Going … Going …

Over the past two or three decades, there has been a well-publicized amount of consolidation within the paint and coatings industry that has often trudged behind the demise of large customers such as Sears, Roebuck and Co. (1889–2018).

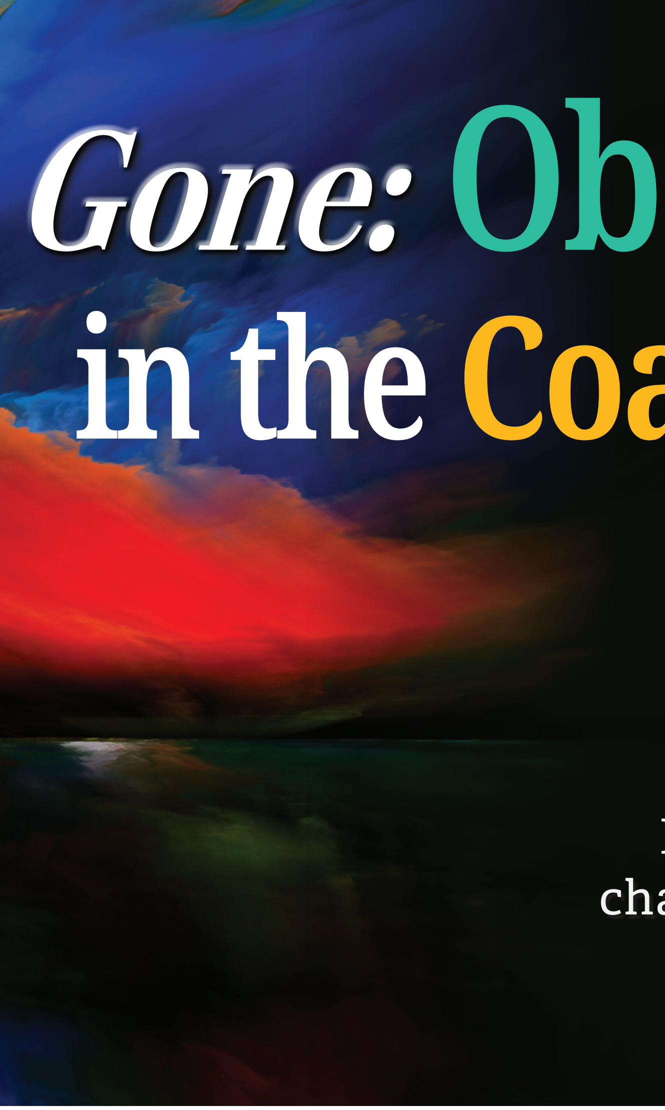
Sears-branded paint accounted for 43% of DeSoto Paint Co. coatings, and losing this large customer was the beginning of the end. One of my personal favorite house paints of all time was the Sears Ultralight Latex Interior House Paint, which—with almost imperceptible drops of color added to a gallon of white satin paint—provided a subtle, color-shifting visage to any room. Hints of color danced on the walls, depending on the day's weather—sunny or cloudy—and even upon the type of light bulbs used in lamps and chandeliers. Unfortunately, both DeSoto and Sears are now distant memories, swallowed up by other companies or private equity groups, their products visible in aging family photographs.

While the Sears/DeSoto saga is a recent example of obsolescence, the coatings world has been reinventing itself for millennia. Pigments, which are the cornerstone of paint, have come and gone since prehistoric times. The first pigments were ground earth or clay held together by liquid or fat. Surprisingly, many of those colors have survived to this day, as seen by the cave paintings often highlighted in *National Geographic*. Modern synthetic pigments are laboratory chemistry experiments designed to replicate the colors used by Renaissance masters—while eliminating some of the less-desirable poisonous effects.

Resins and binders that surrounded pigments have also evolved. The Renaissance masters used egg yolk and oil in their paintings and frescoes encased in plaster while multifaceted polymer families are used in modern paints. Modern biobased paints are trying to return to the plant and animal derivatives of bygone centuries but are hampered by the need for large scale production, not generally needed in earlier times.

