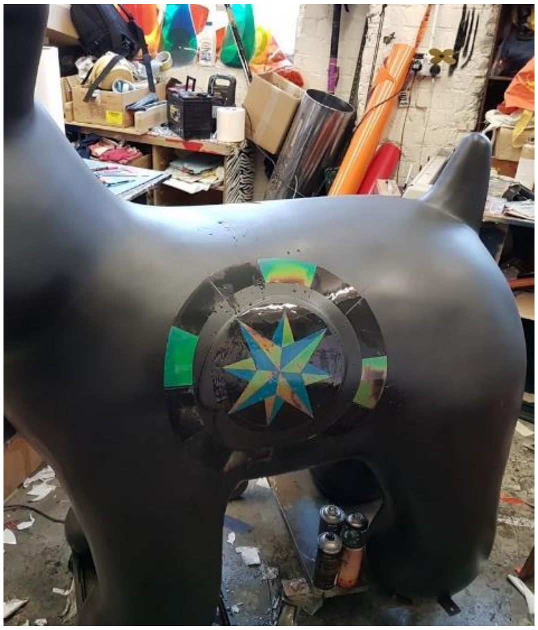

Fig. 1. Snow Dog under construction, right side from

O'Rourke, Andy. Personal Interview. 9 July 2019.

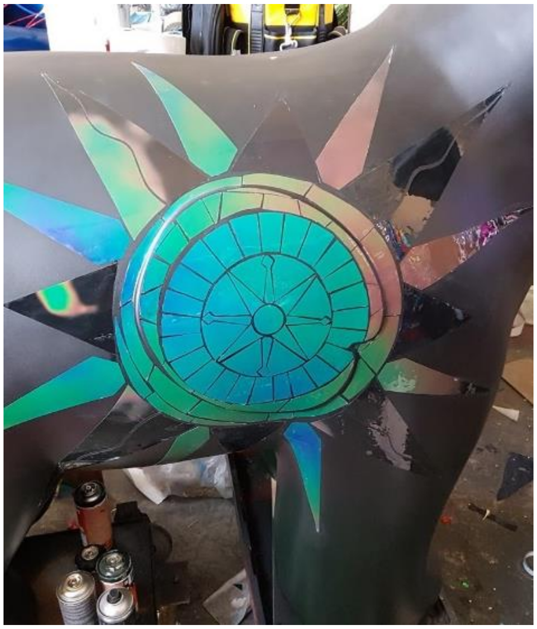

Fig. 2. Snow Dog under construction, left side

O'Rourke, Andy. Personal Interview. 9 July 2019.

Fig. 3. Snow Dog on display, cloudy day

O'Rourke, Andy. Personal Interview. 9 July 2019.

Fig. 4. Snow Dog in display, sunny day

O'Rourke, Andy. Personal Interview. 9 July 2019.

the money was given to charity, so it hasn't been possible to track down the sculpture to see how well it has fared. However, it can be reasonably expected that in a few years the chemicals will be worn down by UV light and the sculpture won't be going through brilliant colors as it once did.

But what if the artist wanted to keep the sculpture functioning for as long as possible? In order to prolong the lifetime of thermochromic materials, they must be protected against all environmental stresses. This includes possible contact with certain organic solvents, moisture and UV light. The first one is the easiest to insure against, as it is unlikely to start raining acetone or chloroform in the foreseeable future. Simply making sure that the material doesn't come in contact with methoxy propyl acetate, methyl ethyl ketone, ethyl acetate or any other solvents it isn't compatible with should be enough (*Documents*). In the unlikely and unfortunate event that they do come in contact, the microcapsules that contain the thermochromic molecules will be irreversibly damaged and the material will lose its color changing properties. Once the thermochromic material has substantially dried, painting over it with non-corrosive agents shouldn't interfere with the microcapsules. Care should be taken as to what kind of chemical is being painted or sprayed over a thermochromic material and if available, solvent compatibility charts from the manufacturer regarding their products should be consulted.

Moisture and UV light are familiar adversaries to any artist, since they threaten traditional pigments as well. Just like artwork employing traditional pigments, thermochromic components can be covered with protective media, such as a lacquer or coating as in the case of the Snow Dog. There are many such sprayable protective chemicals available from a multitude of manufacturers, and since research is ongoing for their improvement, there can be no definitive answer as to which one currently offers the best protection. One can rest easy however, as the decision of choosing the best or the most expensive UV protection is often not going to be the chief determinant of the lifetime of a thermochromic artwork.

Research into thermochromic materials' applications in smart architecture has shown that UV protection alone does not offer statistically significant increases in the lifetime of such products, as certain bonds in organic chemicals can be weak enough to be broken by light in the visible part of the electromagnetic spectrum (Karlessi and Santamouris). Covering materials with a blue filter on top of a UV filter offers little to no protection for example, as blue light passing through the filter has high enough energy to degrade sensitive organic compounds. Covering materials with a red filter on top of a UV filter offers the best protection, but even that is only slightly better than only covering with a UV filter. As such, there still doesn't exist a simple method that can significantly extend the lifetime of thermochromic materials. It should also be noted that commercially available coatings never guarantee UV protection for outdoor applications.

For the chemist or the manufacturer, increasing the stability of liquid crystals is an active area of research for applications in electronics, photonics and industries larger than the paint and coating industry (Chen et al.). Strides made in the frontiers of science slowly find their way into the formulations of manufacturers that produce thermochromic materials, however the chemical composition of any product is a well-guarded secret for good reason. Thus, it isn't possible to compare the relative stabilities of any two commercially available thermochromic materials at a glance. If desired, an artist can order small batches of different materials to subject them to a simple lightfastness test: covering half of the surface of a thermochromic material covered object and leaving it under direct sunlight for a week. More detail on methods of comparison can be found in books that compare the lightfastness of traditional pigments.

As opposed to organic solvents and moisture, the tools of protection against UV light exposure at an artist's disposal are much more limited. Direct exposure to sunlight must be avoided and materials must be well covered with protective chemicals for outdoor applications of thermochromic materials to increase their lifetime. Over time, light will eat away at the thermochromic material until no visible color change occurs and the material remains dull and inert. Therefore, logistic considerations can be employed to improve the lifetime of an artwork; the amount of light an artwork is exposed determines the rate at which it decays and depends on many factors. The geographical latitude of the exposure site, altitude, season of year, air quality, orientation of the artwork, shade cover and many environmental factors can drastically affect exposure. It would be wise to follow heuristics employed by conservators to preserve traditional artwork when it comes to thermochromics as well. Even though they will decay at a much faster rate than traditional pigments, what retards decay in the former will do so in the latter too.

The good news is, temperature can be incorporated into thermochromic artwork through many means that don't require direct exposure to sunlight: via conduction by direct contact with a heating-cooling medium, through convection in the surrounding environment, and even by radiation just as long as it's of a wavelength that isn't small enough to break organic bonds. Microwave radiation for example, like the one we use to heat up water, is harmless. Or, if a daily or seasonal temperature change cycle is to be reflected in the artwork, the thermochromic material can very well absorb the heat from its ambient atmosphere or solids it's in contact with and doesn't require direct sunlight to be heated up. It is up to the artist to think like an engineer to come up with insightful ways to supply the thermochromic material with heat while shielding it from light.

EXAMPLE: RELAYING ENERGY

In 2018, Tania Bruguera created an installation at Tate Modern, London. On the floor of the Turbine Hall she pasted a giant portrait of Yousuf (fig. 5), a young migrant that fled the war in Syria and came to London, whose personal story she knew about (Tate). The name of the piece changed every day to represent the number of migrants who had been displaced or had passed away until that day (vortexdz). Bruguera collaborated with a team of scientists and designers at the UK based Material Evolution Lab, who sprayed the portrait with black thermochromic. When visitors touched the floor and warmed it with their body heat, the ink turned colorless and revealed the portrait beneath it. For the artist, the piece was about "how we can make migrants our neighbors, how can we negotiate new values into our society and making sure people understand their responsibility in what's happening around them" (*Ask the Artist | Questions for Tania Bruguera | TateShots - YouTube*). The macroscopic picture of visitors working together to drive change in the artwork by channeling their energy was paralleled in the microscopic picture where the warm body parts relayed their heat to the surface they came in contact with (fig. 6).

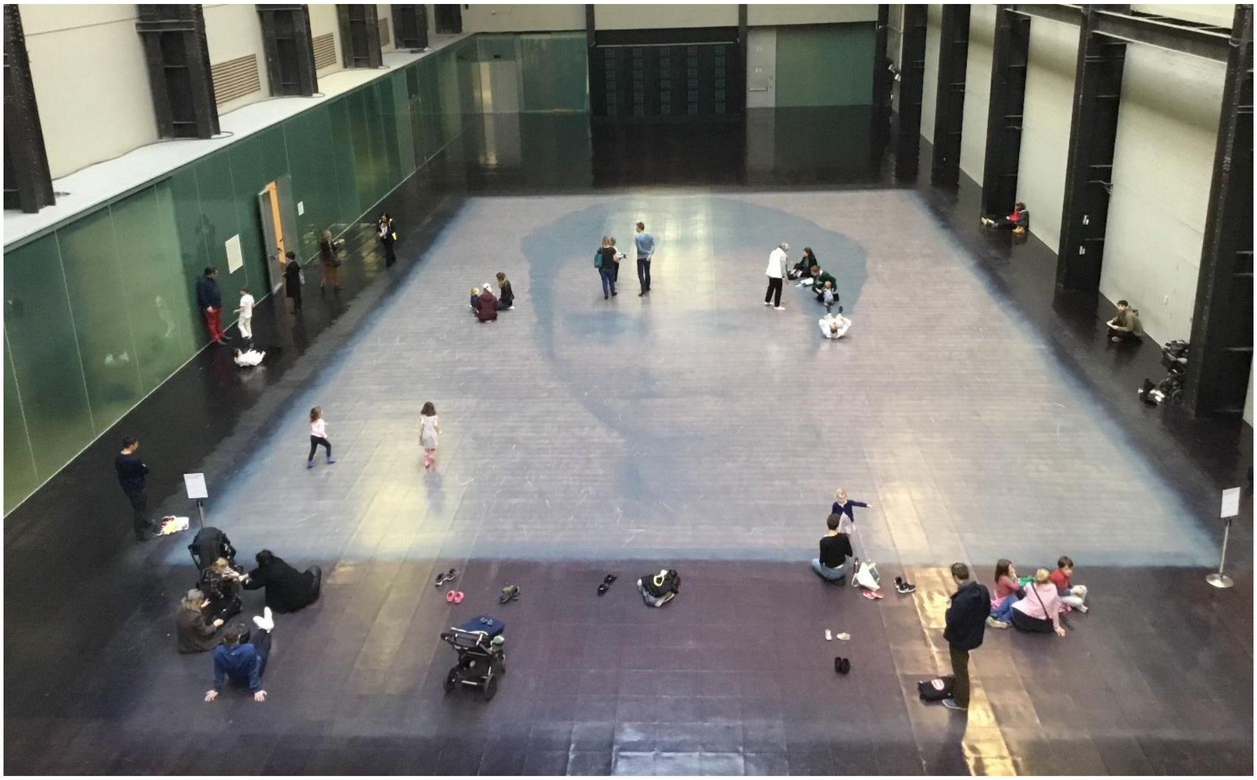

Fig. 5. The portrait of Yousuf pasted on the floor at Turbine Hall from vortexdz. "10,148,451 Tania BRUGUERA." Maja Hill, 20 Mar. 2019, https://majahill.wordpress.com/2019/03/20/10148451-tania-bruguera/.

