

RECREATING ACID STAINS ON HISTORIC CONCRETE

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To my mother, with gratitude...

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Chapter 1: Introduction

Jackson Lake Lodge is a mid-century modern lodge located in Wyoming's Grand Teton National Park. It was designed in 1955 by Gilbert Stanley Underwood, a well-known National Park Service architect, for John D. Rockefeller Jr.'s Grand Teton Lodge and Transportation Company and built by Morrison and Knudsen, a contracting firm located in Boise, Idaho (Wiesner-Chianese 2015,166).

The central lodge is a long and low, blocky concrete structure designed to showcase the view of the Grand Teton Mountains. It was constructed in the International Style and is the first modernist building to have been built within a National Park (Engle 2008, 3). The building replaced a smaller, outdated lodge of the same name, and was intended to provide modern accommodations for visitors who were arriving to the park via automobile.

Jackson Lake Lodge was designated a National Historic Landmark in 2003 and is considered to be one of the earliest motor lodges in the country and an important precursor to Mission 66 (Engle 2008, 3). As evidence of Underwood's full embrace of modernity, parking and car access were incorporated into the heart of the lodge's design. The entrance of the main lodge opens onto a sprawling parking lot, while the guest cottages each feature a parking spot in close proximity to the front door. According to the NHL nomination, Underwood's unique and transformative design for the Lodge was significant:

...The state-of-the-art complex of buildings would break the long-established tradition of Rustic-styled architecture in National Parks. At the same time the facilities at the complex reflected the expectations of the post-World War II traveling middle class, with emphasis placed on progress, leisure time and perceived affluence. (Reed and Wallace, NHL Nomination – Jackson Lake Lodge. 16).

In the aftermath of World War II, visitation to the national parks increased significantly; however, rather than arriving by rail as was the norm before the war, most visitors now traveled



Figure 1. Jackson Lake lodge after 1966. Note the scale of the parking at the center of the complex. Image Credit: Rockefeller Archive Center.



Figure 2. Jackson Lake lodge c. 1955. Note guest cabins with adjacent parking. Image Credit: Rockefeller Archive Center.

to the National Parks by automobile. During the war the parks received little funding, therefore by the 1950's many of the existing accommodations were rundown and out of date. Mission 66 was a ten-year initiative undertaken by the National Park Service in 1956 to create expanded visitor services, including modern, sanitary lodgings. Park Director, Conrad L. Wirth, who pioneered Mission 66, actively looked to Jackson Lake Lodge as a guide for the design and function of future National Park architecture. Jackson Lake Lodge's International style and use of modern materials – concrete, steel and glass– informed and supported the National Park Service's Mission 66 Plan, published in 1956, which guided development in the National Parks in the mid-20th century.

Although a significant departure from the forms and natural materials that defined early 20th century Rustic architecture in the parks, the Lodge's concrete attempted to replicate wood siding and its horizontal form nestled into the surrounding landscape. G.S. Underwood was a pioneer in using modern fireproof materials – particularly textured and stained concrete – to reinterpret the traditional 'rustic architecture' in the National Parks. Prior to designing Jackson Lake Lodge, Underwood used stained and textured concrete for the construction of the Ahwahnee Hotel at Yosemite in 1927 and The Sun Valley Lodge in Idaho in 1938. However, in these earlier lodges the stained and textured concrete was used in imitation of wood-beam construction. With the design of Jackson Lake, how the fireproof concrete was employed and its resulting visual impact changed dramatically.

The surface treatment Underwood used for the concrete on the main lodge at Jackson Lake Lodge is an unusual form of board-finished or "fair-face" concrete that characterized mid-century Brutalist architecture. The building was cast with sandblasted, Douglas Fir plywood-formwork, which imprinted the concrete with a very pronounced wood-grain texture. Underwood referred to this casting technique as "Shadowood"¹. The concrete was then finished with three

¹ It should be noted that most concrete is cast using plywood formwork, therefore traces of wood graining can be seen on many concrete buildings. The surface at Jackson Lake Lodge is markedly different. The texture is approximately ¼" in depth and much more visually significant than most board-marked finishes.



Figure 3. Jackson Lake lodge, Grand Tetons National Park. Built 1955. Note acid-stained concrete, which appears like redwood plywood. Image Credit: Rockefeller Archive Center.



Figure 4. Ahwahnee Hotel, Yosemite National Park. Built 1927. Note brown, acid-stained concrete and natural stone exterior. Image Credit: www.easytobook.com.



Faulty concrete color or finish Kemiko Stain with Col-r-tone Finish will produce uniformity and profound beauty on faded pigmented concrete or on surfaces that are dusting, stained, unevenly textured, patched or worn.

Brief Specification Greater satisfaction and economy will result if KEMIKO is specified in the General Specifications under Concrete Finishes. Because "acid Staining" is an ambiguous term, often applied to such materials as vegetable dyes, oil stains, etc., misunderstanding and disappointment will be avoided by specifying as follows:

"All concrete areas to be colored as described in these specifications or as indicated on the plans are to be treated by the KEMIKO PROCESS."

Complete detailed information, custom color guide, and specifications will be gladly supplied upon request.

KEMIKO

**KEMIKO BEAUTY AND PROTECTION
CHOSEN FOR FAMOUS**

Jackson Lake Lodge

The snow-crested Grand Teton mountains are inspiring, colorful surroundings for Wyoming's famous, \$6,000,000 Jackson Lake Lodge. To harmonize with the natural beauty of the setting exterior lodge walls of concrete were cast against Shado-Wood, then stained with Kemiko's rich Malay Tan, highlighted with Colorado Brown and Black. Through sub-zero winters and summer sun, the stain provides permanent, maintenance-free color. A John D. Rockefeller, Jr. interest, the lodge is operated on a non-profit basis for tourists by Jackson Hole Preserve, Inc. Close-up illustrates natural beauty of concrete wall.

Figure 5. Kemiko Advertisement c. 1956. This advertisement was produced by Kemiko – the company that manufactured the stain that were originally applied to Jackson Lake Lodge. The insert contains the only color, detail shot of the original concrete finish. Image Credit: <http://www.kemikostainforconcrete.com/history.html>.

different colors of acid-stain – tan, brown and black, which created a translucent, variegated finish that closely resembled redwood.

This finish was integral to the lodge's original aesthetic and to Underwood's design. Although suggesting a wooden exterior, the surface of the Lodge was articulated by an abstract grid of rectangular panels that defined the overall massing of the building without imitating the log or board construction found at his earlier lodges. After almost 45 years of exposure, the original acid-stain finish had begun to show its age. Around 2000, Jackson Lake Lodge was re-coated in a monochromatic, brown resinous stain, which obscured the texture and color of the variegated concrete. Unlike the original stain, which was visually dynamic, the current stain is flat and bereft of life.

As with many modernist designs, Jackson Lake Lodge is largely devoid of decorative embellishments; rather the emphasis is on the simplicity and materiality of the design. Therefore seemingly small alterations to the building have significant consequences for the aesthetic integrity of the overall design. The colors, textures, and appearance of the Lodge's different building materials, and especially its concrete skin, are essential to its interpretation and preservation. Therefore conservation/restoration treatments for mid-century modern buildings, like Jackson Lake Lodge have an inherently narrow tolerance for change.

The Jackson Lake Lodge is currently undergoing a comprehensive restoration, which will include addressing the appearance of the exterior of the building. Given the national significance of the building and how important the materiality of the original structure was to its overall design, it is essential that careful consideration be given to the selection of a new exterior treatment. Re-creating the original finish would be an important step in restoring Underwood's original design for the Lodge. Given that the original acid-finish was not only a unique aesthetic, but also an exemplary use of a modern material, this thesis considers whether the Lodge can be retreated with an acid-stain as part of its upcoming restoration program.



Figure 6. West elevation of Jackson Lake Lodge in 2014. Note the modern stain. Image Credit: Joseph Elliott.



Figure 7. Detail of modern stain taken in 2015 Image Credit: Julianne Wiesner-Chianese.

Evaluating whether it will be feasible to retreat the exterior concrete at Jackson Lake Lodge with acid-stains can only be determined through laboratory and field performance testing. The first phase of testing, which is the focus of this thesis, aims to analyze and characterize the original acid-stains, to accurately recreate the original appearance of the stains, and to develop performance standards for their replication using accelerated weathering protocols. The second phase of testing, which is beyond the scope of this thesis, will determine if the concrete at Jackson Lake Lodge still has the appropriate chemical composition and physical properties to accept another generation of acid-based stains and quantify the extent to which the acid-stains may weaken the surface of the existing concrete. If the acid-stains are unable to react with the historic substrate due to diminished alkalinity, or if they result in an uneven application due to differential porosities and rates of absorption across the substrate, an alternative high performance finish will be required to achieve the same variegated appearance of the original stain.

Chapter 2: International Style Buildings and Their Preservation

Original Design

Although Jackson Lake Lodge is still easily distinguishable as an International Style building, throughout its lifetime there have been several campaigns of changes that have compromised Underwood's original articulation of the International Style. When looked at individually none of the exterior alterations is too drastic, but when examined as a whole, it is clear that the building has lost some of the finer detailing that is definitive of 1950's era modernism.

The International Style is among the most clearly defined architectural styles of the 20th century. In 1932, Henry-Russell Hitchcock and Philip Johnson organized an exhibition and publication titled *The International Style*, in which they both codified the appearance of the style and expounded upon the reasons for and the importance of the choices that were indicative of that style. They outlined the three over-arching principles that define the style:

The distinguishing aesthetic principles of the International Style as laid down by the authors are three: emphasis upon volume – space enclosed by thin planes or surfaces as opposed to the suggestion of mass and solidity; regularity as opposed to symmetry or other kinds of obvious balance; and, lastly, dependence upon the intrinsic elegance of materials, technical perfection, and fine proportions, as opposed to applied ornament. (Hitchcock and Johnson 1932, 29)

In the two decades that passed between the publishing of *The International Style* and the opening of Jackson Lake Lodge, the International Style continued to proliferate. At its inception Jackson Lake Lodge had all the hallmarks of the style; it was cubic in form, and featured clean lines, large expanses of glass and steel, cantilevered overhangs, simple shed roofs, and was free of ornamentation. The overall form of the lodge was strongly horizontal and rectilinear; as such, it was clearly distinct from, and did not compete with, the surrounding landscape, which was another important principle of the International Style (Hitchcock and Johnson 1932, 88). Underwood used a simple grid pattern to orient the openings and to visually break up the building's mass. The



Figure 8. East elevation of Jackson Lake Lodge c. 1959. Image Credit: Grand Teton Lodge Company.



Figure 9. West elevation of Jackson Lake Lodge before 1960. View shows relationship between the lodge and the surrounding landscape. Image Credit: Grand Teton Lodge Company.

grid, which is created by deep, v-shaped expansion joints between the individual concrete panels, is most evident on the western elevation. The three horizontal bands of windows are arranged in relation to the squares of the grid, so that the vertical and horizontal expansion joints extend from the corners of the windows. This draws the eye across the elevation, creating a sense of rationality.

The predictability and regularity of the grid not only emphasizes the horizontality of the structure, but it also allows the texture and variegated coloring of the concrete to stand out from rest of the façade. Hitchcock and Johnson acknowledge this by saying "... the more consistently a surface is arranged, the more conspicuous will be its character as a surface." (Hitchcock and Johnson 1932, 60). In effect, the lack of ornamentation and the predictable nature of the fenestration pattern calls attention to the decorative concrete and makes it a defining characteristic of the overall design.

Beyond the rough wood-textured surface of the concrete, the building has virtually no ornamentation. This creates a sleek aesthetic that is defined by the consistency of the concrete surface. These dominating elements give the overall design a sense of order described by Hitchcock and Johnson as follows: "The fact that there is so little detail today increases the decorative effect of what there is. Its ordering is one of the chief means by which consistency is achieved in the parts of a design." (Hitchcock and Johnson 1932, 82). This sense of order is synonymous with legibility, and, therefore, it is essential that the materiality and details of the Lodge's original design be maintained.

Alteration to the Original Design

Throughout Jackson Lake Lodge's lifetime several characteristics that define the lodge as International Style have been significantly altered. First, the addition of the Blue Heron Bar in 1988, which protrudes from the western elevation, compromised the original rectilinear plane of



Figure 10. West elevation of Jackson Lake Lodge c. 1959. View shows the window arrangement within the grid. Image Credit: Grand Teton Lodge Company.



Figure 11. West elevation of Jackson Lake Lodge 2014. View shows the window alterations and the addition of the Blue Heron Bar. Image Credit: Joseph Elliott.

the main lodge. In Underwood's design, the different cubic volumes of the building intersected at right angles only; however, the Blue Heron Bar addition meets the original structure at forty-five degree angle. This addition not only projects from the western elevation in an unexpected way, but it defies the rational system that gives order to the overall design.

Second, the replacement of the original double hung windows with larger casement windows destroyed the relationship between the grid and the windows. Additionally the horizontal meeting rails of the original double-hung windows, which were purposely arranged to match the proportions of the grid, further emphasized the horizontality of the building. Several windows in the middle band of windows on the western elevation were replaced with glass block. This alteration not only interrupts the grid pattern, but it also gives the elevation a sense of mass that the original design did not have.

The original window frames were aluminum and painted wood, and were both light gray in color, which created a contrast between the dark-colored concrete. In contrast, the window frames of the replacement windows are dark brown; the loss of color contrast diminishes the punctuating effect that the windows had on the façade. This effect contributed to the regularity and clean lines that dominated the original design. The alterations to the windows are made more pronounced by poor detailing around the replacement windows. In order to accommodate the larger span of the new windows, new lintels and sills were cut into the concrete façade, interrupting the "shadowood" effect and further disrupting the grid. These poorly designed and executed details compromise the integrity of the original design, as careful detailing is a critical aspect of the International Style. As the detailing of the Lodge has been compromised, its overall sense of order has been diminished and the enthusiastic embrace of modern, machine-made materials that defined mid-century modern design is significantly less legible.

Finally the original acid-stain, which created a translucent, variegated finish on the textured concrete that replicated redwood, has been obscured. Around the year 2000, after 40



Figure 12. Addition of the Blue Heron Bar. View shows the angle that the addition meets the rest of the building. Image Credit: Architectural Conservation Lab.



Figure 13. Image of replacement window with poor detailing. Image Credit: Architectural Conservation Lab.

years of exposure, the acid-stained surface was re-coated. Prior to the application of the existing brown stain, the exterior surface of the concrete was chemically cleaned, rinsed with pressurized water and then acid etched. The new coating is an opaque, monochromatic, brown stain that conceals the materiality of the concrete and diminishes the effect of the wood grain texture. The new stain is completely flat and no longer appears like redwood. This loss of materiality significantly changed the visual appearance of the lodge and compromises the aesthetic role the concrete skin plays in the overall design.

Preserving the Recent Past

When preserving a building of national significance it is essential to understand the elements for which that building is significant. All buildings change and evolve overtime, and it is inevitable that alterations to the original design will occur either due to changing tastes or to changing needs. Inevitably there will be alterations to the building, which compromise the integrity of the original design, but improve the functionality and/or performance of the building. Often it is neither possible nor desirable to reverse these alterations, as they provide necessary functions. With that in mind, it is essential to identify the character defining features of a building and, to every extent possible, ensure that necessary alterations do not affect these specific features.

At Jackson Lake Lodge several of the character defining features have been compromised. Therefore all future work on the lodge should be done with an eye towards both preserving the surviving elements of the original design and to restoring the elements that have been lost. One of the most important and most feasible elements of the original design to reinstate would be the original appearance of the concrete finish. Restoring the original finish and completing necessary concrete repairs would significantly contribute to restoring the aesthetic importance of the concrete skin and would make the other alterations appear less pronounced. It could also help to maintain the performance of the concrete as it ages in a particularly severe climate.

A comprehensive re-treatment of the concrete would provide the opportunity to apply a water-repellent coating that is both compatible with the restored finish and protective of the underlying concrete. The wood-grain texture of the concrete at Jackson Lake Lodge is equally, if not more, important than the finish. Therefore ensuring the long-term preservation of the concrete's texture should be the primary objective of the new finish campaign. Since the concrete was originally acid-stained and acid-etched prior to the application of the current coating, it is safe to say that it is likely that the cementitious paste on the surface of the concrete was rendered more porous. Additionally as concrete ages, its surface neutralizes making the ferrous reinforcement more vulnerable to corrosion. Fortunately very little damage related to rebar corrosion is visible at Jackson Lake Lodge. Nevertheless, the replication of the original finish should be paired with a water-repellent coating, to ensure the long-term protection of the concrete from water penetration.

Over the last few decades there has been much discussion about how best to preserve our recent architectural history – an era of building that is defined by its enthusiastic embrace of modern, experimental materials and construction technology. Preserving buildings from this era presents an interesting predicament, as the materiality of a design is often simultaneously essential and sometimes inherently flawed. Perhaps the best example of this is asbestos containing materials. Consequently when details from this era are replicated, there are often questions about whether the original flaws should be recreated, preserved, or simply covered over.

One specific project where this debate was at the core of the preservation decisions was the re-surfacing of Frank Lloyd Wright's Solomon R. Guggenheim Museum in New York. Ultimately it was decided that, despite the fact that they were not part of Wright's intended aesthetic for the building, the "gunite formwork marks [were] worth preserving and not concealing.... [as they were] historic evidence of the techniques used..." (Huevel et al. 2008, 375). Later patches, on the other hand, were intentionally concealed. Similar questions will inevitably come up when re-creating the original and inherently imperfect finish at Jackson Lake Lodge.

When it comes to decisions about how the materiality of modern buildings should be preserved, DoCoMoMo International has been one of the most vocal participants. Iva Hammer, who was a contributor to the Proceedings from the 10th International DoCoMoMo Conference, asserts: “The original idea or intention of an artist is not real without the material substrate which brings the artist’s ideas and intentions to life” (Huevel et al. 2008, 369). At the other end of the spectrum, Paola Ascione declares that “[m]aintaining architectural value certainly means preserving materials from decay, but it is above all about keeping alive the innate creativity of the project” (Heuvel et al. 2008, 347).

Clearly there is a diversity of thought about how authenticity of the fabric, the form and the intent must be coordinated in the preservation of modern architecture. The approach at Jackson Lake Lodge will have to determine how much variability in the finish is acceptable or even desired. This decision will inform whether Underwood’s original intent can be recreated in-kind, or if more controllable substitute materials and methods that meet new requirements of protection and preservation and environmental safety would be more appropriate.

Chapter 3: Concrete

Throughout the past 200 years the way that concrete has been used has changed dramatically; this change in use necessitated changes in the way that concrete buildings have been designed, constructed, decorated and finished. As concrete experimentation progressed and the understanding of cement chemistry improved, different building pathologies have revealed themselves and continue to do so to date. The study of these pathologies has not only informed how the design of concrete buildings evolved over time, but it has also informed conservators about how best to conserve concrete structures. This section discusses some of the decay mechanisms that pertain to the performance of acid-stains and the long-term impacts of re-applying acid-stains on concrete; it does not purport to be a comprehensive summary of concrete decay mechanisms. Additionally this discussion pertains only to deterioration that occurs after casting; there is a whole subset of issues that can be caused from improper mix design, casting methods and curing conditions, which are not discussed here.

Concrete has been a building material for thousands of years; however, until concrete was reinforced with steel its use for general building construction was limited. The introduction of reinforcing steel members provided concrete with the tensile strength that it lacks, and, in doing so, it opened the door to a whole new array of design possibilities. In the late nineteenth century and the beginning of the twentieth century, concrete was used primarily as a back-up material and faced with brick or stone, as the look of raw concrete was considered unappealing. However this shifted dramatically when the modernist movement in the 1920s and 1930s began to consider fair-faced concrete an acceptable finish material. As a result of this change in the way that concrete was used, there was new demand to create visually appealing concrete surfaces that would remain unblemished overtime. Therefore, the new appreciation of raw concrete surfaces not only inspired a plethora of new practices and products that would give the concrete texture and

color, but it also provoked an interest in understanding what caused concrete to deteriorate and how those deterioration mechanisms could be mitigated.

The primary cause of large-scale damage in reinforced concrete is corrosion and rust-jacking of the interior, ferrous reinforcing structure (Macdonald 2003, 140). The reinforcing members in concrete are susceptible to corrosion over time if they are not properly protected from the elements; the primary protection of these ferrous members is concrete coverage. Freshly cured concrete has a pH ranging from approximately 12–13.5 (Macdonald 2003, 142). When steel is surrounded by alkaline material with a pH of 11 or higher a protective oxide that inhibits corrosion is formed. However as the concrete ages, it begins to adsorb carbon dioxide from the air through a process called carbonation. Carbon dioxide is an acid gas that reacts with the calcium hydroxide in the concrete substrate to form calcium carbonate. This carbonation reduces the pH of the concrete overtime, diminishing its ability to perform as a protective barrier. As the concrete ages the carbonation penetrates progressively deeper into the substrate; corrosion can begin at any pH below 11 if there is adequate moisture and oxygen present. The rate that carbonation advances is dependent on both the porosity of the concrete and on the level of exposure to the elements.

Once the ferrous reinforcing elements are no longer protected by the pH of the concrete they will inevitably begin to corrode. As the rebar corrodes, it increases in volume, causing the surrounding concrete to crack and eventually spall. These cracks and spalls increase the exposure of the ferrous reinforcements to moisture, which further accelerates their degradation. The risk of corrosion and the consequences of the resulting damage will only increase over the lifespan of the building if the sources of deterioration are not addressed.

Corrosion can also occur as a result of chloride attack; chloride attack is when salts from the environment or that were part of the original concrete mix become solubilized within the concrete matrix. If these chlorides come into contact with the ferrous rebar, they can initiate corrosion. A thorough petrographic analysis of the concrete would conclusively determine if chloride

attack is a potential threat at Jackson Lake Lodge. The best defense against corrosion caused by either carbonation or chloride attack is adequate concrete coverage of the reinforcing elements. Since the application of an acid-stain lowers the pH of the surface concrete, when casting concrete for which the intended surface finish is acid-staining, additional concrete coverage should be provided.

Surface erosion is another common pattern of deterioration on concrete buildings. Surface erosion occurs where water frequently runs down the face of the building. As water washes over the concrete, the cementitious paste washes away, leaving the aggregate exposed. These areas generally appear more textured than the surrounding concrete, or they may be a different color if the underlying aggregate is highly pigmented. Jackson Lake Lodge was designed with deep overhangs; therefore, it is likely that the concrete surface has been fairly well protected from surface erosion. Since acid-stains become integral to the concrete matrix, erosion of the surface would most likely erode an existent stain. Additionally, since the appearance of freshly applied acid-stain is affected by the porosity of the concrete substrate, surface erosion will also affect the appearance of a future application of acid-stain.

Another condition that can occur in concrete, which is exacerbated by acid-staining is efflorescence. Efflorescence is when certain salts, which are solubilized within the concrete matrix, migrate to the surface of the concrete and create crystalline deposits. These formations are not only unsightly but they are also indicative that salts are crystallizing within the concrete matrix- subfluorescence - which could lead to further surface spalling. The production of efflorescence is more common on concrete that has been treated with a dark acid-stain, as the chemical composition of the stain contributes to salt crystallization. Currently there is evidence of efflorescence on the over-hanging eaves at Jackson Lake Lodge²; this condition should be addressed prior to retreating the building, regardless of whether acid-stain are used. However this

² A comprehensive conditions survey of Jackson Lake Lodge was conducted by Architectural Conservation Lab in 2014.

problem should be given especially careful consideration if acid-stains are used, as dark colored acid-stains would only exacerbate this pre-existing condition.

There are a variety of other concrete pathologies that alter the surface of the concrete and therefore impact the appearance of acid-stains – such as scaling and laitance. However, if the necessary and sufficient factors for these decay mechanisms were inherent to the Lodge's concrete or induced by the weathering exposure that is typical to Wyoming, it is likely these pathologies would have already presented themselves. Therefore it is reasonably safe to assume that they will not occur in the near future if maintenance of the building continues.

Chapter 4: Acid-Stains

Chemistry of Acid-Stains

As concrete has become an increasingly popular building material, many finishing techniques have been developed to alter the color and texture of concrete to create a greater range of surface effects. One method that was developed was acid-staining. Acid-staining is an integral coloring method that precipitates colorants inside the concrete matrix, creating a permanent, durable color that does not obscure the natural texture of the concrete. Despite their durability, acid-stains were primarily utilized as interior finishes, thus their use at Jackson Lake Lodge is somewhat atypical. Unlike other kinds of pigmentation, acid-stains color the concrete via chemical reaction with the alkaline concrete substrate (Goodman 2005, 5). Therefore, they are inherently unpredictable, as their successful application depends not only on their careful application but also on the homogeneity of the chemical composition of the concrete substrate. The aesthetic appearance is also affected by the porosity and density of the concrete. Therefore large-scale projects that require batched concrete production and placement, like Jackson Lake Lodge, will inevitably introduce more variability into the appearance of acid-stains³.

Due to their unpredictable nature, acid-stains tend to be relegated to flat-surface, interior finishes where it is easier to control their application and where complications that can result from weather exposure during the application period can be limited. As a result, they are most commonly found on floors and countertops. In fact, the floors throughout Jackson Lake Lodge are also acid-stained, albeit to resemble honed sandstone. The use of acid-stains on vertical surfaces is further complicated by the very low viscosity of the stain, which causes the stain to run down the wall, often resulting in streaking. At Jackson Lake Lodge this streaky appearance was exploited to give the illusion of vertical wood graining.

³ It is important to note that in many applications the natural variability of acid-stains is considered to be a desirable characteristic, not a hindrance.

There is very little published information about the chemistry of acid-stains and how they actually work. The information that does exist is superficial and is written by commercial applicators who specialize in acid-stained concrete floors; the intended audience of this literature is homeowners and less experienced contractors (Nasvick, 2006). As such, the primary focus of this literature is on decorative techniques. Published literature repeatedly acknowledges that the results obtained from acid-staining are highly unpredictable and that sometimes acid-stains will not work. However, little has been written about the underlying chemistry that is responsible for both the ability for the stains to react and the intensity and appearance of the stain's reaction. For more information about industry publications about acid-stains, consult the literature review in Appendix A.

To better understand the chemistry of acid-stains, the author conducted several interviews with Stan Stratton, Director of Technology Development at Scofield Chemical⁴. Scofield Chemical is a company that specializes in concrete coloring, texturizing and performance, located in Douglasville, Georgia. Scofield Chemical produces a hydrochloric based acid-stain, called Lithochrome Chemstain Classic, in addition to a variety of other concrete coloring products. Stan is a concrete chemist by trade, and most recently has been developing several patents for high-solar reflectance index (SRI), integral, coloring methods for concrete. My conversations with Stan revealed the complexities of acid-staining, which only reinforced how remarkable their use at Jackson Lake Lodge was for its time.

Acid-stains for concrete are comprised of transition metals that are solubilized in an acid. Hydrochloric acid⁵, which is a solution of hydrogen chloride gas ($\text{HCl}(\text{g})$) dissolved in water, is the most common acid used in concrete staining; however, phosphoric acid can also be used. Unlike hydrochloric acid, phosphoric acid is a weak acid, which means that it does not

4 All of the information pertaining to the chemistry of acid-staining in this chapter came from my interview with Stan Sutton, unless otherwise cited.