The most fascinating changes have taken place in the world of pigments. Pigments are defined as colored, black, white, or fluorescent particulate organic or inorganic solids, which are insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in which they are incorporated.[1] The first pigments are believed to be the minerals limonite and hematite (red ochre, yellow ochre, and umber), charcoal (carbon black), burned bones (bone black), and ground calcite (white, lime white, or chalk).

Ancient Egyptians, Romans, and Greeks developed inorganic iron oxide pigments, again making red ochre, yellow ochre, and umber. "Lead white" and "lead red," which were made through chemical reactions in lead vessels, were colors favored by artists because of the brilliance and depth they added to make a painting shimmer. Vermillion is still a highly favored color,



Gone: Obsolescence in the Coatings World

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Exploring the most captivating changes in the realm of pigments.

even though it was originally made with mercury sulfide.[2]

While red ochre, yellow ochre, and umber can still be made today in the traditional way, pigments containing lead, mercury, and sulfide are generally no longer available.

Paleolithic cave paintings started with red and black. Over time, the color palette expanded. The Lascaux cave paintings in France, accidentally discovered by four boys in 1940, were still vivid and clear—probably protected by the cave's darkness and its secluded area. These paintings, which researchers believe were drawn during the Ice Age, used a basic palette of red, yellow, black, brown, and white to create vivid, vibrant depictions of animals, scenery, and life.

In 1948, the owner of the land above the caves opened the door to tourists, and more than 400,000 people visited annually. The visitors' collective breath, the warm air intruding into the cold caves, and the installation of electric lights caused these vivid colors, once preserved for thousands of years, to fade away into invisibility in only 20 years[3] —a stark reminder of art's vulnerability and impermanence.

As Victoria Finaly wrote in *The Brilliant History of Color in Art*, "And this is another element of the history of colors in art: they are there and then they go. They do not stay the same, and when you look at a painting, you're also, in a tiny way, changing it."[3]

Another example of aiding and abetting obsolescence in the coatings world.

Pigments were not used only for aesthetic depictions. The Tiwi (meaning "We, the only people") population on the Tiwi Islands used color primarily from natural ochre pigments to ensure that marriages did not occur between people that were too closely related. Children were identified as a "color" at a very young age. Red (sun), black (stone), white (pandanus bush), and yellow (mullet fish) identities determined who could marry (or not). Reds could marry yellows or whites, but not reds or blacks. Whites and yellows could marry blacks. In this culture, color was forever synonymous with destiny and even the afterworld as depicted on funeral poles. These color norms are still in place, but are being challenged by the younger generation.[4]

Bygone Pigments

Many pigments have become extinct or unavailable for a number of very good reasons. Among those are scarcity (or expense) of raw materials, moral and ethical sourcing considerations, health and safety disasters, and better alternatives brought about by modern manufacturing advances. However, artists still lament the loss of some of the original pigments because the color, luster, depth, hue, or texture of the paint can only be simulated by modern alternatives, not truly duplicated. It is sort of like using Cr^{+6} as a corrosion protectant: to this day, nothing has its efficacy.

One of the most beautiful and most poisonous colors in history was Scheele's green, also known as Schloss green, which was used from 1775 to 1895.[5,6] It was a cupric hydrogen arsenite ($CuHAsO_3$). Napoleon Bonaparte was thought to have been poisoned by the beautiful Scheele green wallpaper in his luxurious bathhouse when he was in exile on a remote island in the Atlantic Ocean. When exposed to long-term humidity, the pigment develops mold, which results in the release of arsenic gas. In fact, high levels of arsenic were found in Napoleon's hair long after his death. Needless to say, this pigment is now banned everywhere.

Another poisonous green, Paris green, was composed of copper and arsenic pigments. It is thought to have contributed to Cezanne's diabetes and Monet's blindness.[2] Interestingly enough, it was also an effective rodenticide and insecticide. This pigment combination was banned forever in 1960.[7]

Radium green was one of the first glow-in-the-dark paints made from radium (Ra-226), zinc sulfide, and a glue binder.[8] Madame Curie discovered radium in 1898, and it was initially used as a cure for cancer and ultimately as a health tonic. Radium salts were used for all kinds of personal care items and as an elixir for fatigue.[9] By 1908, radium green was used to illuminate dials on military compasses and watches to aid in night excursions. Civilian and military luminous alarm clocks and wristwatches were made with Ra-226 well into the 1960s until it was replaced by tritium in the 1970s.