The portrait was fully covered by layers of black thermochromic ink that prevented what was beneath from being recognized. When visitors pressed their palms down on it and waited for heat to be conducted, the black color faded into transparent and remained that way for minutes before turning black again. The heat didn't dissipate radially outward as much as it did into the ground, which meant that the handprints and other marks made by the body part of the visitors retained their shape until they turned back to black. Over the course of the day, most of the portrait remained covered in black. Even when many visitors laid on the portrait side by side to warm up larger chunks, only the areas that remained in full contact with their body parts transitioned from black to colorless. These visual effects stem from the thermal properties of the ink, which are not so different than the thermal properties of other coatings (*The Chemistry and*

Physics of Coatings). The chemical and physical properties of thermochromic coatings, like paints and inks, alter the kinetics of the color transition, which dictates the visual effect achieved and thus influence meaning that is relayed through the material.

Fig. 6. Marks left by audience members from "Cuban Artist Tackles Global Migrant Row At Tate Modern." Star2.Com, 12 Oct. 2018, https://www.star2.com/culture/2018/10/12/cuban-artist-bruguera-global-migrant-crisis-tate-modern-london/.

One can imagine, if the initial or final color of the transition had been different or the layer of paint had been thickly painted with brushstrokes visible, the artwork would have been different. Those changes in application and choice of material can be exercised by the artist, who is knowledgeable about color theory and techniques of painting. In a similar fashion, understanding the thermal properties of coatings will allow the artist to exercise full command of the thermochromic medium they are handling. For example, with a basic understanding of heat, the artist should be able to predict that a thicker layer of paint would require more heat to warm up, thus change color, than a thinner layer. Based on the First Law of Thermodynamics, the thermal energy required to heat a substance by a single degree Celsius is equal to the product of the mass and the specific heat capacity of the object. This can be denoted with the simple formula $Q = mc_p\Delta T$, where Q is the heat energy, m is the mass, c_p is the specific heat capacity at constant pressure and ΔT is the change in temperature. Increasing the thickness of the paint layer increases the mass of paint that must be heated, thus the amount of energy required for the activation temperature of the color transition to be achieved. Since it takes time to transfer thermal energy from the audience's body to the thermochromic material covering the artwork, the time it takes for someone interacting with the artwork to reveal the underlying portrait also increases with the thickness of the material.

In the case of Tania Bruguera, a thin layer of ink was spray painted, which meant that the reaction time of the surface was kept short. The ink heated up when touched, the black color fading to reveal the underlying image; but it also cooled down very fast, turning fully black in a few minutes. The effect was the same whichever part of the portrait one interacted with, because the ink had been spread uniformly. This meant that no area was thicker than the other or required more heat to reach the same temperature. Although the exact measurements of how rapidly heat will be absorbed depends on other thermal properties the material an artist is using, altering the thickness and uniformity of the coating has a simple universal effect on each material: thicker areas have more mass, and require more heat energy to reach the same temperature. Therefore, paint or ink that is spread non-uniformly over a surface won't exhibit uniform thermochromic behavior.

The second component of the thermal energy equation, specific heat capacity, is an intensive property of materials that doesn't depend on the amount of material that's at hand. It is a measure of how much heat energy is required to increase the temperature of a certain mass of material by one degree, Celsius or Kelvin. The specific heat capacity of paint, ink or other pigment including mixtures stems from the complex relationship between the different materials found in the mixture. It changes over time as the mixture dries and volatile solvents evaporate. Increasing the specific heat capacity of a mixture would increase the time it takes to warm up any segment of it, thus increasing the amount of work that must be put into the material to drive color change, a similar effect to increasing the mass. However, isolating an intensive property of a mixture and adjusting it is not as simple as painting a thicker layer of paint. It can be done by adding fillers to the mixture, as is done in many industries, but that will change other thermal properties as well. Specific heat capacity is tricky to temper with in isolation, but important to understand as other thermal properties depend on it.

Let's assume for example, that Bruguera didn't want the audience to leave handprints on the surface but desired a more diffuse visual effect. This way, when multiple people huddled together on the ink surface, instead of patchy transparent clearings, an entirely transparent area would form and allow what is beneath the ink to be seen. For such a visual effect, rather than the exact surfaces that come in contact with the heat source (in this case, the body part of the audience interacting with the piece) becoming transparent, the heat would have to dissipate uniformly from the source through the medium of the material, turning a circular area transparent. This would require the material to conduct thermal energy more readily, rather than containing it locally at the area where thermal contact occurs. In order to achieve this effect, the artist must manipulate the thermal diffusivity of the thermochromic mixture they are working with. Thermal diffusivity, α, depends on density, ρ, thermal conductivity, λ, and the specific heat capacity at constant pressure c_p with the equation $\alpha = \frac{\lambda}{\rho c_p}$. It measures the rate at which thermal energy is relayed through a material from the hot end to the cold end. In this example, the hot end is the area where a body part is in contact with the surface and the cold end is the edge of the coating material.

Increasing the thermal conductivity of the mixture or decreasing the product of density and specific heat capacity for the material would increase thermal diffusivity (M. H. Wit). Thermal conductivity, λ, is the proportionality constant between how much heat energy flows through an area, given a temperature difference. Aluminum, silver and copper particles have been added to polymer mixtures to increase their thermal conductivity, usually 20-40% by volume (Huang et al.). This is because metals are, among other things, good thermal conductors. There are organic options too: graphite, graphene, carbon nanotubes and graphene nanoplatelets have accomplished similar improvements in thermal conductivity with only 10-30% additions by volume. Carbon derivatives usually have higher specific heat capacities than metals, but metals are denser (*Densities of Common Materials*; Evans). When all three factors that contribute to thermal diffusivity are considered, carbon composites, copper, silver and aluminum are all good candidates as fillers to increase the thermal diffusivity of a mixture according to engineering data (*Thermal Diffusivity Table | Engineers Edge | Www.Engineersedge.Com*; *Thermal Conductivity of Common Materials and Gases*).

The artist can vary the ratio of filler particles added to the paint mixture until the desired thermal diffusivity is reached. All these fillers will affect the color, vibrance and mattness of the paint. The artist should exercise restraint by beginning with a small amount of filler to observe the effects, as the high percent by volume values taken from literature are usually meant to increase the thermal conductivity of their target material by four-fold to twenty-fold. Such an increase might not be necessary for the needs of the artist. The particle size of the fillers should be fine enough as to not change the application properties of the paint or ink. Such particles can be ordered from chemical or raw material producers online.

If tempering with the paint composition is not desired by the artist, there are simpler means of manipulating thermochromic visual effects. They involve adding another layer on top of the thermochromic coating to work as a thermal liaison. Covering the surface of the thermochromic material containing mixture after it has dried up with a transparent layer of cheap, easy to work with lacquer, glaze, glass or plastic would delay the response time of the mixture (Justus). When touched, or warmed through other means, the transparent layer would have to first absorb the heat and then conduct it to the underlying thermochromic paint layer, functioning as a thermal buffer. That would increase the time delay between first contact and color change.

The final visual element to note from Bruguera’s work that will offer insights to other artists is that no matter how long an audience member kept their hand pressed on the surface, they wouldn’t be able to reveal the entire portrait all by themselves. This was important for Bruguera, as she wanted to show that “sometimes you need two-three hundred people” to make a change (*Ask the Artist | Questions for Tania Bruguera | TateShots - YouTube*). What if she wanted to draw attention to a different number, maybe the number of politicians from a governing body, the number of seats that a political district controls, or some other number that was of importance? She would then need to adjust the size of the color changing area a single person could sustain; larger the area a single person can reveal, lesser the amount of people necessary to reveal the entire portrait.

Although thermal diffusivity plays a role in the spreading the heat and thus the color changing area, adjusting it wouldn't significantly change the limited circular area centered on the point of thermal contact that is being sustained. This is because the thermochromic paint is in thermal equilibrium with its surroundings: the floor it was painted on and the air that surrounds it. The printed portrait between the thermochromic ink and the floor is thin enough to be negligible. When the ink is touched and warmed, that equilibrium is temporally disrupted. Thermal energy pours into the material from the heat source and diffuses through the material. A hypothetical area that is at or above an arbitrary temperature forms, then expands. If the temperature is chosen to be the activation temperature of the thermochromic coating, then the expanding area has a visual equivalent: the area that has changed color. At a certain point the energy that is flowing into the material from the heat source will be equal to the energy that is being dissipated to the surroundings, which is when the expanding area reaches its limit.

That limit is defined by the temperature difference between the heat source and the coating, the area of contact, the activation temperature of the thermochromic mixture and the thermal effusivity of the surface it was painted on. The first two are related through the formula $\frac{Q}{t} = \frac{\mathrm{A}\lambda\Delta T}{d}$, where *Q/t* is the rate of heat flow, *A* is the area of contact, ΔT is the temperature difference between the heat source and material, λ is the thermal conductivity and *d* is the depth of the material. It should come intuitively that if a person laid down on the thermochromic ink, they would be able to heat up a larger area than if someone had pressed down their hand. It should also make sense that if a hot iron plate was pressed on the ink, it would be able to sustain a larger heated area than a warm iron plate. This is because both the area of contact and temperature difference correlate positively with heat flow. Depth, denoted *d*, refers to the distance that heat is being conducted through, and in this case, it is negligible as the thermochromic ink is so thin that it can be treated as two dimensional.

