Examination of Surface Washing Agents for Conservation of Oiled Historic Materials

Phase III

October 2019– September 2021

Note 1:	The U.S. Department of the Interior sponsored the subject study.
Note 2:	The U.S. Environmental Protection Agency provided the list of registered Surface Washing Agents selected for the subject study.
Note 3:	This subject report is exactly as originally published with the exception that Spillclean® has been highlighted throughout in yellow.

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1. Executive Summary

Beginning in January 2018, this project aims to identify (1) commercial products and (2) application methods best suited to remove crude oil from historic architectural substrates. The premise of the study is to expose surrogate historic materials to oil and examine surface washing agents as potential conservation treatments in a controlled setting. Products deemed successful are those that best restore the physical and chemical properties that a material possessed before oil exposure, as measured qualitatively and quantitatively.

The data presented in this report was collected as a part of Phase III of a three-part study to take place over 2 years. The study seeks to remove one of two classes of oil, West Texas Intermediate (WTI) from Galveston, TX, U.S.A or Access West Winter Blend (AWW) from Alberta, Canada, with one of the seven surface washing agents (SWAs) that are selected from the Environmental Protection Agency (EPA) National Contingency Plan Product Schedule. Products selected in the third phase of this study were based on the success of SWAs with active ingredient as ethoxylated alcohols in Phase I and II. Earlier research from 2011 established that SWA with D-limonene as the active ingredient was successful in the removal of oil. The surfactants used for fracking and drilling in the oil industry have a high percentage of ethoxylated alcohols between 30-40%

Products examined in the second phase of this study include Premier 99, Spillclean, Naturama G3A-5, Gold Crew SW, De-solv-it Industrial formula apart from Simple Green 2013 Reformulation which was used in Phase I of this study, and Nokomis 5-W, which was examined in Phase I and II of this study and was selected once again to establish continuity. The substrate used in this phase include – Concrete, Yellow Pine, Brick, and Sandstone.

The goal of this phase was to explore more SWAs from the EPA product schedule based on the success of the SWAs from Phase I and II of the project.

Phase III employs the same treatments methods explored in the Phase II to remove crude oil which were:

1. To attempt a two-part treatment, aiming first to remove bulk oil on the surface and then to remove residual oil and staining on and below the surface
2. To increase the number and volume of water rinses to remove residual oil and SWA

Success of a treatment is measured by data describing changes in color, gloss character, surface roughness, penetration depth and aptitude for water vapor transmission.

The data presented shows the successful SWA for the four substrates in all four conditions. WTI applied on concrete was best removed by SWA Premier 99. Naturama G3 A-5 was most successful on unweathred samples of yellow pine contaminated with WTI and Spillclean for the weathered samples. Spillclean and Nokomis 5W were successful on WTI contaminated Brick. The De-Solv-it Industrial formula and Naturama G3 A5 were most successful on AWWB on concrete and sandstone. Naturama G3 A-5 was most successful in removing AWWB contamination from yellow pine and weathered AWWB from brick. Gold crew SW was most successful on removing fresh AWWB from brick. Overall Naturama G-3 A5 was considered a good SWA for removal across all four substrates.

2. Background to the research

Since the beginning of petroleum industry in the late 1850s[1]the oil has been circulated on land and water. Transporting barrels of oil on wagons and flat boats evolved to the emergence of first pipeline 1862 at the well of Phillips No. 2 in Oil Creek Valley, Pa.[2]. First oil well was drilled in 1859, near Titusville, Pennsylvania also causing one of the first oil spills on land during transportation from this well[3]. The use of petroleum increased with the discovery of steam engine and later petrochemical products such as plastics, textiles, etc. The crude oil and gas industry provide for 60% of worlds primary energy needs[4.] With this substantial need for crude oil, the transportation by trucks, rails, pipelines, and ships increased in the last century making spills inevitable. The spills lead to indiscriminate contamination of surrounding environments, including cultural and historical sites[5]. Release of crude oil into the environment can occur during transportation over water or land, as a result of operational discharge, faulty equipment, human error, disaster, or via a damaged pipeline[6].

In the recent past spills of various types and sizes were seen. In May 2015 approximately 100,000[7] gallon oil spill just North of Refugio State Beach in California coating 4 miles of the shoreline. This oil spill impacted the cultural resources which include artifacts made up of native stones, bones, cemeteries and grave goods[8.] The most recent spill, February 2021 in Israel, was an ecological disaster in which more than 12,000 tons of petroleum and tar was piled up on beaches. The cleanup would take several months, and it is known to have impacted sea turtles, sea birds, fishes and a young whale. At present Chaco Canyon, a UNESCO World heritage site in New Mexico is at threat. It was a major center of ancestral Pueblo culture between 850 and 1250, was a focus for ceremonials, trade and political activity for the prehistoric Four Corners area. There has been a growth of oil and gas wells in its 15 miles radius since 2000 making oil or gas spill probable.

Despite the physical and chemical threat to cultural resources presented by crude oil contamination, little is understood about how best to respond to this type of spill[9]. As compared to the cultural resource specialists, oil spill responders and SCAT teams are acquainted with the spills, its identification, and have appropriate response options to minimize impacts. With the varied range of cultural resources - archaeological sites, historic bridges, cultural landscapes, historic buildings and their respective cultural materials, the methods implemented by first responders such as power washing and largescale treatments are not suitable. As the oil response protocol specifies the use of products enlisted on Environmental Protection Agency's National Contingency Plan Product Schedule, for oil remediation include the Surface Washing Agents (SWAs). This study seeks to identify both products and application methods appropriate for removal of crude oil while minimizing the physical and chemical impacts on cultural resources[10.]

With a lack of research on the oil spill response for cultural materials, it was required to have a broad range of application- oils, SWA's, and substrates. Two oils of different viscosities were selected for understanding different oil absorptions of substrates. The first phase included four substrates and six SWA's varied in oil removal mechanisms. The treatment application was performed in two phases of poultice treatments. The second phase of the research included on successful SWA from Phase I and two new SWA's to test the efficacy of the alternate treatment application i.e., spray and agitate method followed by two phases of poultice treatments on one substrate. The success of two SWA's and tripartite treatment method continued to the Third Phase. In addition to two, five new SWA's selected were based on the similar chemical compositions for application on four substrates.

The National Center for Preservation Technology and Training (NCPTT) is a National Park Service center whose mission is to apply science and technology to historic preservation. With the support of the U.S. Department of the Interior Inland Oil Spill Preparedness Project (IOSPP) this research began with Phase I, taking place from January 2018- May 2019. The second phase of this work was carried out from June 2019-August 2019. The third phase of this research, presented in this report, was done from October 2019 –June 2021.