5 Hydrochloric acid is commonly referred to as muriatic acid.

entirely deprotonate when it is in the presence of a solvent; therefore the amount of product that results from these equations can be highly variable based on different conditions (Atkins and Jones 2008, 398). Chemical reactions involving strong acids, such as hydrochloric acid, are generally more predictable because when the acids react, they do so completely. The original stains that were used at Jackson Lake Lodge and the acid-stains that were used throughout this testing program were all comprised of hydrochloric acid. So this discussion of acid-stains only pertains to stains that are hydrochloric acid-based. The composition of the concrete substrate is equally responsible for the appearance of the acid-stains; therefore, concrete that is made with different binders will create starkly different results. Acid-base stains are most successful on concrete

that is made with Portland Cement; which is the material that was used at the Jackson Lake Lodge. The following discussion pertains only to hydrochloric acid-based stains that are applied to Portland cement; it does not address the chemistry of weak acid-based stains or the performance of HCl stains on concrete that utilizes other binders, such as lime.

When the transition metals are combined with the hydrochloric acid, they react to create metallic salts, and hydrogen gas. Metallic salts are simply ionic compounds that are comprised of metal elements; in the case of acid-stains the salts that are produced are metallic chlorides. These metallic chlorides are held in solution by the hydrochloric acid and are very stable until the stain is applied to the concrete.

The stains that were used for the testing portion of this thesis were Kemiko Products, manufactured by Empar Corp. Kemiko produced the stains that were originally applied to Jackson Lake Lodge, and they are still making the same products today. As part of her 2015 thesis, Julianne Wiesner-Chianese confirmed with the manufacturer that the formulation of the stains is the same as it was in the 1950s.

Based on the ingredient information that was listed on the Material Safety Data Sheet (MSDS), which was confirmed by ED-XRF analysis, the transitional metals that form the

pigments in the three different stains that were used at Jackson Lake Lodge were identified as follows. The tan (Malay Tan) stain was colored with ferrous chloride. The brown (Cola) stain was colored with manganese chloride and ferrous chloride. The ED-XRF analysis also identified a source of chromium in the brown stain, which was not listed in the ingredients, however, the exact compound is unknown. The black stain was colored with sodium dichromate and manganese chloride. For details about how the composition of the stains at Jackson Lake Lodge was verified, see the section on Energy Dispersive X-Ray Fluorescence.

When the acid-stain is applied to the concrete substrate, the first reaction to take place is the dissolution of the calcium carbonate on the surface of the concrete, which causes a slight etching of the concrete surface, increasing the porosity. Calcium carbonate naturally forms on the surface of the concrete when carbon dioxide in the atmosphere reacts with the calcium hydroxide in the concrete (Torraca 2009, 63). As the concrete ages, the carbonation will slowly penetrate deeper into the substrate. Generally this calcium carbonate is not a problem for acid-staining, however if too much of the calcium hydrate has been converted to calcium carbonate, the stains may have no reaction. The initial etching of the surface that occurs as the calcium carbonate is dissolved helps the stain be absorbed into the surface of the concrete. However this etching also dissolves some of the cementitious paste that is at the surface of the substrate; this weakens the surface making it less resistant to abrasion.

Once the calcium carbonate has been consumed, the acid-stain solution reacts with the alkalinity in the concrete causing the pH of the solution to rise. This process is referred to as neutralization. The metallic chlorides in the solution react with the calcium hydroxide in the concrete substrate to create metallic oxides or hydroxides. Unlike metallic chlorides, metallic oxides and hydroxides are highly insoluble, and can only be held in solution by a very acidic solvent. Therefore as the pH rises, the metallic oxides and hydroxides precipitate out of solution and become embedded into the pores of the concrete matrix. However, the different metallic oxides or hydroxides do not precipitate out of solution all at once; rather different metals will fall out

of solution at different pHs. The pH at which a given metal will precipitate out of solution is a function of that specific chemical compound's solubility product constant (K_{sp}). Each chemical compound has a solubility product constant that is unique. The smaller the solubility product constant, the lower the pH required for the stain to precipitate out and color the substrate. In other words, the more insoluble the colorant, the less neutralization of the stain is necessary to get that colorant to drop out of solution. It is difficult to say precisely if and when the metals will drop out of solution, because, like all chemical reactions, the reaction can be affected by the temperature or the presence of other reactants. Once embedded in the concrete matrix, the metallic hydroxide and oxide pigments are extremely stable as they are also light-fast.

When dealing with freshly cast concrete, the solubility product constants of the individual transition metals that comprise the stain are virtually irrelevant because the strong alkalinity that is inherent in freshly cast Portland cement will force all the metals to precipitate. However when applying stains to historic concrete, in which the alkalinity has been reduced by carbonation, the pH at which a metal will precipitate becomes increasingly important. Since the different metals precipitate at different levels of pH, it is possible that when the stain are applied to historic concrete some colors will form, while others will not. Additionally stains that derive their color from a combination of different metals could only partially precipitate, which could produce an unintended color. Therefore when applying acid-stains to historic concrete, it is important to know the pH of the existing substrate and the chemical composition of each stain used, to gauge the stain's potential for performance. In short, acid-stains, which are naturally unpredictable, only become more unpredictable when they are applied to aged concrete.

Kemiko Stain Color	Compound in Solution	Compound in Precipitate	Chemical Formula	K_{sp} Value
Malay Tan®	Ferrous Chloride	Iron (II) hydroxide	$Fe(OH)_2$	2.9×10^{-39}
Cola®	Ferrous Chloride	Iron (II) hydroxide	$Fe(OH)_2$	2.79×10^{-39}
	Chromic Chloride	Chromium (III) Hydroxide	$Cr(OH)_3$	6.3×10^{-31}
	Manganese Chloride	Manganese (II) Hydroxide	$Mn(OH)_2$	1.9×10^{-13}
Black®	Manganese Chloride	Manganese (IV) Hydroxide	$Mn(OH)_4$	1.9×10^{-13}
	Sodium Dichromate	Sodium Dichromate Functions as an Oxidizing Agent	$Na_2Cr_2O_7$	N/A

Table 1: Table showing the different metallic compounds in each stain and their K_{sp} values.

By looking at the K_{sp} values of the compounds that were used in the stains at Jackson Lake Lodge, predictions can be made about which colorants will be easiest and most difficult to precipitate out of solution. Based on the K_{sp} value, it can be determined that the ferrous oxides, which have a K_{sp} value of 2.79×10^{-39} will be the easiest to form. Therefore the tan (Malay Tan) stain is the mostly likely colorant to form on the aged concrete and will give the most reliable results since its color is produced by a single chemical compound. The second compound to drop out of solution will be the chromium(III) hydroxide which has a K_{sp} of $Cr(OH)_3$ 6.3×10^{-31} . The colorant that will require the highest level of neutralization in order to drop out of solution is manganese (II) hydroxide, as its K_{sp} is 1.9×10^{-13} . Therefore, if there is not enough residual alkalinity in the historic concrete, it is likely that both the brown (Cola) and the black (Black) stain will not precipitate out to achieve the desired reaction.

Depth of Penetration

The acid-stains are drawn into the concrete via absorption, so the depth of penetration is dependent on the density and permeability of the concrete substrate, not on the properties of the stain itself. Highly porous concrete bodies will allow the acid-stain to be absorbed deeper into the

concrete, whereas less porous concrete will limit the depth of penetration. Discrepancies in porosity can occur across a single slab, which accounts, in part, for the natural variation that occurs when using acid-stains. Generally speaking, trowel finished concrete is the most difficult kind of concrete to stain, because the troweling process compacts the surface of the substrate, making it impervious to the stains. Acid-staining is much more successful on board-marked surfaces, like those found at Jackson Lake Lodge, because their more porous nature facilitates better penetration. As concrete ages, it naturally becomes more porous as the cementitious paste at the surface erodes. This suggests that acids stains that are applied to aged concrete will penetrate further in to the concrete surface than they would on freshly cured concrete.

Since all of the concrete that comes into contact with the acid-stain will have a reduction of pH, it is particularly important to know the depth of the concrete coverage of the underlining reinforcements to ensure that the pH of the concrete surrounding the rebar remains as high as possible. Generally speaking, historic concrete buildings have less concrete coverage and more porous concrete substrates than modern buildings due to a limited understanding of the causes of concrete deterioration at the time of their construction. Therefore careful analysis of the concrete substrate should be conducted prior to embarking on a re-application of acid-stains.

Applying Acid-Stains on Historic Concrete

When replicating an acid-stain it is essential to be familiar not only with the appropriate application techniques to achieve the desired effect, but also with the chemistry, condition and repair history of the existing concrete substrate. The appearance, durability, success, and weathering patterns of acid-based stains are integrally linked to the concrete mix design and its long-term performance.

The way the concrete has weathered on the different elevations of the building, due to varying amounts of exposure to water and UV radiation, will affect how the stains react across the

substrate. Areas that have experienced surface erosion due to water run-off will have a different texture and less cementitious paste. The loss of cementitious paste will result in less alkalinity and these areas will react differently with the acid-stains. Additionally it is important to be familiar with the alteration and repair history of the building, as additions and later patches will likely have a higher pH, and, thus, have a stronger reaction with the stain than the surrounding historic concrete. These differences in reactivity could cause large blotches or areas of color difference that would interrupt the surface regularity that is an essential component of the Lodge's original exterior finish. Furthermore, in order to maintain the uniformity of the concrete skin, existing patches and future repairs will have to be custom matched to the surrounding concrete using diluted proportions of stain to disguise the more reactive, new concrete.

There are a variety of techniques that can be used to improve the results of acid-staining on historic concrete. First, acid-stains should be applied in very small amounts in dilute concentrations, because if there is a small amount of reactivity that is still present in the concrete, that reactivity could be easily overwhelmed by a large concentration of acid. Applying the stains gradually in a very controlled manner will help to maximize an aged, concrete substrate's potential to be re-stained. A second method that can be utilized to achieve better results is to apply a baking soda (NaHCO_3) or washing soda (Na_2CO_3) solution to the concrete prior to staining. This solution would temporarily raise the pH and restore some alkalinity back into the substrate, which would improve the chances of reactivity. Baking soda has a pH of approximately 8.5, while washing soda has pH of 10.5, so of the two, washing soda would restore more alkalinity to the concrete.

Finally, Scofield Chemical creates a product called Chemstain EnhancerTM that also restores the alkalinity to the concrete substrate, but is more effective and reliable than a baking soda or washing soda solution. According to the manufacturer's data, the formulation of the product is only compatible with Scofield Chemical's line of acid-stain. If the substrate proves to be

too neutral and an application of Chemstain Enhancer™ is necessary to get the stains to react, the Kemiko colors would have to be matched to products in the Scofield Chemical line. Whether or not Scofield Chemical manufactures acceptable color alternatives can only be determined by further testing. Switching product lines should be considered only after all other options have been exhausted.

Chapter 5: Methodology

Recreating the Original Stain

Regardless of whether acid-stains are ultimately used in the next campaign of restoration work, recreating the original finish with the original technique is an essential step in determining what the original finish looked like. Very little documentation about how the stains were applied to the concrete exists, as there were no specifications for the acid-stain finish. Therefore how the finishes looked immediately after application is unknown. The only written documentation about the stain application appears in a letter dated July 1st, 1954 that was exchanged between Gilbert Stanley Underwood and Rohloff and Co., the company that sold the stains, which were made by Kemiko.

The letter states that Underwood's objective was to "get the naked concrete showing thru a very dark brown stain...(Underwood, 1954)". It goes on to explain that three coats of the Kemiko Colorado Brown stain were applied to a test area, but the application still was not dark enough. When applied, the brown stain appeared much lighter than it did on the sample card that Rohloff and Co. had provided. Due to the budget restraints of the project, Underwood stated that they could only afford two coats of stain. Therefore he suggested that a wash of black stain could be applied over the brown. He mentioned that both the brown and the black stain would be applied with a Dupont sponge. Advertisements from the era suggest that a Dupont sponge is simply a cellulose sponge (Dupont Magazine 1955, 26). In the last paragraph of the letter Underwood stated that the stain was being applied by painters, who were being trained how to use acid-stains on site. However he mentions that they may be interested in having Rohloff and Co.'s experts apply the stain. This correspondence, combined with the lack of specifications, suggests that the finish application was somewhat experimental.

To further complicate the recreation of the original stain, there are almost no color photos that show what the stain looked like when applied originally. While many color photographs

were taken of the lodge after completion, no detail shots of the exterior concrete surface were taken. The best photographic documentation of the stain appears in a 1956 Kemiko ad, which features Jackson Lake Lodge (See Figure 5). The advertisement states that the building was “stained with Kemiko’s rich Malay Tan, highlighted with Colorado brown and Black.” (Kemiko Advertisement, c. 1956). This advertisement is the first and only mention of the third color, Malay Tan. It also includes a detail photograph of the surface of the concrete; however, the advertisement has a very orange hue to it, which was typical of publications of that time. Therefore, it is difficult to know if the photograph accurately represents the color of the original finish. It does, however, show the level of color variation and the wood-grained appearance that was achieved.

Another important piece of information that helped in the recreation of the stain was an area of the original stain, preserved on the west elevation of the original Lodge, that was enclosed by the addition of the Blue Heron Bar in 1988. This area of concrete shows the

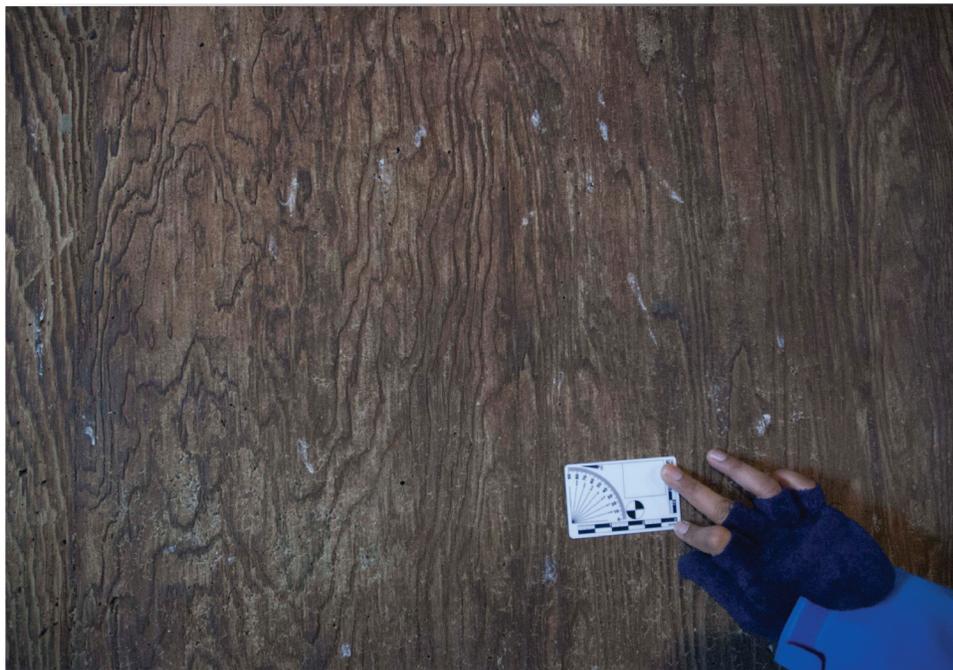


Figure 14. Area of original stain enclosed above the Blue Heron Bar. Image Credit: Architectural Conservation Lab.



Figure 15: Stains used to make facsimile samples. Image by author.

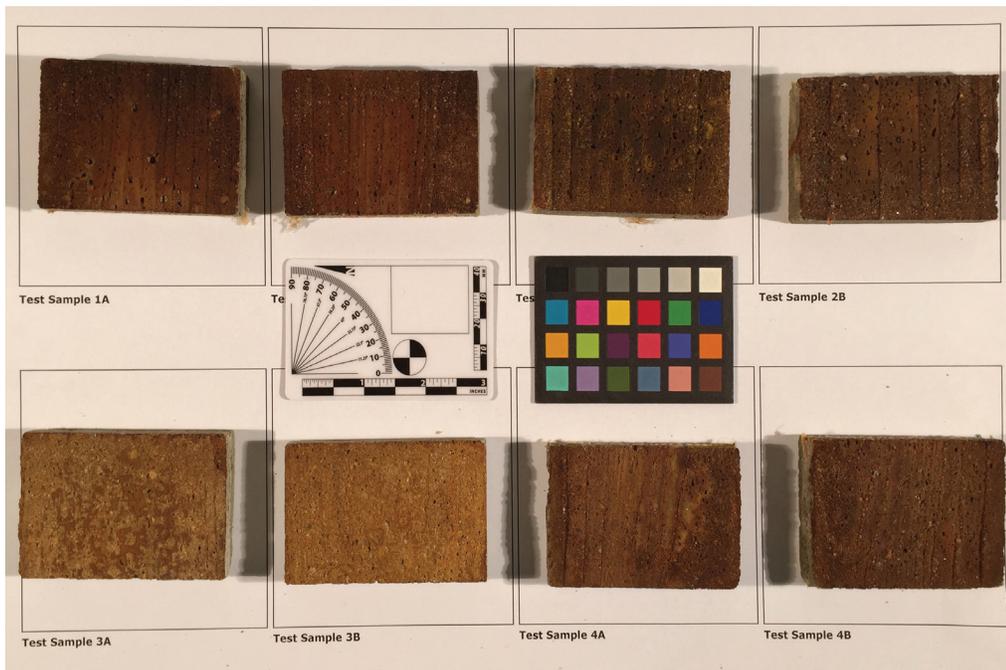


Figure 16: Examples of mock-ups that were made to determine the stain application process. Image by author.

original stain after over 30 years of exposure. It is clear that the stain has altered over time, as it is somewhat grayed, but the three distinct colors are still easily observable. Both the archival documentation and physical remains of the original stain informed the creation of the mock-up samples.

Due to the lack of documentation on the application technique, several samples were made to determine the order and method of stain color application. Variables included sequence, dilution, and application method of the stains until the appropriate appearance was reached. See Appendix B for sample schedule. The samples represent the best effort to replicate the appearance of the original finish based on archival and product research and cross-sectional comparison of original and replica finishes; however, there is still some degree of speculation.

Sample Creation

The profile and texture of the concrete is an integral part of the original surface finish



Figure 17: Molds that were made to cast facsimile samples. Image by author.

at Jackson Lake Lodge. Therefore, in order to re-create the original finish, it was essential that the facsimile samples have the same pronounced, wood-grain texture that the original concrete featured. It was also essential that the facsimile samples were sized to fit into the QUV Weatherometer brackets. To accomplish this, wooden molds were constructed that would create samples with the appropriate size and texture for staining and testing purposes.

The wooden molds were built out of a combination of three-quarter inch birch-plywood and solid wood. The four sides of the mold were constructed with the plywood; the corners of the molds were connected with simple butt joints and secured with duct tape. Utilizing duct tape insured that the joints were both tight and easy to release after the concrete had hardened. The bottom piece of each mold was constructed with either Cypress or Douglas Fir, and then blasted with abrasive media. This media abrasion eroded the early wood, which is softer, but left the late wood; which created an exaggerated wood-grain texture on the surface of the concrete. A total of 32 molds were created, which insured that each mold only had to be used twice to obtain the necessary number of samples.

The concrete was mixed in the proportions laid out in Underwood's original specifications for the building. The original specifications give the concrete ratio by weight; it calls for ½ part cement, ½ part water, 1 part fine aggregate, and 2 parts coarse aggregate. Since the cast samples had to be ½" or less in depth to fit into the Weatherometer, coarse aggregate was not used as it would have created samples that were too thick, and it would have interfered with the surface texture. Finer aggregate was used in its place, and the samples were cast using a ratio of ½ part cement, ½ part water, and 3 parts concrete sand, by weight. Each batch contained 1200 grams of concrete sand, 200 grams of Type I/II gray Portland cement, and 200 grams of distilled water.

The concrete was mixed in accordance with the ASTM C192/C132M and utilized the machine mixing protocols, which are discussed in Section 7.1.2. A 10-quart capacity HOBART

C-100 industrial stand mixer with a flat beater (R-61628) was used to mix the concrete. The concrete mixing procedure is as follows. The dry ingredients were added to the mixing bowl and a small amount of the water was added on top to prevent dust from forming when the mixer was turned on. Once the dry ingredients and this small amount of water were well-combined, the rest of the water was added. The ingredients were mixed for three minutes on the lowest speed (144 RPM); then the mixer was turned off and the concrete was allowed to rest for three minutes. At the beginning of the rest period, the sides of the mixing bowl were scraped with a rubber spatula to ensure all ingredients were well-combined. Following the rest, the concrete was mixed again for two minutes on medium speed (258 RPM) (Hobart Manufacturing 1972, 3).

Once the concrete was mixed, it was spooned into the individual molds. Prior to use, all of the molds were coated with a generous layer of mineral oil. Mineral oil was selected as a lubricant for the molds because the original specifications called for mineral oil to be applied to the formwork as a release agent. The mineral oil was allowed to soak into the wood molds for several hours until the wood appeared saturated. Immediately prior to casting, the molds were re-brushed with a generous coat of mineral oil, so that they appeared glossy. If a release agent had not been used, the wooden fibers on the surface of the molds or formwork would have become embedded into the surface of the concrete.

The first lift of concrete was tamped down with a rectangular tamper, which measured 1 cm x 2cm, and then shaken back and forth in both directions until the lift was level. Next a rectangular piece of burlap was pressed into the surface of the concrete. The purpose of the burlap was to give tensile reinforcement to the sample, to prevent cracking when the sample was removed from the mold. Following the burlap a second lift was added; it was also tamped down and the mold was shaken back and forth until each sample was level and appeared well compacted. Finally, the molds were tapped forcefully against the counter so that any air bubbles in the concrete were forced to the surface.



Figure 18: Adding water to the concrete mix. Image credit: Jean Jang.



Figure 19: Tamping the concrete into the molds. Image credit: Jean Jang.

The samples were allowed to dry in the molds for 48 hours, after which they were removed from the molds and allowed to cure with the grain side up for at least 28 days prior to staining. Since the objective was for the samples to be fully carbonated prior to staining, the curing environment was not closely controlled. The samples were cured in an enclosed room with no windows and with a temperature of approximately 70 degrees F.

Although the concrete was mixed in accordance with the original specifications, it is important to note that several options for substitutions were written into the specifications. Therefore it is not possible to know for sure whether the method used to create the facsimiles is the same as the method that was used for the cast concrete at Jackson Lake Lodge. Additionally it is possible that different materials could have been used in different parts of the building based on the availability of materials or the weather conditions at the time of casting. Therefore there is almost certainly some variability in the properties of the original concrete substrate.



Figure 20: Samples after they were removed from the molds. Image by author.

Sample Preparation

After the samples were removed from the molds and prior to staining, each sample was washed with tap water and scrubbed with a nylon toothbrush to remove any residual mineral oil or laitance. Laitance is a thin, crusty layer comprised of fines that can form on the surface of concrete after casting; this layer is particularly friable and obscures the intended surface texture. Once the samples were washed and scrubbed, they were allowed to air dry for 24 hours prior to staining.

The samples were then stained using Kemiko® Stone Tone acid-stains in the following colors: Malay Tan, Cola, and Black. Kemiko® Stone Tone acid-stains are comprised of transition metal chlorides suspended in a hydrochloric acid solution. Each stain was diluted to a 1:1 ratio, per the manufacture's instructions, and was applied using a natural bristle brush. Each color was applied with a clean brush to prevent cross contamination. Discussions with the manufacturer in 2015 confirmed that the composition of the stains is the same today as in 1954.

The brown stain was applied first; a thin coat was brushed onto the surface and allowed to soak into the concrete. Once the stain had been absorbed, a second layer was brushed on to ensure that the sample was completely saturated. This layer of brown was allowed to dry for four hours. When it was checked, it did not appear dark enough, so another layer of brown was applied in the same manner as the first at the four-hour mark. After the second application, the brown stain was allowed to dry for an additional eight hours before the black stain was applied. After eight hours, the black stain was brushed on top of the brown stain. Once again an initial coat was brushed on; after the initial coat was absorbed, a second coat was applied to ensure adequate saturation. The stain was then allowed to dry for eight hours. After eight hours the tan stain was brushed on using the same technique described above and allowed to dry overnight.

During the drying process, residual solids were left on the surface of the sample. In order to both achieve the intended color and to neutralize the acidity of the stain, the samples had to



Figure 21: Applying stains to the test samples. Image Credit: Joe Mester.



Figure 22: Samples soaking in the neutralizing baking soda bath. Image by author.

be rinsed. The samples were again washed under cold, running, tap water and brushed with a nylon brush. These processes were repeated until the samples could be blotted with a cotton rag and leave no residue. Once the solids were removed, the samples were placed, two at a time, facedown in a bath of a one molar solution of NaOH³. The samples were allowed to soak for two minutes and then they were removed, blotted with a clean cotton rag, and allowed to air dry.

After all the samples were stained, each sample was numbered. A Roman numeral was scribed into the back of each sample using a Dremel tool with a reinforced fiberglass bit. Twelve samples were stained for accelerated weathering tests. From the twelve samples, two were kept as controls, five were weathered as is, and five were treated with a water repellent and then weathered.

Once the samples were dry, a waterborne, silane/siloxane water repellent Repels® was spray applied on top of the acid-stain, using a Preval® Sprayer. To ensure even coverage the spray stream was begun several inches beyond the edge of the sample; the spray gun was moved slowly back and forth across the sample, delivering several thin coats of water-repellent. Once the sample was sufficiently coated, the sample was rotated 90 degrees and the coating was applied again, once again with the stream of the spray beginning and ending several inches to either side of the sample. Each sample was coated until it appeared saturated, per the manufacturer's instructions. The water-repellent was then allowed to dry for 48 hours before the weathering cycles were begun⁶.

It is important to note that this testing program does not aim to evaluate the efficacy of different waterproof coatings; however one common concrete water-repellent was chosen to test

⁶ The water repellent that was applied to the samples for this testing program is not the recommended sealer by the manufacturer; Epmar Corp. recommend that the Stone Tone Acid® stains should be sealed with Stone Tone Sealer II®. However the intended application of the Stone Tone acids stains is for concrete floors, which experience high impact use. Consequently, Stone Tone Sealer II® creates a very thick finish layer, which would compromise the texture of the concrete. Additionally this sealer has a high-gloss finish, whereas the original finish was matte. Therefore Stone Tone Sealer II® was not an appropriate choice for this application. Repels® was selected because it was the only product in the Kemiko line that had a matte finish and would not compromise the texture of the concrete.

with the stains to determine their effect relative to untreated stained samples. This testing program simply aims to determine if applying a water-repellent to the acid-stain is essential to the stain's long-term performance.

Energy-Dispersive X-Ray Fluorescence

In order to make predictions about whether the concrete at Jackson Lake Lodge has enough residual pH for the metallic ions in the stains to precipitate, it is essential to know which metals create the pigments in each of the different stains. The Material Safety Data Sheets provided by the manufacturer list the potentially hazardous chemicals found in their products, however, they do not disclose all the ingredients in a given product. Therefore Energy-Dispersive X-Ray Fluorescence Spectroscopy (ED-XRF) was used to confirm each stain's composition.