The limit of the area that has changed color can be adjusted by picking a different activation temperature. Let's say that the room temperature is 20^{o}C and the ink is in thermal equilibrium with the room. An ink transitioning from black to transparent at 24^{o}C would require less heat to transition than an ink with an activation temperature of 31^{o}C. That would mean that a larger area of color change can be sustained with the lower activation temperature than the higher one, given that all other factors are the same. One could visualize this by assigning body temperature 36^{o}C to the point of contact between the audience member and the ink. Then, drawing imaginary concentric lines starting from that point, extending all the way to the edge of the ink covered surface. The temperature gradient parallel to these lines will be decreasing, such that the temperature some distance away from the center will be 28^{o}C, an arbitrary example temperature. If the activation temperature is lower than that, the color changing area will have a radius larger than this hypothetical distance, and if the activation temperature is higher than 28°C, the color changing area will be smaller than this distance.

That leaves the final thermal property to be discussed, thermal effusivity, which measures the ability of a material to exchange thermal energy with its surroundings. It is denoted as e, which depends on density, ρ, thermal conductivity, λ, and the specific heat capacity at constant pressure c_p, with the equation $\mathrm{e} = \sqrt{\lambda \rho c_p}$. These parameters can all be tempered with for a thermochromic mixture; however, the thermochromic mixture itself along with any fillers added would have higher effusivity than the other two environments the coating is in contact with (*Thermal Properties of Common Materials | Thermal Analysis Labs*). The prime importance is therefore on the surfaces in contact with the coating; because the thermal effusivity of concrete is almost two orders of magnitude greater than that of air, thermal energy is most rapidly lost at the interface between the coating and the surface it has been painted on. This knowledge allows for a quick remedy to the heat loss problem. Reducing the thermal effusivity of the surface that is painted over, or rather picking a thermally insulating surface, will lower the heat loss. Since thermal equilibrium is reached when the energy input is equal to the energy loss, lowering the energy loss means that less energy must be put into the mixture to sustain the same temperature. In other words, if the energy input is the same, lowering the energy loss means that a larger area of color change will be sustained. There is an incredible variety of low thermal effusivity, thermally insulating materials available, the simplest being plastics and their derivatives. The artist can choose one of these materials as an insulating layer below the thermochromic mixture.

Thinking like an engineer, trying to tweak properties of the material they are working with and gazing at formulas might come as tedious for an artist. However, with dynamic materials such as thermochromic pigments, the very nature of the physical and chemical processes governing the visual effects are be part of the artwork. The science isn’t separate from the art, rather an element of it. Key elements of Bruguera’s work, such as the nature of driving change, working together, sharing and spreading are all paralleled in the molecular level by the conduction, dispersion and dissipation of heat. As Bruguera says: “For me science in this project is the metaphor, is the way to enter into the metaphor of the project, because it’s what delivers the meaning of the project”. As such, the knowledge and manipulation of materials become essential tools for the artist, just as vital as color theory or perspective.

Photochromic materials have been known to the scientific world since the beginning of the 20th century and have been developed to be used in many practical applications, including solar panels, optical information storage, display media and color changing glasses . As chemicals and dry pigments, they have been available since the 1980s and their properties have been extensively studied. This allows for many creative examples of usage from different disciplines to serve as inspiration for the artist. Their availability as artist materials is at a comparable level to thermochromics paints and pigments; most manufacturers that produce one also produce the other. However, due to the longer market presence of photochromics, concerns related to fickle supply are more applicable to thermochromics.

PHOTOCHROMIC PAINTS AND PIGMENTS

Photochromic paints and pigments change color when exposed to UV light. The source of UV light can be natural or artificial. Sunlight, arc lamps and blacklight are the most common sources (Ritter, "Colour- and Optically Changing Smart Materials"). Color change will occur as long as the material is irradiated and stop when exposure is discontinued. The mechanics and kinetics of how the color reverts to its original form varies and is the prime interest of this chapter. The color change of the material will depend on the duration of exposure, intensity of the UV component found in the light and the conditions of the non-exposure period.

Photochromic materials come in a wide variety of colors. There are two types of transitions possible: colorless-to-color and color-to-color (*Photochromics | TMC Hallcrest*; "SFXC® Photochromic Sun Sensitive Reversible Pigment Powder"; *Sun Activated Products | Atlanta Chemical Engineering*). Colorless-to-color materials contain a single photochromic chemical in their recipe and are transparent or white when not exposed to UV light. Color-to-color transitions can sometimes employ an inert pigment as a base color, such as blue, along with a photochromic pigment, such as colorless-to-pink (Marinov). When combined, the mixture will appear blue when not exposed to UV light, and turn violet due to the photochromic pigment attaining its pink hue. Certain photochromic molecules also exhibit a direct color-to-color transition without the need for a base color, however these are rare.

It is possible to find many colors for colorless-to-color transitions, however the exact hue an artist desires might not be available. For example, one is sure to find colorless-to-blue material, but whether it's ultramarine, cobalt, navy or Prussian won't be on the label and will have to be tested once the artist acquires the paint or pigment. Since the primary concern for manufacturers isn't to offer a wide selection of hues for a given color, like producers of classic paints, if the artist desires different hues of a given color, then ordering from various producers is the best bet to create variety. The same goes for color-to-color transitions, it would often be best to acquire the colorless-to-color component from a manufacturer and add the inert pigment as desired rather than going on searching for the exact color-to-color transition.

Photochromic pigments contain a microencapsulated photochromic dye, usually with certain additives like a synthetic resin or an organic solvent to provide extra stability and protection from chemicals used in the manufacture of coatings and plastics (“Photochromic Pigment”). The contents of the microcapsule can vary from manufacturer to manufacturer since they are not integral to the basic mechanism of color change as they were in the three-component system employed in thermochromic pigments. The properties of a photochromic pigment therefore depend mostly on the chemistry of the photochromic molecule employed. The medium in which the pigment is dispersed and any additives into the microcapsule function as auxiliary determinants for the overall visual effect.

Although they derive their color change from UV light, photochromic leuco dyes and other conjugated molecules aren’t completely resistant to its deteriorative effects. Each molecule has a different average cycle count between its two forms before it bleaches, which is called fatigue (Durasevic; Irie et al.). Manufacturers do their best to keep the cycle count high and research is constantly conducted to improve the photostability of all kinds of chromic compounds (*Photochromics | TMC Hallcrest*).

Photochromic pigments can be divided into two based on the molecular mechanism exhibited by their organic dye molecule: ring opening leuco dyes and ring forming leuco dyes. Photochromic glasses on the other hand, contain silver halides and are subject to different mechanisms than paint or pigments, thus are beyond the scope of this book (*Experimenting with Photochromism - YouTube*; *4363 JR Reversacol Brochure*). They are quite common in our daily lives and research about their workings is abundant if the artist is interest in utilizing them.

MECHANISM: RING-OPENING LEUCO DYES

There are many classes of ring-opening photochromic molecules, triarylmethanes, nitrones, naphthopyrans, spiropyrans, and spiro-oxazines being the most common ones (*Chemistry and Application of Leuco Dyes*; Nakazumi; Muthyala and Lan). Because these chemicals transition between two forms, one of which is colorless, they are also referred to as leuco dyes. Generally, the colorless form of the molecule absorbs in the UV region of the electromagnetic radiation spectrum, but not in the visible region. This is because its cyclic systems of the molecule are separated by a carbon with tetrahedral geometry, which essentially prevents them from joining together and allowing absorption of light with less energy (light with longer wavelength). Manufacturers don’t label the exact chemical they use in their products, but it is possible to understand and manipulate common properties shared by these classes of organic molecules.

These photochromic leuco dyes exhibit a common mechanism of color change. On irradiation with UV light the molecule undergoes a ring opening reaction, more specifically a heterolytic cleavage of the carbon–oxygen bond (or other spiro bond), to form the colored isomer, which is sometimes referred to as the merocyanine form (Nakazumi). In this new “open ring” form, the cyclic systems are joined and conjugated along the entire molecule, which is virtually planar. This lowers the energy requirement for photonic absorption; thus, the molecule can absorb longer wavelengths of light, including visible light. Since the photochromic reaction is unimolecular, a tri-component system isn’t necessary unlike the thermochromic leuco dye mechanism.

When the UV source is removed, the molecule can relax to its original geometric conformation, the closed spiro form with the carbon–oxygen bond reforming (Nakazumi). The observable visual effect is a return to the colorless state. This bond breaking and reforming process is dynamic and reversible, which is why the two forms of the molecule are said to be in equilibrium. When UV light is present, the forward reaction forming the colored form is favored. When it isn’t present, then the reverse reaction forming the colorless form is favored. The favorability of the reactions is a thermodynamic term, as such it only refers to the direction of the reaction and not the rate. The kinetics of the reaction, which pertain to the speed at which the forward and the backward reaction occur, will be discussed later.

Although the colorless-to-color transition of photochromic molecules is activated by UV light, the reverse reaction can be driven by both thermal energy and visible light. If the back reaction is thermally driven, it is referred to as T-type photochromism; if it is photochemically driven, then it is referred to as P-type photochromism (Corns et al.). Most commercially available paints and pigments employ T-type photochromism, but some show P-type photochromism as well (Corns et al.). Every property of photochromic molecules can be manipulated in the lab, from color to stability to transition rates between forms, either through direct chemical substitution or the alteration of the environment of the molecules (Chen et al.; Wen et al.). However, the microencapsulated pigment form of a photochromic molecule, either as is or pre-dispersed in ink or paint, is a finished product which the artist can’t chemically tinker with. Thus, the vast amount of research available that can tweak the chemical properties, which directly influence the visual properties, of leuco dyes isn’t of much use to the practicing artist. The thermal component of the back reaction is the simplest aspect of photochromism for an artist to manipulate, and it remains largely unaffected by the fact that the molecules have been microencapsulated, which is why it will be further discussed.

MECHANISM: RING-FORMING PHOTOCHROMIC DYES

Separate from photochromic materials that exhibit only the T-type or both the T-type and P-type behavior, there are also classes of chemicals that only exhibit P-type behavior: the two most-studied being diarylethenes and fulgides (Corns et al.; Durasevic; Bouas-Laurent and Dürr, *International Union of Pure and Applied Chemistry Organic Chemistry Division Commission on Photochemistry* Organic Photochromism*; Ritter, “Colour- and Optically Changing Smart Materials”). Research on them has only intensified in the last few decades for the sake of technological applications, and they are available as dyes but not as pigments. Eventually manufacturers might make pigments containing only P-type dyes, but until then the artist must acquire them in dye form.