3. Phase I & II

The first phase of the project started in January 2018 and commenced in May 2019. The materials chosen based on the frequency and proximity to crude oil circulation inland routes in the country, which included brick, concrete, Yellow pine, and Douglas fir. The two classes of oil chosen were West Texas Intermediate and Access Western Winter Blend. After the oil exposure half of the samples were exposed to artificial weathering in QUV. The SWAs were selected from the Environment Protection Agencies list based on their oil removal mechanism, toxicity, pH, etc. The selected products were BG-Clean 401, Cytosol, Nokomis5-W, PES-51, Petro Clean, and Simple Green. The samples were exposed to two treatments of poultice to reduce the presence of oil on the materials.

Success of a treatment as defined in Phase I is by changes in data which is difference in final and initial measurements. The data was collected for color, gloss, character, surface roughness, penetration depth and aptitude for vapor transmission. Based on the analyses, Simple Green delivered via a cellulose poultice is recommended to reduce WTI staining on all substrates when treated within twenty-one days (defined as "un-weathered "for the purpose of the research). For the weathered samples, Nokomis 5-W is recommended to reduce presence of WTI. PES-51 and Nokomis 5-W treated AWWB contaminated best in the six selected SWAs. As staining persisted after treatment of AWW on concrete and pine (quantified by color change, ΔE) needed more effective treatments for AWW remediation.

As it was difficult to remove diluted bitumen, alternate tripartite treatment method was planned in second phase of the study. It included SWAs- Accell Clean SWA, AQUACLEAN, and with the success of Nokomis 5-W in the phase I was used to establish continuity. The experimental substrate used was brick. The AWWB was weathered in a rotatory evaporator (30% evaporative mass loss) prior to application.

The main objective of this phase was to improve on the treatment methods to remove crude oil from Phase I. Two alternate methods were devised first included removing bulk oil on the surface and remove oil absorbed by the substrate. The number of water rinses was also increased to remove any residual oil and SWA. The second alternate method was to reduce the time between treatments and not letting samples dry. After the bulk removal of oil poultice treatments were followed and the data was collected after that. The brick substrates treated with Nokomis 5W had the lowest color change when exposed to fresh WTI and AWWB.

The data showed that brick substrates that were treated with Nokomis 5-W had the lowest color change when exposed to both fresh WTI and AWW. Treatment with Aquaclean had the least effect on the substrate's ability to transmit water vapor and resulted in lowest gloss change. The Access Clean performed slightly better than the other two products on samples exposed to weathered AWWB. The second alternate method to apply the three treatments without collecting data and letting the samples dry did not increase the effectiveness of the treatments to remove AWW. While the tripartite application was more successful than Phase I in removing AWWB, more effective treatments are needed for AWW remediation as the residual oil persisted on the samples.

4. Materials

Crude Oils

To establish continuity between Phase I and Phase II of this research, the same crude oils that were used for Phase I of the experiment will be used for Phase II. West Texas Intermediate is a medium-viscosity crude oil with a reported density of 0.8594 g/mL (0% Evaporative Mass Loss). Access Western (Winter) Blend is a comparatively heavy oil with a reported density of 0.9253 g/mL (0% Evaporative Mass Loss). In addition to presenting a good comparison based on density, these oils were selected because they both regularly travel by pipeline, rail, or truck, making them more likely to affect inland historic sites in the case of a spill.

Surface Washing Agents (SWA)

The aim of the Phase III is to evaluate additional Surface Washing Agents from the National Contingency Plan Product Schedule. As the successful SWAs from Phase I and Phase II were Nokomis – 5W and Simple green reformulation the composition of the two were studied which had primary component as ethoxylated alcohols. Therefore, Simple Green reformulation from Phase I and Nokomis 5-W from Phase I & II of this project were selected to continue on into Phase III. Four SWAs were selected with primary ingredient as ethoxylated alcohols which were – Gold crew SWA, Premier 99, Naturama G3 A-5, and Spillclean. Earlier research from 2011 established that solvent based SWA with D-limonene as the active ingredient was successful in the removal of oil. Therefore, De-Solv-it industrial formula was selected. Information about the seven SWA's examined here in presented in Table 1.

Fig. 1 The SWA's used for this project from left to right – Naturama G3-5, De-Solv-it industrial formula, Simple Green 2013 reformulation, premier 99, Gold Crew – SW, Nokomis 5W, and Spill clean.

Table1: The SWA's used for Phase III and their properties.

	New Products added in Phase III					Repeated Products from Phase I	Repeated Products from Phase I and II
Surface Washing Agents	**Premier 99 (Water Based) (formerly D-41)**	**Gold Crew SW**	**Naturama G3 A-5**	**Spillclean**	**De-Solv-it INDUSTRIAL FORMULA**	**Simple Green 2013 Reformulation**	**Nokomis 5-W**
Made by:	Gold Coast Chemical Products	Gold Crew Products & Services	Green Life Development, Inc.	Super Sat Ventures	Orange-Sol Blending and Packaging	Sunshine Makers, Inc.	Mar-Len Supply, Inc.
Easily obtainable?	Yes(phone) 1 gallon and 55 gallon size	Yes (email) 5and 55 gallon	Yes (email) 1 gallon, and special batch creation	Yes (phone/email) 5 gallon	Yes (phone/email) 1, 5, and 55 gallon size	Yes (phone/email) 1,5, and 55 gallon size	Yes (phone)
Mechanism:	**Lift and Disperse**	**Lift and Disperse**	**Lift and Disperse**	**Lift and Disperse**	**Lift and float**	**Lift and Disperse**	**Lift and Disperse.**
Ingredients	Sodium Hydroxide Hydroxyethyl Isodecyloxypropylamine Oxide, **Nonylphenol Ethoxylate**, Sodium metasilicat, Ethylene Diamine Tetra Acetic Acid	Proprietary Blend of **Ethoxylated Octylphenolic** Surfactants	C9-11, Tomadol 91 - 2.5 **Ethanol, 2(2 butoxyethoxy)**-Stepanate, SXS 40%	**Nonylphenyl Ethoxylate**, Isopropanol	**D-limonene,** non-ionic proprietary surfactants and solvents. Biodegradable.	**ethoxylated alcohol,** Na citrate N,N-bis(carboxymethyl)L-glutamate, citric acid, isothiazolinone mixture	**Ethoxylated alcohols**
pH	11.5	9.76	8.39	7.2	6.6	9	10.4
Toxicity (LC50 for menidia beryllina)	565.70 96-hr ; 94.70 48-hr	13.80 96-hr, 20.40 48-hr	577.68 96-hr ; 482.97	24.30 96-hr; 10.00 48-hr	37.71 96-hr ; 4.57 48-hr	27.90 96-hr 77.60 48-hr	(10.47ppm/ 96-hr)