ED-XRF is a non-destructive testing technique that is used in conservation to determine the elemental composition of a material. The machine bombards a sample with x-rays, which excite the atoms in the material. This excitation forces the atoms to give up an inner shell electron. As this electron is released, another electron from a higher shell drops down to fill the void causing a secondary x-ray to be produced. The radiation that is produced is referred to as fluorescence. Each element has a characteristic pattern of fluorescence, which can be used for identification.

Three stain samples were analyzed using ED-XRF by Catherine Matsen, Associate Scientist and Affiliated Assistant Professor at Winterthur, on November 11th, 2015. Non-destructive, qualitative ED-XRF spectroscopy was performed to determine the sample area's elemental composition. Analysis was performed with the Bruker Tracer III-SD XRF spectrometer using a rhodium tube (40kV high voltage, 9.6 μ A anode current, 25 μ m Ti/305 μ m Al) for 60 seconds live-time irradiation. The spot size is oblong in shape, approximately 1cm \times 0.5cm. Spectra were interpreted using the PXRF1 software.

The samples that were tested were created by the stain manufacturer, Empar Corp., as standard color swatches for their Kemiko® Stone Tone product line. Each stain was applied to the surface of a thin concrete sample and coated with a water repellent. The stain and water repellent are sold by the manufacturer as a two-part system. The colors that were analyzed were Black, Cola, and Malay Tan. The applied water repellent is called Kemiko® Stone Tone Sealer II, which is an acrylic, water-based sealer. Since Kemiko® Stone Tone Sealer II is waterborne it did not interfere with determining the composition of the underlying stains.

The ED-XRF analysis began by scanning the backside of one of the samples where the untreated concrete surface was exposed. Once the composition of the concrete substrate was determined, the stained face of each sample was scanned. The results from each stain scan were compared with the results from the scan of the concrete substrate to determine which elements were components of the substrate and which elements were components of the stain.

The spectra produced by the ED-XRF analysis were compiled and analyzed by the instrument's software. On the graphs that were produced, the red peaks represent the composition of the concrete substrate. The blue peaks represent the individual stains. The software program labels the largest peak that is associated with a given element. If elements generate more than one characteristic peak, the secondary peaks are not labeled.

The ED-XRF scans revealed that the concrete substrate is made up of potassium, calcium, manganese, iron, rubidium, strontium, yttrium, and zirconium. The black stain derives its color from chromium and manganese. The Cola stain, which is brown in color, derives its color from chromium, manganese, and iron. And finally the Malay Tan stain, which is orange-brown in color, derives its color from iron.

These results confirm that the information provided in the MSDS is largely accurate. All of the ingredients that appeared in the MSDS for the Malay Tan and Black stain appeared in the scan. Interestingly, the Cola stains showed traces of manganese, which was not listed in the MSDS. Since an area of the concrete substrate without acid-stains was also scanned, it is

possible to conclude that the manganese is part of the stain, not inherent to the concrete.

Measuring the pH

Understanding the pH of the substrate and how it is altered throughout the acid-staining process is essential to not only determining whether or not acid-stains will work on a given surface, but also for understanding the condition of the concrete substrate more generally. The success of acid-staining hinges on adequate pH in the substrate. See the section on acid-staining for further discussion about the role that pH plays in the process of acid-staining.

A pH measurement is a measurement of the negative logarithm of the hydronium ion molarity in solution (Atkins and Jones 2009, B23). Measurements of pH determine if a given solution is alkaline or acidic. As defined by the Bronstead-Lowery acid-base theory, an acid is a proton donor, while a base is a proton acceptor (Atkins and Jones 2009, F73). A pH measurement greater than 7 is alkaline, a value of 7 is neutral, and a pH measurement less than 7 is acidic. The transfer of hydronium ions is the crux of neutralization reactions.

Since pH is a critical factor in the performance of the stain, the pH of the concrete was monitored throughout the different steps of the testing process. The pH was measured according to the procedures outlined in ASTM D4262 Standard Test Method for pH of Chemically Cleaned or Etched Concrete Surfaces. The pH was measured with a reactive pH strip that was dipped in water. Prior to contact with the concrete the pH of the water was measured; then the pH paper that was dipped into water that was allowed to sit on the surface of the concrete sample. The pH paper's sensitivity ranged from 1 to 14 and was capable of measuring in 1.0 increments. ASTM D4262 requires that the samples should be measured with pH paper that is capable of measuring in 0.5 increments, however pH strips with this level of resolution were not available.

Eight samples were selected at random to establish the pH of the concrete samples after they had cured but prior to staining. All of the samples that were tested had a pH of 11. After

Surface pH of the Concrete Samples

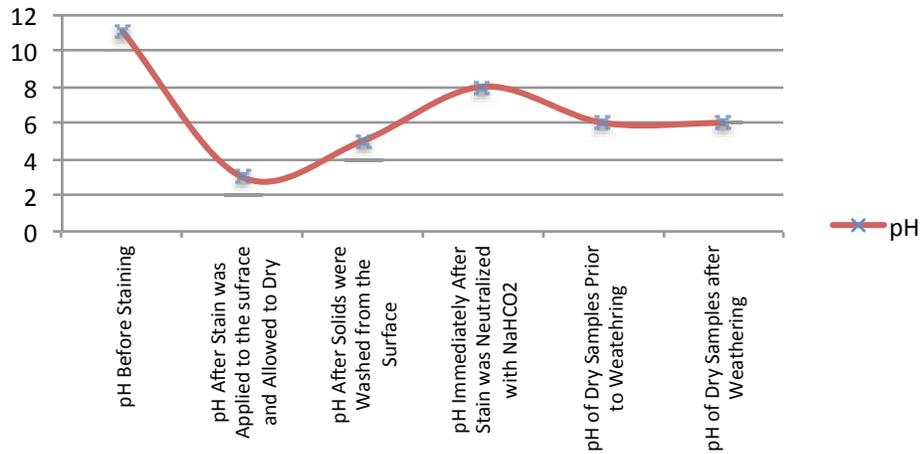


Table 2: Graph depicting pH fluctuations during staining process.

the stains were applied and allowed to dry on the surface of the samples, the pH of the concrete was 3. Once the solid residue that was left behind by the stain was removed by washing the sample with water and scrubbing it with a nylon brush, the pH of the sample was 5.

Following washing, the samples were soaked in a 1 Mol/Liter solution of NaHCO₂ to neutralize any residual acid. After the samples were removed from the NaHCO₂ bath, the pH of the concrete was 8. After the samples were dry the pH dropped down to 6. The application of the water repellent had no effect on the pH of the samples. The pH of all the samples at the start of the weathering cycles was 6. After the samples were removed from the Weatherometer, the pH of the concrete was 6; there was no difference in pH in the water repellent treated samples. For each of these pH measurements a minimum of five samples was selected at random from the larger cohort.

Samples that were removed from the site for Julianne Wiesner-Chianese's 2015 thesis were also measured for pH. The samples that were tested included a large core that was taken in 2014 and a spalled fragment that was collected in 2014. Each sample was measured three

times, to ensure the accuracy of the reading. The surface of the core and the side of the core both had a pH of 7. A small piece was broken off the large spall to expose a fresh surface; the pH of the broken face was also 7. A neutral pH is to be expected for concrete that has been exposed to the elements for over 50 years.

This comparison shows that the pH of the original concrete is significantly lower than the pH of the freshly cast, facsimile samples. Whether the pH of the original concrete is sufficient to achieve full precipitation of the metallic ions in the acid-stains will have to be determined by further field testing or by the acquisition of larger samples for laboratory testing.

Spectrophotometry

The primary method of testing was used to determine the color stability of the acid-stains was spectrophotometry. Evaluating the color of an object is inherently difficult because one's perception of a color changes based on the ambient lighting and on the surrounding colors. A spectrophotometer is a device that utilizes an established color system to accurately measure a color; these quantified measurements can then be used for comparative purposes.

The human eye is capable of perceiving three different variables of color: hue, saturation, and lightness. The spectrophotometer measures these three variables to determine if and how a color changes. For this testing series, measurements were taken with the CIELAB color system, which was developed in 1976. Each measurement taken in CIELAB color space has an L*, a* and b* value. The L* value represents the light to dark value, with 100 representing pure white and 0 representing pure black. The a* value represents the greenness or redness of a color, with negative values representing green, positive values representing red and zero representing a neutral value. Similarly, the b* value represents the blueness or yellowness of a color, with negative values representing blue, positive values representing yellow and zero, once again, representing a neutral value. When these three values are combined they identify a unique, standardized color within the CIELAB color space.

Prior to weathering each of the samples was measured to get a baseline reading of the stain's color. By design, the samples have an inherent amount of variability, since they were stained with three different colors and were deeply textured. Therefore each sample was measured five times in five different locations, and then the computer software averaged the results of these five measurements. In order to be as consistent as possible the measurements were taken in the same approximate location each time. A measurement was taken in each of the four corners and then a final measurement was taken in the center of the sample. The averaged value was utilized for comparison between samples.

During the weathering process, the Weatherometer was paused approximately every 120 hours and the samples were removed from their brackets and color measurements were taken. Stopping the machine at approximately 120 hour intervals ensured that the samples were always dry when they were removed from the machine. Each time the samples were removed, five measurements were taken using the same method described above and averaged. The objective of these intermediary measurements was both to determine how many hours of exposure were necessary to initiate damage, and to track the rate of progression once damage had begun.

After the weathering testing was complete, the Delta E (ΔE^*) was calculated to determine the amount of color change before and after weathering. The equation used for the calculation is as follows:

$$\Delta E_{ab}^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

This equation calculated the overall change in color in the samples, while calculating the difference for each variable showed the amount of change that occurred on each axis. By isolating the color into different variables it is possible to determine not only how much a color has changed, but also the manner in which it changed (e.g. became more blue, less green etc.). For further discussion about how the color of the samples changed throughout the weathering cycles, see Chapter 6.

T-Test

To determine if the differences between the before and after readings that were detected by the spectrophotometer were statistically significant, A paired T-test was run on the results. A t-test is an equation that compares the recorded data with the normal distribution of a data set, which falls along the Gaussian curve. The calculations were done using Microsoft Excel and the results of the t-test can be found in Appendix G. The t-test equation is as follows:

$$t = \frac{\overline{x_1} - \overline{x_2}}{\sqrt{\frac{S_1^2}{N_1} + \frac{S_2^2}{N_2}}}$$

$\overline{x_1}$ = the mean of the first sample set

$\overline{x_2}$ = the mean of the second sample set

S_1^2 = the variance (squared standard deviation) of data set 1

S_2^2 = the variance (squared standard deviation) of data set 2

The results of the t-test are discussed in Chapter 6.

Accelerated Weathering

The samples were weathered in a QUV Weatherometer. The Weatherometer is a machine that artificially weathers materials in an accelerated timeframe by exposing samples to repeated wetting and drying cycles and intense amounts of ultra violet light. The weathering cycles are designed to simulate years of material degradation, which results from prolonged exposure to rain, sunlight and water vapor within a few weeks (QUV Accelerated Weathering Tester, 1993). The kinds of damage that can be induced include fading, loss of color, loss of sheen, crazing, hazing, chalking, embrittlement and loss of strength. The results of the accelerated weathering can then be used to project how a material will perform when exposed to natural weather patterns.

Although the weatherometer can provide information about the durability of a given material or treatment, particularly when utilized comparatively, it is important to acknowledge that it is not possible to determine a precise lifespan for a given material based on accelerated weathering data. Material degradation patterns and rates will vary based on the local climate and the specific weathering patterns materials are exposed to. Additionally artificial weathering machines cannot accurately simulate the level of variability and intermittent extremes that occur in the natural environment; therefore it is not possible to make a direct comparison between natural and artificial weathering. The primary purpose of lab-based artificial weathering tests is to create repeatable, accelerated deterioration in a material to establish performance standards, not to determine a specific lifespan (Wypych 2008, 211). Although artificial weathering is a valuable tool in understanding the durability and performance of different materials, it does not provide all the answers. The best method for determining the long-term durability of a material in a specific situation is an in situ mock-up. Therefore, in order to determine if it will be feasible to re-treat the exterior concrete of Jackson Lake Lodge with acid-stains, the next critical phase of testing will be in situ mock-ups.

Description of how the Machine Works

The QUV Weatherometer consists of a 54" by 21" weathering chamber, supported on a corrosion resistant rolling frame. Inside the weathering chamber there are eight fluorescent UV lamps that are arranged in rows of four on either side. This arrangement ensures equal exposure across all samples in the machine. In the space between the two center light tubes there are six spray nozzles, which deliver a fine mist of cold water at specified intervals and durations. At the base of the weathering chamber there is a tray, which collects the water from the spray cycle. There is also a plumbed connection to the chamber that will fill the tray if the water feed unit indicates that the water level is too low; the water level in the tray must remain between 10mm

and 15mm to produce adequate condensation. In an ideal set up, the plumbed connection would provide deionized water for the spray cycle, however, regular tap water was used for this testing series. Below the collection tray, there is a heating element. The heating element warms the water causing it to evaporate, which fills the chamber with water vapor. The relative humidity inside the chamber during the condensation cycle is 100%.

The samples are placed in brackets that are aligned parallel to the lamps. There is a small gap between the trays that hold the samples and the doors that swing down over them. When the samples are in the Weatherometer, it is essential that all gaps between the sample brackets are filled either by additional brackets outfitted with flat aluminum panels or by flat metal panels that are sized to fit the gaps that occur depending on the size of the bracket utilized for the testing program. This creates a seal so the samples (and their brackets) form the wall of the chamber, which encapsulates the condensation. The back side of the samples is exposed to the ambient air temperature, which is much cooler than the interior of the chamber. This temperature

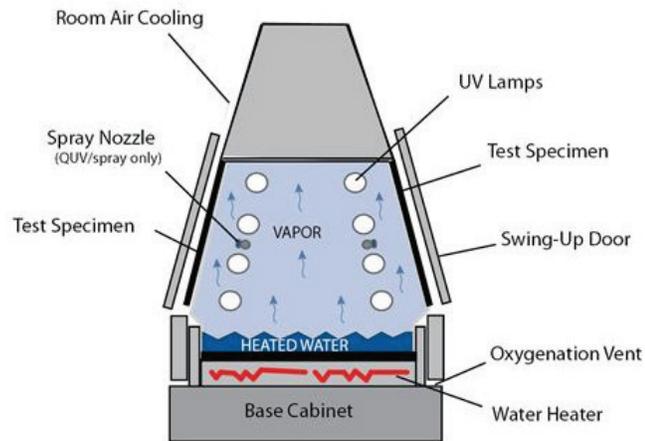


Figure 23: Cross section of the QUV Accelerated Weathering machine. Image credit:

differential between the front and the back of the sample creates the necessary and sufficient conditions for condensation to be produced.

Light Source

The Weatherometer can be used with either a UVA-340 or UVB-313 light bulb. The wavelength for UVA light ranges between 400 and 315 nm, while the wavelength of UVB light ranges between 280 and 315 nm. There is a direct correlation between the size of a light's wavelength and its ability to cause damage; the smaller the wavelength the more photo degradation it causes. The rate of damage that results when using the UVA bulbs is more similar to the rate of deterioration in natural weathering. However, UVB bulbs were utilized in this testing regimen because exposing the samples to the most intense, most damaging light possible would allow UV degradation to be more likely detected in the condensed time frame of this thesis.

Cycle Selection

There are three typical cycles that are used with UVB-313 light bulbs in a QUV Weatherometer. The first option has an irradiance, which is a measurement of the intensity of the light exposure per unit of surface area, of $0.63 \text{ Wm}^{-2}\text{nm}^{-1}$ at wavelength 310 nm and paired with alternating four hour cycles of UV and condensation. The temperature during the UV cycle was $63\pm 3^\circ\text{C}$ and the temperature during the condensation cycle was $50\pm 3^\circ\text{C}$ (Wypych 2008, 186).

The second standard cycle has an irradiance of $0.55 \text{ Wm}^{-2}\text{nm}^{-1}$ at wavelength 310 nm paired with an eight hours UV cycle followed by a four-hour condensation cycle. The temperature during the UV cycle was $70\pm 3^\circ\text{C}$ and the temperature during the condensation cycle was $50\pm 3^\circ\text{C}$ (Wypych 2008, 186).

The third standard cycle has an irradiance of $0.44 \text{ Wm}^{-2}\text{nm}^{-1}$ at wavelength 310 nm paired with an twenty hours UV cycle followed by a four-hour condensation cycle. The

temperature during the UV cycle was $80\pm 3^{\circ}\text{C}$ and the temperature during the condensation cycle was $50\pm 3^{\circ}\text{C}$ (Wypych 2008, 186).

Each standard could also incorporate a spray cycle at the beginning of each condensation cycle, which was intended to induce thermal shock. The spray cycle could last anywhere from one minute to an hour.

For this testing program the first standard was selected with a five minute spray cycle at the beginning of each condensation cycle. The first standard was utilized because it exposed the samples to the most damaging intensity of UV light. The climate in Wyoming, where the lodge is located, experiences extremely high levels of UV radiation, therefore the ability of the samples to withstand UV degradation was of particular interest in this testing program.

Irradiance Control

The Weatherometer is equipped with a solar eye panel, which allows the UV-B light bulb to be calibrated so that it always emits a consistent amount of irradiance. Under normal circumstances the level of irradiance that a light bulb produces fluctuates with the ambient temperature; when the temperature rises, the amount of irradiance emitted is decreased (QUV Accelerated Weathering Tester, 1993). Additionally as the light bulbs age, they give off less irradiance. The solar eye panel eliminates these fluctuations by keeping the light bulbs calibrated to emit a specified amount of irradiance regardless of changes in the ambient temperature. The panel also monitors the life cycle of the light bulbs, and alerts the user when the bulbs are no longer capable of producing the necessary threshold of irradiance for a given testing program (QUV Accelerated Weathering Tester, 1993).

Securing the Samples

Although the samples were sized to fit the Weatherometer brackets, it was still necessary to secure them into the brackets to ensure that they would remain in place during the weathering cycles. The samples were secured with a piece of polyethylene foam on one side and a wooden tongue depressor on the other. A narrow strip of polyethylene foam was placed on the left side of the bracket first, then the sample was set into place in the center of the bracket. To create a tighter fit, the samples were pressed into the foam to create a small gap on the right side of the bracket, and the tongue depressor was wedged into place. This created a pressure fit between the sample and the walls of the bracket. The foam gave the samples an appropriate amount of cushion. Prior placement, which utilized a tongue depressor on each side of the bracket, resulted in chipping the edges of the samples. In addition to the foam, a block of wood was placed at the base of the bracket to prevent the samples from sliding down below the exposure window.



Figure 24: Samples in their brackets in the weatherometer. Image by author.

Testing Schedule

The samples were removed from the Weatherometer approximately every 120 hours, which is equivalent to every 30 cycles. Each time the samples were removed they were photographed and measured with the spectrophotometer. ASTM D 4587 – 11 calls for the samples to be checked every 100 hours; however, if the machine had been stopped every 100 hours, the samples would have been evaluated at different points during the weathering cycles, which means that sometimes they would be wet while at other times they would be dry. Since the performance of the stain was being evaluated by color, this measurement schedule would result in unusable data. Therefore the ASTM protocols were modified and the machine was stopped every 120 hours, which fell halfway through the UV cycle. This ensured that the samples would be dry when the photos and measurements were taken, and that the samples would have ample time to reheat during the second half of the UV cycle. It is essential that the samples are hot at the beginning of the condensation cycle so that they experience thermal shock when the water spray turns on at the beginning of the condensation cycle.

Microscopy

Microscopy was performed on the concrete samples that were removed from Jackson Lake Lodge in 2015 and on fragments of the facsimile samples that were cast for this thesis. The objective of the microscopic analysis was to learn more about the characteristics of the original stain and to compare the stains on the facsimile samples to those that were found on the building. Another objective was to determine the depth of the stain's penetration.

Samples JJJL_1 thru JJJL_5 were taken from a large fragment of concrete, approximately 5 to 7 inches, that had spalled off the building. The spalled fragment is coated with the modern, resinous stain that was applied c. 2000; however, it is likely that traces of the original finish

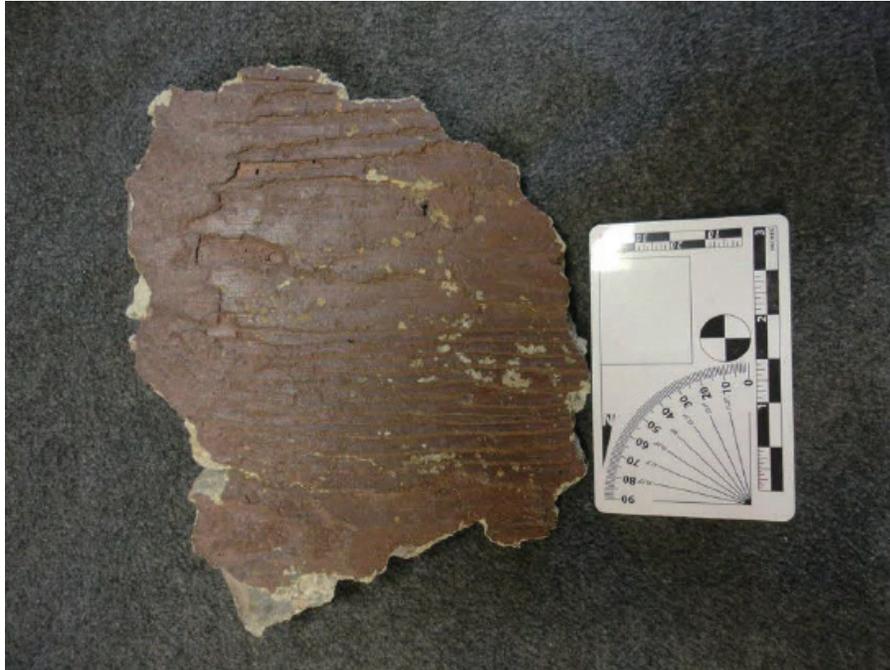


Figure 25: Large spall that samples JLL_1 thru JLL_5 were cast from. Image credit: Julianne Wiesner-Chianese.

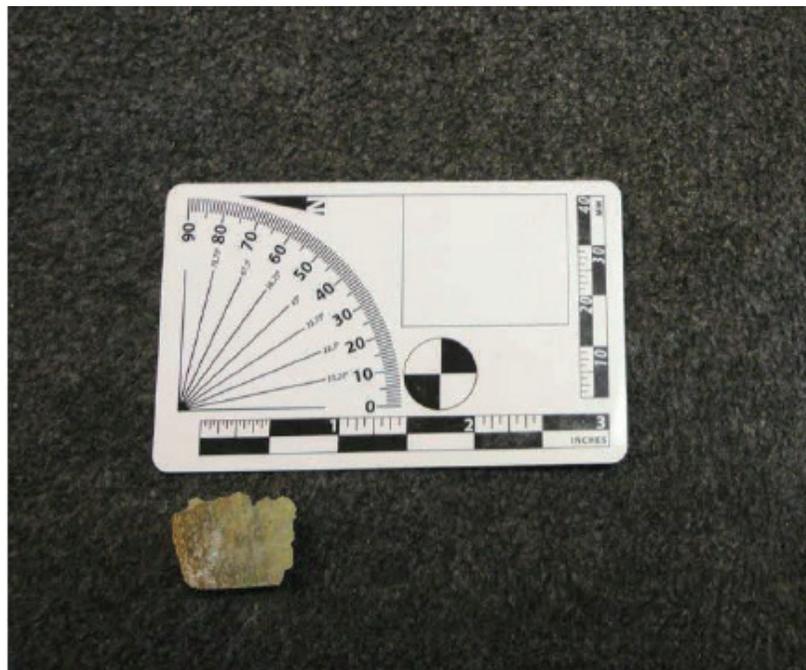


Figure 26: Fragment removed from about the Blue Heron Bar that samples JLL_6 and JLL_7 were cast from. Image credit: Julianne Wiesner-Chianese.

were still present underneath the modern stain. Therefore samples were cast to determine if the original stain survived on any of the concrete surfaces. Additionally, the original stain was reportedly stripped and acid etched before the application of the modern resinous stain; therefore, the samples were examined for traces of stripping or acid etching.

Samples JLL_6 and JLL_7 were cast from a portion of the concrete that was removed from the area above the Blue Heron Bar that was enclosed by the 1988 addition where the original stain is still exposed. The fragment, from which the samples JLL_6 and JLL_7 were taken, was removed from the Lodge by Frank Matero in 2015. It was a very small sample of concrete and allowed for only limited finishes analysis. Due to time and scope limitations, a thorough investigation of the remaining finishes was not conducted. When conducting a finish analysis the sample locations are essential to the accuracy of the study's findings. Therefore in order to determine if these samples are representative of the original finish a much more in depth study would have to be conducted. However, a site visit was not part of the scope of this thesis, therefore the samples that were removed in 2015 as part of a different scope of work were the only samples that were available for the finish analysis. This enclosed area of the original stain appears to be very different in color from historic images of the lodge. It has a grayish brown color and appears more like driftwood than redwood, which was how the original stain was described. Therefore these samples were examined to determine if there was a perceptible difference between any traces of the original stain that might be found beneath the modern stain. These samples were also examined for any evidence of a leaching deposit or an encrustation, which could be responsible for the concrete's gray appearance in this area.

Finally fragments of the facsimile samples were also cast. These samples were examined to see how similar the lab applied stains were to the original. These samples also allowed the porosity of the concrete in the modern samples to be compared with the porosity of the original concrete.

Casting Process

The first step in the casting process is to isolate small fragments from the larger bulk samples. The selected fragments were embedded in BioPlast™, which is a polyester casting resin. Once embedded, the resin hardens over several hours creating a plastic cube. After the resin had hardened, parallel cuts were made through the samples with a Buehler Isomet 1000 precision saw to reveal a cross-section. The cross-section was then polished using different grades of abrasive cloths to remove the saw marks and to improve the visibility of the samples. Once the samples were polished they were mounted to a glass slide for microscopic evaluation.

Microscopic evaluation

The samples were examined with a Nikon Alphaphot-2 YS2⁷ microscope using both visible and filtered ultraviolet (UV) light. UV light is used to reveal auto-fluorescence, which is a characteristic of many finish materials. The presence of auto-fluorescence can help identify different layers of finishes, and, in some circumstances, it can help reveal finish composition. The samples were thoroughly examined and pertinent data recorded. Representative photographs were also taken of the samples in both visible and UV light using a Nikon DS Fi-1 Camera and NIS Elements BR Software. These photos can be found in Appendix E.

Observations

On samples JLL_1 thru JLL_5 the original stains were present under the modern resinous coating. Variation in the color of the base layer can be seen across the substrate. This suggests that the initial layer of stain did not fully coat the concrete substrate. Rather it may have been applied sporadically, so that when the subsequent stains were applied, they overlapped the bottom coat of stain in some areas but not in others. The predominant color that can be seen is an

⁷ This microscope was retrofitted to include Ultraviolet Light.

orange-brown; however, there is significant variation within this color range. A dull blackish-gray is also visible in some areas. The depth or penetration varies widely across the samples. In some areas it is as shallow as approximately 50 mm; in other areas it is as deep as approximately 300 mm. This is consistent with historical descriptions of the application of the colors by applying and wiping the individual colors to create a variegated appearance.

Although the five samples show consistent findings, they were all removed from the same large spall. Therefore, it is not possible to know if these samples are representative of what might be found on the entire building. The samples do, however, confirm that the original stains exist under the modern stain and that a comprehensive paint study, analyzing samples from multiple locations on the building, could potentially yield important information about the original finish on the building.