They don't exhibit a ring-opening mechanism, but rather a ring-closure or ring-formation mechanism upon irradiation with UV light (Bouas-Laurent and Dürr, "Organic Photochromism (IUPAC Technical Report)"). This usually occurs in a position where two cyclic moieties can form a mutual bond that allows the overall molecule to obtain fused rings, rather than rings connected by a non-cyclic conjugated system. Therefore, the forward reaction is a photocyclization and the reverse reaction is a ring-opening. Based on the same principal of expanding the conjugated system and lowering of the absorption energy, the closed form of the molecule can absorb longer wavelengths of light than the open form. For diarylethenes, the open form is colorless, absorbing light in the UV region of the spectrum, while the closed form is colored, absorbing light in the visible part of the spectrum. For fulgides, both forms are colored, the open form absorbing wavelengths of light that are more energetic than the closed form (absorbing yellow in the open form and red in the closed form for example) (Bouas-Laurent and Dürr, "Organic Photochromism (IUPAC Technical Report)"). Upon irradiation with the wavelengths of light that are specific to the dye molecule, the fused rings open again and allow the molecule to transition from its closed form to the open form.

What makes these molecules of interest to the artist isn't the color range they offer, as a wider spectrum is available for T-type photochromics. It is the fact that the reverse reaction doesn't occur thermally, but instead requires absorption of certain wavelengths of light. This yields the dyes, and the systems that they are dispersed in, novel photochromic properties that can be manipulated in unique ways. Because thermal energy that is always present in the environment doesn't initiate the reverse reaction, the color of the molecules isn't constantly fading. The equilibrium between the forward and backward reactions can be disturbed if the wavelengths of light that initiate the backward reaction are prevented from reaching the molecules. Whereas for T-type photochromism, the fading rate could be manipulated to a certain extent depending on its thermal dependence, in solely P-type photochromics the fading can be brought to a halt. This allows the artist to more precisely control when the color change will take place, UV and reverse-reaction-initiating radiations working like switches to turn on the forward and backward reactions respectively. That is how P-type photochromics are being developed in technological applications as well, to work as photonic switches and logic gates (Irie et al.).

Before preventing the reverse-reaction-initiating wavelengths, the artist must be aware of what they are. This can either be done by consulting with the manufacturer or knowing the exact chemical name of the dye and looking up scientific literature for its absorbance. Once the wavelengths are known, different filters can be utilized to prevent light of those wavelengths from passing through. The filters can be thin sheets of acrylic, thicker slabs glass, or some form of plastic in between, but the general idea behind them is the same. A red filter would allow the passage of light with wavelengths in the red region of the spectrum, a blue filter would allow blue. Other filters that allow the passage of larger ranges of wavelengths can be bought as well.

Then, it is up to the artist to construct a photochromic system that is exposed UV or reverse-reaction-initiating radiations in the desired amount during intended intervals.

If the reverse-reaction-initiating wavelengths aren't known, they could be experimentally determined by the artist by first exposing the photochromic material to UV light to change its color and then subjecting it to light passed from different filters to see which one results in faster fading. This might seem like a primitive way of going about, but if the artist only has access to limited types of filters, this test is more useful than knowing exactly which wavelengths of light trigger the back reaction. If the artist has access to a few filters, knowing which ones allow the passage of light that causes a faster fading rate in the photochromic system could be enough to manipulate the reverse reaction rate. The filters and the light reaching the photochromic artwork can be manipulated in a multitude of ways that are familiar to the artist: they could be moved, partially blocked, the radiation can be reflected or refracted. P-type photochromism allows the color of a material to be tied to visible light as well as UV light, which expands the number of interactions the artist can tap into between color and light.

EXAMPLE: EMBEDDING PHOTOCHROMISM

In 2011, Tomoko Hashida and Takeshi Naemura from the University of Tokyo and Yasuaki Kakehi from Keio University, presented their experimental photochromic sculpture. They were aiming to demonstrate the concept of "contactless color control" on a volumetric space to create a dynamic sculpture that could display shapes and forms depending on the light shining on it (fig. 7 and 8). They coated laminated plates with photochromic spiropyrans granules and manipulated their activation with projected light. Their UV light source had a wavelength of 365 nm and the transparent plates which were placed on top of each other transmitted this wavelength (Hashida et al.).

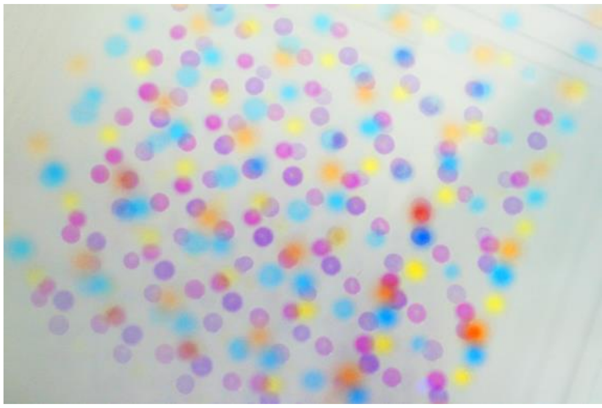

Fig. 7. Multicolored spiropyrans from Hashida, Tomoko, et al. Photochromic Sculpture: Volumetric Color-Forming Pixels. 2011, doi:10.1145/2037703.2037714.

Fig. 8. Volumetric color formation from Hashida, Tomoko, et al. Photochromic Sculpture: Volumetric Color-Forming Pixels. 2011, doi:10.1145/2037703.2037714.

By forming a structure with high transparency which does not require electronic control to change color, they were aiming to demonstrate the viability of such sculptures. They showed that by controlling the time, strength the pattern of the projected UV light, it possible to control the position and activation duration of various colors synchronously (fig. 9). Their sculpture employs a straightforward application of paint, which is the coating of a surface. However, a sculptor wanting to experiment with different media can utilize photochromic dyes and pigments in more ways by embedding photochromism to different materials rather than simply coating them.

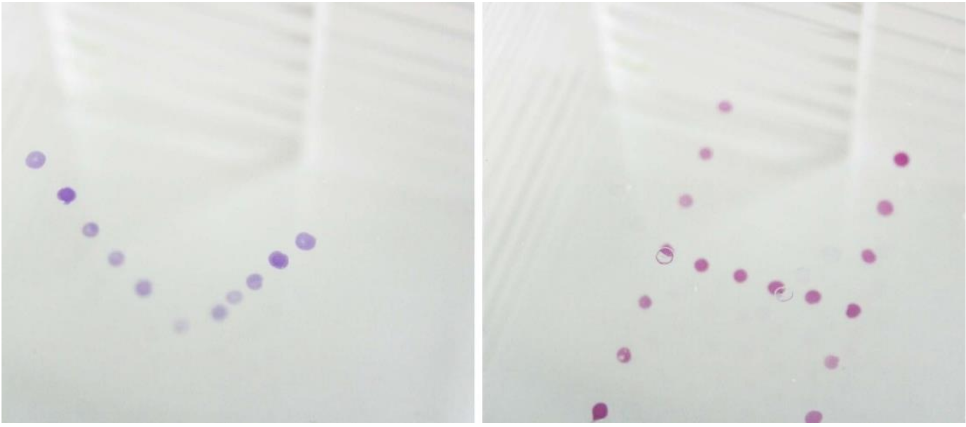

Fig. 9. Controlled illumination patterns from Hashida, Tomoko, et al. Photochromic Sculpture: Volumetric Color-Forming Pixels. 2011, doi:10.1145/2037703.2037714.

An important difference between photochromics and thermochromics is that the former is commercially available in many forms while the latter requires microcapsules to preserve its function. Photochromic materials are available as dyes, pigments, paints, inks and glasses to the artist. Among those, both the dye and the pigment can be dispersed in a multitude of media. The availability of the dye form allows the artist to create a wider range of photochromic materials without worrying about damaging the microcapsule surrounding the pigment.

The pigment and dye forms must be carefully distinguished before subjecting them to chemical procedures or dispersing them in a medium. The pigment form has been microencapsulated and is suitable to be dispersed in either aqueous or organic mixture. The dye form is the unaltered organic molecule itself and is soluble in various solvents. When bought as a powder, both forms can look quite similar, if not outright the same. If the powders have been separated from the labels somehow and the artist needs to distinguish between them, then subjecting them to UV light will be enough. The pigment contains the dye and a solvent in its capsules, and it will turn colored; the dye will not acquire color in its solid powder form, because it needs to be dissolved in a solvent or embedded in a matrix for the photochemical reaction to occur (Corns et al.; *How Do Reversacol^{TM} Photochromic Dyes Work?*).

The dye form opens many interesting venues for the artist to explore. While the pigment can be mulled into paint, the dye form can be mixed into plastics, molded, dispersed in inks or dissolved in liquid media. The most apparent downside of the dye form is the limited commercial availability as artists' materials and the cost of acquiring dyes that are intended as scientific materials. The dye is essentially just a chemical and the only limit as to what can be done with it is the artist's imagination, but there is precedent in certain types of applications and the literature that exists for the usage of industry can offer the artist some guidance, if not inspiration.

One of the most well-studied applications of photochromic dyes is in thermoplastics (Corns et al.; Ritter, "Colour- and Optically Changing Smart Materials"). Photochromic dyes can be chemically attached to polymers as side chains or dispersed in polymer matrices before they are molded. The latter is more suitable for artists with less chemical expertise. The most common T-type dyes work best in polymer matrices that do not restrict the changes in conformation that the dyes undergo upon UV irradiation. Either or both the forward and the backward reaction can be inhibited, as the activation energies of the reactions increase due to geometric challenges. Materials with high rigidity should be avoided and instead materials with relatively low flexural moduli and glass transition temperatures should be used (Corns et al.). One rule of thumb from literature suggests that polymers with a flexural modulus higher than 2GPa, like polycarbonates, styrenics or acrylonitriles, will give a poor photochromic effect, while polymers with lower flexural moduli, like polyolefins, polyvinyls and rubbers, will give better photochromic results (Corns et al.). Small molecules called plasticizers can be added to the polymer mixture to get between the polymer chains, effectively increasing the free volume and lower the glass transition temperature; this would improve the photochromic properties of a polymer-dye mixture (*The Glass Transition*). Plasticizers can be commonly bought and should be familiar to the artist familiar with making their own materials.