			48-hr				
Recommended application:	Apply by spray, mop, or pressure washer, etc. Agitate severe spots. Rinse thoroughly for residue free surface.	Apply through hand pump sprayer and allow to soak	Product may be applied by any method (e.g., drum pump, pressurized spray applicator, brush, or aqueous wash tank), depending on the surface; and type and viscosity of the oil/contamination.	Squeeze product directly around outside perimeter of oil/gasoline/antifreeze spill using squeeze bottle container. This process is designed to "contain" the contaminant and keep it from migrating down a hard surface.	Pour, spray, wipe onto problem area. Allow sufficient time for product to penetrate (penetration time will vary with different applications); wipe off or rinse with mild soap and clean water for residue free surface	Apply SIMPLE GREEN® or diluted solution of Simple Green® to oiled surface via sponge, mop, coarse spray, foaming applicator, or pressure washer.	Spray onto surface, brush or agitate, rinse with water.
Recommended concentration for heavy contamination	1:10	1:8	1:5	No dilution	No dilution	1:10	20%
Solubility in water:	100%	100%	Miscible in oil, water, and solvents	Water soluble	Not miscible or difficult to mix	100%	100%
Materials to avoid:	NA	NA	NA	For land only, shouldn't be used around water bodies.	Do not leave for extended periods of time on rubber, butyl, some styrene products or EPDM.		NA
Flammable?	no	no	no	Flammability: >210°F	No	no	No

Historic Materials

The substrates used in the first phase of this research were historic brick, concrete, yellow pine, and Douglas fir. For the Phase II due to time constraints, one surrogate material, historic brick was selected. From Phase I – historic brick, and concrete were continued. Due to similarities in data between Douglas fir and Yellow pine, former was discontinued in phase III. The fourth material to reflect the historic architecture materials of the regions of the country which was intersected with oil pipelines was Sandstone.

The concrete selected is most likely cast in the 1960s which comprises white Portland cement as popular in the 1920s. Southern yellow pine used is a weathered piece from the 1930s. The brick used for Phase I &II of the research was Atlanta, Texas bricks, which were manufactured until World War II. For Phase III, due to lack of availability of Atlanta Texas Brick in the quantities required, bricks from 1900's St. Louis red were procured. The difference in the two bricks is more of the mineral compositions; the WWII bricks are moderately high-fired bricks that are hard but porous, ranging from yellow-brown to red-brown with uniform iron inclusions. The St. Louis bricks are uniformly colored which are made from high quality refractory red clay which can withstand high temperatures. The clay mines had beds of coal, fire clays, shales and brick clays[11]. There is not a considerable difference in the porosity, which is an important aspect for cleaning the oiled substrates.

Many brick companies had started in St. Louis in late 1800's, because of its geographical location in between two rivers: the Missouri and the Mississippi. The richest clay deposits in the country were found on the Eastern side of the state of Missouri. The surface clay deposited by these rivers was typical of the Mississippi Valley and ideal for the construction of brick. Deeper beneath the surface clay, shale deposits offered a more durable and fire-resistant clay, ideal for kilns[12]. This fine-grade clay and an abundance of accessible coal made it possible to mass-produce affordable, high-quality brick[13]. By 1900 St. Louis became the largest brick-making city in the world, shipping bricks across the United States and overseas. With its mass use and manufacturing makes it an ideal choice for this research.

The sandstone used for the Phase III was the compact sandstone from Colorado Plateau aquifers. The pipeline map of the country was overlaid with the sites on the National Register of Historic Places, protected Native American lands and sandstone aquifers. Based on the four layers we found that many buildings in Wyoming and Colorado were built with the Colorado Plateau sandstone. Also, Chaco Culture National Historical Park, a UNESCO World Heritage site in New Mexico is built in Colorado Plateau sandstone which has oil and gas well pads in its vicinity.

Fig. 2 substrates for Phase III – brick, sandstone, timber-yellow pine, and concrete

5. Methods

With the success of the three-step treatment in the Phase II, it was continued to Phase III which is Spray-Agitate followed by two treatments of Poultice. The spray- agitated method, as described in Procedure 4, was intended to remove bulk oil deposited on the surface of the surrogate material. As described in Procedure 5, a surface washing agent mix poultice was applied twice to remove absorbed oil. The progress after each subsequent treatment was documented.

A simplified experiment matrix, showing the number of samples for each combination of the 2 oils and 7 surface washing agents on historic substrates, is shown below.

Table 2: Experiment Matrix, Phase III

	West Texas Intermediate		Access Western Blend	
	Un-weathered	Weathered	Un-weathered	Weathered Oil**
brick	14* samples 1 control	14 samples 1 control	14 samples 1 control	14 samples 1 control
concrete	14 samples 1 control	14 samples 1 control	14 samples 1 control	14 samples 1 control
wood	14 samples 1 control	14 samples 1 control	14 samples 1 control	14 samples 1 control
stone	14 samples 1 control	14 samples 1 control	14 samples 1 control	14 samples 1 control
Total	224 samples, 14 oiled controls, 4 un-oiled controls = 242 *14 samples = 2 samples/product ** Oil weathered before it is applied to the material (Procedure 2)			

Procedure as defined in Phase II

Procedure 1: Material Preparation
Equipment - Ecomet 4: Variable Speed Grinder-Polisher (preparation) - Symphony ultrasonic cleaner (preparation) - Mettler Toledo Classic Plus scale (mass) - CR-400 Chroma-Meter (color) - BYK Gardner micro-TRI-gloss meter (gloss) - KEYENCE VR 300 3-D scanning macroscope (surface roughness/rugosity) - Nikon D750 camera with Nikon DX AF-S Nikkor 32 mm lens (Imaging) Prepare the materials: 1. Obtain naturally weathered, aged samples of each material to act as surrogate historic materials for treatment testing.

2. Prepare coupons by using a circular saw to cut the material into 3 x 2.5 x 0.5 in. coupons. Ensure that each coupon has one 3 x 2.5 in. face that was an exterior face of the material prior to cutting. This face will serve as the substrate for oiling and treatment.
3. Polish all other faces using a circular grinder/polisher fitted with 120 grit sand paper. Do not polish the front face of the substrate.
4. Clean inorganic samples using an ultrasonic cleaner with water at ~27°C. Do not clean wood in ultrasonic cleaner.
5. Label samples on back face with serial number using a Dremel tool.
6. Place samples in closed chamber conditioned to 50 ± 2% RH for 48-hrs prior to oiling.

Collect Pre-Oiled Data:

1. Collect the following data from the un-oiled samples:
    a. Mass (n*=3)
    b. Color (n=5)
    c. Gloss (n=5)
    d. Surface roughness profile
    e. Imaging (Settings: f/8, ISO 320, 2 Fiilex P180w – 40 W bulbs)

*n= number of measurements taken per sample and then averaged

Procedure 2: Weathering the Dilbit (before applying to materials)

Equipment:

- Rotary Evaporator
- Round-bottom flask
- Flat, glass pan

Weathering by Rotary Evaporation(Fig 1)*:

1. Place diluted bitumen in a round-bottom flask and record the mass.
2. Set up warm water bath to maintain a temperature of 80°F (this will help to maintain homogeneity of the oil).
3. Place in the flask in the rotary evaporator and lower into water bath. Leave air release open to facilitate weathering process. Do not turn on vacuum feature.
4. Allow the rotary evaporator to operate for a fixed amount of time (TBD)
5. Remove the flask from the rotary evaporator and record to the mass
6. Use the Evaporation Equation for the specific oil (included in the SDS) to calculate the evaporative mass loss at the given temperature and time of exposure.