Samples JLL_6 and JLL_7 are significantly more gray than samples JLL_1 thru JLL_5. The altered appearance of these samples may be due to weathering, or the finish in this area may have been altered when it was enclosed as part of the 1988 addition. Further finish investigation, with multiple samples from the different elevations of the Lodge, will have to be undertaken in order to determine if either hypothesis is correct.

Samples JLL-8 thru JLL-12 showed that the facsimile samples were much more porous than the original concrete substrate. This is not a revelation, as it was clearly apparent with the naked eye. This difference in porosity can be attributed to the different casting methods. In the molds, the textured "face" of the concrete was on the bottom, whereas when the original concrete was cast the textured "face" would have been on the side. Therefore, gravity caused the aggregate in the molds to settle on the "face" side of the sample. Additionally, the original formwork would have absorbed water from the concrete, which would have drawn the paste towards the plywood creating a less porous surface. The difference in porosity caused the stain to penetrate more deeply into the facsimile samples than the original concrete. Finally the sheer

mass of the large volume of concrete poured into the formwork on site would have created greater pressure and compacting of the surfaces than on the small hand-packed replicate samples.

The depth of penetration was also likely affected by the fact that the original stains were applied to a vertical concrete surface and the stain was applied to the facsimile samples while they were lying face-up on a tray. Therefore, the acid-stains stayed on the surface of the facsimile samples longer than they would have stayed on the surface of original concrete.

Despite the difference in porosity the stain appears to have reacted with the facsimile samples in a similar manner to the original. The stain appears as an orange-brown color with a considerable amount of color variation. There are some sections where the darker stain is clearly visible. The appearance of the facsimile samples is consistent with early descriptions of the building.

Chapter 6: Results

The accelerated-weathering testing program utilized two cohorts of five. The first cohort of 5 (Numbers A_I thru A_5) were stained with four coats of acid-stain and then coated with Repels®, which is a waterborne silane/siloxane emulsion that is manufactured by Empar Corp. and is part of the Kemiko product line. The second cohort (Numbers A_VI-A_X) was stained with the same application of acid-stain, but was not coated with the water repellent.

Once the spectrophotometry data were compiled, they were analyzed statically to determine if the changes that were observed were statistically significant. According to this analysis the sealed cohort showed a statistically significant change for both the A and B values. That translates to a change on the black to white spectrum and on the red to green spectrum. The mean value of the pre-weathering L* measurements was 34.13, while the mean of the post-weathering L* measurements was 33.34. Therefore, after weathering, the sealed cohort was slightly whiter than it was at the start of testing. The mean value of the pre-weathering a* measurements was 12.64, while the mean of the post-weathering a* measurements was 11.14. Therefore after weathering the sealed cohort was slightly less red. This finding is consistent with the weathering patterns seen on the area of original concrete that was enclosed during the addition of the Blue Heron Bar.

The unsealed cohort shows a statistically significant change in the L value only. Therefore it only exhibited changes on the black to white spectrum. The mean of pre-weathering L* value was 35.29, with the mean of the post-weathering L* values was 31.52. Therefore the unsealed cohort was also slightly whiter post-weathering. However no other statistically significant changes were observed.

It is possible that although the water repellent that was applied to the first cohort improved the water repellency of those samples, it did not prevent the color of the acid-stains from changing. Initial testing suggests that it may have affected the red pigmentation of the

stain; however retesting with a larger number of samples size would more conclusively determine if the Repels® water repellent does in fact have a negative impact on the performance of the acid-stains.

Reinforcing the analysis of the data compiled for this thesis, the color change before and after weathering was virtually imperceptible with the naked eye. It is possible that if the accelerated weathering had continued, there might have been visually perceptible changes in the color. However, the performance of the stains in this thesis, the documentation of their use on historic buildings, and their specific performance on the Jackson Lake Lodge prove that acid-stains are a stable and durable finish for exterior concrete.

Chapter 7: Conclusions and Recommendations

It is clear from the accelerated weathering testing that acid stains applied to freshly cast concrete create a durable stain. During the testing program they endured tremendous amounts of UV exposure, as well as repeated wetting/drying cycles and thermal shocking, with little impact. However the next question to be addressed is if the stains could be applied to the historic concrete. As mentioned in the chapter on acid stains, it is possible that some colors will not work on the historic substrate, or that they may result in an unintended color if all of the metallic salts are unable to precipitate out. Additionally, the pH of the substrate is most likely not uniform across the building; therefore, different portions of the building could be more reactive, creating patches of more intense color. Undeniably, retreating the lodge with acid based stains will be complicated and labor intensive. However once it is done, testing suggests that it will prove to be a durable, high performing stain.

Historic photos confirm that the original stains, were never perfectly uniform – some areas appeared streaky or splotched from the start. Establishing how much variation in color will be tolerated, will be an essential step in determining if the lodge can be retreated with acid stains. Another important decision that will inform the preservation choices made for the Jackson Lake Lodge will be determining if the experimental use of materials, which was typical of mid-century architecture, is going to be a facet of the lodge's interpretation. If so, the tolerance for variation and imperfection would likely be higher.

If acid stains can be used, additional testing will have to be conducted to ensure that the surface texture of the concrete is not harmed by the reapplication of an acid stain. Preliminary testing on the weathered samples showed that it might be possible to retreat concrete with a pH as low as 6. However, the neither the samples size nor the samples themselves were large enough to determine if the stains would reliably precipitate on concrete with such a low pH, or if the appearance of stains would be at all consistent across larger surfaces.

Preliminary tests of the historic concrete substrate reveal that it has a pH of approximately 7. However only two small samples of the historic concrete were available for pH testing; therefore, it is not possible to say whether the pH readings from those samples are at all representative of the overall substrate at Jackson Lake Lodge. Large scale field mock-up are a necessary next step to determine if the acid stains are a viable candidate to recreate the original stain.

An on-site testing program should be developed that includes several large scale mock up on different areas of the building where the concrete is known to be of different ages, and where the historic concrete show signs of deterioration due to exposure. In these areas, the existing modern finish should be stripped, and the acid stains should be applied. Since the acid-stains have already been tested for long-term durability in the lab, the primary goals of the field testing will be to evaluate the ability of the stains to replicate the original "redwood" color and the consistency of the color on large areas of the exterior concrete. A certain amount of natural variation, which is typical of acid-stains, is to be expected. However, large blotches of color within one panel or a drastic difference in the color development between two panels could be evidence that acid stains will not perform well on a large scale.

If the acid stains do perform well on the original substrate, tests should be conducted to determine if the stains have any compromising effects on the strength of the concrete. To do this, small samples could be removed from the mock-up area where acid based stains were applied and from an area where the concrete was stripped but not re-stained. These samples should then be tested for differences in both porosity and abrasion resistance.

If acid stains to not perform adequately on the historic substrate, alternative high-performance coatings should also be mocked up – first on a small scale and then on a larger scale. Two possible kinds of coating that should be tested are mineral silicate paints and polymer stains.

Like acid stains, mineral silicate paints react chemically with the concrete substrate rather than forming a film on top. The paints combine water glass, which is a potassium silicate solution, with color pigments (Wilson 1964, 112). The potassium silicate solution functions as a binder with the concrete substrate, embedding the pigments in the matrix. Mineral silicate paints have a history of high durability and performance due to their colorfast pigments and high levels of vapor permeability (Wilson 1964,112). Since the paints bond with the concrete matrix, rather than forming a film on top, they would not obscure the materiality of the concrete, which might make them a good candidate for reproducing the original translucent aesthetic that once defined the Lodge.

Another media that should be tested are reactive polymer stains for concrete. Many of the companies that sell acid-based stains for concrete are selling reactive polymer stains as an alternative. These stains use acrylic and inorganic silicate polymers to bind with the cement substrate, creating a durable, UV resistant coating (Scofield Systems, 2014. 1). These stains are capable of creating the same translucent appearance that is typical of other reactive stains (Envirostain Website). The stains were specifically design as an acid-free alternative for acid stains, so it is likely that they could produce similar results as the original products.

Regardless of what product is used to recreate the original “redwood” appearance of the concrete, it is essential that a water repellent is incorporated into the next exterior finish treatment. In order for the water repellent to be beneficial it must be highly vapor permeable, so moisture is not trapped within the concrete. As previously mentioned, excess moisture in the concrete is one of the principle causes of deterioration in concrete structures, as it causes the embedded ferrous reinforcements to corrode. Therefore to ensure the long-term preservation of the Lodge, this added level of protection against the elements is necessary. The water repellent should be carefully researched and tested prior to its widespread application to ensure that it will not obscure the texture and restored color of the concrete.

Restoring the original appearance to the exterior concrete of Jackson Lake Lodge is one of many important tasks that the Grand Teton Lodge Company will have to undertake as the stewards of this significant, and greatly underappreciated, National Landmark. The Jackson Lake Lodge is an important International Style building within the rich architectural heritage of America's National Parks. Its use of acid-stained concrete to replicate natural finishes is a significant character-defining feature of Underwood's design. Future work should be directed towards replicating the Lodge's original exterior finishes, using both the testing and data assembled for this thesis and future field testing. Furthermore, Underwood's intentionality can be seen throughout his design of Jackson Lake. Given the character of the International Style of Architecture, it is essential that future alterations to Jackson Lake Lodge be done with the same intentionality.

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Appendix A: Literature Review

Literature Review

History of Concrete

Concrete is one of the most economical and versatile building materials in world. Freshly-mixed concrete has the consistency of wet plaster but as it cures it takes on many of the physical properties as stone, such as durability and compressive strength; when it is used in conjunction with reinforcing steel, which provides tensile strength, it can be sculpted into any shape imaginable (Addis & Bussell, 2003).

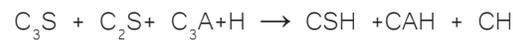
Although concrete was used during ancient times, the technology was largely lost during the middle ages and was not rediscovered until the late 1700's when John Smeaton, of England, rediscovered hydraulic cements. Experimentation with cement continued throughout the following decades and resulted in many technological advances including the creation of Portland cement by Joseph Aspdin in 1824 in England. Portland cement was introduced in the United States in 1868 (Loewenberg, 1987, Torraca, 2009). After the creation of Portland cement, concrete began to slowly be incorporated as a building material, but was mostly limited to foundations, masonry back-ups and experimental structures. The widespread usage of concrete didn't really take off until the World Wars in the 20th century, which necessitated the use of cheap, quick building materials.

Concrete Composition

Portland cement is produced by burning limestone and clay to create clinker; Clinker is comprised of tri-calcium silicate, di-calcium silicate, tri-calcium aluminate and calcium aluminum ferrite. The clinker is then finely ground and mixed with a small amount of gypsum, which reduces the set time of the concrete (Torraca, 2009).



Modern concrete is comprised of four different elements: cement, aggregate, admixtures and water. Water combines with the cement initiating the hydraulic reaction which causes the cement to harden and to create an alkali paste that binds the aggregate together. The aggregate provides volume and compressive strength and the admixtures are used to alter specific properties of the concrete including, set time, strength, plasticity etc. (Macdonald, 2005). During the mixing process the of tri-calcium silicate, di-calcium silicate, tri-calcium and water react to form calcium silicate hydrate, calcium aluminate hydrate and free lime (Torraca, 2009). The setting reaction of Portland Cement is as follows (Torraca, 2009):



Once the concrete has formed it quickly begins to absorb carbon dioxide from the air causing the concrete to carbonate from the outside surface in. The carbonation process significantly reduces the pH of the concrete (Torraca 2009).

Curing Concrete

The presence of water is required for hydraulic cement to undergo a chemical reaction necessary to become an alkali paste. If the water evaporates from the freshly-mixed concrete too quickly, the strength of the paste is compromised. Therefore retaining the water in the concrete by controlling the rate of evaporation is essential to the final strength of the finished product. This process is referred to as curing (Wilson, 1962, Macdonald, 2005).

Decorative Concrete

When concrete was first introduced in the United States it was primarily used as a back up material for masonry veneers. Beginning in the early 20th century J.J. Earley began to experiment with surface decoration so that the concrete could be left exposed. (Earley, 1918).

These experiments included adjusting the color using pigments or colored aggregates. Throughout the first half of the 20th century a wide variety of surface treatments were developed for concrete, including tooling, texturing and abrading. These techniques allowed the concrete to remain exposed (Loewenberg, 1987). By the middle of the 20th century the modernism movement had embraced the look of raw concrete and the importance of formwork came to the forefront (Wilson, 1962).

Acid Stains

Acid stains are comprised of hydrochloric acid and metallic salts. The hydrochloric acid reacts with the calcium hydroxide in the concrete, etching the surface, and allowing the metallic salts to penetrate into the concrete and bond with the substrate. Acid stains penetrate between 1/8th and 1/16th of an inch, depending on the porosity of the concrete (Goodman, 2005).

Mineral Silicate Paints

Mineral silicate paints are paints that utilize sodium and potassium silicate as a binder. This composition is not affected by the alkalinity of the cement and is vapor permeable (Wilson, 1962).

Accelerated Weathering

A QUV Weatherometer is an accelerated aging device that is designed to expose samples to extreme weather patterns in an effort to predict their long term performance. The standard test time is 1000 hours, which is roughly 6 weeks. During this time the samples are exposed to repeated wetting and drying cycles, high heat, and extreme levels of UV (Wypych, 2013).

Appendix B: Mock-up List

Mock-up List

Sample Number	Stain Sequence	Stain Dilution	Application Method
1A	Cola Black Tan	1 1 1	Brush
1B	Cola Black Tan	1 1 1	Sponge
2A	Cola Tan Black	1 1 1	Brush
2B	Cola Tan Black	1 1 1	Sponge
3A	Tan Cola Black	1 1 1	Brush
3B	Tan Cola Black	1 1 1	Sponge
4A	Tan Black Cola	1 1 1	Brush
4B	Tan Black Cola	1 1 1	Sponge
5A	Black Cola Tan	1:1 1:1 1:1	Brush
5B	Black Cola Tan	1:1 1:1 1:1	Sponge
6A	Cola Black Tan	1:1 1:1 1:1	Brush
6B	Cola Black Tan	1:1 1:1 1:1	Sponge
7A	Tan Cola Black	1 1:1 1	Brush
7B	Tan Cola Black	1 1:1 1	Sponge
8A	Tan Cola Black	1:1 1:1 1	Brush
8B	Tan Cola Black	1:1 1:1 1	Sponge
9A	Cola Black	1 1	Brush
9B	Cola Black	1 1	Sponge
10A	Cola Tan Black Black	1:1 1:1 1:1 1:1	Brush
10B	Cola Tan Black Black	1:1 1:1 1:1 1:1	Sponge

Table 3: Table showing the different sequences, dilutions and application methods that were tested.

Appendix C: Material Safety Data Sheets



SAFETY DATA SHEET

Print date:

Revision Date: 04/01/2015

Revision Number: 1

1. COMPANY AND PRODUCT IDENTIFICATION

Product identifier

Product Name: KEMIKO® REPELS
Product code: K51-1

Other means of identification

Synonyms No information available.

Application

Recommended Use Water Repellent
Uses advised against For industrial use only

Supplier/Manufacturer:

Supplier:
EPMAR Corporation
13240 E. Barton Circle
Whittier, CA 90605-3254
Phone: 562-946-8781
FAX: 562-944-9958
E-mail: she@quakerchem.com
(For Health and Safety Questions)

Emergency telephone number:

* 24 HOUR TRANSPORTATION:
**CHEMTREC: 1-800-424-9300
+703-527-3887 (Call collect outside of US)
* 24 HOUR EMERGENCY HEALTH & SAFETY:
**(800) 523-7010 (Within US only) Outside of US call (703)
527-3887

2. HAZARDS IDENTIFICATION

Classification

OSHA Regulatory Status

This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

Reproductive toxicity	Category 2
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K51-1 - KEMIKO® REPELS

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Revision Date: 04/01/2015

Label Elements

Emergency Overview

WARNING		
Hazard Statements Suspected of damaging fertility or the unborn child		
		
Appearance Colorless	Physical State Liquid	Odor Characteristic

Precautionary Statements - Prevention

Obtain special instructions before use
Do not handle until all safety precautions have been read and understood
Use personal protective equipment as required

Precautionary Statements - Response

IF exposed or concerned: Get medical advice/attention

Precautionary Statements - Storage

Store locked up

Precautionary Statements - Disposal

Dispose of contents/container to an approved waste disposal plant

Hazards not otherwise classified (HNOC)

None known

Other Information

None known

Unknown acute toxicity

0% of the mixture consists of ingredient(s) of unknown toxicity

3. COMPOSITION/INFORMATION ON INGREDIENTS

Components	CAS No.	Weight %
Octamethylcyclotetrasiloxane	556-67-2	<1%

This product does not contain any hazardous ingredients as defined under 29 CFR 1910.1200.

The exact percentage (concentration) of composition has been withheld as a trade secret.

4. FIRST AID MEASURES

General advice:

Show this safety data sheet to the doctor in attendance. Remove contaminated clothing and shoes. Wash contaminated clothing before re-use. Wash off with soap and water. If symptoms persist, call a physician.

Eye contact:

Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes.

Skin contact:	Remove contaminated clothing and shoes. Wash contaminated clothing before re-use. Wash off immediately with soap and plenty of water.
Ingestion:	If swallowed, seek medical advice immediately and show this container or label. Do not induce vomiting without medical advice. Never give anything by mouth to an unconscious person.
Inhalation:	Move to fresh air in case of accidental inhalation of vapors. If breathing is difficult, give oxygen. If not breathing, give artificial respiration. Consult a physician.
Note to physician:	Treat symptomatically.
Medical condition aggravated by exposure:	Dermatitis.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media:	Use dry chemical, CO2, water spray or `alcohol` foam.
Specific hazards:	Do not allow material to contaminate ground water system.
Special protective equipment for fire-fighters:	As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.
Specific methods:	Water mist may be used to cool closed containers.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions:	Ensure adequate ventilation. Avoid contact with skin, eyes and clothing. Do not breathe vapour/dust. Use personal protective equipment. Wash thoroughly after handling
Environmental precautions:	Do not flush into surface water or sanitary sewer system. Prevent further leakage or spillage if safe to do so.
Methods for cleaning up:	Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Sweep up and shovel into suitable containers for disposal.

7. HANDLING AND STORAGE

Handling

Technical measures/precautions:	Provide sufficient air exchange and/or exhaust in work rooms.
Safe handling advice:	In case of insufficient ventilation, wear suitable respiratory equipment. Do not breathe vapors or spray mist. Avoid contact with skin and eyes. Wash thoroughly after handling.

Storage

Technical measures/storage conditions: Store at room temperature in the original container

Incompatible products: Strong oxidizing agents

Safe storage temperature: 15 - 40 °C

Shelf life: 6 months

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering measures: Ensure adequate ventilation.

Personal Protective Equipment:

General: Eye Wash and Safety Shower

Respiratory protection: If engineering controls do not maintain airborne concentrations to a level which is adequate to protect worker health, a NIOSH-certified respirator with organic vapor/P100 filter should be worn.

Eye protection: Safety glasses with side-shields.

Hand protection: Neoprene gloves

Skin and body protection: Long sleeved clothing

Hygiene measures: Avoid contact with skin, eyes and clothing.



9. PHYSICAL AND CHEMICAL PROPERTIES

Physical State	Liquid
Appearance	Colorless
Odor	Characteristic
Odor Threshold	No information available.
pH:	5.88
pH Dilution	No information available
Melting/freezing point	No information available
Boiling Point/Range	~ 100 °C / 212 °F
Flash Point	No information available

Method	No information available
Evaporation rate	No information available
Flammability Limits in Air	
upper flammability limit	No information available.
lower flammability limit	No information available.
VOC Content	No information available
Vapor pressure	No information available.
Vapor density	No information available.
Specific Gravity (g/cc, 15 C)	0.998
Bulk Density (lb/gal, 15 C)	8.33
Water Solubility	Completely soluble
Solubility in other solvents	No information available.
Partition coefficient: n-octanol/water	No information available
Autoignition temperature	No information available
Decomposition Temperature	No information available
Kinematic viscosity	No information available
Dynamic viscosity	No information available
Molecular Weight	No information available

10. STABILITY AND REACTIVITY

Stability:	Stable under recommended storage conditions.
Conditions to avoid:	None known.
Materials to avoid:	Strong oxidizing agents.
Hazardous decomposition products:	None under normal use.
Hazardous Polymerization:	Not applicable.

11. TOXICOLOGICAL INFORMATION

No toxicological information is available on the product. Data obtained on components are summarized below.

Information on likely routes of exposure

Inhalation	May cause irritation of respiratory tract.
Eye Contact	Contact with eyes may cause irritation.

Skin Contact Prolonged contact may cause redness and irritation.

Ingestion Ingestion may cause gastrointestinal irritation, nausea, vomiting and diarrhea.

Components	LD50 Oral	LD50 Dermal	LC50 Inhalation
Octamethylcyclotetrasiloxane	1540 mg/kg (Rat)	794 µL/kg (Rabbit) 2400 mg/kg (Rat) 4640 mg/kg (Rabbit)	12.7 mg/kg (Rat) 4 h 17.6 mg/L (Rat) 1 h

Delayed and immediate effects as well as chronic effects from short and long-term exposure

Carcinogenicity The table below indicates whether each agency has listed any ingredient as a carcinogen

Components	IARC Carcinogens	NTP	OSHA - Select Carcinogens
Octamethylcyclotetrasiloxane	Not listed	Not listed	Not listed

Sensitization No information available.

Mutagenic effects: No information available.

Reproductive Toxicity Product contains a componet that is classified as a reproductive hazard. No testing has been conducted on the product itself.

Developmental Toxicity No information available.

Teratogenic No information available.

Specific target organ systemic toxicity (single exposure) No information available.

Specific target organ systemic toxicity (repeated exposure) No information available.

Aspiration hazard No information available.

Additional information on toxicological effects

No information available

12. ECOLOGICAL INFORMATION

Components	Ecotoxicity - Fish Species Data:	Ecotoxicity - Freshwater Algae Data:	Ecotoxicity - Water Flea Data:
Octamethylcyclotetrasiloxane	1001 500.5	No data	EC50 (Daphnia magna - 24h) = 25.2 mg/L

13.965% of the mixture consists of components(s) of unknown hazards to the aquatic environment

Persistence and Degradability No information available.

Bioaccumulation No information available.

Components	Octanol/water partition coefficient
Octamethylcyclotetrasiloxane	-

Mobility: No data available

Ozone: No data available

13. DISPOSAL CONSIDERATIONS

Waste from residues/unused products: Waste disposal must be in accordance with appropriate Federal, State, and local regulations. This product, if unaltered by use, may be disposed of by treatment at a permitted facility or as advised by your local hazardous waste regulatory authority.

Contaminated packaging: Do not re-use empty containers

Methods for cleaning up: Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Sweep up and shovel into suitable containers for disposal.

14. TRANSPORT INFORMATION

U. S. DEPARTMENT OF TRANSPORTATION:

Proper shipping name: Not Regulated

TDG (CANADA):

Proper shipping name: Not Regulated

IMDG/IMO:

Proper shipping name: Not Regulated

IATA/ICAO:

Proper shipping name: Not Regulated

15. REGULATORY INFORMATION

Federal Regulations

OSHA Hazard Communication Standard: This product is considered to be hazardous under the OSHA Hazard Communication Standard.

CERCLA/SARA Information:

SARA (311, 312) hazard class: This product possesses the following SARA Hazard Categories:

Immediate Health (Acute): Yes
 Delayed Health (Chronic): No
 Flammability: No
 Pressure: No
 Reactivity: No

Components	Hazardous Substances and RQs	Extremely Hazardous Substances and TPQs	SARA 313 Emission Reporting

Octamethylcyclotetrasiloxane	Not listed	Not listed	Not listed
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Clean Air and Clean Water Acts:

Components	Hazardous Air Pollutants	CWA - Hazardous Substances	CWA - Toxic Pollutants	CWA - Priority Pollutants
Octamethylcyclotetrasiloxane	Not listed	Not listed	Not listed	Not listed

U.S. STATE REGULATIONS (RTK):

Components	California Proposition 65	PARTK	MI Critical Materials	NJRTK	MARTK
Octamethylcyclotetrasiloxane	Not Listed	Not Listed	Not Listed	Not Listed	Not Listed

California Proposition 65 Status: No components are listed

RCRA Status: Not regulated

CANADIAN REGULATIONS:

Canada - WHMIS Classification Information: This product has been classified according to the hazard criteria of the CPR and the SDS contains all the information required by the CPR.

Canadian Product Classification: None Required

Product Classification Graphic(s):

Component Classification Data:

Components	WHMIS hazard class	CEPA Schedule I	Challenge Substances
Octamethylcyclotetrasiloxane	None	Not listed	Listed

INVENTORY STATUS:

United States TSCA - Sect. 8(b) Inventory: This product complies with TSCA

Canada DSL/NDSL Inventory List Compliance has not been determined

16. OTHER INFORMATION

Sources of key data used to compile the data sheet: Material safety data sheets of the ingredients.

Prepared by: Safety, Health and Environmental Department

Revision Date: 04/01/2015

Reason for revision: New Format.

Personal protection recommendations should be reviewed by purchasers. Workplace conditions are important factors in specifying adequate protection.

Disclaimer

This product's safety information is provided to assist our customers in assessing compliance with safety/health/environmental regulations. The information contained herein is based on data available to us and is believed to be accurate. However, no warranty of merchantability, fitness for any use, or any other warranty is expressed or implied regarding the accuracy of this data, the results to be obtained from the use thereof, or the hazards connected with the use of the product. Since the use of this product is within the exclusive control of the user, it is the user's obligation to determine the conditions for safe use of the product. Such conditions should comply with all regulations concerning the product. The company referenced in this Safety Data Sheet assumes no liability for any injury or damage, direct or consequential, resulting from the use of this product unless such injury or damage is attributable to the gross negligence of such company.

End of Safety Data Sheet



A QUAKER CHEMICAL COMPANY

SAFETY DATA SHEET

Print date:

Revision Date: 03/27/2015

Revision Number: 1

1. COMPANY AND PRODUCT IDENTIFICATION

Product identifier

Product Name: KEMIKO® ACID STAIN MALAY TAN 37N-1
Product code: 37N-1

Other means of identification

Synonyms No information available.