Being polycyclic organic compounds, photochromic dyes are soluble in non-polar solvents. Their solubility in toluene, which is structurally comparable to turpentine, ranges from a dozen grams to a few hundred grams per liter depending on the dye (*4363 JR Reversacol Brochure*). Their solubility drops considerably to less than a few grams per liter in methanol however, which goes to show that polar solvents like water would be even poorer choices to dissolve the dye in. Furthermore, the inherent amphoteric nature of water can to cause a series of redox reactions to occur with the photochemically activated dye molecule, rendering the molecule unstable in aqueous environments. The intermolecular interactions between the solvent molecule and the photochromic dye might affect the equilibrium constant for the photoisomerization reaction, which could change the intensity of observed color; or it could alter the chroma of the observed color, which is called solvatochromism. Wavelength shifts, for the absorbance of the dye, of up to 20 nm have been observed in different media (*4363 JR Reversacol Brochure*). Such effects are case specific, and the artist should experiment with different dye-solvent combinations until the desired visual effect is found.

The kinetics of color change will change depending on the medium in which the dye has been dispersed in. The easier it is for the molecule to change its conformation, the lower the activation energy for such a change and thus the faster the rate of coloration and discoloration.

Polymers can hold the dye in a favorable conformation within their matrix to allow for rapid photoisomerization or lock it in the non-colored closed form and thus inhibit photochromism. A dissolved dye should experience no such inhibitions, as such the activation energy of the photoisomerization should be at its lowest in liquid media. The fading rate would be quite high, and almost instantly fading photochromic solutions have been engineered for technological applications (*Rapid Color Fading of Photochromic Naphthopyrans - YouTube*; Irie et al.). Depending on the needs of the artist, different media with different fading rates and properties can be chosen and the visual effects achieved through photochromism further manipulated.

EXAMPLE: A DRESS FOR EVERY WEATHER

In 2018, the fashion label Anrealage showcased their newest 2019 Spring/Summer Collection, which included garments with photochromic components. The garments were designed to be black when exposed to sunlight and white or translucent when worn indoors (*Anrealage Spring 2019 Ready-to-Wear Collection - Vogue*). During the showcase, the color change was demonstrated by exposing the garments to UV light backstage to turn them black (fig. 10 and 12) and letting the color fade out over time as the models made their way down on the podium (fig. 11 and 13) (*Slow Photochromism - Anrealage Installation - YouTube*).

The collection, named “A Light Un Light”, explored material and lighting, relying heavily on black and white as colors (“ANREALAGE OFFICIAL | COLLECTION”). The head designer, Kunihiko Morinaga, is interested in bringing together opposites: “I think that there is both a science technology and a human technology in technology. I am interested in making clothes by crossing over these two different technologies” (Balmat). On one hand, the dresses employed cutting edge technology through the usage of photochromic materials, on the other hand, the garments were produced primitively by hand. The photochromic nature of the dresses added onto this metaphor about the dualities that exist within production: the photochromic material the dresses are made from is a singular entity, yet it exists in two forms and oscillates between two colors.

The collection was made possible by the collaboration between Anrealage and Mitsui Chemicals Material Oriented Laboratory (*Mitsui Chemicals Serves as Material Advisor for ANREALAGE’s Paris Fashion Week Spring/Summer 2019 Show | 2018 | Press Release / MITSUI CHEMICALS, INC.*). If it had been simple to produce photochromic garments, then the interest shown in photochromic dyes as a means of producing novel effects in apparel would have already been matched by commercial success in the fashion industry. However, it is difficult to apply industrial photochromic dyes by conventional textile coloration techniques due to their poor lightfastness and durability (Corns et al.). The team therefore took a different approach; they combined the dyes with thermosetting resin that was molded into buttons, balls, studs, fibers and other embellishment parts, which were then sown or otherwise attached to garments (Matsunaga). The photochromic molecules were pre-mixed into a liquid polymer mix

Fig. 10. Opaque form of dress with circular buttons

Fig. 11. Transparent form of dress with circular buttons

Fig. 12. Opaque form of dress with hexagonal buttons

Fig. 13. Transparent form of dress with hexagonal buttons

all from "ANREALAGE." LVMH PRIZE, http://www.lvmhprize.com/designer/anrealage/. Accessed 8 Sept. 2019.

of either thiourethane or polyurethane for the embellishment parts and the synthetic fibers employed as base material for the clothes were polypropylene. The addition of photochromic dyes in-mass to polymeric mixtures is a different process by nature than handling paint and pigment to coat surfaces, but the kinetics of color change obey the same rules as commercially available photochromic material (*How Do Reversacol^{TM} Photochromic Dyes Work?*). An artist, a painter and a fabric manipulator might have slightly different concerns, but the rate of color change is a common element of art in all their practices.

The manipulation of kinetics is therefore vital to skillfully manipulate the temporal element of photochromic media. If the designers wanted the black color of the dress to fade almost immediately when the wearer went indoors, or if they wanted a more subtle change that took place over hours, where the untrained eye wouldn't be able to tell that the dress was changing color, they would have to tinker with the kinetics of color change. The same question of how fast the color of a photochromic material should fade is relevant to any artist utilizing photochromic paints or pigments. In order to achieve the desired visual effect, the artist must first understand that the photochemical reaction between the two forms of the dye molecule is referred to as a chemical equilibrium. At any given point in time, in a batch of photochromic mixture, colored forms are transitioning into the colorless form and colorless forms are transitioning into the colored form. The two transitions are facilitated by different sources of energy, and the balance of the equilibrium along with the difference in the rate of the reactions is responsible for the dynamic color change that is observed.

Irradiation with UV light facilitates the ring-opening reaction for example, shifting the balance of the equilibrium so that the concentration of the colored form increases, which is observed as an intensification of color. Removal of the light source has the opposite effect, the equilibrium shifting towards the colorless form of the dye, which is seen as fading. In T-type photochromism, the reverse reaction is driven thermally; raising the temperature speeds up decay of the colored form to the colorless. This shifts the equilibrium further away from the colored form, which is perceived as a reduction in the intensity of color. If temperature is sufficiently high, then even if UV light is applied to the photochromic material, the forward and backward reaction rates might be too close. In that a case, since roughly the same number of molecules are transitioning into the colored state as the molecules that are transitioning to the colorless state, no net color change will be observed. The same idea applies to P-type photochromism: instead of the thermal energy regulating the reverse reaction, some wavelength of light specific to the dye molecule does so. Increasing the intensity of the reverse reaction facilitating light will reduce the intensity of color. At a sufficiently high intensity, the back reaction will match the forward and no color change will be observed.

One can think of the forward and backward reactions as two arms locked in an arm-wrestling match. It is the power difference between the arms that results in one of them being lowered: just as two strong athletes can be tied, so can two regular adults. When thinking about the rate and intensity of color change in photochromism, it is crucial to consider both the forward and backward driving forces. On a bright sunny day, there is ample UV radiation, but the temperature is also hotter and there is more visible light coming from the sun. On a cloudy and dark day, there is less UV light that can penetrate the cloud cover, but the temperature might also be colder and there would be less visible light coming from the sun. In both cases the perceived color change could be the same. The visual effect depends on the innate properties of the photochromic material at hand: its fading rate, the thermal dependence of the fading rate and the temperature at which it is irradiated. As such, the artist shouldn't formulate their expectations about the behavior of photochromic material on heuristics that rely solely on the availability of UV light.

In Anrealage's show the fading rate was quite rapid: the dresses that were fully colored on the runway minutes ago were introduced for a second time to the runway completely colorless ("ANREALAGE OFFICIAL | COLLECTION"). The fading rate of a photochromic molecule depends on its chemistry, more specifically how easily it can transition back to its original form. This can be adjusted in the lab by adding or removing chemical groups that cause steric hindrance for the geometric reorganization. To achieve a rapid fading rate, Mitsui Chemicals utilized technology designed for photochromic lenses to pick a rapidly fading photochromic dye and then disperse it in-mass in polymers material. This offers longer lasting photochromic effects than simply coating a material with a pigment while preserving the fast rate of fading.

This kind of chemical expertise might not be available to the artist. Furthermore, if the organic dye has been microencapsulated, then it would be challenging to disperse it in a plastic medium or glass and subject it to high molding temperatures without damaging it. When working with microencapsulated photochromic pigments, the artist can inquire about the fading rate before buying it, and if the manufacturer doesn't have the necessary data, two photochromic paints can be compared side by side to see which one fades quicker. To do this, simply controlling all variables other than pigment type, such as dispersion medium, amount of paint/pigment and ambient temperature, and observing which pigment turns colorless first after being exposed to UV light would be enough. If two photochromic paints are each painted in equal amounts, yet one of them fully colors under UV light much faster than the other one, that would indicate that they contain different amounts of pigment in their composition. In that case the fading rate should be tested once both paints have fully acquired their colors by transitioning to their UV-light activated form.

There is huge variety in the fading rates of photochromic materials. The rates are measured and denoted as the time it takes for the colored form to lose a quarter, a half and three quarters of its intensity, denoted as $T_{1/4}$, $T_{1/2}$ and $T_{3/4}$ respectively. These could be as fast as 4, 8 and 16 seconds for a rapidly fading dye, or as slow as a minute, 6 minutes and half an hour for a slow fading dye (*4363 JR Reversacol Brochure*). The fading can happen linearly, exponentially or logarithmically over time. For example, the time for half-fading, $T_{1/2}$, could be 6 minutes for two different dyes. But the $T_{1/4}$ of the first dye could be longer than the second, and the $T_{3/4}$ could be shorter. This would mean that the first dye would start to fade slowly, but then speed up and catch the second dye around half discoloration, becoming fully colorless much sooner. The thermal fading of the colored form follows first-order kinetics for most commercially available molecules, which would have one think that the thermal fading would occur linearly. However, intermolecular interactions, changes in absorption and refractivity of the dye or other bulk properties might delinearize the fading curve, leading to dyes that have different fade-over-time curves.

The thermal dependence of the fading rate is also an innate chemical property of photochromic materials, as such it can't be manipulated by the artist. One can be aware of it during the artistic process and inquire about it when acquiring paint or pigment from a manufacturer. Historically, materials that exhibited somewhat uniform behavior across a temperature range were favored, so most commercially available paints and pigments have fading rates with low temperature dependence (*4363 JR Reversacol Brochure*). The dye form offers more variety, as it is more of a raw substrate rather than a finished product; if the artist desires highly thermally dependent fading rates, those can be acquired in the dye form rather than the microcapsulated pigment or pre-dispersed paint form. Data is scarce when it comes to the thermal dependence of the fading rate of paints and pigments; different products must be tested by the artist to compare them. To do this, the thermal fading test explained above should be repeated, but at temperatures that differ by a constant amount, such as 10 °C, 20 °C and 30 °C.