Fig 3: Weathering of AWWB using Rotatory evaporator.

Weathering by Pan Evaporation:
1. Log mass of oil in a flat, open container.
2. Leave container open to air for a fixed amount of time (TBD)
7. Use the Evaporation Equation for the specific oil (included in the SDS) to calculate the evaporative mass loss at the given temperature and time of exposure.

*Only one methods of weathering (Rotary Evaporation or Pan Evaporation is necessary)

Procedure 3: Oil Application

Equipment:
- Mettler Toledo Classic Plus scale (mass)
- CR-400 Chroma-Meter (color)
- Fume hood
- Flat, glass container
- Vertical lab clamps affixed to horizontal holder (Fig. 2)
- BYK Gardner micro-TRI-gloss meter (gloss)
- 3D Measurement Macroscope VR-3200 (surface roughness/rugosity)
- Nikon D500 camera with Nikon DX AF-S Nikkor 32 mm lens (Imaging)
- QUV artificial weathering machine

Fig 4: The concrete samples oiled with West Texas Intermediate are hung with clamps.

Apply Oil:
1. In fume hood, pour fresh oil from canister into flat, glass container so that it coats the bottom (~0.5 in. deep). Apply to material immediately.
2. Hold the front-face of the sample in contact with the oil. Take care to ensure that only the front-face of the sample makes contact with the oil.
3. Hang sample face-down using a vertical laboratory clamp.
4. Repeat process manually for each sample.
5. When soiling with West Texas Intermediate, dip twice more for a total of three instances of material-oil contact, allowing samples to hang face-down for ten minutes between each instance of contact with oil. (Samples soiled with Access Western Blend are only dipped once)
6. Let samples hang face-down for 4 hours in a fume hood before placing face-up on a tray.
7. Calculate the volume of oil applied and estimate the mass.

a. Record the thickness of the oil coating using a wet-film thickness gauge.
b. Multiply the thickness of the coating by the dimensions of the front face of the sample, ensuring that units are consistent. (Note that this estimation will be low as some of the oil will have penetrated the surface of the material.)
c. Estimate the mass of oil added by multiplying the above volume and the density reported on the SDS. Compare estimated mass to the mass calculated by subtracting the mass of the un-oiled coupon from the oiled coupon.

8. Allow 24 hours to pass before collecting the following data (so not to transfer oil to instruments):
   a. Mass
   b. Color
   c. Gloss
   d. Surface roughness profile
   e. Imaging

Artificial Weathering:

1. Expose half of the samples oiled with West Texas Intermediate to artificial weather conditions in a QUV. Place samples in QUV and set to run 400 hours at ASTM G154 (Standard Practice for Operating Fluorescent Ultraviolet Lamp Apparatus for Exposure of Nonmetallic Materials).
   i. UV: 8 hrs, 60° C
   ii. Condensate: 4 hrs, 50° C
   iii. Cycle for 400 hours
2. Record analytical data after artificial weathering.
   a. Mass
   b. Color
   c. Gloss
   d. Surface Roughness profile
   e. Imaging

Procedure 4: Spray-Agitate Treatment

Equipment:

- Mettler Toledo Classic Plus scale (mass)
- Spray bottles
- Soft-bristle brushes
- CR-400 Chroma-Meter (color)
- BYK Gardner micro-TRI-gloss meter (gloss)
- 3D Measurement Macroscope VR-3200 (surface roughness/rugosity)
- Nikon D500 camera with Nikon DX AF-S Nikkor 32 mm lens (Imaging)
- Recirculating pump (rinsing)

Apply Spray Treatment

1. Prepare SWA solutions, diluting as directed by manufacturers.
2. Spray fixed amount ~5 mL (5 squirts from squirt bottle) of SWA solution onto the oiled

surface of each sample. Allow 10 minutes of contact.

3. After 10 minutes, agitate with a soft-bristle brush.
4. Spray additional 5 mL allocate of product. Agitate. Spray final allocate (total of ~15 mL of SWA solution/sample) and allow 10 additional minutes of contact.
5. Agitate treated oil with soft bristle brush for 30 seconds.
6. Rinse thoroughly with 250 mL deionized water using a recirculating pump to regulate rate of flow.
7. Apply poultice treatment (Procedure 5)

Procedure 5: Poultice Treatment

Equipment:

- Commercial Blender
- Mettler Toledo Classic Plus scale (mass)
- CR-400 Chroma-Meter (color)
- BYK Gardner micro-TRI-gloss meter (gloss)
- 3D Measurement Macroscope VR-3200 (surface roughness/rugosity)
- Nikon D500 camera with Nikon DX AF-S Nikkor 32 mm lens (Imaging)
- Recirculating pump (rinsing) with deionized water.

Fig. 5 - Poultice treatment on weathered yellow pine and concrete samples contaminated with WTI

Apply the Poultice

1. Prepare SWA solutions, diluting as directed by manufacturers.
2. In a blender, mix 3 cups (loosely packed) shredded cotton linters with 300 mL SWA solution(amount of cotton and SWA solution may vary depending on the amount of samples to be treated, but ratio should remain the same). A pulp will emerge after about 1 minute.
3. Measure ~40 g of the SWA-cotton pulp and flatten onto a piece of plastic wrap. The piece of plastic wrap should be big enough to secure the edges around the sample.
4. Place the sample face-down, ensuring that the pulp makes even contact with the front-face of the sample
5. Secure the edges of the plastic wrap around the sample with low-adhesion tape
6. Leave the poultice sealed and in contact with the sample for 4 hours
7. After 4 hours, remove the poultice.
8. Agitate remaining product with a soft bristle brush for 30 seconds
9. Use a recirculating pump to dispense distilled water in a steady stream. Disperse ~250 mL

water and then scrub for 10 seconds.

10. Repeat this process of rinsing and scrubbing for a total of three rinses (~750 mL water). Do not scrub after the final rinse to avoid recontamination.
11. Allow samples to dry before collecting analytical data:
    a. Mass
    b. Color
    c. Gloss
    d. Surface roughness profile
    e. Imaging
12. If needed, repeat poultice treatment a second time for all samples (Steps 1-11) and collect analytical data.