Application

Recommended Use Acid Stain
Uses advised against For industrial use only

Supplier/Manufacturer:

Supplier:
EPMAR Corporation
13240 E. Barton Circle
Whittier, CA 90605-3254
Phone: 562-946-8781
FAX: 562-944-9958
E-mail: she@quakerchem.com
(For Health and Safety Questions)

Emergency telephone number:
* 24 HOUR TRANSPORTATION:
**CHEMTREC: 1-800-424-9300
+703-527-3887 (Call collect outside of US)
* 24 HOUR EMERGENCY HEALTH & SAFETY:
**(800) 523-7010 (Within US only) Outside of US call (703)
527-3887

2. HAZARDS IDENTIFICATION

Classification

OSHA Regulatory Status

This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

37N-1 - KEMIKO® ACID STAIN
MALAY TAN 37N-1

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Revision Date: 03/27/2015

Acute toxicity - Inhalation (Gases)	Category 4
Skin corrosion/irritation	Category 1
Serious eye damage/eye irritation	Category 1
Chronic aquatic toxicity	Category 3
Corrosive to metals	Category 1

Label Elements

Emergency Overview

DANGER

Hazard Statements
 Harmful if inhaled
 Causes severe skin burns and eye damage
 Harmful to aquatic life with long lasting effects
 May be corrosive to metals



Appearance Dark yellow Green **Physical State** Liquid **Odor** Strong, Pungent

Precautionary Statements - Prevention

Use only outdoors or in a well-ventilated area
 Do not breathe dust/fume/gas/mist/vapors/spray
 Wash face, hands and any exposed skin thoroughly after handling
 Wear protective gloves/protective clothing/eye protection/face protection
 Avoid release to the environment

Precautionary Statements - Response

Immediately call a POISON CENTER or doctor/physician
 Specific treatment (see first aid on this label)
 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing Immediately call a POISON CENTER or doctor/physician
 IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower Wash contaminated clothing before reuse
 IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing Call a POISON CENTER or doctor/physician if you feel unwell Immediately call a POISON CENTER or doctor/physician
 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting

Precautionary Statements - Storage

Store locked up

Precautionary Statements - Disposal

Dispose of contents/container to an approved waste disposal plant

Hazards not otherwise classified (HNOC)

None known

Other Information

May be harmful if swallowed Harmful to aquatic life

Unknown acute toxicity 0% of the mixture consists of ingredient(s) of unknown toxicity

3. COMPOSITION/INFORMATION ON INGREDIENTS

Components	CAS No.	Weight %
Ferrous chloride	7758-94-3	10 - 20%
Hydrochloric acid	7647-01-0	5 - 10%

The exact percentage (concentration) of composition has been withheld as a trade secret.

4. FIRST AID MEASURES

General advice:	Show this safety data sheet to the doctor in attendance. Remove contaminated clothing and shoes. Wash contaminated clothing before re-use. Wash off with soap and water. If symptoms persist, call a physician.
Eye contact:	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes.
Skin contact:	Remove contaminated clothing and shoes. Wash contaminated clothing before re-use. Wash off immediately with soap and plenty of water.
Ingestion:	If swallowed, seek medical advice immediately and show this container or label. Never give anything by mouth to an unconscious person. Do not induce vomiting without medical advice.
Inhalation:	Move to fresh air in case of accidental inhalation of vapors. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Consult a physician.
Note to physician:	In case of ingestion, the stomach should be emptied by gastric lavage under qualified medical supervision. Material is corrosive. It may not be advisable to induce vomiting. Possible mucosal damage may contraindicate the use of gastric lavage.
Medical condition aggravated by exposure:	Dermatitis and asthma.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media:	Use dry chemical, CO ₂ , water spray or `alcohol` foam.
Specific hazards:	Do not allow material to contaminate ground water system.
Special protective equipment for fire-fighters:	As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.
Specific methods:	Water mist may be used to cool closed containers.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions: Ensure adequate ventilation. Avoid contact with the skin and the eyes Do not breathe vapour/dust. Use personal protective equipment. Wash thoroughly after handling
Avoid contact with skin, eyes and clothing.

Environmental precautions: Do not flush into surface water or sanitary sewer system. Prevent further leakage or spillage if safe to do so.

Methods for cleaning up: Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Sweep up and shovel into suitable containers for disposal.

7. HANDLING AND STORAGE

Handling

Technical measures/precautions: Provide sufficient air exchange and/or exhaust in work rooms.

Safe handling advice: In case of insufficient ventilation, wear suitable respiratory equipment. Avoid contact with skin and eyes. Do not breathe vapors or spray mist. Wear personal protective equipment. Wash thoroughly after handling. Keep container tightly closed.

Storage

Technical measures/storage conditions: DO NOT FREEZE Store in original container Keep containers tightly closed in a dry, cool and well-ventilated place. Keep away from direct sunlight

Incompatible products: See Section 10, Materials to avoid.

Safe storage temperature: 40 - 100 ° F

Shelf life: 12 months

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Components	ACGIH Exposure Limits	OSHA TWA (final)	NIOSH - Pocket Guide
Ferrous chloride	1 mg/m ³ (TWA)	None	1 mg/m ³ (TWA)
Hydrochloric acid	None	None	5 ppm (Ceiling) 7 mg/m ³ (Ceiling)
Iron oxide	5 mg/m ³ (TWA)	10 mg/m ³ 15 mg/m ³	5 mg/m ³ (TWA)

Engineering measures: Ensure adequate ventilation.

Personal Protective Equipment:

General: Eye Wash and Safety Shower

Respiratory protection: If engineering controls do not maintain airborne concentrations to a level which is adequate to protect worker health, a NIOSH-certified respirator with organic vapor/P100 filter should be worn.

Eye protection: Goggles. Face-shield.
Hand protection: Neoprene gloves
Skin and body protection: Chemical resistant apron Long sleeved clothing
Hygiene measures: Avoid contact with skin, eyes and clothing.



9. PHYSICAL AND CHEMICAL PROPERTIES

Physical State	Liquid
Appearance	Dark yellow Green
Odor	Strong, Pungent
Odor Threshold	No information available.
pH:	1
pH Dilution	No information available
Melting/freezing point	No information available
Boiling Point/Range	~ 100 °C / 212 °F
Flash Point	No information available
Method	No information available
Evaporation rate	No information available
Flammability Limits in Air	
upper flammability limit	No information available.
lower flammability limit	No information available.
VOC Content	No information available
Vapor pressure	No information available.
Vapor density	No information available.
Specific Gravity (g/cc, 15 C)	1.13
Bulk Density (lb/gal, 15 C)	9.43
Water Solubility	Insoluble
Solubility in other solvents	No information available.
Partition coefficient: n-octanol/water	No information available

Autoignition temperature	No information available
Decomposition Temperature	No information available
Kinematic viscosity	No information available
Dynamic viscosity	No information available
Molecular Weight	No information available

10. STABILITY AND REACTIVITY

Stability:	Stable under recommended storage conditions.
Conditions to avoid:	Heat, flames and sparks.
Materials to avoid:	Alkali metals. Strong bases. Potassium. Sodium. ethylene oxide. Gives off hydrogen by reaction with metals.
Hazardous decomposition products:	HCl, Cl ₂ . iron oxides.
Hazardous Polymerization:	Not applicable.

11. TOXICOLOGICAL INFORMATION

No toxicological information is available on the product. Data obtained on components are summarized below.

Information on likely routes of exposure

Inhalation	Harmful if inhaled.
Eye Contact	Corrosive to the eyes and may cause severe damage including blindness.
Skin Contact	Contact causes severe skin irritation and possible burns.
Ingestion	Ingestion may cause gastrointestinal irritation, nausea, vomiting and diarrhea.

Components	LD50 Oral	LD50 Dermal	LC50 Inhalation
Ferrous chloride	450 mg/kg (Rat)	-	-
Hydrochloric acid	700 mg/kg (Rat)	5010 mg/kg (Rabbit)	3120 ppm (Rat) 1 h

Delayed and immediate effects as well as chronic effects from short and long-term exposure

Carcinogenicity The table below indicates whether each agency has listed any ingredient as a carcinogen

Components	IARC Carcinogens	NTP	OSHA - Select Carcinogens
Ferrous chloride	Not listed	Not listed	Not listed
Hydrochloric acid	Not listed	Not listed	Not listed

Sensitization No information available.

Mutagenic effects: No information available.

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Reproductive Toxicity	No information available.
Developmental Toxicity	No information available.
Teratogenic	No information available.
Specific target organ systemic toxicity (single exposure)	Respiratory system.
Specific target organ systemic toxicity (repeated exposure)	No information available.
Aspiration hazard	No information available.

Additional information on toxicological effects

No information available

12. ECOLOGICAL INFORMATION

Components	Ecotoxicity - Fish Species Data:	Ecotoxicity - Freshwater Algae Data:	Ecotoxicity - Water Flea Data:
Ferrous chloride	No data	No data	No data
Hydrochloric acid	No data	No data	No data

0.2842% of the mixture consists of component(s) of unknown hazards to the aquatic environment

Persistence and Degradability No information available.

Bioaccumulation No information available.

Components	Octanol/water partition coefficient
Ferrous chloride	-
Hydrochloric acid	-

Mobility: No data available

Ozone: No data available

13. DISPOSAL CONSIDERATIONS

Waste from residues/unused products: Waste disposal must be in accordance with appropriate Federal, State, and local regulations. This product, if unaltered by use, may be disposed of by treatment at a permitted facility or as advised by your local hazardous waste regulatory authority.

Contaminated packaging: Do not re-use empty containers

Methods for cleaning up: Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Sweep up and shovel into suitable containers for disposal.

14. TRANSPORT INFORMATION

U. S. DEPARTMENT OF TRANSPORTATION:

UN/NA ID Number:	UN3264
Proper shipping name:	Corrosive liquid, acidic, inorganic, n.o.s.(hydrochloric acid, ferrous chloride)
Hazard class:	8
PG:	II
RQ	Ferrous chloride, RQ kg = 419
DOT ERG:	ERG 154
Additional DOT Information:	Not applicable for packages of 5 gallons or less

TDG (CANADA):

UN nr:	UN3264
Proper shipping name:	Corrosive liquid, acidic, inorganic, n.o.s.(hydrochloric acid, ferrous chloride)
TDG Hazard Classification:	8
Packing group:	II

IMDG/IMO:

UN nr:	UN3264
Proper shipping name:	Corrosive liquid, acidic, inorganic, n.o.s.(hydrochloric acid, ferrous chloride)
Class:	8
Packing group:	II
EMS:	F-A, S-B
Limited quantity:	0.5 L

IATA/ICAO:

UN nr:	UN3264
Proper shipping name:	Corrosive liquid, acidic, inorganic, n.o.s.(hydrochloric acid, ferrous chloride)
Hazard Class:	8
Packing group:	II
Maximum quantity for cargo only:	60 L
Maximum quantity for passenger:	5L
Limited quantity:	0.5 L

15. REGULATORY INFORMATION

Federal Regulations

OSHA Hazard Communication Standard: This product is considered to be hazardous under the OSHA Hazard Communication Standard.

CERCLA/SARA Information:

SARA (311, 312) hazard class: This product possesses the following SARA Hazard Categories:

Immediate Health (Acute):	Yes
Delayed Health (Chronic):	Yes
Flammability:	No

Pressure: No
 Reactivity: No

Components	Hazardous Substances and RQs	Extremely Hazardous Substances and TPQs	SARA 313 Emission Reporting
Ferrous chloride	100 lb	Not listed	Not listed
Hydrochloric acid	5000 lb	500 lb	1.0 %

Clean Air and Clean Water Acts:

Components	Hazardous Air Pollutants	CWA - Hazardous Substances	CWA - Toxic Pollutants	CWA - Priority Pollutants
Ferrous chloride	Not listed	Listed	Not listed	Not listed
Hydrochloric acid	Listed	Listed	Not listed	Not listed

U.S. STATE REGULATIONS (RTK):

Components	California Proposition 65	PARTK	MI Critical Materials	NJRTK	MARTK
Ferrous chloride	Not Listed	Environmental hazard	Not Listed	0930	Present
Hydrochloric acid	Not Listed	Environmental hazard	Not Listed	1012	Extraordinarily hazardous

California Proposition 65 Status: No components are listed

RCRA Status: To be disposed of as characteristic hazardous waste: characteristic: Corrosive D002

CANADIAN REGULATIONS:

Canada - WHMIS Classification Information: This product has been classified according to the hazard criteria of the CPR and the SDS contains all the information required by the CPR.

Canadian Product Classification: Class E - Corrosive Material
 Class D1

Product Classification Graphic(s):



Component Classification Data:

Components	WHMIS hazard class	CEPA Schedule I	Challenge Substances
Ferrous chloride	E	Not listed	Not listed
Hydrochloric acid	D1A E	Not listed	Not listed

INVENTORY STATUS:

United States TSCA - Sect. 8(b) Inventory: This product complies with TSCA

Canada DSL/NDL Inventory List This product complies with DSL

16. OTHER INFORMATION

Sources of key data used to compile the data sheet: Material safety data sheets of the ingredients.

Prepared by: Safety, Health and Environmental Department

Revision Date: 03/27/2015

Reason for revision: New Format.

Personal protection recommendations should be reviewed by purchasers. Workplace conditions are important factors in specifying adequate protection.

Disclaimer

This product's safety information is provided to assist our customers in assessing compliance with safety/health/environmental regulations. The information contained herein is based on data available to us and is believed to be accurate. However, no warranty of merchantability, fitness for any use, or any other warranty is expressed or implied regarding the accuracy of this data, the results to be obtained from the use thereof, or the hazards connected with the use of the product. Since the use of this product is within the exclusive control of the user, it is the user's obligation to determine the conditions for safe use of the product. Such conditions should comply with all regulations concerning the product. The company referenced in this Safety Data Sheet assumes no liability for any injury or damage, direct or consequential, resulting from the use of this product unless such injury or damage is attributable to the gross negligence of such company.

End of Safety Data Sheet



A QUAKER CHEMICAL COMPANY

SAFETY DATA SHEET

Print date:

Revision Date: 03/27/2015

Revision Number: 1

1. COMPANY AND PRODUCT IDENTIFICATION

Product identifier

Product Name: KEMIKO® ACID STAIN COLA 37R-3
Product code: 37R-3

Other means of identification

Synonyms No information available.

Application

Recommended Use Acid Stain
Uses advised against For industrial use only

Supplier/Manufacturer:

Supplier:
EPMAR Corporation
13240 E. Barton Circle
Whittier, CA 90605-3254
Phone: 562-946-8781
FAX: 562-944-9958
E-mail: she@quakerchem.com
(For Health and Safety Questions)

Emergency telephone number:
* 24 HOUR TRANSPORTATION:
**CHEMTREC: 1-800-424-9300
+703-527-3887 (Call collect outside of US)
* 24 HOUR EMERGENCY HEALTH & SAFETY:
**(800) 523-7010 (Within US only) Outside of US call (703)
527-3887

2. HAZARDS IDENTIFICATION

Classification

OSHA Regulatory Status

This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

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Acute Toxicity - Oral	Category 4
Acute toxicity - Inhalation (Gases)	Category 4
Skin corrosion/irritation	Category 1
Serious eye damage/eye irritation	Category 1
Chronic aquatic toxicity	Category 3
Corrosive to metals	Category 1

Label Elements

Emergency Overview

DANGER

Hazard Statements
harmful if swallowed
Harmful if inhaled
Causes severe skin burns and eye damage
Harmful to aquatic life with long lasting effects
May be corrosive to metals



Appearance Dark green **Physical State** Liquid **Odor** Strong, Pungent

Precautionary Statements - Prevention

Wash face, hands and any exposed skin thoroughly after handling
Do not eat, drink or smoke when using this product
Use only outdoors or in a well-ventilated area
Do not breathe dust/fume/gas/mist/vapors/spray
Wear protective gloves/protective clothing/eye protection/face protection
Avoid release to the environment

Precautionary Statements - Response

Immediately call a POISON CENTER or doctor/physician
Specific treatment (see first aid on this label)
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing Immediately call a POISON CENTER or doctor/physician
IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower Wash contaminated clothing before reuse
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing Call a POISON CENTER or doctor/physician if you feel unwell Immediately call a POISON CENTER or doctor/physician
IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell Rinse mouth Do not induce vomiting

Precautionary Statements - Storage

Store locked up

Precautionary Statements - Disposal

Dispose of contents/container to an approved waste disposal plant

Hazards not otherwise classified (HNOC)

None known

Other Information

Harmful to aquatic life

Unknown acute toxicity

1.1E-05% of the mixture consists of ingredient(s) of unknown toxicity

3. COMPOSITION/INFORMATION ON INGREDIENTS

Components	CAS No.	Weight %
Ferrous chloride	7758-94-3	10 - 20%
Hydrochloric acid	7647-01-0	5 - 10%
Chromic chloride, basic	50925-66-1	1 - 5%

The exact percentage (concentration) of composition has been withheld as a trade secret.

4. FIRST AID MEASURES

General advice:	Show this safety data sheet to the doctor in attendance. Remove contaminated clothing and shoes. Wash contaminated clothing before re-use. Wash off with soap and water. If symptoms persist, call a physician.
Eye contact:	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Call a physician immediately
Skin contact:	Remove contaminated clothing and shoes. Wash contaminated clothing before re-use. Wash off immediately with soap and plenty of water. Remove and wash contaminated clothing before re-use. Call a physician immediately.
Ingestion:	If swallowed, seek medical advice immediately and show this container or label. Do not induce vomiting. If victim is conscious, give water. Never give anything by mouth to an unconscious person. Do not induce vomiting without medical advice.
Inhalation:	Move to fresh air in case of accidental inhalation of vapors. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Consult a physician.
Note to physician:	In case of ingestion, the stomach should be emptied by gastric lavage under qualified medical supervision. Material is corrosive. It may not be advisable to induce vomiting. Possible mucosal damage may contraindicate the use of gastric lavage.
Medical condition aggravated by exposure:	Dermatitis and asthma.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media:	Use dry chemical, CO2, water spray or `alcohol` foam.
Specific hazards:	Do not allow material to contaminate ground water system.
Special protective equipment for fire-fighters:	As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.

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Specific methods: Water mist may be used to cool closed containers.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions: Ensure adequate ventilation. Avoid contact with the skin and the eyes Do not breathe vapour/dust. Use personal protective equipment. Wash thoroughly after handling
Avoid contact with skin, eyes and clothing.

Environmental precautions: Do not flush into surface water or sanitary sewer system. Prevent further leakage or spillage if safe to do so.

Methods for cleaning up: Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Sweep up and shovel into suitable containers for disposal.

7. HANDLING AND STORAGE

Handling

Technical measures/precautions: Provide sufficient air exchange and/or exhaust in work rooms.

Safe handling advice: In case of insufficient ventilation, wear suitable respiratory equipment. Avoid contact with skin and eyes. Do not breathe vapors or spray mist. Wear personal protective equipment. Wash thoroughly after handling. Keep container tightly closed.

Storage

Technical measures/storage conditions: DO NOT FREEZE Store in original container Keep containers tightly closed in a dry, cool and well-ventilated place. Keep away from direct sunlight

Incompatible products: See Section 10, Materials to avoid.

Safe storage temperature: 40 - 100 ° F

Shelf life: 12 months

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Components	ACGIH Exposure Limits	OSHA TWA (final)	NIOSH - Pocket Guide
Ferrous chloride	1 mg/m ³ (TWA)	None	1 mg/m ³ (TWA)
Hydrochloric acid	None	None	5 ppm (Ceiling) 7 mg/m ³ (Ceiling)
Iron oxide	5 mg/m ³ (TWA)	10 mg/m ³ 15 mg/m ³	5 mg/m ³ (TWA)

Engineering measures: Ensure adequate ventilation.

Personal Protective Equipment:

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General:	Eye Wash and Safety Shower
Respiratory protection:	If engineering controls do not maintain airborne concentrations to a level which is adequate to protect worker health, a NIOSH-certified respirator with organic vapor/P100 filter should be worn.
Eye protection:	Goggles. Face-shield.
Hand protection:	Neoprene gloves
Skin and body protection:	Chemical resistant apron Long sleeved clothing
Hygiene measures:	Avoid contact with skin, eyes and clothing.



9. PHYSICAL AND CHEMICAL PROPERTIES

Physical State	Liquid
Appearance	Dark green
Odor	Strong, Pungent
Odor Threshold	No information available.
pH:	1
pH Dilution	No information available
Melting/freezing point	No information available
Boiling Point/Range	~ 100 °C / 212 °F
Flash Point	No information available
Method	No information available
Evaporation rate	No information available
Flammability Limits in Air	
upper flammability limit	No information available.
lower flammability limit	No information available.
VOC Content	No information available
Vapor pressure	No information available.
Vapor density	No information available.
Specific Gravity (g/cc, 15 C)	1.22
Bulk Density (lb/gal, 15 C)	10.18

Water Solubility	Insoluble
Solubility in other solvents	No information available.
Partition coefficient: n-octanol/water	No information available
Autoignition temperature	No information available
Decomposition Temperature	No information available
Kinematic viscosity	No information available
Dynamic viscosity	No information available
Molecular Weight	No information available

10. STABILITY AND REACTIVITY

Stability:	Stable under recommended storage conditions.
Conditions to avoid:	Heat, flames and sparks.
Materials to avoid:	Alkali metals. Strong bases. Potassium. Sodium. ethylene oxide. Gives off hydrogen by reaction with metals.
Hazardous decomposition products:	HCl, Cl ₂ . iron oxides.
Hazardous Polymerization:	Not applicable.

11. TOXICOLOGICAL INFORMATION

No toxicological information is available on the product. Data obtained on components are summarized below.

Information on likely routes of exposure

Inhalation	Harmful if inhaled.
Eye Contact	Corrosive to the eyes and may cause severe damage including blindness.
Skin Contact	Contact causes severe skin irritation and possible burns.
Ingestion	Harmful if swallowed.

Components	LD50 Oral	LD50 Dermal	LC50 Inhalation
Ferrous chloride	450 mg/kg (Rat)	-	-
Hydrochloric acid	700 mg/kg (Rat)	5010 mg/kg (Rabbit)	3120 ppm (Rat) 1 h
Chromic chloride, basic	-	-	-

Delayed and immediate effects as well as chronic effects from short and long-term exposure

Carcinogenicity	The table below indicates whether each agency has listed any ingredient as a carcinogen
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Components	IARC Carcinogens	NTP	OSHA - Select Carcinogens
Ferrous chloride	Not listed	Not listed	Not listed
Hydrochloric acid	Not listed	Not listed	Not listed
Chromic chloride, basic	Not listed	Not listed	Not listed

Sensitization No information available.

Mutagenic effects: No information available.

Reproductive Toxicity No information available.

Developmental Toxicity No information available.

Teratogenic No information available.

Specific target organ systemic toxicity (single exposure) No information available.

Specific target organ systemic toxicity (repeated exposure) No information available.

Aspiration hazard No information available.

Additional information on toxicological effects

No information available

12. ECOLOGICAL INFORMATION

Components	Ecotoxicity - Fish Species Data:	Ecotoxicity - Freshwater Algae Data:	Ecotoxicity - Water Flea Data:
Ferrous chloride	No data	No data	No data
Hydrochloric acid	No data	No data	No data
Chromic chloride, basic	No data	No data	No data

1.89461% of the mixture consists of component(s) of unknown hazards to the aquatic environment

Persistence and Degradability No information available.

Bioaccumulation No information available.

Components	Octanol/water partition coefficient
Ferrous chloride	-
Hydrochloric acid	-
Chromic chloride, basic	-

Mobility: No data available

Ozone: No data available

13. DISPOSAL CONSIDERATIONS

Waste from residues/unused products: Waste disposal must be in accordance with appropriate Federal, State, and local regulations. This product, if unaltered by use, may be disposed of by treatment at a permitted facility or as advised by your local hazardous waste regulatory authority.

Contaminated packaging: Do not re-use empty containers

Methods for cleaning up: Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Sweep up and shovel into suitable containers for disposal.

Components Chromic chloride, basic
50925-66-1

RCRA - Hazardous Constituents - Appendix:	hazardous constituent - no waste number
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14. TRANSPORT INFORMATION

U. S. DEPARTMENT OF TRANSPORTATION:

UN/NA ID Number: UN3264
Proper shipping name: Corrosive liquid, acidic, inorganic, n.o.s.(hydrochloric acid, ferrous chloride)
Hazard class: 8
PG: II
RQ Ferrous chloride, RQ kg = 236
DOT ERG: ERG 154
Additional DOT Information: Not applicable for packages of 5 gallons or less

TDG (CANADA):

UN nr: UN3264
Proper shipping name: Corrosive liquid, acidic, inorganic, n.o.s.(hydrochloric acid, ferrous chloride)
TDG Hazard Classification: 8
Packing group: II

IMDG/IMO:

UN nr: UN3264
Proper shipping name: Corrosive liquid, acidic, inorganic, n.o.s.(hydrochloric acid, ferrous chloride)
Class: 8
Packing group: II
EMS: F-A, S-B
Limited quantity: 0.5 L

IATA/ICAO:

UN nr: UN3264
Proper shipping name: Corrosive liquid, acidic, inorganic, n.o.s.(hydrochloric acid, ferrous chloride)
Hazard Class: 8
Packing group: II
Maximum quantity for cargo only: 60 L
Maximum quantity for passenger: 5L
Limited quantity: 0.5 L

15. REGULATORY INFORMATION

Federal Regulations

OSHA Hazard Communication Standard: This product is considered to be hazardous under the OSHA Hazard Communication Standard.

CERCLA/SARA Information:

SARA (311, 312) hazard class: This product possesses the following SARA Hazard Categories:

Immediate Health (Acute): Yes
Delayed Health (Chronic): Yes
Flammability: No
Pressure: No
Reactivity: No

Components	Hazardous Substances and RQs	Extremely Hazardous Substances and TPQs	SARA 313 Emission Reporting
Ferrous chloride	100 lb	Not listed	Not listed
Hydrochloric acid	5000 lb	500 lb	1.0 %
Chromic chloride, basic	Not listed	Not listed	Not listed

Clean Air and Clean Water Acts:

Components	Hazardous Air Pollutants	CWA - Hazardous Substances	CWA - Toxic Pollutants	CWA - Priority Pollutants
Ferrous chloride	Not listed	Listed	Not listed	Not listed
Hydrochloric acid	Listed	Listed	Not listed	Not listed
Chromic chloride, basic	Listed	Not listed	Listed	Not listed

U.S. STATE REGULATIONS (RTK):

Components	California Proposition 65	PARTK	MI Critical Materials	NJRTK	MARTK
Ferrous chloride	Not Listed	Environmental hazard	Not Listed	0930	Present
Hydrochloric acid	Not Listed	Environmental hazard	Not Listed	1012	Extraordinarily hazardous
Chromic chloride, basic	Not Listed	Environmental hazard	100 lb	2245	Not Listed

California Proposition 65 Status: No components are listed

RCRA Status: To be disposed of as characteristic hazardous waste: characteristic: Corrosive D002

CANADIAN REGULATIONS:

Canada - WHMIS Classification Information: This product has been classified according to the hazard criteria of the CPR and the SDS contains all the information required by the CPR.

Canadian Product Classification: Class E - Corrosive Material
Class D1

Product Classification Graphic(s):



Component Classification Data:

Components	WHMIS hazard class	CEPA Schedule I	Challenge Substances
Ferrous chloride	E	Not listed	Not listed
Hydrochloric acid	D1A E	Not listed	Not listed
Chromic chloride, basic	None	Not listed	Not listed

INVENTORY STATUS:

United States TSCA - Sect. 8(b) Inventory: This product complies with TSCA

Canada DSL/NDL Inventory List This product complies with DSL

16. OTHER INFORMATION

Sources of key data used to compile Material safety data sheets of the ingredients.
the data sheet:

Prepared by: Safety, Health and Environmental Department

Revision Date: 03/27/2015

Reason for revision: New Format.

Personal protection recommendations should be reviewed by purchasers. Workplace conditions are important factors in specifying adequate protection.