Radium had great glow properties but was also a million times more radioactive than uranium, with a half-life of 1,600 years. A slow poison, radium's devastating effects remained unknown—or perhaps more correctly stated, *unacknowledged*—for a long time. This in spite of the fact that the women artists painting wristwatches and compasses began to lose facial bone and ultimately died from exposure as early as the 1920s.[10]

In 1968, radium green was phased out and eliminated from use–not because of any threat posed to the watch wearers, but because of the grave health consequences suffered by the artists along with some help from the courts. Kate Moore, author of *Radium Girls*, says that almost everything we know about radiation poisoning is attributed to the studies conducted on the New Jersey "Radium Girls" after they stopped painting watches.[11] Since the mid-1990s, non-toxic, non-radioactive strontium aluminate-based photoluminescent pigment replaced Ra-226 in luminous dials.

While green pigments were considered the worst health hazards, yellow pigments were a notoriously close second. Orpiment, or king's yellow, has been found on ancient Egyptian papyrus scrolls.[12] Since this pigment is arsenic sulfide, the fumes were not only poisonous, but most likely, quite smelly.

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It was not only the "before-our-time" yellows that posed health and safety hazards. Around 1939, American school busses were directed to be painted a special bright yellow called National School Bus Chrome to make these vehicles uniform and very visible, and to enhance safety. Unfortunately, a heavy loading of hexavalent chrome made the paint very toxic to manufacturing plant workers.[13] The paint has since been reformulated, keeping the glossy attention-grabbing yellow color, while becoming safer for workers.

Indian yellow was a result of feeding cows in rural India only water and mango leaves and harvesting the urine to make a luminously rich yellow color. A favorite of Van Gogh's, this full-bodied paint was a much-loved earthy mustard color that could easily be thinned down to neon yellow. But there were two problems. First, the process was ultimately banned because it was considered very cruel to the cows. Second, while initially beautiful, the paint tended to fade over time.

Red pigments generated gorgeous colors but were also often fraught with health hazards. The vibrant (and many say unreproducible) vermillion red was made with mercury. Dating to ancient times, vermillion red has been considered the only "true red" at all viscosity levels.

The original Fiesta dinnerware was all the rage until 1969. Available in several colors, Fiesta red was a favorite–and is still sought by collectors today. Between 1936 and 1943, this color was manufactured by adding as much as 14% uranium oxide to the 0.2 mm thick glaze. Researchers estimate that each plate contained 4.5 grams of uranium.[14]

After the war effort ended, uranium was once again available, so depleted uranium was used in Fiestaware production between 1959 and 1969. Many other deep orange/red ceramic glazes of that period also contained uranium, which was often used to enhance other colors. As a result, 2 million pieces of dinnerware produced between 1959 and 1969 are considered radioactive.[14] This particular formulation was discontinued in 1969 and supplanted by alternative pigment technologies until 1973 when manufacturing of the original Fiestaware line and its infamous red glaze ended for good.[14]

This discussion cannot end without a mention of lead pigment in paint. In the 4th century B.C., lead metal was soaked in vinegar in sealed vats.[12] The resulting lead carbonate flake and powder was scraped off and used in the famous paint color known as "lead white." This paint had creamy, luminous tones second to none—even to this day.

In the 17th century, the process was "improved" whereby cow and horse manure were layered on lead and soaked with vinegar. After three months in a sealed room, flakes of pure white lead were obtained to make the widely coveted lead white color.[2] Artists say that the modern pigments of zinc and titanium provide a poor alternative because the depth of hiding and creamy tones are missing.

Van Gogh used thick layers of paint with high lead content, particularly lead white and chrome yellow (lead chromate). His descent into madness was later believed to be a result of lead exposure. At the very least, many artists developed "painter's colic," which was actually lead poisoning. These paints containing lead were functionally banned in the 1970s because most manufacturers stopped production. Artists can still get small amounts of real lead white through a few specialty paint vendors thanks to the Labeling of Hazardous Materials Act of 1988. The paints are sold in small quantities with safety data sheets and detailed labeling.