Parameters for analysis

The ability of a treatment to restore the original appearance of a historic material is integral to its relevance as a viable conservation treatment. In the context of this experiment, a successful conservation treatment facilitates the restoration of the physical and chemical properties that a material possessed before exposure to crude oil. In order to measure and track the changes associated with oil contamination, photographs and data describing the mass, surface roughness, gloss character, and color were collected at each of the following stages:

i. Before exposure to oil
ii. After exposure to oil
iii. After first treatment
iv. After second treatment
v. After third treatment

Analysis of these data allows for a quantitative and qualitative comparison of the treatments that were performed on each material.

Color

The ability of the SWAs to remove stains created by crude oil contamination as measured by color change was the prime parameter for success. Konica Minolta Chroma Meter CR-400 was used to measure color values which were L*(light to dark), a*(green to red), and b*(blue to yellow). In each reading the colorimeter took five measurements and the data was average of the readings. The measurements were taken at five different points on the sample.

The color change (ΔE) was considered by two methods. First, was considered to evaluate the capacity of each product to remove oil staining, with lower ΔE values corresponding to less color change following oiling and treatment. This method was utilized for AWWB and WTI. The second method was limited to WTI, higher ΔE values corresponding to high color change between oiling and treatment.

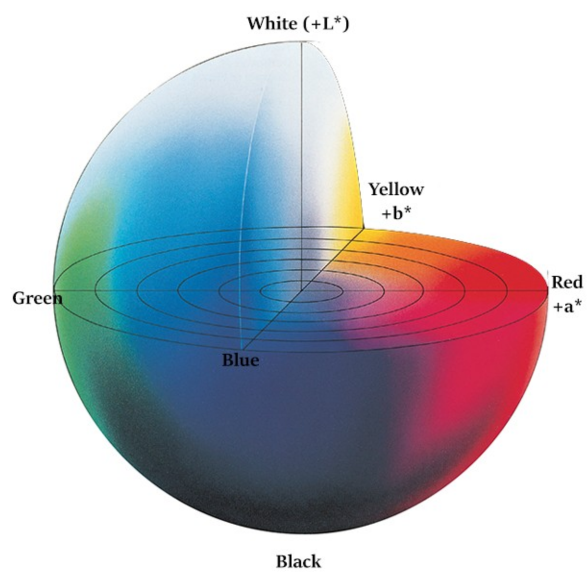


Fig.6-Color space[14] with l*, a*, and b*

The light and color shifts were used to calculate total color change, ΔE, using the CIE L*a*b* equation[15]:

$$\Delta E^{*}_{ab} = \left[\left(\Delta L^{*}_{ab} \right)^2 + \left(\Delta a^{*} \right)^2 + \left(\Delta b^{*} \right)^2 \right]^{\frac{1}{2}}$$

An appropriate conservation treatment should remove the crude oil without damaging or altering the material integrity of the substrate to maintain the values and significance associated with the cultural resource. As it was established in the Phase I of the research, a ΔE of 20 or greater is considered great enough to render a treatment inappropriate for this experiment. According to research and standards, ΔE ≤ 1 is barely perceptible to the human eye, and comparing two surfaces side by side is ΔE ≥ 2 is clearly perceptible and ΔE ≥ 5 the difference is visible without direct comparison.[16]

Gloss

Gloss is the physical character of the surface to reflect light and it was measured in gloss unites (GU) by using BYK Gardner micro-TRI-gloss meter. The gloss measurements were recorded at the angle of incidence 85° degrees, as the values were <10 GU for all the substrates over the different stages of the study. For each measurement five readings were taken along the width of the sample and an average of readings was used. Similar to color change, the difference in gloss character was considered by two methods, before oil exposure and after treatment, and between after oil contamination and treatment for WTI exposed samples.

An increase in gloss character can be indicative, of oil or product residue. Similar to color change the gloss character from before oiling to after treatment is preferred closer to zero.

Mass

The mass of the samples was recorded using the Mettler Toledo Classic Plus scale. At each stage an average of three measurements were taken of the samples. Before the treatment of the samples the mass of the samples were taken after keeping the samples in a closed container for 2 days with an 50 ± 2% RH. After oiling and subsequent stage the samples were kept in the fume hood, to avoid contamination. The RH in the fume hood fluctuated with high range of 65 to low range of 50 throughout the timeline of the project therefore RH at each stage was also recorded.

The difference in mass was considered by two methods as mentioned for gloss and color.

Surface Roughness: 3-D Profilometry

The surfaces were examined using the KEYENCE VR 300 3-D scanning macroscope. Using the VR-3000 G2 Series Analyzer software, the following measurements of the surface roughness were calculated

- Spc
- Sdr
- Spd

Spc refers to the arithmetic mean peak curvature, or the arithmetic mean of the principal curvature of the peaks on the surface, where a smaller value correlates to a more rounded peak shape and a larger value to a more pointed peak shape. *Spc* is measured in 1/mm (Fig. 3).[17]

Spd is the density of peaks or the number of peaks per unit area, measured in $1/mm^2$ (Fig. 4).[18] A large number indicates more peaks per unit area. As oil filled the pores and surfaces were agitated, the peaks were found to have flattened as compared from the initial stage.

Sdr, parameter is the percentage of the additional surface area contributed by the texture as compared to its planar definition(Fig. 5 & 6).[19]. As the weathered historic substrates are uneven in texture, this parameter helped understanding the change in the 'unevenness' of the surface with the residues from oil, products and also agitation of brushes.

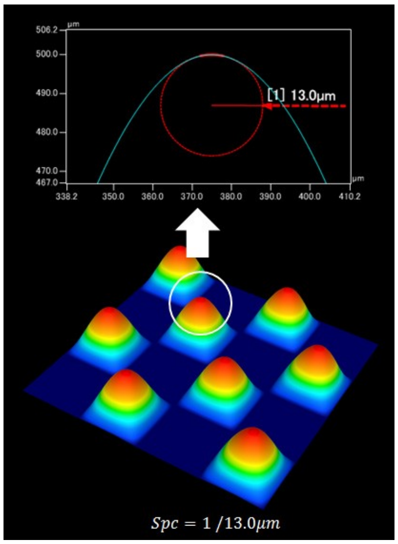


Fig. 7: *Spc* is a parameters that indicates the roundedness or pointiness of peaks on the measurement surface, with larger values indicating more rounded peaks.

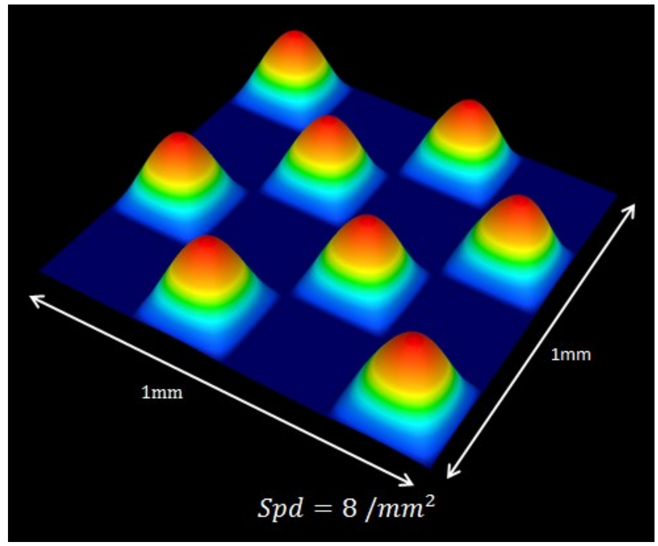


Fig. 8: *Spd* represents the number of peaks per unit area.