Disclaimer

This product's safety information is provided to assist our customers in assessing compliance with safety/health/environmental regulations. The information contained herein is based on data available to us and is believed to be accurate. However, no warranty of merchantability, fitness for any use, or any other warranty is expressed or implied regarding the accuracy of this data, the results to be obtained from the use thereof, or the hazards connected with the use of the product. Since the use of this product is within the exclusive control of the user, it is the user's obligation to determine the conditions for safe use of the product. Such conditions should comply with all regulations concerning the product. The company referenced in this Safety Data Sheet assumes no liability for any injury or damage, direct or consequential, resulting from the use of this product unless such injury or damage is attributable to the gross negligence of such company.

End of Safety Data Sheet



A QUAKER CHEMICAL COMPANY

SAFETY DATA SHEET

Print date:

Revision Date: 03/27/2015

Revision Number: 1

1. COMPANY AND PRODUCT IDENTIFICATION

Product identifier

Product Name: KEMIKO® ACID STAIN BLACK 37B-1
Product code: 37B-1

Other means of identification

Synonyms No information available.

Application

Recommended Use Acid Stain
Uses advised against For industrial use only

Supplier/Manufacturer:

Supplier:
EPMAR Corporation
13240 E. Barton Circle
Whittier, CA 90605-3254
Phone: 562-946-8781
FAX: 562-944-9958
E-mail: she@quakerchem.com
(For Health and Safety Questions)

Emergency telephone number:
* 24 HOUR TRANSPORTATION:
**CHEMTREC: 1-800-424-9300
+703-527-3887 (Call collect outside of US)
* 24 HOUR EMERGENCY HEALTH & SAFETY:
**(800) 523-7010 (Within US only) Outside of US call (703)
527-3887

2. HAZARDS IDENTIFICATION

Classification

OSHA Regulatory Status

This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

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BLACK 37B-1

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Revision Date: 03/27/2015

Acute Toxicity - Oral	Category 4
Acute toxicity - Inhalation (Dusts/Mists)	Category 4
Skin corrosion/irritation	Category 1
Serious eye damage/eye irritation	Category 1
Respiratory Sensitization	Category 1A
Skin Sensitization	Category 1
Germ cell mutagenicity	Category 1B
Carcinogenicity	Category 1B
Reproductive toxicity	Category 1B
Specific target organ toxicity (repeated exposure)	Category 1
Chronic aquatic toxicity	Category 2
Oxidizing liquids	Category 2
Corrosive to metals	Category 1

Label Elements

Emergency Overview

DANGER

Hazard Statements
harmful if swallowed
Harmful if inhaled
Causes severe skin burns and eye damage
May cause allergy or asthma symptoms or breathing difficulties if inhaled
May cause an allergic skin reaction
may cause genetic defects
May cause cancer
may damage fertility or the unborn child
Causes damage to organs through prolonged or repeated exposure
Toxic to aquatic life with long lasting effects
May intensify fire; oxidizer
May be corrosive to metals



Appearance Dark brown **Physical State** Liquid **Odor** Strong, Pungent

Precautionary Statements - Prevention

Obtain special instructions before use
Do not handle until all safety precautions have been read and understood
Use personal protective equipment as required
Wash face, hands and any exposed skin thoroughly after handling
Do not eat, drink or smoke when using this product
Use only outdoors or in a well-ventilated area
Do not breathe dust/fume/gas/mist/vapors/spray
In case of inadequate ventilation wear respiratory protection
Contaminated work clothing should not be allowed out of the workplace
wear protective gloves
Avoid release to the environment

Precautionary Statements - Response

Immediately call a POISON CENTER or doctor/physician
Specific treatment (see first aid on this label)
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing Immediately call a POISON CENTER or doctor/physician
IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower Wash contaminated clothing before reuse If skin irritation or rash occurs: Get medical advice/attention
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing Call a POISON CENTER or doctor/physician if you feel unwell Immediately call a POISON CENTER or doctor/physician
IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell Rinse mouth Do not induce vomiting
Collect spillage

Precautionary Statements - Storage

Store locked up

Precautionary Statements - Disposal

Dispose of contents/container to an approved waste disposal plant

Hazards not otherwise classified (HNOC)

None known

Other Information

Toxic to aquatic life

Unknown acute toxicity 0.0005% of the mixture consists of ingredient(s) of unknown toxicity

3. COMPOSITION/INFORMATION ON INGREDIENTS

Components	CAS No.	Weight %
Manganese chloride	7773-01-5	10 - 20%
Sodium dichromate, dihydrate	7789-12-0	1 - 5%
Hydrochloric acid	7647-01-0	1 - 5%

Physico-chemical properties: Sodium dichromate is an oxidizer

The exact percentage (concentration) of composition has been withheld as a trade secret.

4. FIRST AID MEASURES

General advice:	Show this safety data sheet to the doctor in attendance. Remove contaminated clothing and shoes. Wash contaminated clothing before re-use. Wash off with soap and water. If symptoms persist, call a physician.
Eye contact:	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes.
Skin contact:	Rinse immediately with plenty of water for at least 15 minutes. Remove and wash contaminated clothing before re-use. Wash off with soap and plenty of water. Discard contaminated shoes. Consult a physician. Wash off immediately with soap and plenty of water. Call a physician immediately.
Ingestion:	If swallowed, seek medical advice immediately and show this container or label. Do not induce vomiting. If victim is conscious, give water. Never give anything by mouth to an unconscious person. Do not induce vomiting without medical advice.
Inhalation:	Move to fresh air in case of accidental inhalation of vapors. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Consult a physician.
Note to physician:	Massive overexposure to this product could lead to kidney failure and death. Ascorbic acid administered intravenously and locally is an effective antidote (converting Cr6 to Cr3) in preventing renal tubular failure. Up to 10 grams Ascorbic acid in stomach. Plus I.V. Ascorbic acid 1 gram in divided doses. Monitor blood chemistries, force fluids for diuresis (of chrome). Do not attempt chelation! Protect renal tubules. Contact with broken skin may lead to formation of firmly marginated "chrome sores.". Skin ulcers may be treated by removal from exposure, daily cleansing, debridement, and application of antibiotic cream and dressing.
Medical condition aggravated by exposure:	Dermatitis and asthma.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media:	Carbon dioxide (CO2) Dry chemical
Specific hazards:	Do not allow material to contaminate ground water system.
Special protective equipment for fire-fighters:	As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.
Specific methods:	Water mist may be used to cool closed containers.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions:	Ensure adequate ventilation. Avoid contact with the skin and the eyes Do not breathe vapour/dust. Use personal protective equipment. Wash thoroughly after handling Avoid contact with skin, eyes and clothing.
Environmental precautions:	Do not flush into surface water or sanitary sewer system. Prevent further leakage or spillage if safe to do so.
Methods for cleaning up:	Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Sweep up and shovel into suitable containers for disposal.

7. HANDLING AND STORAGE

Handling

Technical measures/precautions: Provide sufficient air exchange and/or exhaust in work rooms.

Safe handling advice: In case of insufficient ventilation, wear suitable respiratory equipment. Wear personal protective equipment. Keep away from combustible material. Keep container tightly closed. Avoid contact with skin and eyes. Do not breathe vapors or spray mist. Wash thoroughly after handling. Remove and wash contaminated clothing before re-use

Storage

Technical measures/storage conditions: DO NOT FREEZE Store in original container Keep containers tightly closed in a dry, cool and well-ventilated place. Keep away from direct sunlight

Incompatible products: See Section 10, Materials to avoid.

Safe storage temperature: 40 - 100 ° F

Shelf life: 12 months

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Components	ACGIH Exposure Limits	OSHA TWA (final)	NIOSH - Pocket Guide
Manganese chloride	0.02 mg/m ³ (TWA) 0.1 mg/m ³ (TWA)	None	1 mg/m ³ (TWA)
Sodium dichromate, dihydrate	0.05 mg/m ³ (TWA)	5 µg/m ³	0.0002 mg/m ³ (TWA)
Hydrochloric acid	None	None	5 ppm (Ceiling) 7 mg/m ³ (Ceiling)

Engineering measures: Use only in area provided with appropriate exhaust ventilation.

Personal Protective Equipment:

General: Eye Wash and Safety Shower

Respiratory protection: If engineering controls do not maintain airborne concentrations to a level which is adequate to protect worker health, a NIOSH-certified respirator with organic vapor/P100 filter should be worn.

Eye protection: Goggles. Face-shield.

Hand protection: Neoprene gloves

Skin and body protection: Long sleeved clothing Chemical resistant apron

Hygiene measures: Avoid contact with skin, eyes and clothing. Contaminated work clothing should not be allowed out of the workplace.



9. PHYSICAL AND CHEMICAL PROPERTIES

Physical State	Liquid
Appearance	Dark brown
Odor	Strong, Pungent
Odor Threshold	No information available.
pH:	1
pH Dilution	No information available
Melting/freezing point	No information available
Boiling Point/Range	~ 100 °C / 212 °F
Flash Point	No information available
Method	No information available
Evaporation rate	No information available
Flammability Limits in Air upper flammability limit lower flammability limit	No information available. No information available.
VOC Content	No information available
Vapor pressure	No information available.
Vapor density	No information available.
Specific Gravity (g/cc, 15 C)	1.15
Bulk Density (lb/gal, 15 C)	9.60
Water Solubility	Soluble in water
Solubility in other solvents	No information available.
Partition coefficient: n-octanol/water	No information available
Autoignition temperature	No information available
Decomposition Temperature	No information available
Kinematic viscosity	No information available
Dynamic viscosity	No information available

Molecular Weight

No information available

10. STABILITY AND REACTIVITY

- Stability:** Stable under recommended storage conditions.
- Conditions to avoid:** Heat, flames and sparks.
- Materials to avoid:** Combustible material. Organic materials. Strong bases. Alkali metals. Potassium. Sodium. Zinc powder.
- Hazardous decomposition products:** HCl, Cl₂. Sodium oxides. Chromium oxides.
- Hazardous Polymerization:** Not applicable.

11. TOXICOLOGICAL INFORMATION

No toxicological information is available on the product. Data obtained on components are summarized below.

Information on likely routes of exposure

- Inhalation** Harmful if inhaled.
- Eye Contact** Corrosive to the eyes and may cause severe damage including blindness.
- Skin Contact** Contact causes severe skin irritation and possible burns. May cause sensitization by skin contact.
- Ingestion** Harmful if swallowed.

Components	LD50 Oral	LD50 Dermal	LC50 Inhalation
Manganese chloride	250 mg/kg (Rat)	-	-
Sodium dichromate, dihydrate	-	-	-
Hydrochloric acid	700 mg/kg (Rat)	5010 mg/kg (Rabbit)	3120 ppm (Rat) 1 h

Delayed and immediate effects as well as chronic effects from short and long-term exposure

Carcinogenicity The table below indicates whether each agency has listed any ingredient as a carcinogen

Components	IARC Carcinogens	NTP	OSHA - Select Carcinogens
Manganese chloride	Not listed	Not listed	Not listed
Sodium dichromate, dihydrate	Group 1 (Carcinogenic to Humans)	Known Carcinogen	Present
Hydrochloric acid	Not listed	Not listed	Not listed

Sensitization Product contains a component that is classified as a skin sensitizer. No studies have been conducted on the product itself.

Mutagenic effects: Product contains a component that is classified as a mutagen. No testing has been conducted on the product itself.

Reproductive Toxicity	Product contains a component that is classified as a reproductive hazard. No testing has been conducted on the product itself.
Developmental Toxicity	No information available.
Teratogenic	No information available.
Specific target organ systemic toxicity (single exposure)	Respiratory system.
Specific target organ systemic toxicity (repeated exposure)	May cause disorder and damage to the, Respiratory system.
Aspiration hazard	No information available.

Additional information on toxicological effects

No information available

12. ECOLOGICAL INFORMATION

Components	Ecotoxicity - Fish Species Data:	Ecotoxicity - Freshwater Algae Data:	Ecotoxicity - Water Flea Data:
Manganese chloride	No data	No data	No data
Sodium dichromate, dihydrate	No data	No data	No data
Hydrochloric acid	No data	No data	No data

0% of the mixture consists of component(s) of unknown hazards to the aquatic environment

Persistence and Degradability No information available.

Bioaccumulation No information available.

Components	Octanol/water partition coefficient
Manganese chloride	-
Sodium dichromate, dihydrate	-
Hydrochloric acid	-

Mobility: No data available

Ozone: No data available

13. DISPOSAL CONSIDERATIONS

Waste from residues/unused products: Waste disposal must be in accordance with appropriate Federal, State, and local regulations. This product, if unaltered by use, may be disposed of by treatment at a permitted facility or as advised by your local hazardous waste regulatory authority.

Contaminated packaging: Do not re-use empty containers

Methods for cleaning up: Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Sweep up and shovel into suitable containers for disposal.

Components Sodium dichromate, dihydrate
7789-12-0

RCRA - Hazardous Constituents - Appendix:	hazardous constituent - no waste number
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14. TRANSPORT INFORMATION

U. S. DEPARTMENT OF TRANSPORTATION:

UN/NA ID Number: UN3264
Proper shipping name: Corrosive liquid, acidic, inorganic, n.o.s. (contains sodium dichromate and hydrochloric acid)
Hazard class: 8
Subsidiary risk:
PG: II
RQ Sodium bichromate, RQ kg = 91
DOT ERG: ERG 154
Additional DOT Information: Not applicable for packages of 5 gallons or less

TDG (CANADA):

UN nr: UN3264
Proper shipping name: Corrosive liquid, acidic, inorganic, n.o.s. (contains sodium dichromate and hydrochloric acid)
TDG Hazard Classification: 8
Subsidiary class:
Packing group: II

IMDG/IMO:

UN nr: UN3264
Proper shipping name: Corrosive liquid, acidic, inorganic, n.o.s. (contains sodium dichromate and hydrochloric acid)
Class: 8
Subsidiary class:
Packing group: II
EMS: F-A, S-B
Limited quantity: 1 L

IATA/ICAO:

UN nr: UN3264
Proper shipping name: Corrosive liquid, acidic, inorganic, n.o.s. (contains sodium dichromate and hydrochloric acid)
Hazard Class: 8
Subsidiary class:
Packing group: II
Maximum quantity for cargo only: 30 L
Maximum quantity for passenger: 1 L
Limited quantity: 0.5 L

15. REGULATORY INFORMATION

Federal Regulations

37B-1 - KEMIKO® ACID STAIN
BLACK 37B-1

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Revision Date: 03/27/2015

OSHA Hazard Communication Standard: This product is considered to be hazardous under the OSHA Hazard Communication Standard.

CERCLA/SARA Information:

SARA (311, 312) hazard class: This product possesses the following SARA Hazard Categories:

Immediate Health (Acute): Yes
Delayed Health (Chronic): Yes
Flammability: No
Pressure: No
Reactivity: No

Components	Hazardous Substances and RQs	Extremely Hazardous Substances and TPQs	SARA 313 Emission Reporting
Manganese chloride	Not listed	Not listed	1.0 %
Sodium dichromate, dihydrate	10 lb	Not listed	0.1 %
Hydrochloric acid	5000 lb	500 lb	1.0 %

Clean Air and Clean Water Acts:

Components	Hazardous Air Pollutants	CWA - Hazardous Substances	CWA - Toxic Pollutants	CWA - Priority Pollutants
Manganese chloride	Listed	Not listed	Not listed	Not listed
Sodium dichromate, dihydrate	Listed	Listed	Listed	Not listed
Hydrochloric acid	Listed	Listed	Not listed	Not listed

U.S. STATE REGULATIONS (RTK):

Components	California Proposition 65	PARTK	MI Critical Materials	NJRTK	MARTK
Manganese chloride	Not Listed	Environmental hazard	Not Listed	2324	Not Listed
Sodium dichromate, dihydrate	developmental toxicity	Environmental hazard Special hazardous substance Present	Not Listed	1695 3575 2245	Present
Hydrochloric acid	Not Listed	Environmental hazard	Not Listed	1012	Extraordinarily hazardous

California Proposition 65 Status: May contain trace amounts of listed chemicals: hexavalent chromium.

RCRA Status: To be disposed of as characteristic hazardous waste: characteristic: Corrosive D002
Chromium compounds: D007

CANADIAN REGULATIONS:

Canada - WHMIS Classification Information: This product has been classified according to the hazard criteria of the CPR and the SDS contains all the information required by the CPR.

Canadian Product Classification: Class E - Corrosive Material
Class D1

Product Classification Graphic(s):



Component Classification Data:

Components	WHMIS hazard class	CEPA Schedule I	Challenge Substances
Manganese chloride	D2B	Not listed	Not listed
Sodium dichromate, dihydrate	C D1A D2A D2B	Not listed	Not listed
Hydrochloric acid	D1A E	Not listed	Not listed

INVENTORY STATUS:

United States TSCA - Sect. 8(b) Inventory: This product complies with TSCA

Canada DSL/NDSL Inventory List Compliance has not been determined

16. OTHER INFORMATION

Sources of key data used to compile the data sheet: Material safety data sheets of the ingredients.

Prepared by: Safety, Health and Environmental Department

Revision Date: 03/27/2015

Reason for revision: New Format.

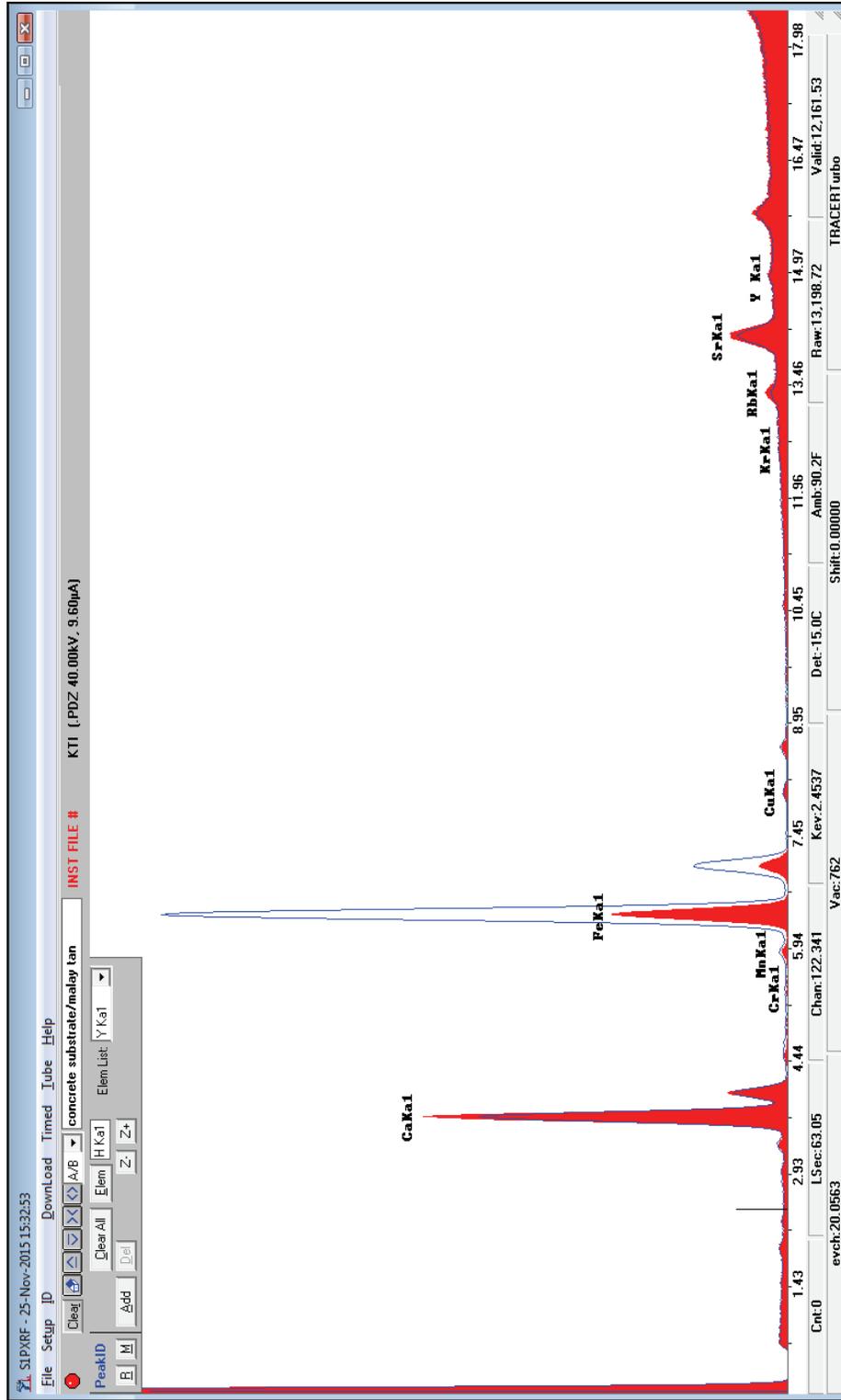
Personal protection recommendations should be reviewed by purchasers. Workplace conditions are important factors in specifying adequate protection.

Disclaimer

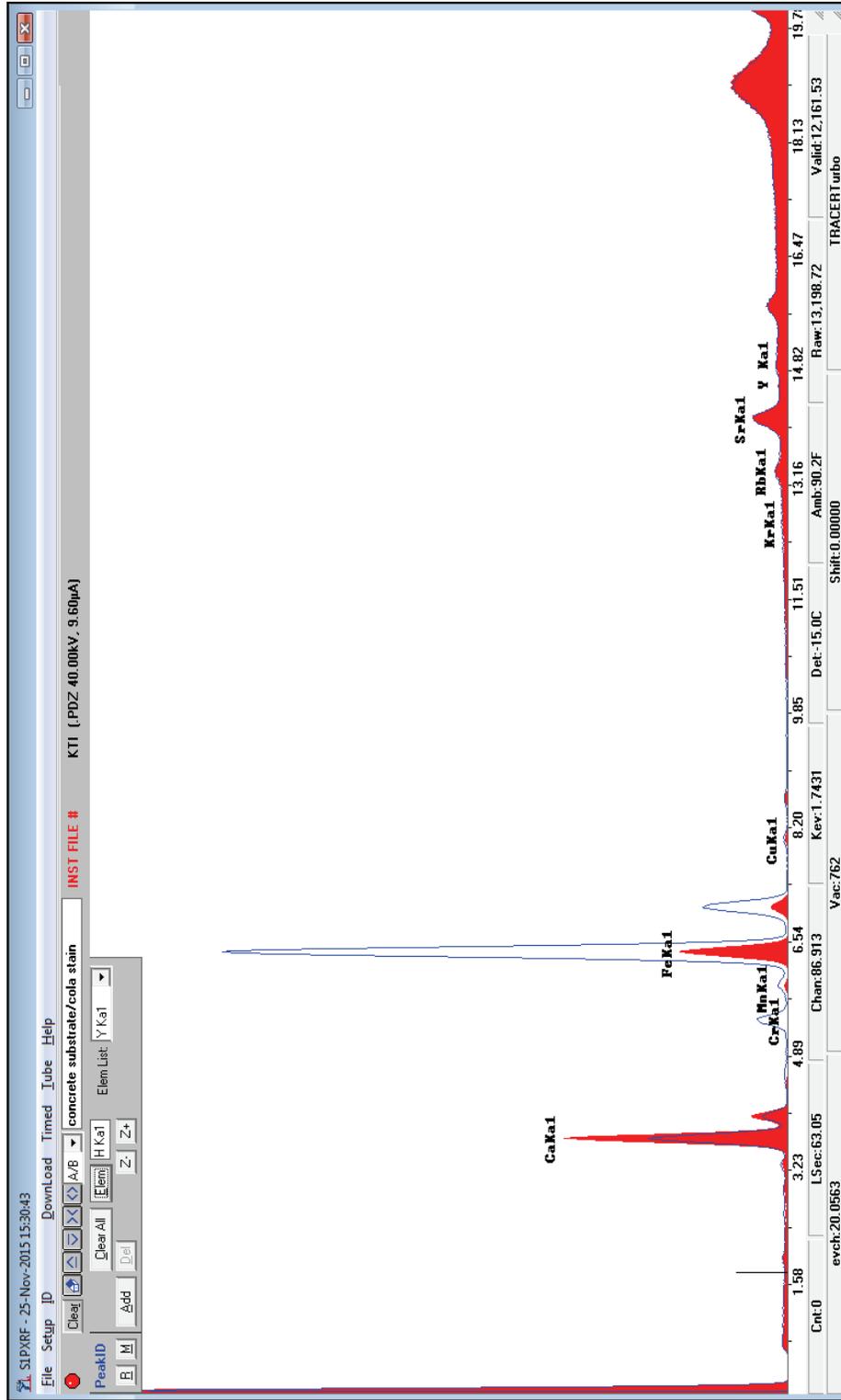
This product's safety information is provided to assist our customers in assessing compliance with safety/health/environmental regulations. The information contained herein is based on data available to us and is believed to be accurate. However, no warranty of merchantability, fitness for any use, or any other warranty is expressed or implied regarding the accuracy of this data, the results to be obtained from the use thereof, or the hazards connected with the use of the product. Since the use of this product is within the exclusive control of the user, it is the user's obligation to determine the conditions for safe use of the product. Such conditions should comply with all regulations concerning the product. The company referenced in this Safety Data Sheet assumes no liability for any injury or damage, direct or consequential, resulting from the use of this product unless such injury or damage is attributable to the gross negligence of such company.

End of Safety Data Sheet

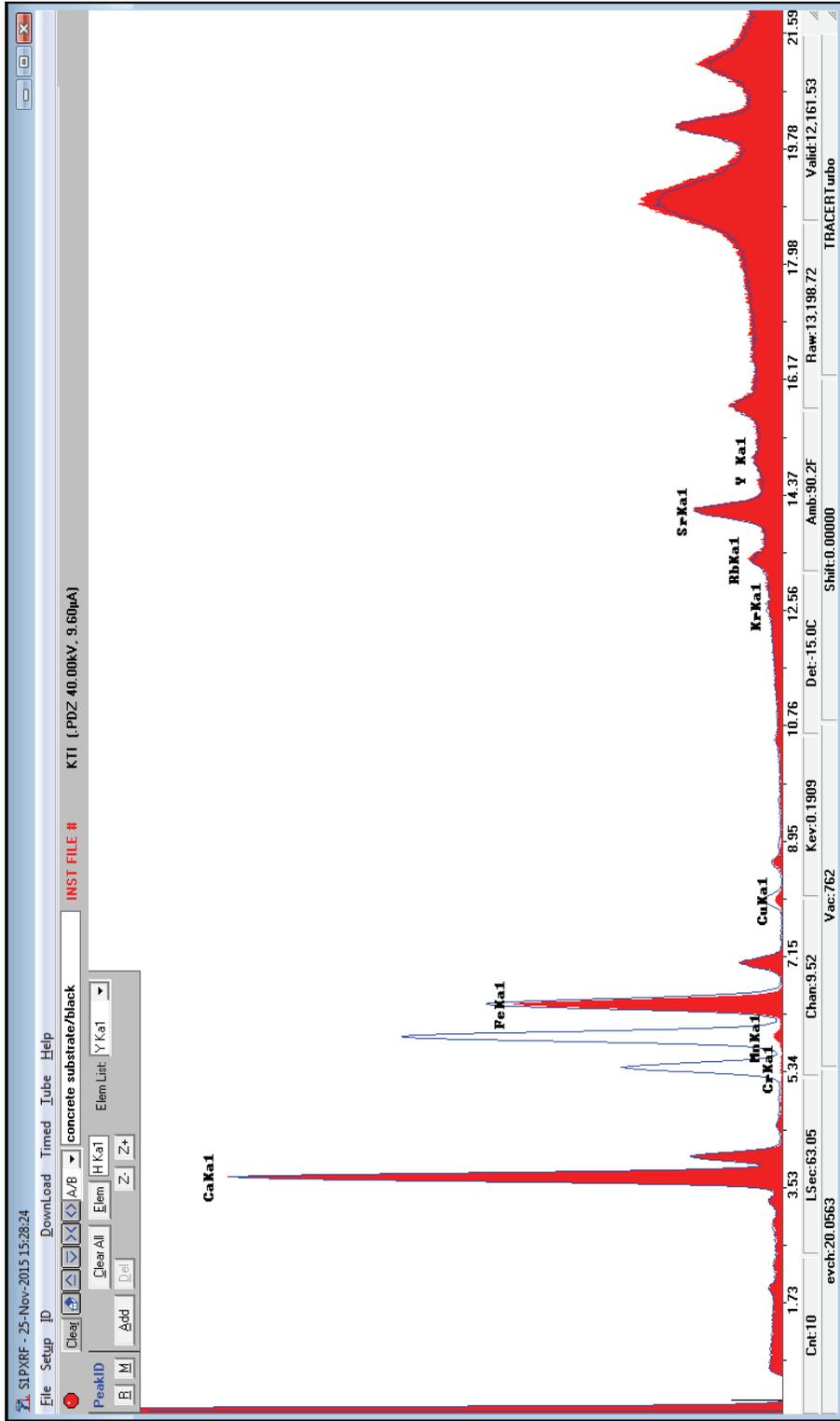
Appendix D: ED-XRF Spectra



Appendix D. Figure 1: Red spectrum represents the concrete which includes the following elements (Potassium (K), Calcium (Ca), Manganese (Mn), Iron (Fe), Rhodium (Rb), Strontium (Sr), Yttrium (Y), Zirconium (Zr)). The blue spectrum represents the Malay Tan stain Iron (Fe).