House paints containing lead were banned in the United States in 1978. While lead paint is still used in some low-risk industrial applications, there are calls for an all-out ban on lead paint. This may yet happen as paint technology advances to provide the color and hiding that many artists covet and is—at this time—only found in lead white.[12]

Not Available to the General Public

Sometimes paints are obsolete because only certain people or companies can use them. One example is "Mystic," the very first color-shifting paint used on a production car. Exactly 2,000 1996 Ford Cobra Mustangs were painted with Mystic, which was patented by BASF. Although not illegal, use of the paint was tightly controlled. Using the same dye that the federal government uses to print money, the body color shifted between green, purple, gold, brown, and shades in between.

To use the paint, a Ford representative had to be present during painting, the paint shop had to be licensed, and all residue and extra paint had to be removed from the premises.[15] This formulation is no longer manufactured; it has since been replaced with "Mystichrome," which does not use federal reserve dye. Mystichrome was used to paint the 2004 Ford Mustang SVT Cobra.[16]

Vantablack®, a black pigment coating developed in 2014, can absorb 99.965% of visible light from ultraviolet to beyond the terahertz spectral range. It is an array of nanotubes made of vertically aligned pure carbon regularly spaced on a surface. The light enters the space between nanotube forest and repeatedly reflects off the nanotubes until it is absorbed. Hence, the name is an acronym of **V**ertically **A**ligned **N**ano **T**ube **A**rray **B**lack. It is being used for deep space imaging, auto sensing, optical systems, military camouflage, and art. The material is extremely fragile and must not be touched or marred.[17]

When it comes to art applications, Vantablack is only available to sculptor Anish Kapoor, who holds the exclusive license to use this coating for art. A rival artist retaliated by creating several other colors that are available for everyone in the world *except* Anish Kapoor. Another company created a somewhat-similar color called Singularity Black, which is available to everyone. But for now, Kapoor is the only artist allowed to take advantage of the unique, highly absorbent Vantablack.[6]

Substrate Influences

Coatings systems can also become obsolete because of advances in the underlying metal substrates. Zincrometal® was the first large scale production prepainted material for the automotive industry from 1970 to 1990. Millions of pounds of cold rolled steel (CRS) were coil coated on one side with a Dacromet® primer and a Zincromet® topcoat. The primer was an inorganic chromium oxide/zinc oxide matrix containing zinc particles and applied at a 0.1 mil thickness. The topcoat was an organic epoxy binder heavily loaded with zinc dust applied at 0.4 mils. When applied to the unexposed side of exterior body panels, this formable, weldable, paintable, bondable coating provided an additional measure of chemical and barrier corrosion protection without disturbing the aesthetics of the exposed side.

The advent of nitrogen finishing on corrosion resistant galvanized steel allowed for acceptable exposed automotive surface appearance with minimized spangle and improved distinctness of image (DOI). Galvanized steel allowed for better corrosion resistance and downgauging, which essentially ended the need for Zincrometal® as CRS was phased out.

Electrogalvanized steel became popular for exposed automotive body panels in the 1990s. However, in Japan, high electricity costs led to the manufacture of an electrogalvanized alloy known as zinc-nickel. Unfortunately, this coating was very brittle and cracked when formed into body panels. To improve corrosion resistance, FirstCoat® was coil coated onto the unexposed side of the substrate. This two-coat system was comprised of a thin chrome coating (measured in coating weight) and a clear, thin epoxy topcoat. This addition greatly improved the corrosion resistance without any adverse effects on stamping, forming, welding, DOI, or appearance. Once the Japanese-transplant automotive companies in the United States switched to nitrogen-finished, hot-dipped galvanized or phosphated galvanneal, this coating also became obsolete.

Final Thoughts

The examples provided here are just some of the more interesting ones. They show that the world of paint and coatings is ever changing, governed by a desire to replicate beauty, tempered by ethics, health, and safety, along with availability, sourcing options, and geopolitical forces. Today, the industry is moving toward making coatings BPA-free and figuring out the challenge of what to do with and about PFAS. As technology advances, obsolescence is inevitable. Hopefully, that same technology will provide robust alternatives to serve all coatings constituencies. ❇

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