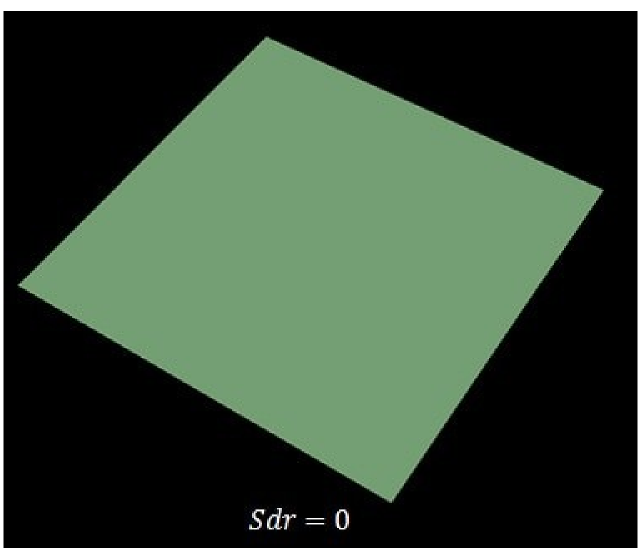


Fig. 9: When surface is flat the value is 0

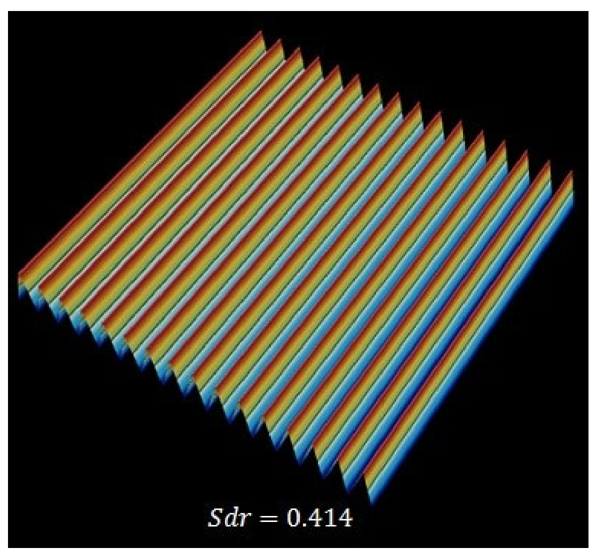


Fig. 10: When a surface has any slope, its Sdr

value becomes larger.

Water Vapor Transmission

This test is to measure the rate of transfer of water through the material. In a sealed container with a defined amount of water, the substrate is attached on the top such that vapor must travel through it to evaporate. Most historic buildings are made of permeable materials like stone, brick, timber, lime, clay, etc. and tend to absorb and release moisture. In a situation where the pores of material are clogged by either oil or SWA, impacting the breathability of the material, entrapment of moisture and further decay.

The test was followed as described in Phase II. 100mL of distilled water was placed in a Tupperware container, with top sealed and the substrate placed on top of that. The container lid had a rectangular cut for the vapor to transfer through the material. This assembly was placed in a closed container with 50 ± 2% RH. The RH was based on ASTM Standard E96;[20] however, all the parameters described in the ASTM Standard were not followed[1] due to restrictions on time and equipment, which is not unprecedented.[21] The mass measurements were taken on the Mettler Toledo Classic plus scale every minute for 24 hours. The data was plotted as mass (g) vs. time (h) and the rate, or the slope of the resulting line, was compared across treated sampled and untreated controls. One sample from each successful sample set was run for each SWA that was successful in cleaning the samples. The size of the cutout was kept uniform over different substrates, oils and SWAs to maintain uniformity.

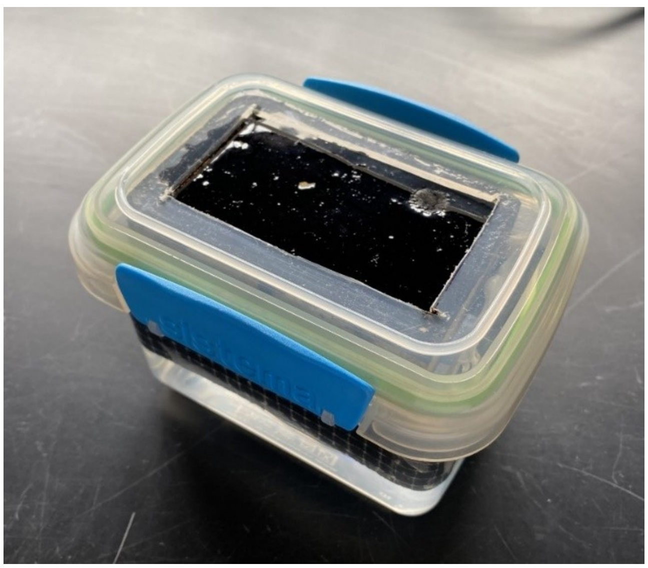


Fig. 11: Closed chamber to conduct water vapor transmission test on concrete substrate.

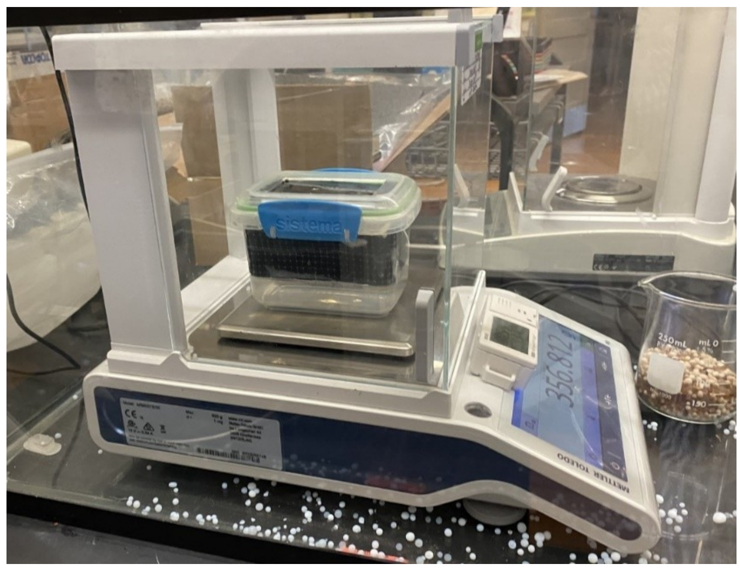


Fig. 12: Closed chamber on the weighing scale taking weight readings every minute.