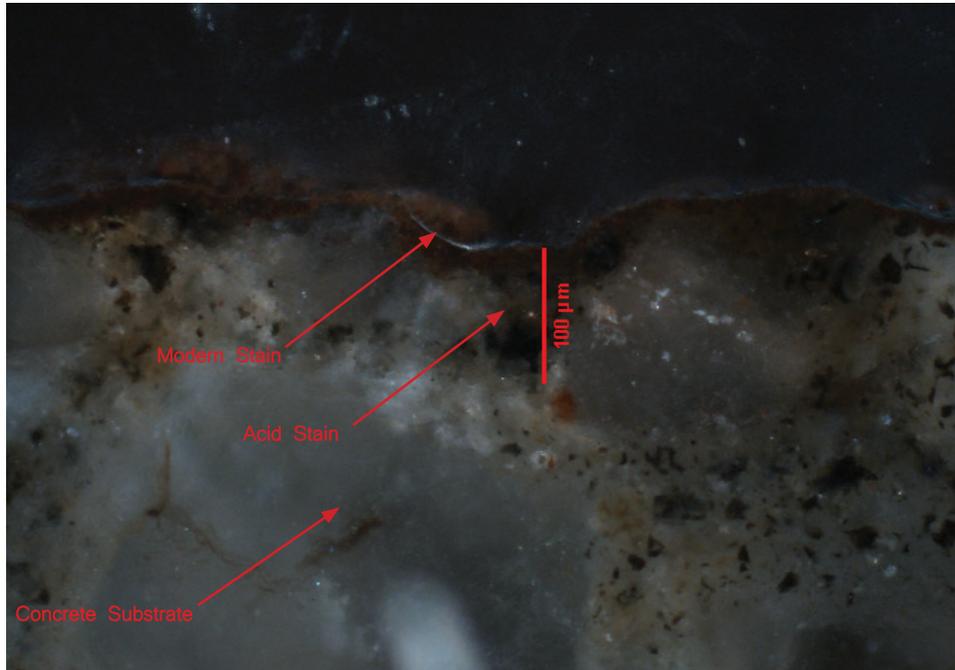


Appendix D. Figure 2: Red spectrum represents the concrete which includes the following elements (Potassium (K), Calcium (Ca), Manganese (Mn), Iron (Fe), Rhodium (Rb), Strontium (Sr), Yttrium (Y), Zirconium (Zr)). The blue spectrum represents the Cola stain Chromium (Cr) and Manganese (Mn) and Iron (Fe).

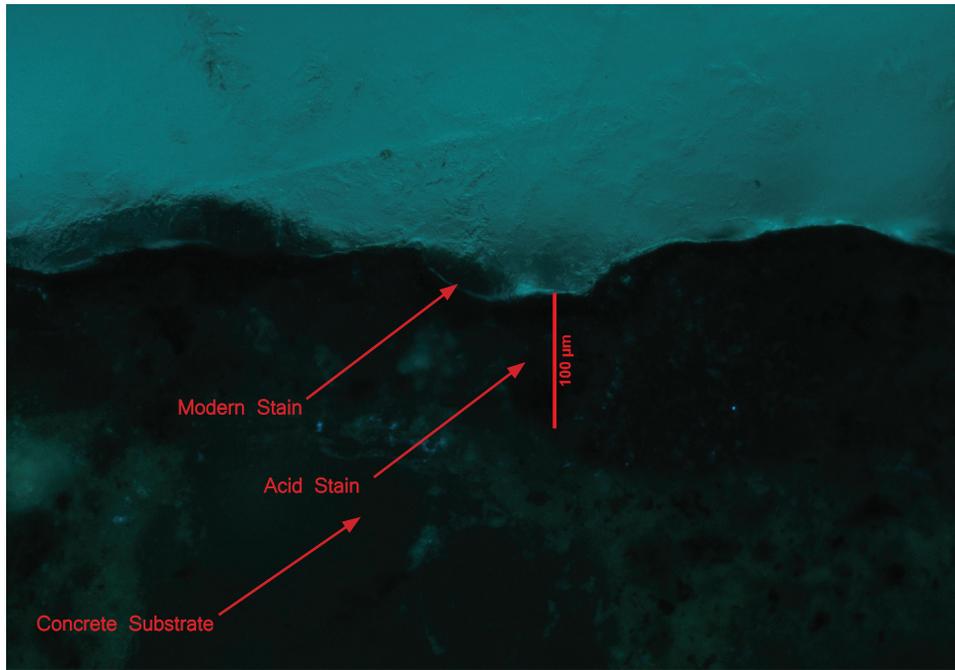


Appendix D. Figure 3: Red spectrum represents the concrete which includes the following elements (Potassium (K), Calcium (Ca), Manganese (Mn), Iron (Fe), Rhodium (Rb), Strontium (Sr), Yttrium (Y), Zirconium (Zr)). The blue spectrum represents the Black stain Chromium (Cr) and Manganese (Mn) .

Appendix E: Microscopy



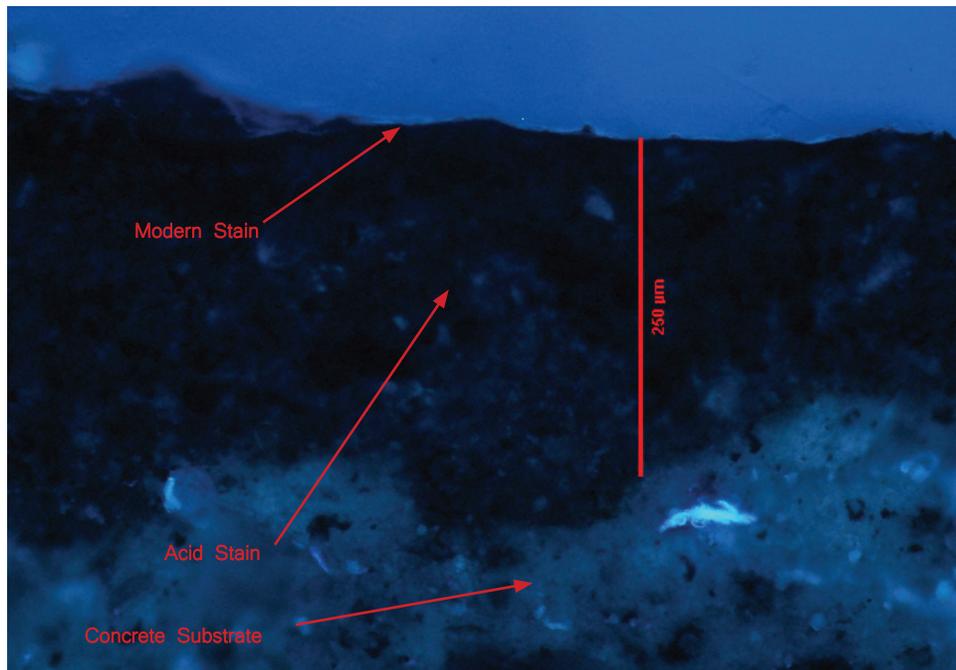
Appendix E. Figure 1. Sample JLL_1. Fragment of large spall removed from site in 2014. 100x. Reflected Light.



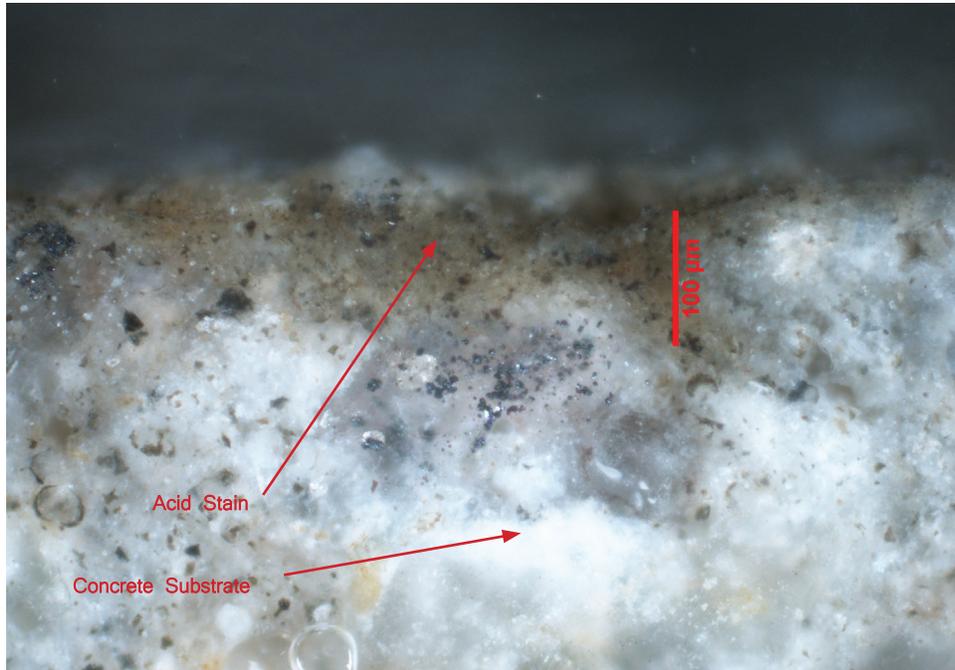
Appendix E. Figure 2. Sample JLL_1. Fragment of large spall removed from site in 2014. 100x. Ultraviolet Light.



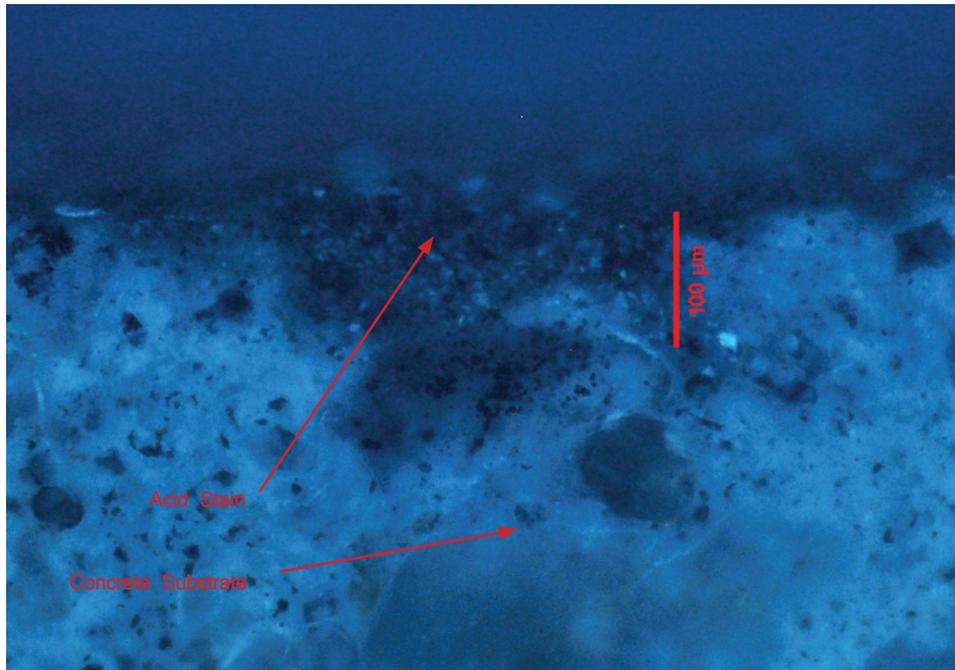
Appendix E. Figure 3. Sample JYL_2A. Fragment of large spall removed from site in 2014. 100x. Reflected Light.



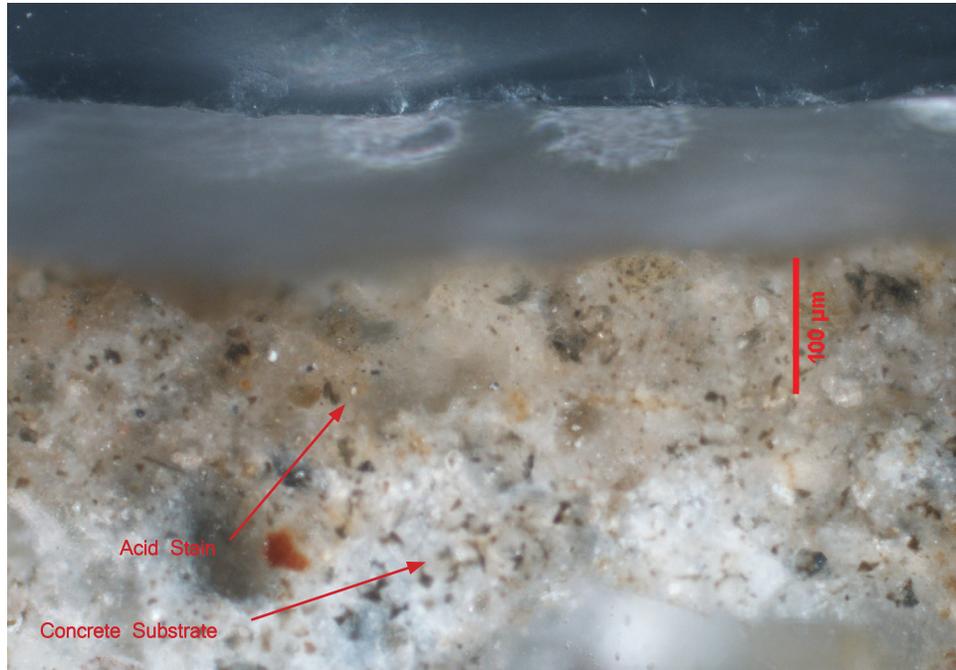
Appendix E. Figure 4. Sample JYL_2A. Fragment of large spall removed from site in 2014. 100x. Ultraviolet Light.



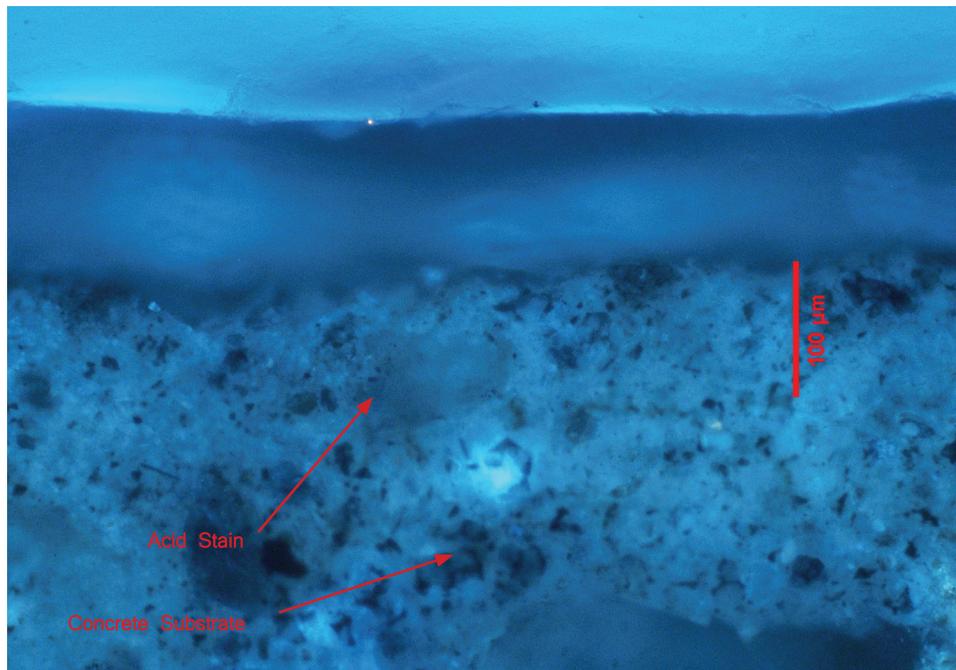
Appendix E. Figure 5. Sample JJJ_6. Fragment removed from the enclosed are above the Blue Heron Bar, with original finish. 100x. Reflected Light.



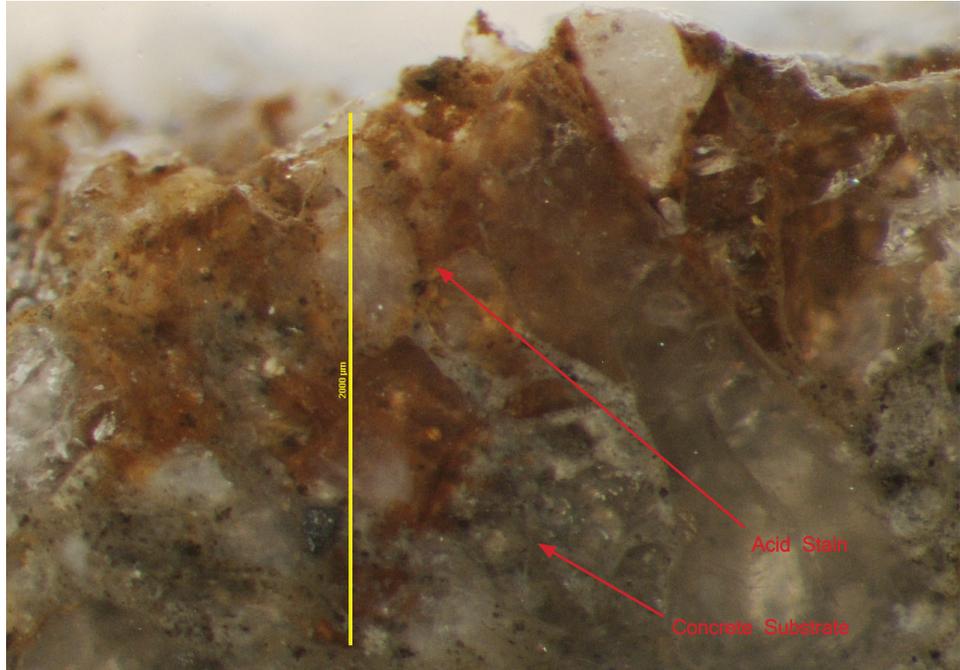
Appendix E. Figure 6. Sample JJJ_6. Fragment removed from the enclosed are above the Blue Heron Bar, with original finish. 100x. Ultraviolet Light.



Appendix E. Figure 7. Sample JLL_6. Fragment removed from the enclosed are above the Blue Heron Bar, with original finish. 100x. Reflected Light.

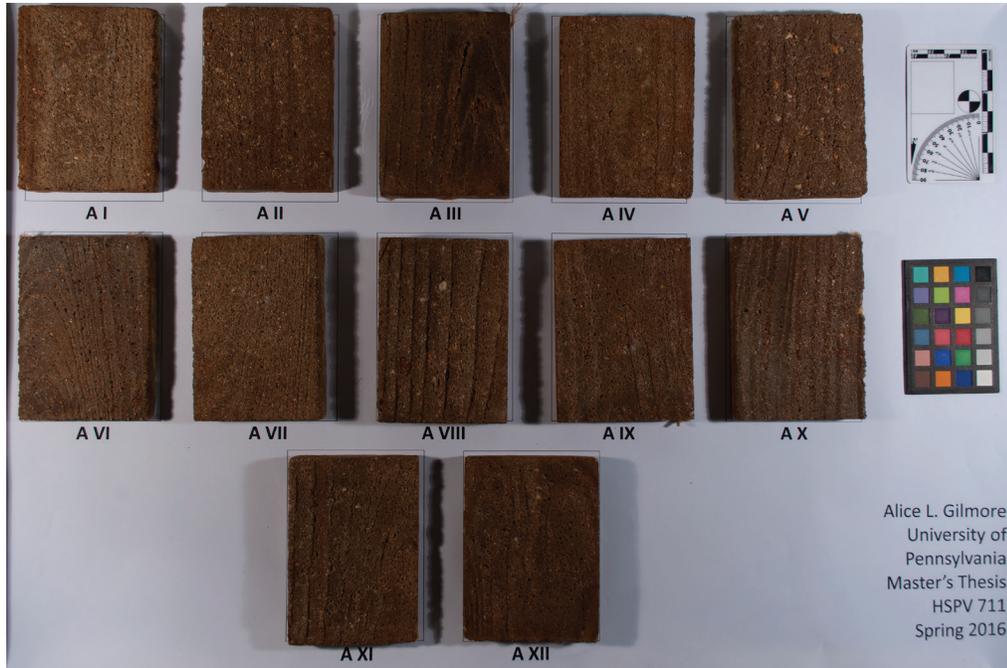


Appendix E. Figure 8. Sample JLL_7. Fragment removed from the enclosed are above the Blue Heron Bar, with original finish. 100x. Ultraviolet Light.

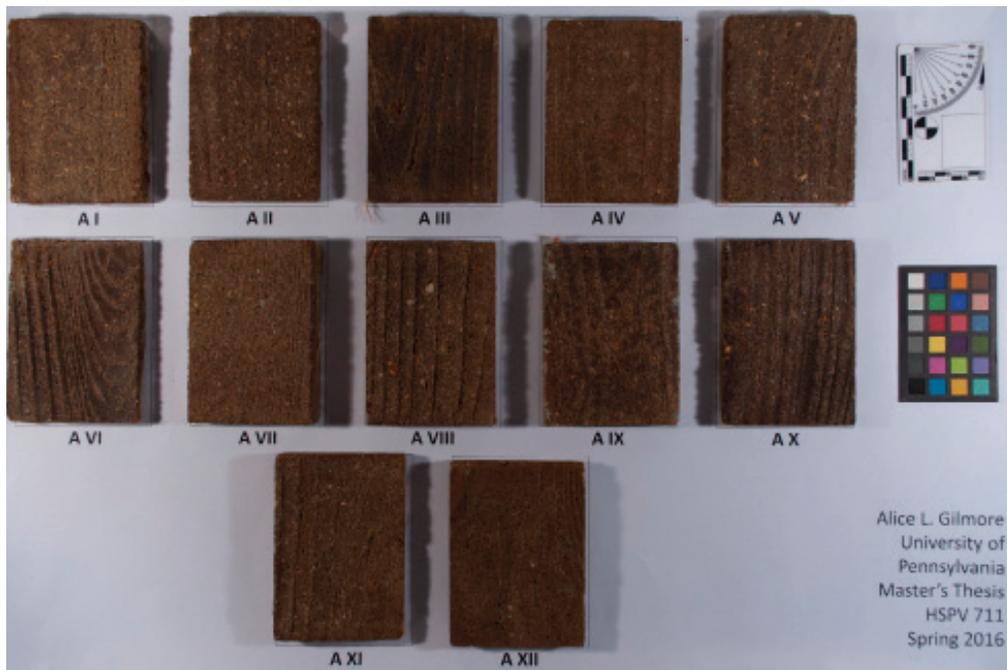


Appendix E. Figure 9. Sample JLL_9. Facsimile sample with acid stains. 10x. Reflected Light.