In the case of Anrealage's collection, formulating the polymeric components with a highly thermally dependent photochromic dye would yield garments with high seasonal variation in the color change they exhibit. With a fast fading rate and high thermal dependence, the same dress when worn outside on a sunny day in summer would be much paler in color than when worn in winter. In cold weather the fading rate would be sufficiently slow for the UV light to sustain coloration, but in hot weather the fading rate would be fast enough to compete with the forward reaction. With a sufficiently slow fading rate and high thermal dependence, the dress would remain colored in both winter and summer. This is because the change in temperature wouldn't be able to speed up the very slow fading rate enough to be competitive with the forward reaction.

To predict the visual effect achieved when the garments go from outdoor space to an indoor space, the simple "winter equals cold weather, summer equals hot" heuristic doesn't hold, however. The effect of heating and cooling in buildings must be considered alongside the loss of UV light for outdoor to indoors transitions. When a T-type photochromic garment with highly thermally dependent photochromic material goes from a cold UV light environment to a warmer non-UV light environment, its forward reaction rate plummets and its backward reaction rate increases. On the other hand, if the material goes from a hot UV light environment to a colder non-UV light environment, the forward reaction rate plummets and its backward reaction rate increases. This means that going indoors during winter would cause a much sharper and rapid decoloration than going indoors during summer, this distinction between the seasons being heightened by the thermal dependence of the photochromic material.

If the thermal dependence of the photochromic dye was low enough to be negligible, then these seasonal variation in the visual effects wouldn't occur. Whether the dress could remain intensely colored when worn outdoors would only depend on the fading rate: a fast-enough fading rate would compete with the forward reaction, one too slow would allow for full color intensity to occur. If the photochromic material exhibited P-type photochromism, the fading rate would exhibit light dependence. Heat and light are just different forms of energy, as such the previous arguments about T-type photochromics would still hold for P-types. Simply substituting the availability of thermal energy in the previous discussion with the availability of the wavelength of light that facilitates the reverse reaction would be enough to conceptually translate T-type kinetics to P-type kinetics.

Whereas in thermochromic systems a physical phase change dictates color change, and thus the material can be controlled more physically, manipulations of photochromic materials require understanding of the chemical reactions taking place. As such, instead of thinking about thermal energy alone and tinkering with its conduction like an engineer, working with photochromic media requires the artist to don the coat of a chemist, taking into account both thermal and radiant energy.

The fact that ambient humidity can change the way colors are perceived has been known to those who deal with inks, dyes, coatings and textiles for a long time. Often regarded as a phenomenon that makes quality control or color matching challenging in different environments, hydrochromism, sometimes referred to as hygrochromism, is the observed color or opacity change in a material due to changes in ambient humidity or contact with water (Gordon). Developed more recently than thermo- and photochromic materials, paints and inks exhibiting hydrochromic properties are now available to artists. Although available through more sources across continents, there is much less variety in hydrochromic paints and inks compared to thermo- and photochromics.

HYDROCHROMIC PAINTS AND PIGMENTS

Hydrochromic pigments change color when they come in contact with water. They are most commonly available in a printable sprayable ink or brushable paint form. Both share a common color change mechanism and only the viscosity of the medium and intended application method distinguishes which products are labeled as “inks” or “paints” by a manufacturer. Hydrochromic inks and paints both create a reversible white print which turns clear on contact with water and in its transparent state reveals the color of the underlying substrate (*How It Works - Hydrochromic*). Upon drying out, the white color returns, hiding the underlying print. The ink can be manipulated with a brush as if it were a fast-drying water based medium, like acrylics.

The color range of the ink is quite limited, as white gives the best results for color-to-transparent transitions. Inert pigments can be added to the composition to change the transparent hue to a light color; however, this is usually avoided as it affects the opacity of the transparent state as well. As the coating weight of hydrochromic ink is increased, its transparency when wet is reduced and colors other than white would give poor results. Multiple layers might be necessary to hide the layer beneath the ink. The surface on which the hydrochromic ink is applied to affects the results as well, although paper, plastic, wood, metal and glass can be covered by the ink, the surfaces must all be flat. A non-uniform surface would affect the transparency of the wetted state because the depressions or holes in the surfaces can get clogged by the ink in a way that prevents the absorption of water.

The “pigment” employed in hydrochromic inks or paints can be a mixture of many inorganic compounds. There are patents for numerous salt combinations including but not limited to carbonates, bicarbonates, silicates, bisulfates, hydroxides of alkali metals and alkaline earth metals (Kanakkanatt and Kanakkanatt; Klofta et al.). There can also be certain aluminum compounds, some chlorides, oxides and nitrates. These chemicals are mixed with other solid particles that either increase the stability and improve the adhesive properties of the resulting film, or act as porosigens that allow water to be transmitted throughout the film. Then, the pigment is dispersed in a medium and water is added until the desired consistency is achieved.

MECHANISM: WET-REVEAL HYDROCHROMIC INKS

The hydrochromic property of the ink or paint comes from the physical changes that take place once the pigments form a film on a surface. When dry, the film is opaque and white, as expected from the solid-state appearance of the chosen chemicals. When the surface is wetted with water, the film absorbs water and the air that filled the spaces inside the film is replaced with water (Ritter, “Matter-Exchanging Smart Materials”). Thus, the film acquires a viscosity such that it becomes permeable to light which it used to diffract. This allows light waves to travel through, making the image beneath the film visible. When the surface is dried, the ink film returns to its light impermeable condition, becoming white and opaque again.

The principle behind wet-reveal hydrochromic materials has to do with the index of diffraction of materials, also called the refractive index. When light travels from one medium to another, a portion is always reflected proportional to the difference in the index of diffraction between the two media. The angle at which light shines on a surface also affects reflection, but the porous and jagged microscopic surface structure of the hydrochromic film makes the angle of incidence negligible for reflectivity discussions related to this material. As such, the change in behavior of light at an interface where the difference in the index of diffraction is high compared one where it is low accounts for the change in opacity for hydrochromic materials.

The mechanism with which the film changes its permeability to light is like how other substrates, such as paper, behave when the air filling their inner spaces gets replaced by another substance. The salt fillers between cellulose fibers in paper and the air surrounding them have a high difference in their index of diffraction; so, a large portion of light coming from the air side of the interface is reflected from the paper. When the paper is wet, the difference in the index of diffraction between the water and the paper is low. The difference between water and air is also low enough to let light pass through, so light travels through the media without being fully reflected. A mechanically similar process occurs in the hydrochromic ink or paint layer, in fact some manufacturers sell an adhesive hydrochromic sheet which employs a layer of hydrochromic ink deployed over a transparent plastic sheet. The paper analogy extends perfectly to this product, and when working with white hydrochromic ink the artist can think of it as covering a surface with a thin sheet of paper that becomes transparent when wet.

Just like how paper might become damp but not fully soaked in a humid environment, the film formed by a hydrochromic paint or ink requires enough water to turn transparent. Direct contact with liquid water is the most effective way to fill the interstices between the particles forming the film, because their uptake of water vapor isn’t reliable. Some formulations might result in films that can take up some water molecules into their volume, however the overall effect of humidity in wetting a film isn’t considerable. The water molecules can condense on the surface of the film and the intermolecular attraction between the salts and water can keep them there, but the water molecules wouldn’t be able to penetrate at an appreciable rate below the topcoat of the hydrochromic paint or ink. Since it usually takes a few layers to fully conceal an image, humidity alone wouldn't be able to cause the film to become transparent. Water vapor denser than ambient humidity, in the form of a spray or mist, would be able to accumulate on the surface of a film and penetrate to layers below the topcoat if it came in contact with it.

EXAMPLE: HYGROCHROMISM

In 2006, designers Frederik Molenschot and Susanne Happle at drooglab in collaboration with the tile manufacturer Terratorium created "Solid Poetry", which were concrete tiles with patterns or text printed on them, covered with hydrochromic ink (fig. 14 and 15) (Ferrara and Bengisu). The prototypes of the project were presented at Milan's Saloni del Mobile. Then they paved a square near the Design Academy in Eindhoven and when it rained, the tiles revealed the underlying inscriptions ("Concrete Innovation Part 3"). Since then, there have been both artistic and commercial applications of hydrochromic inks or paints on a variety of surfaces such as concrete slabs, bathroom tiles, shower walls and other architectural water elements (Ritter, "Colour- and Optically Changing Smart Materials"). Some of these designs exist in binary states where they are either fully wet, when it rains or when water runs over the surface for example, or they are fully dry. Other designs exist in a spectrum of wetness and thus transparency: wall tiles in bathrooms where water doesn't directly splash but a strong steady steam condenses on the surface, or concrete facades where morning dew forms. In all these cases, the main concern is making sure the hydrochromic substance is wet enough, so that it can reveal an underlying pattern or image.

If the surface isn't going to be wetted with ample amounts of liquid water, but with some amount of water vapor, the artist should consider the effect of temperature in ensuring the desired transparency is achieved. The hydrochromic paint or ink will be in thermal equilibrium with the surface it has been painted on and the air it is in contact with. The coating will be at a temperature that is in between the solid and gaseous environments, being much closer to that of the solid due to its high thermal conductivity and effusivity. If there is a temperature difference between the two environments, then the coating can be utilized as a condensation surface for water. If warm and humid air is in contact with a hydrochromic coating, which in turn is in contact with a much colder solid, then water will condense at the interstices of the hydrochromic material which is essentially the interface between the gas and the solid. Thus, a hydrochromic material that required direct wetting can be turned transparent by utilizing the ambient humidity and the temperature gradient at the interface of the coating.

Thus "Concrete Poetry" could potentially be set up as a hygrochromic system that doesn't have an obvious "hydro" component. The tiles covered with hydrochromic ink wouldn't be changed, just installed in a different fashion that allowed transparency to be achieved through humidity, the "hygro" component. The larger the temperature difference and higher the ambient humidity gets, the more transparent such a system will appear. The artist could utilize a naturally occurring temperature difference on a rock formation, a building façade or other surface element, paired with ambient humidity. The correct assessment of the environment and proper installment of the hydrochromic system become critical components of the artistic process.

The hygrochromic capabilities of a hydrochromic material can be enhanced through additives. Natural stones and certain coatings that take up water vapor from the environment by absorbing it into their volumes are used in architectural applications to stabilize the humidity in closed environments (Ritter, “Matter-Exchanging Smart Materials”). Grinding such material and mixing it directly into the hydrochromic material can be tempting, however, tempering with the ink formulation could prove to be beyond the scope of the artist. Since the chemical makeup of the ink or paint supplied by the manufacturers isn’t publicly available, it is hard to suggest generalized solutions without risking cross reactions. The artist can either experiment with absorbent additives or seek consultation from the manufacturer for such endeavors.