[1] ASTM E96 calls for a temperature of 90° F and a continuous airflow of uniform velocity.

6. Results and Discussion

The structure of the analysis under each parameter starts from substrates contaminated with WTI followed by AWWB application. The change was measured by capacity of each product to remove oil staining, with lower values corresponding to less change following oiling and treatment. An additional method was used for WTI, where higher change value corresponded to the post oiling and treatment stage to understand the relationship between the oiled to cleaned stage. As the amount of oil absorbed by each sample varied, the two ways analysis process would give us a better understanding of success of surface washing agents. In the case of AWWB, it was difficult to take measurements after oiling as the samples were not dry and would have contaminated the equipment.

Color

Color change (ΔE) was measured as a quantitative means to assess physical change. Treatments that best restore the color of the original substrate prior to oil exposure are considered successful and are identified by a low ΔE in change in color between before oiling with treated and highest removal of oil by high ΔE for the change in color between post oiling to treated.

West Texas Intermediate

Concrete

The concrete substrates that were treated with Spillclean (ΔE 14.72, 20.14) and Premier 99(ΔE 18.81, 17.91) had the lowest color change when contaminated with fresh WTI. Although the values are too close to 20 which is considered inappropriate for this experiment. The two surface washing agents also had the highest when oil was removed Spillclean (ΔE 2.96, 4.88) and Premier 99 (ΔE 1.021, 1.72). As compared to freshly oiled samples the SWAs were more successful in removing oil from artificially weathered samples. Nokomis 5W (ΔE 9.14, 8.58) and Premier 99 (ΔE 10.08, 8.30) had the lowest color change from the initial stage and high with oiled as Nokomis 5W (ΔE 11.02,6.30) and Premier 99 (ΔE 7.41, 4.4)

Fig. 13: Color Change (ΔE) after removal of Fresh WTI from concrete Samples

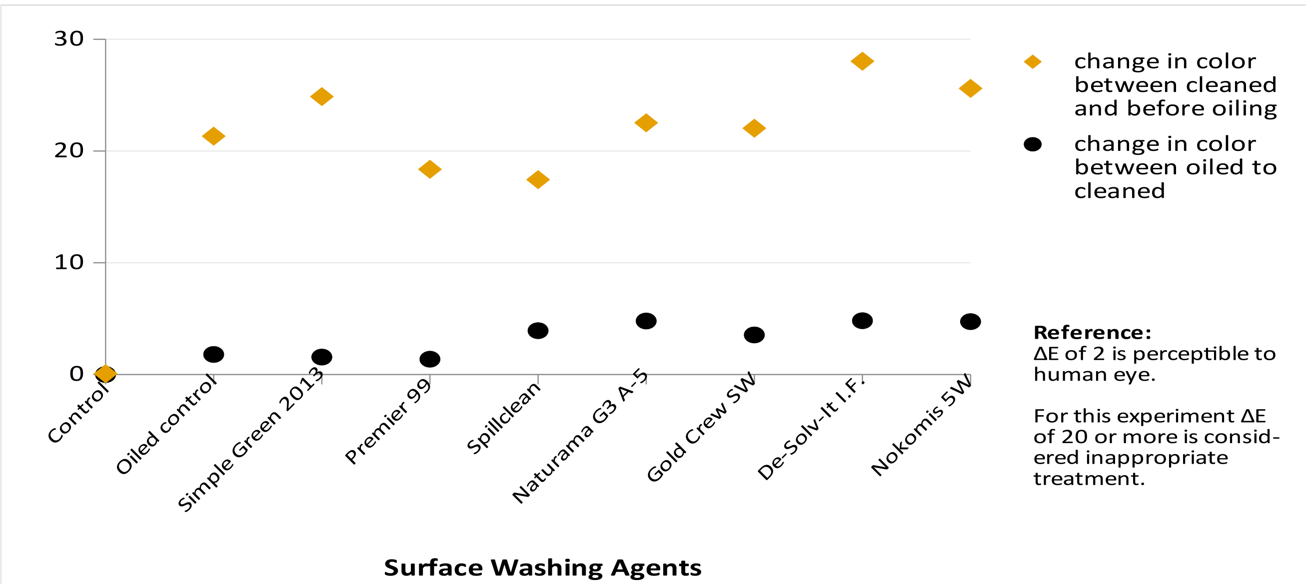
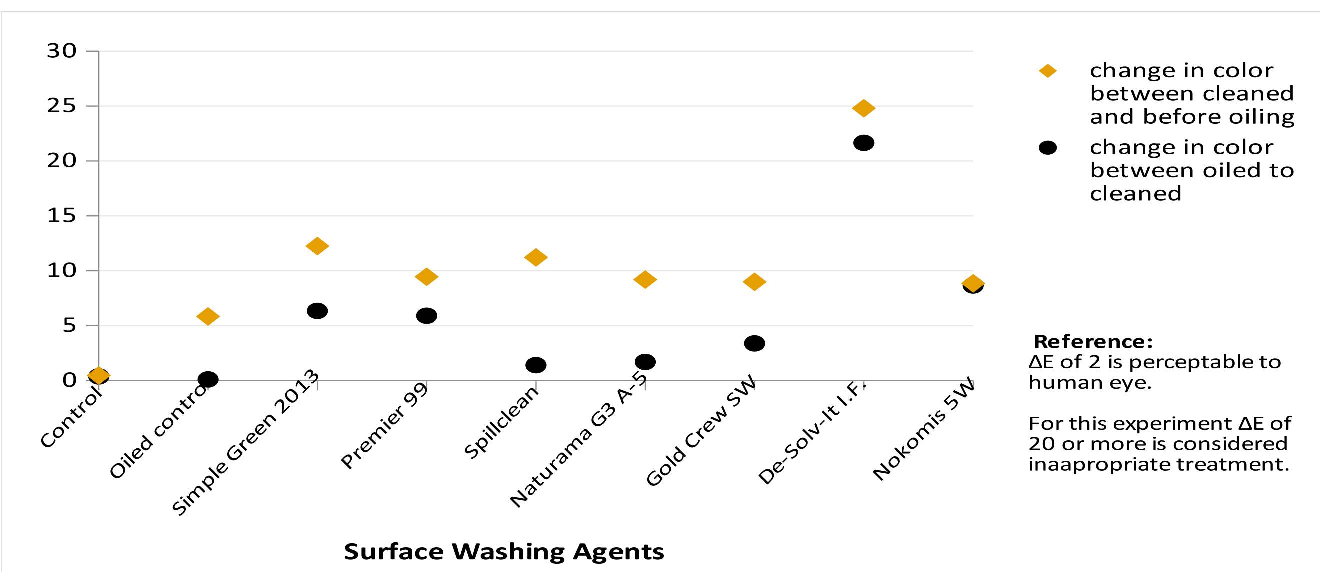