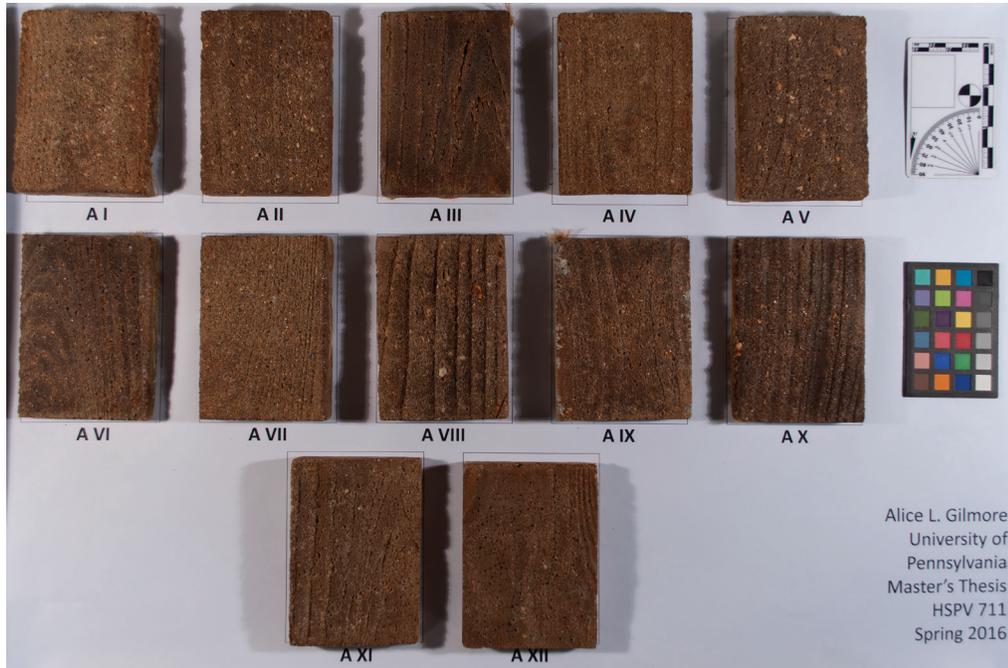
Appendix F: Accelerated Weathering Photos



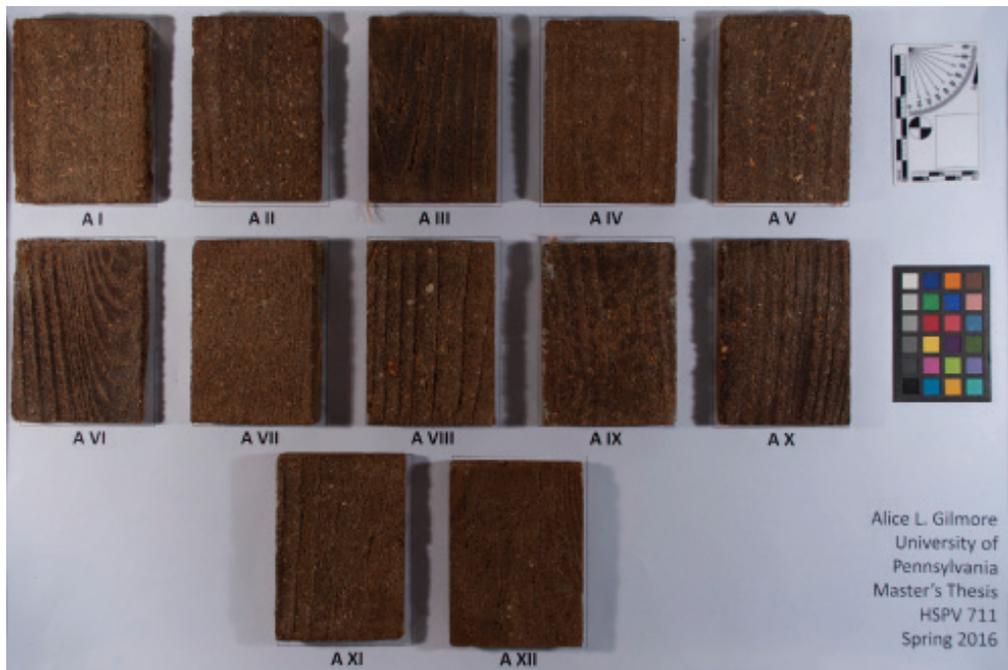
Appendix F. Figure 1. Samples before weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



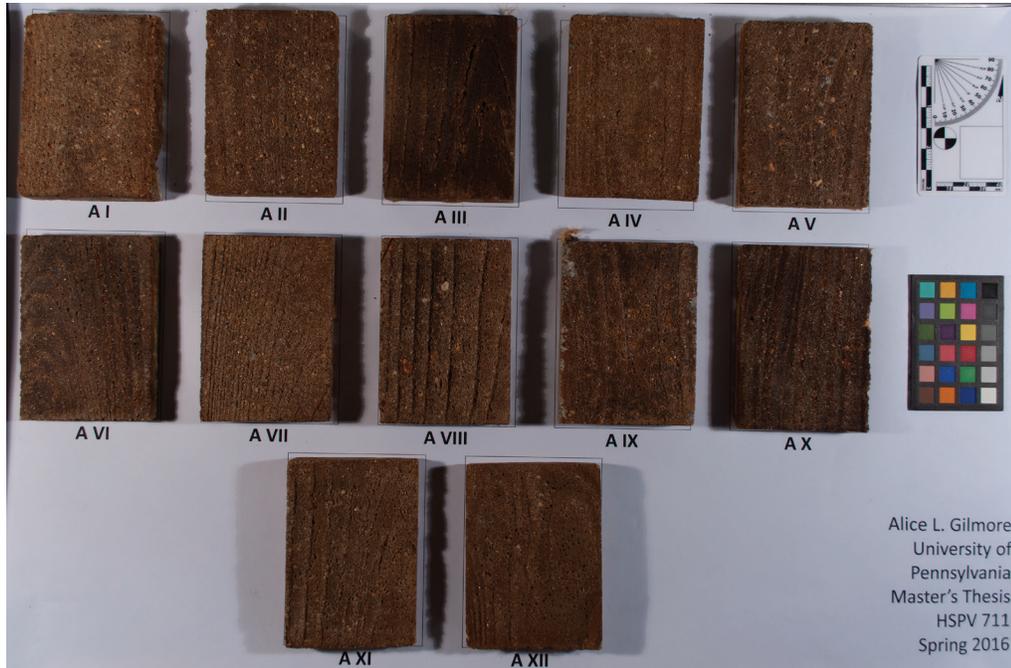
Appendix F. Figure 2. Samples After 845 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



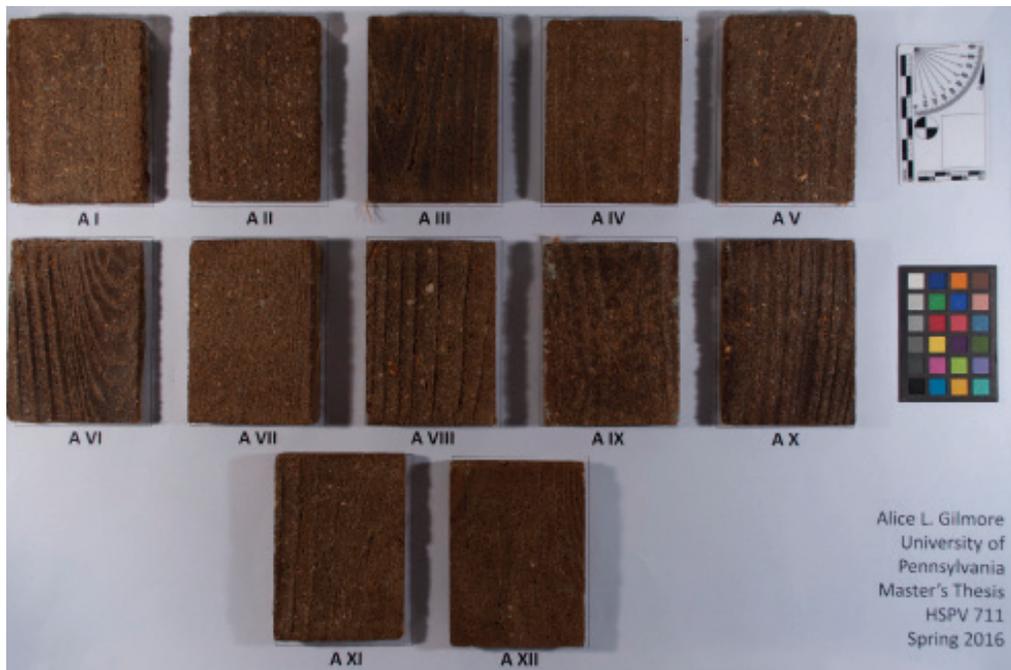
Appendix F. Figure 3. Samples After 125 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



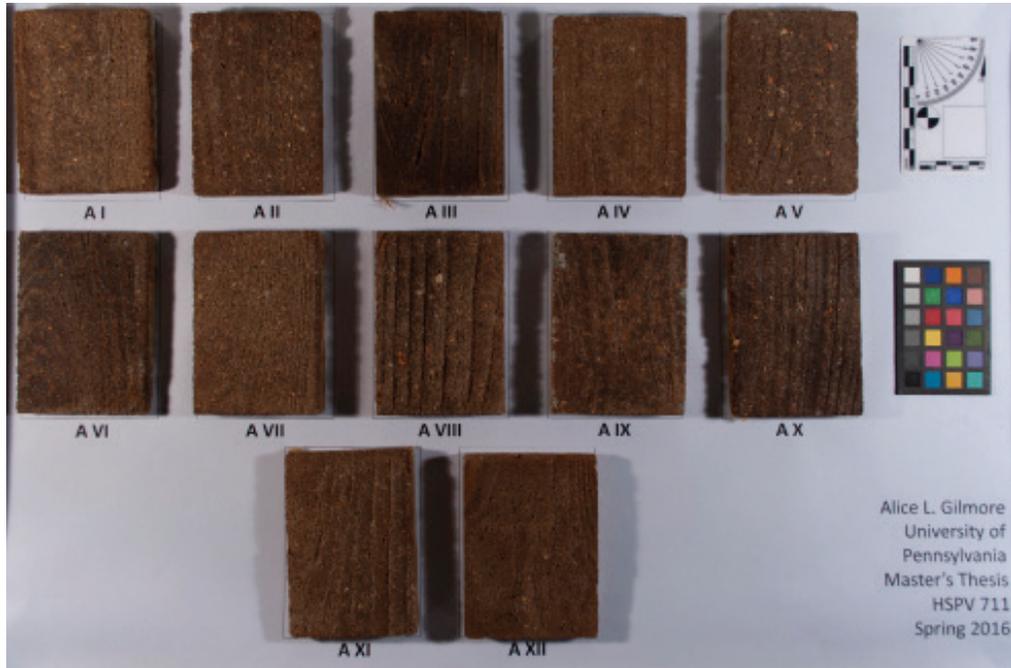
Appendix F. Figure 4. Samples After 845 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



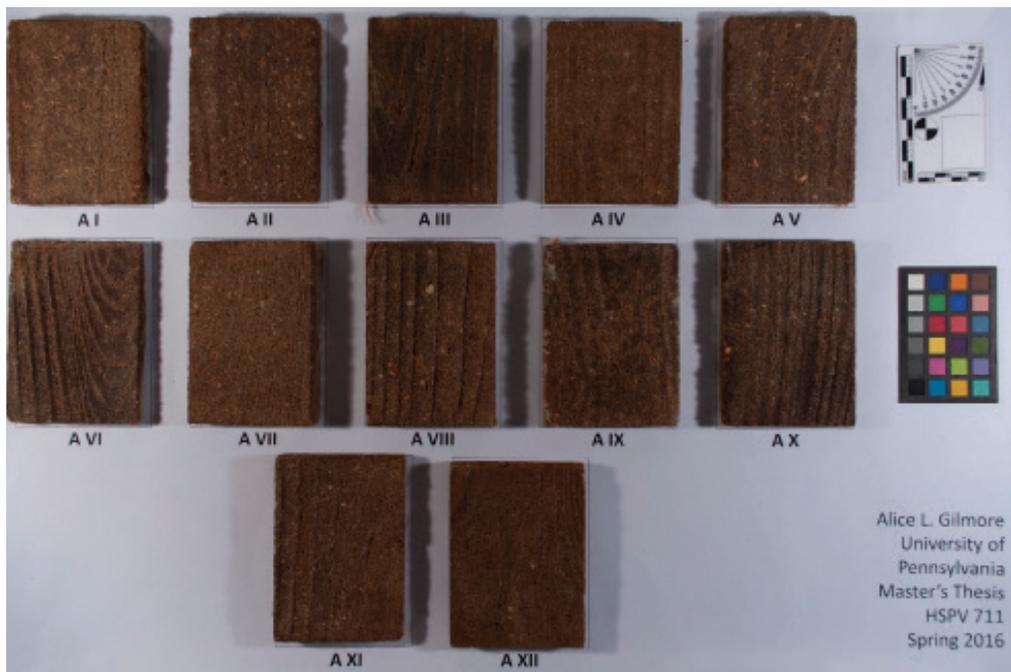
Appendix F. Figure 5. Samples After 245 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



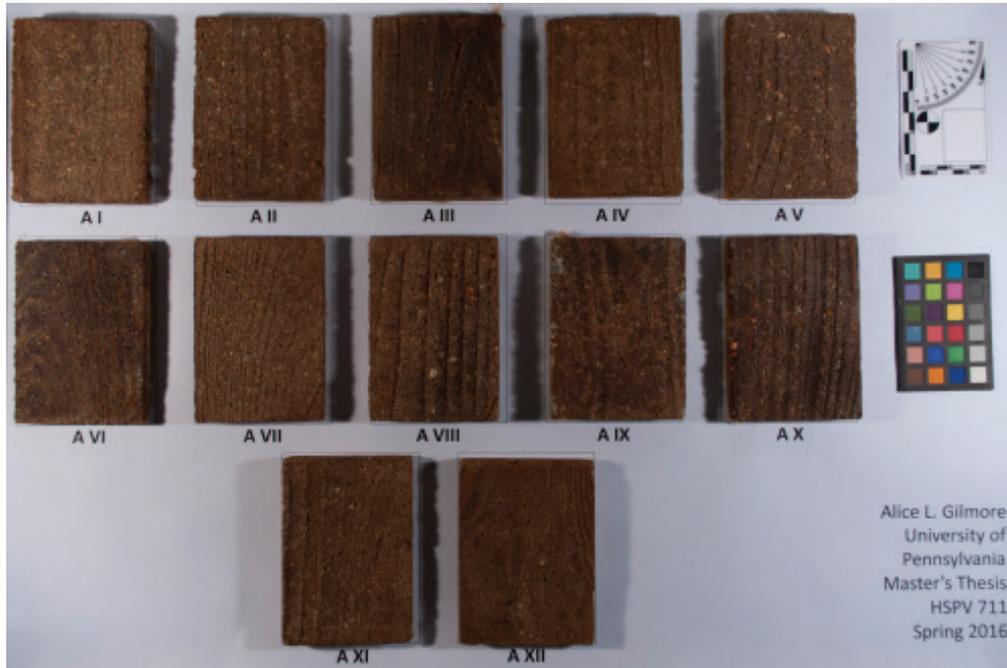
Appendix F. Figure 6. Samples After 845 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



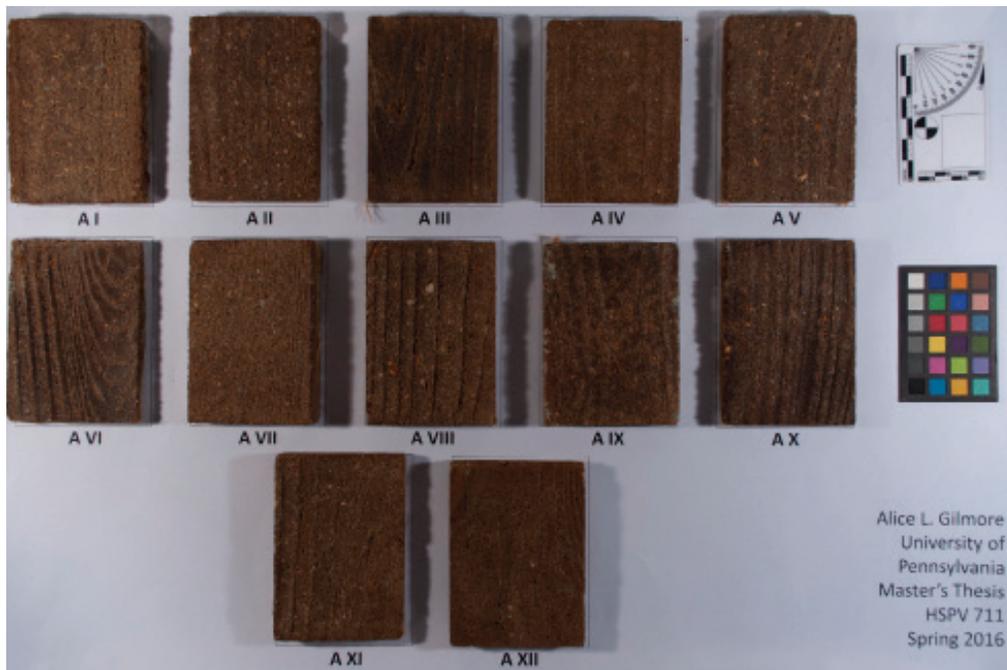
Appendix F. Figure 7. Samples After 381 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



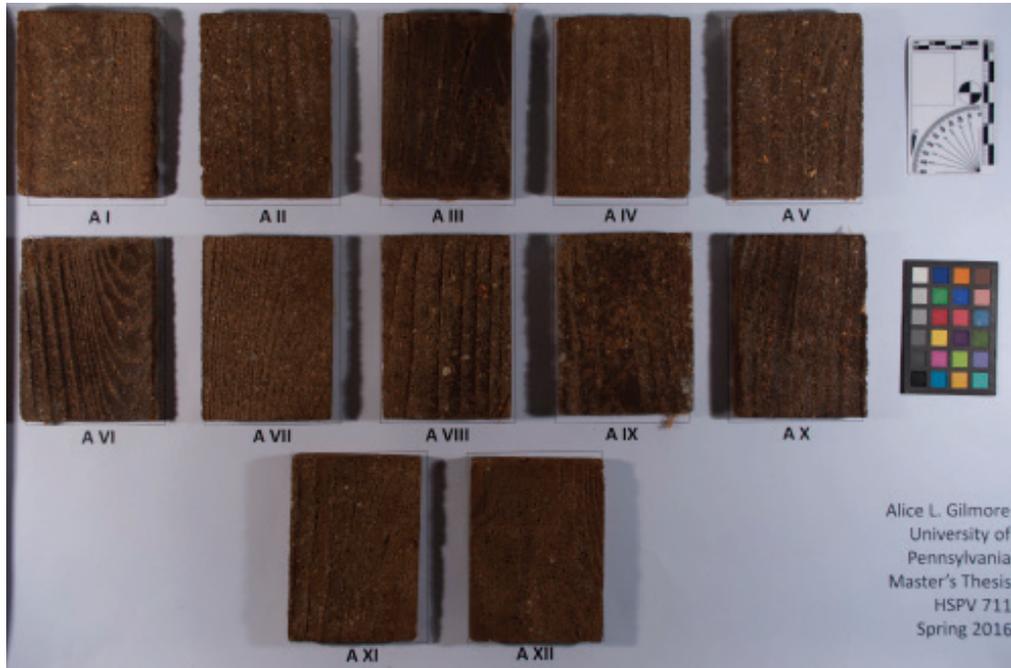
Appendix F. Figure 8. Samples After 845 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



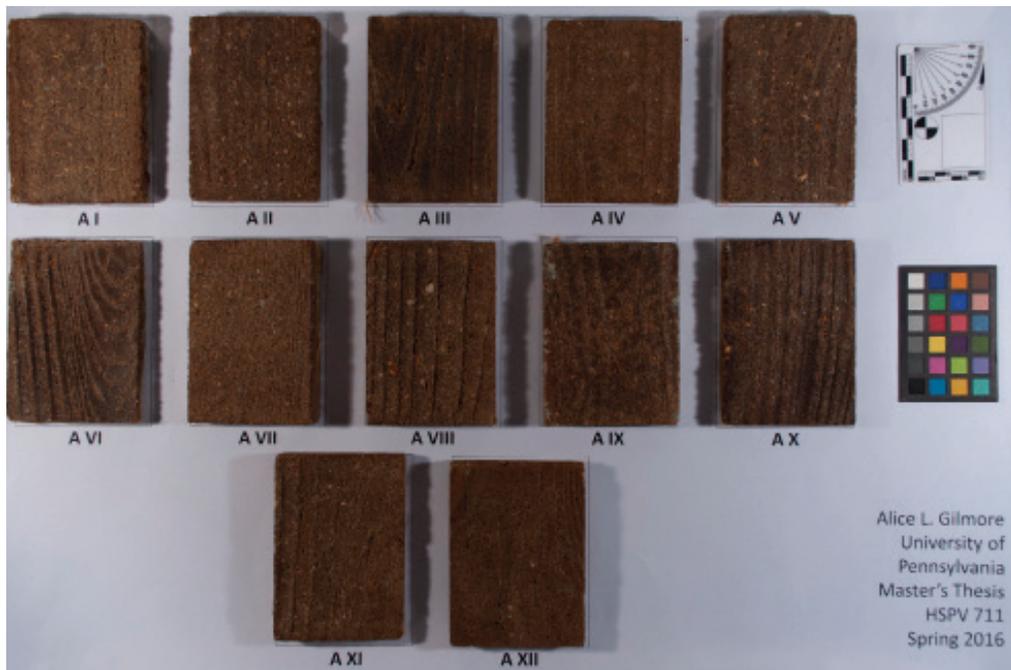
Appendix F. Figure 9. Samples After 486 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



Appendix F. Figure 10. Samples After 845 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



Appendix F. Figure 11. Samples After 608 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.



Appendix F. Figure 12. Samples After 845 hours of weathering. Top row is the cohort that was treated with the water repellent, The second row is the cohort that was left untreated and the bottom two samples are the controls.

Appendix G: Spectrophotometry Data

Before Values Water Repellent Treated Cohort			
Data Name	L*(D65)	a*(D65)	b*(D65)
Pre Weathering A_I	41.82	10.12	28.19
Pre Weathering A_I	41.88	10.03	25.03
Pre Weathering A_I	37.79	11.61	31.93
Pre Weathering A_I	41.69	10.15	27.32
Pre Weathering A_I	37.9	10.81	30.02
Pre Weathering A_II	29.91	13.04	37.48
Pre Weathering A_II	32.02	11.48	30.29
Pre Weathering A_II	33.95	12.37	34.67
Pre Weathering A_II	37.02	11.68	30.1
Pre Weathering A_II	33.44	12.69	34.73
Pre Weathering A_III	28.13	13.66	37.84
Pre Weathering A_III	27.08	13.96	38.92
Pre Weathering A_III	26.12	14.4	39.28
Pre Weathering A_III	21.84	11.76	32.86
Pre Weathering A_III	22.66	12.94	36.32
Pre Weathering A_IV	35.21	14.7	38.89
Pre Weathering A_IV	36.36	13.37	36.23
Pre Weathering A_IV	36.65	13.32	35.49
Pre Weathering A_IV	39.43	13.7	34.97
Pre Weathering A_IV	37.34	12.51	34.66
Pre Weathering A_V	31.79	10.84	28.04
Pre Weathering A_V	42.25	16.2	40.14
Pre Weathering A_V	36.68	15.55	39.45
Pre Weathering A_V	31.34	13.43	38.83
Pre Weathering A_V	33.01	11.56	30.54

Table 4. Table of before values for water repellent treated cohort.

After Values Water Repellent Treated Cohort			
Data Name	L*(D65)	a*(D65)	b*(D65)
845 HRS A_I	36.4	11.37	28.76
845 HRS A_I	40.34	11.04	28.38
845 HRS A_I	38.65	9.91	24.69
845 HRS A_I	37.15	11.54	29.68
845 HRS A_I	39.39	11.07	28.19
845 HRS A_II	36.91	10.27	26.33
845 HRS A_II	32.63	11.93	28.81
845 HRS A_II	29.35	11.23	25.81
845 HRS A_II	31.47	9.78	21.53
845 HRS A_II	29.37	11.02	26.6
845 HRS A_III	21.95	9.73	21.13
845 HRS A_III	25.09	10.32	21.16
845 HRS A_III	26.01	11.74	24.14
845 HRS A_III	24.65	9.42	18.51
845 HRS A_III	26.24	9.99	22.15
845 HRS A_IV	37.03	13.5	32.84
845 HRS A_IV	40.88	10.4	24.13
845 HRS A_IV	35.18	11.78	27.65
845 HRS A_IV	35.79	11.98	31.05
845 HRS A_IV	33.44	11.64	29.23
845 HRS A_V	40.54	14.32	32.41
845 HRS A_V	35.28	10.49	24.25
845 HRS A_V	33.89	10.89	26.04
845 HRS A_V	33.25	11.58	26.27
845 HRS A_V	32.69	11.63	28.59

Table 5. Table of after values for water repellent treated cohort.

Statistical Analysis of Data from the Water Repellent Treated Cohort

L Values

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
L Value Before Values	24	0	24	28.550	42.010	35.286	3.230
L Value After Values	24	0	24	20.260	41.780	32.516	4.806

Difference	2.770
t (Observed value)	4.460
t (Critical value)	2.069
DF	23
p-value (Two-tailed)	0.000
alpha	0.05

A Values

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
A Value Before Values	24	0	24	7.020	12.810	10.398	1.537
A Value After Values	24	0	24	7.960	12.650	10.673	1.233

Difference	-0.275
t (Observed value)	-0.849
t (Critical value)	2.069
DF	23
p-value (Two-tailed)	0.405
alpha	0.05

B Values

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
B Value Before Values	24	0	24	17.790	36.110	27.290	4.686
B Value After Values	24	0	24	18.200	31.950	25.665	3.454

Difference	1.625
t (Observed value)	1.734
t (Critical value)	2.069
DF	23
p-value (Two-tailed)	0.096
alpha	0.05

Before Values Untreated Cohort			
Data Name	L*(D65)	a*(D65)	b*(D65)
Pre Weathering A_VI	32.6	10.78	26.61
Pre Weathering A_VI	31.95	11.15	31.96
Pre Weathering A_VI	33.44	7.02	18.31
Pre Weathering A_VI	34.49	7.42	20.2
Pre Weathering A_VI	34.96	10.32	27.59
Pre Weathering A_VII	42.01	9.74	25.05
Pre Weathering A_VII	40.55	10.96	29.18
Pre Weathering A_VII	38.93	11.2	29.18
Pre Weathering A_VII	36.06	12.13	31.98
Pre Weathering A_VII	41.15	10.58	28.03
Pre Weathering A_VIII	34.02	10.63	27.55
Pre Weathering A_VIII	36.21	10.26	27.59
Pre Weathering A_VIII	34.13	11.35	32.15
Pre Weathering A_VIII	31.26	12.61	36.11
Pre Weathering A_VIII	38.14	9.71	26.62
Pre Weathering A_IX	37.41	10.57	26.36
Pre Weathering A_IX	33.35	12.81	31.58
Pre Weathering A_IX	33.59	11.71	29.36
Pre Weathering A_IX	36.27	9.47	25.04
Pre Weathering A_IX	34.29	11.94	33.96
Pre Weathering A_X	36.25	7.73	17.79
Pre Weathering A_X	34.89	8.42	20.6
Pre Weathering A_X	32.36	11.12	27.5
Pre Weathering A_X	28.55	9.91	24.66

Table 6. Table of before values for untreated cohort.

After Values of Untreated Cohort			
Data Name	L*(D65)	a*(D65)	b*(D65)
845 HRS A_VI	32.34	10.81	28.5
845 HRS A_VI	29.1	11.76	26.67
845 HRS A_VI	28.73	8.19	18.2
845 HRS A_VI	26.7	7.96	20
845 HRS A_VI	30.19	10.37	23.43
845 HRS A_VII	40.23	10.92	26.7
845 HRS A_VII	38.85	10.96	27.32
845 HRS A_VII	36.18	11.53	28.92
845 HRS A_VII	35.55	12.65	30.88
845 HRS A_VII	41.78	9.71	23.9
845 HRS A_VIII	31.5	9.78	23.85
845 HRS A_VIII	34.63	9.6	23.67
845 HRS A_VIII	34.17	11.43	28.72
845 HRS A_VIII	31.9	11.98	31.95
845 HRS A_VIII	36.47	10.16	26.32
845 HRS A_IX	32.74	9.73	20.86
845 HRS A_IX	27.1	9.54	23.03
845 HRS A_IX	32.16	10.69	24.49
845 HRS A_IX	32.58	12.32	25.86
845 HRS A_IX	37.03	11.12	25.99
845 HRS A_X	27.36	12.55	30.59
845 HRS A_X	29.91	10.62	25.64
845 HRS A_X	32.92	10.09	22.48
845 HRS A_X	20.26	11.67	27.98
845 HRS A_X	25.1	12.95	34.65

Table 7. Table of after values for untreated cohort.

Statistical Analysis of Data from the Untreated Cohort

L Values

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
L Value Before Values	24	0	24	28.550	42.010	35.286	3.230
L Value After Values	24	0	24	20.260	41.780	32.516	4.806

Difference	2.770
t (Observed value)	4.460
t (Critical value)	2.069
DF	23
p-value (Two-tailed)	0.000
alpha	0.05

A Values

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
A Value Before Values	24	0	24	7.020	12.810	10.398	1.537
A Value After Values	24	0	24	7.960	12.650	10.673	1.233

Difference	-0.275
t (Observed value)	-0.849
t (Critical value)	2.069
DF	23
p-value (Two-tailed)	0.405
alpha	0.05

B Values

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
B Value Before Values	24	0	24	17.790	36.110	27.290	4.686
B Value After Values	24	0	24	18.200	31.950	25.665	3.454

Difference	1.625
t (Observed value)	1.734
t (Critical value)	2.069
DF	23
p-value (Two-tailed)	0.096
alpha	0.05

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