Once the artist ensures that the hydrochromic material becomes wet enough, how long it will take for the material to get wet and then dry can be considered. The transformation is fully physical in nature for hydrochromism and no apparent hysteresis is observed; there is no lag between the observed transparency and the wetness of the material. The wetting rate depends on how much water is applied to the hydrochromic materials, which is quite straightforward. The drying rate is dependent on the rate at which the water evaporates from the interstices of the hydrochromic material. Most people are familiar with this physical process and it doesn’t require much chemical expertise to know that water evaporates faster when its warmer. However, referring to the chapter on thermochromism and considering the thermal properties of coatings can inspire the artist to think about how varying the coating properties can alter the drying rate.

Fig. 14. Water being poured on a Solid Poetry slab from Solid Poetry by Frederik Molenschot & Susanne Happle | Yanko Design. https://www.yankodesign.com/2007/04/27/solid-poetry-by-frederik-molenschot-susanne-happle/. Accessed 21 Aug. 2019.

Fig. 15. Patterns revealed when wet from “Solid Poetry by Studio Frederik Molenschot.” Stylepark, https://www.stylepark.com/en/studio-frederik-molenschot/solid-poetry. Accessed 20 Sept. 2019.

OTHER REVERSIBLE CHROMISMS

Apart from photochromism, thermochromism and hydrochromism, many other kinds of reversible chromisms exist (Ferrara and Bengisu; Ritter, *Smart Materials in Architecture, Interior Architecture and Design*). Some of these are used almost daily in the scientific world, their mechanisms are well understood, others employ novel mechanisms that are still being investigated (*New frontiers in photochromism*; Publication et al.). The most generic kinds of chromisms have been known for decades, if not for centuries and details about them can be found in simple science textbooks, or more advanced literature.

Some of these reversible chromisms require the addition and removal of certain chemicals into the environment where the chromic material exists. Halochromism is pH induced color change, ionichromism is ion induced color change and chemochromism is a generic term referring to color change due to the presence of gasses or specific chemical agents. Although paints and pigments that change color can be formulated based on these mechanisms, each application would be case specific. Compiling all color forming reactions would be an improbable undertaking to say the least and is beyond the scope of this book.

Solvatochromism is color change caused by the change in solvent polarity and has been briefly mentioned in relation to photochromic dyes. Some molecules acquire different colors when dissolved in different solvents, the reversible nature of the color change arising from the fact that the solute can be separated from the solvent through different means. Solvatochromism only applies to liquid media, and therefore is beyond the scope of this book.

There are reversible chromisms that don’t require the addition or removal of any chemicals, but instead rely on energy input. Tribochromism is friction induced color change, piezochromism is pressure induced color change, mechanochromism is a generic term referring to color change to deformations. Along with electrochromism, these chromisms are briefly touched upon, due to their relative ease of their possible applications in the arts.

MECHANOCHROMIC PIGMENTS

Also referred to as piezochromic pigments in literature, mechanochromic pigments change color when placed under pressure. This can be tensile, compressive or torsional stress (Ritter, “Shape-Changing Smart Materials”). Mostly used in industry applications to visualize mechanical stress and test materials, the availability of mechanochromic pigments and paints as artists’ materials is almost non-existent. Compared to other chromogenic paints and pigments, there are considerably less patents in this field and research is just picking up steam. The technologies aren’t mature yet for widespread commercial availability. This leaves the artist a few options when wanting to work with mechanochromic media.

There is a limited number of manufacturers around the world that supply construction, aerospace, transport and energy industries with mechanochromic materials. Their products are usually formulated based on demand. If desired, the artist can seek their consultation and expertise. Since a general formulation for such paints and pigments isn’t available to analyze and some form of consultation is necessary before an artist can acquire them, it wouldn’t be wise to try and cover all possible mechanisms of mechanochromism or suggest manipulations for them.

If the method of color change is vital for the artist but the source of energy for the change isn’t, then other chromogenic paints and pigments can be substituted for mechanochromic ones in certain cases. Making the color change aspect of an artwork dependent on touch or stimulation received from the audience is possible with other chromogenic materials. Utilizing thermochromic paints that have a transition temperature between room temperature and human body temperature can offer a color change that is triggered by touch. Utilizing photochromic pigments indoors with a UV light source that the audience can control allows color change to be controlled by the audience. These chromogenic materials are more readily available, easier to acquire and cheaper to experiment with, which might prove beneficial for the artist.

ELECTROCHROMIC PAINTS AND PIGMENTS

Electrochromic pigments change color when current is applied to them, in a way “turning on” much like other electronic applications and devices. Because of their applications in technology and research, there is as much research on them as thermo- or photochromic materials. They can come in many forms: as pigment, paint, ink, embedded into polymers or glass (Ritter, “Colour- and Optically Changing Smart Materials”; Ritter, “Energy-Exchanging Smart Materials”). Sometimes the electrochromic property of a material arises from its innate properties rather than the addition of an electrochromic pigment (“Switching Colors with Electricity”). Much like mechanochromics, their availability as ready-to-use artist materials is quite limited. They can be acquired on demand from manufacturers and if the artist has experience working with circuitry and electronics, then incorporating an electrochromic surface into an artwork should be similar practice to adding a lightbulb to a piece.

Electricity is less tangible than heat, light or water, which are almost innately understood by the artist who can feel them through the five senses. As such, electrical work requires an entirely different skillset than painting, sculpting, or other manipulation of physical media. If the artist has limited background in electricity and magnetism, then manipulating electrochromic paints and pigments would require substantial information that is beyond the scope of this book. In such a case, the best solution would be to ask for consultation or collaborate with a party that has experience with the material that the artist would like to work with. As can be seen in examples of other color changing materials, artists often collaborate with scientists or a team of experts to formulate materials that require a high degree of expertise.

PAINT FORMULATIONS

Many artists procure their own materials, like those working with found media or mixing their own paints or inks. The modern artist who makes his own materials does so because the material is not commercially available, for reasons of economy, because the process of producing the material is part of the artistic process, or in order to control the properties of the material (Mayer 9). The craft of paint making has long been an essential part of the skillset for any artist, especially when commercial availability of premixed paints was quite limited in earlier centuries. Nowadays most beginners and even professional artists take advantage of the highly developed paint industry, which produces paints of different varieties, meeting diverse needs. This has taken off the burden of technical know-how from the common artist. Whether that is a curse, or a blessing is subject to debate, but this book offers a chapter on the compatibility of different painting media with color changing pigments for the artist that is interested in mixing their own reversibly color changing paints.

In previous chapters, manipulations specific to the mechanism of color change have been discussed. This chapter is going to touch upon more general considerations that pertain to the medium that is used. There exist large volumes dedicated to the art and craft of mixing, mulling and making paints from pigments. As such, only the properties of paint that are relevant to the mechanisms of color change will be covered. For example, among the traditional factors to consider when making paints from pigment, color stability is rendered obsolete, because color changing pigments don’t have a stable color (Mayer 7). Permanence, a much-desired quality for traditional pigments, is also a touchy subject for color changing pigments, which are not at all lightfast. Chemical inertness if also not applicable, as the foundational premise of color changing pigments is their ability to interact with and respond to atmospheric stimuli.

This leaves interactions between the medium and the pigment, referred to as balance of formula in general. A traditional requirement for a paint pigment which is also applicable for color changing pigments is that a pigment should be a “finely divided, colored substance that imparts color to another material either when mixed intimately with it or when applied over its surface in a thin layer” (Mayer 31). Whether it be thermochromic, photochromic, hydrochromic or any other non-traditional pigment the artist is choosing to work with, it will have to be dispersed in a medium to cover and stick to a surface. Traditionally, no paint is made by simply mixing “pigment and vehicle, grinding with strong pressure is essential to achieve a good mixture with minimal air trapped between pigment particles” (Mayer 3). But when molecules are formed into microencapsulated pigments, as is the case with many of the color changing materials, a different procedure is necessary. A low shear mixer or triple roll mill should be used for large batches, as a higher shear apparatus can damage the capsules. For smaller batches, they can be mixed in a metal or plastic container with a spatula until the desired consistency is achieved. This kind of care must be taken when dispersing microencapsulated pigment in all kinds of media.

The chemistry of paint media differs drastically, and each medium will be discussed separately. The chemical makeup, formulation composition and other relevant properties of the medium will be developed systematically for each case, judging the viability of the medium for different colorants.

OIL

The paint vehicle in oil paint is a mixture of long chain polymers and other organic compounds which exist in a viscous liquid phase to begin with, allowing color to be applied and spread out (Mayer 120). As it dries, complex oxidation reactions cross-link these polymers and cause the paint to stiffen, locking the pigment particles into a film. This protects them from atmospheric or mechanical forces, but also prevents humidity from penetrating into the inner layers of the paint. When oil paint is subjected to volatile environmental conditions, damp or dry air, the film can expand and contract, leading to disastrous consequences such as cracking or flaking. Therefore, oil isn’t a suitable medium for hydrochromic pigments which require constant drying and re-wetting.

If thermochromic and photochromic pigments weren’t microencapsulated, certain oxidation and photochemical reactions would have caused them to cross react with the vehicle, essentially inhibiting their color changing properties. As such, using bare photochromic dyes in oil formulations isn’t suggested. The same reactions already act upon the vehicle and any other particles of dirt that have been deposited on its surface, which is why oils are known to show effects of aging, such as losing their transparency and acquiring a yellow or brown tint. The time scale at which aging occurs is much slower than the rate at which thermochromic and photochromic pigments become bleached, fade out, or in some other way become dysfunctional. Therefore, these pigments are suitable for oil paint applications without too much concern for the color change of the oil to mask the color change of the pigments.

Oil paint has an optical effect, it brings out depth and tone of pigment, giving it a quality different from its dry state (Mayer 120). This has to do with the way light interacts with matter depending on a property called the refractive index. When two substances of varying refractive indices meet, air and pigment bound in a vehicle for example, the light will be reflected from the surface of the more refractive substance. The greater the difference in the refractive index, the greater the sheen. Thus, more reflective vehicles will allow less light to reach the pigment. Most pigments have refractive indexes higher than air and when surrounded with oil in a paint emulsion, the difference in the refractive index is lowered.

If visible light is the source of energy for a color change, either thermochromic or photochromic, then the reflectivity of the dry state of the oil paint must be taken into consideration. UV light operates differently than visible light, some of it being absorbed by the oil rather than reflected. In either case, less light reaches the pigment, which can have one of two effects. It can increase the time required for full color change to occur. Or if the paint is sufficiently reflective of visible light or absorptive of UV light, not enough light might reach the pigment to drive the color change to its full extent. The competing reverse reaction might occur at a rate that is comparable to the forward reaction, which will lead to the overall visual effect of having a color that is in between the two forms of the pigment. A colorless-to-red pigment dispersed in a reflective medium might have only half of its total number of molecules in the colored form at any given moment, which will look pink rather than red against a white background.

Thermo- and photochromic molecules are usually bound within microcapsules; thus, the chemical properties of the capsule are of importance when evaluating its compatibility with different media. Whether the capsule has been formulated to work in aqueous or non-aqueous systems is vital, the same molecule can be bound in two different capsules and sold as separate products. There exist products with names that are confusing and even contradictory to their properties. Instead of the name of the product, which can be a slurry, powder, concentrate, pigment or paint, its compatibility with different solvents should be regarded. For oil paint applications, the product should be compatible with high chain polymers as well as mineral spirits, since turpentine or other thinners are used liberally while painting. Once the paint has adequately dried to a film, it can be painted over with materials that would normally be harmful to the capsule, as long as the topcoat doesn’t dissolve the under painting.

Oils have different surface tensions in their liquid phase, which directly influences the uniformity of their dry phase (Marrion and Reynolds). Stand oil, which can be thinned with turpentine, tends to form uniform films free of brushstrokes (Mayer 123). Aggregation of paint due to stroke quality will create areas of thicker paint, which will heat up, cool down or absorb light at a different rate than areas of thinner paint. This will result in non-uniform changes in color for thermo- and photochromic pigments. The difference in rate of color change in different parts of a non-uniform paint layer will depend on the kinetics of the pigment, physical qualities of the paint vehicle and the manner in which paint was applied to the surface. Such differences might be too pronounced to be macroscopically negligible. When choosing a paint vehicle, if a uniform smooth color change is desired, stand oil should be favored by the artist. If the non-uniform color change, or rather delayed color change, is desired in areas where brushstrokes have been applied accordingly, than the standard mixing material, linseed oil should be favored (Mayer 122). These subtleties in film thickness that can be worked into the work makes oils excellent for thermochromic applications that use heat sources other than physical touch. Oil films take a long time to fully dry and even when they do, they are less sturdy than acrylics and more prone to deterioration.

Certain stabilizers can be added to the oil along with the pigment to manipulate the properties of paint: wax to give a buttery paste, water as an emulsifier or inert pigments such as alumina hydrate to produce shorter pastes are among the most common (Mayer 138).

ACRYLIC

The paint vehicle in acrylics is an acrylic polymer emulsion, which includes a monomer like methyl methacrylate and a catalyst, along with some additives and a solvent (Mayer 259; Mayer 263). All or part of the solvent can be water, taking up to half the volume of the finished paint, which naturally makes acrylic an aqueous medium in which pigment has been dispersed in (Mayer 260). As the water in the composition of the paint and any extra water used in painting evaporates, the monomers polymerize and the paint dries to a plastic film (Skye et al.). There can also be a coalescing solvent in the composition, but a large portion of the paint volume evaporates either way to leave a lighter film on the surface. The paint rapidly loses its solubility, which can present challenges when mulling pigment into an acrylic resin.

Acrylics have been favored for their rapid drying times, compared to oils or other aqueous media, however this property leads to its unique challenges when an artist wants to prepare their own acrylics paints. Hand grinding of acrylics must be done rapidly; if water isn’t added continuously the mixture can become rubbery and useless on the grinding slab. This issue is amended by manufacturers that counteract it through procedural or chemical solutions.

Some acrylics therefore contain retardants such as propylene glycol or ammonia that improve shelf life by preventing film formation inside the tube (Christensen). These basic compounds increase the pH of acrylic paint. Microcapsulated pigments are sensitive to pH; they are not compatible with ammonia or pH higher than 8 (*Documents*). That makes basic acrylic media harmful to microcapsules to the point that if mixed together, the pigments might lose their color changing properties entirely. The artist should be careful when mixing dry pigments with any kind of solvent, not just organic ones, and should check the pH before doing so. This can be done with easily acquired pH-papers, which change color when dipped into a liquid to reveal the degree of its acidity. If the paint vehicle that the artist is planning on dispersing the microcapsulated pigment is too basic, it can be neutralized by the addition of an acid. A few drops of diluted acid should be able to bring the pH down to a workable level, depending on the batch size.

Another issue with microcapsules is their sensitivity to shear. Time is of the essence when mulling acrylics, but strength and speed must not be mixed up. When mulling the pigment, the artist must experiment with finding a balance between applying enough pressure to disperse the pigment properly and not applying too much as to harm the capsules. Since the microencapsulation process produces nanoparticles that don’t clump together easily and have fine enough particle size, too much pressure won’t be necessary to break up pigments. Therefore, as long as some care is taken when mulling, the capsules shouldn’t be harmed.

If the artist has access to the dye form of the pigment that hasn’t been microencapsulated, that can be used as the dry pigment to be dispersed in acrylic media too. The chemistry of each organic dye is different, as well as their interaction with the acrylic monomers that will polymerize, therefore there is no guarantee that cross-reactions won't happen or if they do whether that will affect the color changing properties of the pigment. When it comes to dispersing the dye form in media, even if no cross reactions occur, the rigidity of the resulting plastic film should be considered as discussed earlier in the photochromics chapter. Acrylics produce plastic films that are similar in structure to oil films, the polymers cross-link to form a lattice. Polyacrylates usually have a flexural modulus higher than 2 GPa, the range being between 2.5 and 3.5 GPa for polymethylmethacrylate (*Plastic Rigidity & Material Stiffness, Units, Formula & Table*). That is slightly above the rule of thumb value for photochromism, as such acrylics aren't ideal for photochromic dye dispersions. However, forming much more rigid films than other media, acrylics are ideal for high wear and tear thermochromic applications that employ a touch component.

As discussed in the context of oil paints, the reflectivity of the dry state of the paint must be taken into consideration if light is the source of energy for a color change, either thermochromic or photochromic. Acrylics films can be matte or reflective, and they are opaque even in thin layers. For photochromic applications, it only makes sense to paint a thin layer as neither will UV light penetrate deep into a paint film nor will the color of the innermost photochromic pigments show through the paint layer.

WATERCOLOR

The paint vehicle in watercolors is a mixture and can contain a variety of the following: gum Arabic as a binder, a humectant like glycerol, a sugar as plasticizer, dextrin as a filler and water (Mayer 333). None of these organic molecules are reactive enough to cause immediate concern, therefore both microencapsulated pigments and photochromic dyes are viable in watercolor. For the artist synthesizing at home, only the binder and the plasticizer are required to mull fully functional watercolors, along with finely grinded pigment to produce brilliant glazes and transparent washes (Mayer 332). The same grinding procedure for oils and acrylics can be followed for watercolors, taking care not to harm the microcapsules with the shear of the grinding slab.

No chemical reactions take place during the formation of the watercolor film, the binder simply dries to form a uniform film with pigment dispersed in it. Watercolors leave a mark on paper that is more like a stain than an actual film with thickness and plastic properties. This allows for watercolor to be re-wetted and reworked. It also makes it impractical to use hydrochromic pigments with watercolor, because the water stress would eventually wash away the paint entirely.

Being adequately transparent, watercolors pose no problems with light availability for transitions that use light as an energy source. Overall, the chemical compatibility, ease of mixing and optical properties of watercolor makes it the ideal medium for photochromic applications. It can also be used with thermochromic pigments; however, the fragility of the thin watercolor film makes it undesirable for touch-stimulated thermochromic applications that would cause wear and tear on the watercolor paper.

GOUACHE

Gouache paints are similar to watercolors in all aspects but one, they are opaque (Mayer 338). Thus, all the considerations previously mentioned apply to gouache paints except for one: the amount of light that penetrates a gouache film. Gouache uses the same paint vehicle materials as watercolor, however with a larger percentage of vehicle than is used in watercolor and with the additions of inert pigments like chalk (Mayer 340). This makes gouache inferior to watercolor in applications that require light as an energy source to trigger color change but doesn't make it any sturdier for applications that require touch-activation. As such, gouache can be utilized along with watercolor for diminished photochromic effects but isn't ideal for either thermo- or photochromic applications.

PASTEL

The vehicle that carries the pigment in a pastel stick is usually natural gum, like tragacanth, along with precipitated chalk (Mayer 345). Dry pigment is folded and mixed into the pastel paste, which is then dried to the desired consistency. There are many recipes for making pastels at the studio, with various odd and creative additives used for different effects. The common property of all of them, however, is that chalk is applied as a dry medium, where the pastel grinds against the rough microscopic texture of a surface, leaving chunks attached to the surface. Other dry media produce marks on surfaces with the same principle: friction. As mentioned previously, friction and shear damage microcapsules, which is why pastel isn't a viable medium for thermochromic and photochromic pigments. Photochromic dyes can be folded into the pastel mixture, but redox reactions can occur between the chalk and the organic molecules, which can inhibit their photochromic properties.

Hydrochromic pigments could have been incorporated into pastel, however hydrochromics are only commercially available to the artist the liquid state. The artist can experiment with repetitive drying and grinding processes to obtain the pigment without the liquid paint vehicle from hydrochromic inks or paints, however there is no previous record of it having been done. There just is no theoretical limitation to hydrochromic pigments being applied in pastel form, since they could be just as well be deposited in pastel form as they are ink.

FRESCO

Fresco paintings can be done upon a wet, freshly prepared lime-plaster wall with pigments ground in water only; when the plaster dries it sets with a rocklike cohesion, and the pigments dry with it as an integral part of the surface (Mayer 361). After lime plaster has been applied and dried, the calcium hydroxide reacts with carbon dioxide in the air to form calcium carbonate, which is called the hardening of the mortar (Mayer 372). The pigment particles become cemented to the surface lime in the same manner in which the lime particles bond with each other and with sand. Microscopic examination of a fresco painting reveals definite penetration of the pigment into the interstices of the particles that compose the plaster surface (Mayer 361).

Hydrochromic paint acquires its properties from the microscopic structure of the film it forms, which is quite suited for fresco applications. However, applying white hydrochromic paint on a white fresco would produce results with low contrast. Adding some inert pigment into the lime plaster to make it at least an off white is necessary to acquire a visible color change effect. When dry lime is mixed with water, it forms calcium hydroxide, which is called slaked or hydrated lime (Mayer 368–70). The pH of wet lime plaster can be as high as 12, which is too caustic for microcapsulated pigments and organic molecules. The slaking process also releases heat, enough to cause side reactions or harm microcapsules. The usage of thermo- or photochromic pigments in frescos is not possible as the capsules would quickly be damaged. Photochromic dyes would also be oxidized and lose their color changing properties.

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