Fig. 14: Color Change (ΔE) after removal of WTI from artificially weathered concrete Samples



Yellow pine

The fresh WTI exposed yellow pine substrates that were treated with Premier 99(ΔE 9.40, 12.83) had the lowest color change followed by Gold Crew SW (ΔE 18.02, 15.19) from unoiled to treated stage and had the maximum color change from oiled to treated with Premier 99 (ΔE 18.62, 14.93) and Gold Crew SW (ΔE 13.90, 17.78). The color change results for cleaning in artificially weathered samples of yellow pine were lesser than freshly applied oil. The successful SWA were Spillclean (ΔE 17.15, 13.95) followed by Nokomis 5W (ΔE 11.22, 20.83) with high removal of oil with Spillclean (ΔE 22.08, 13.75) and Nokomis 5W(ΔE 7.5, 11.99)

Fig. 15: Color Change (ΔE) after removal of Fresh WTI from Yellow pine Samples

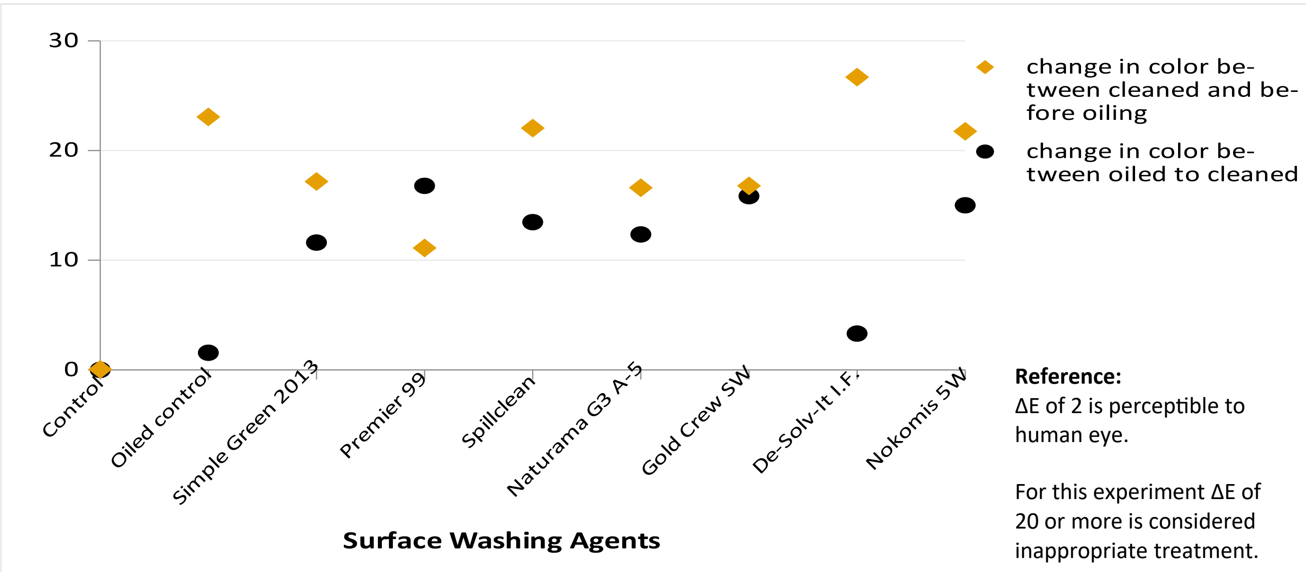
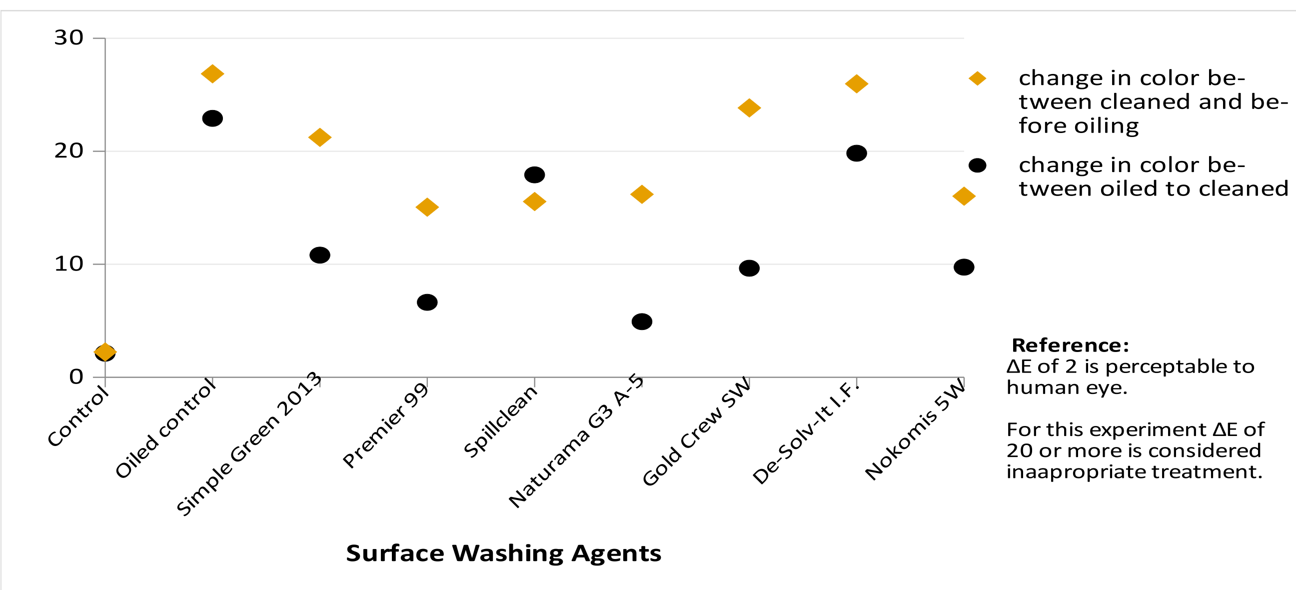


Fig. 16: Color Change (ΔE) after removal of WTI from artificially weathered Yellow pine Samples



Brick

Brick substrates that were contaminated with Fresh WTI treated with Spillclean (ΔE 8.46,7.36) and Nokomis 5-W (ΔE 5.82, 9.20) had the lowest color change when exposed to fresh WTI. The two surface washing agents also had the highest color difference while comparing the oiled and the treated stage – Spillclean (ΔE 2.06,1.77) and Nokomis 5-W (ΔE 0.61,1.73). Similarly for weathered brick samples the Nokomis 5-W (ΔE 7.5, 5.3) and Spillclean (ΔE 6.87, 7.12) were more successful with minimum change in color and maximum change with oil removal Nokomis 5-W (ΔE 8.15,14.77) and Spillclean(ΔE 11.02,14.56).

Fig. 17: Color Change (ΔE) after removal of Fresh WTI from Brick Samples

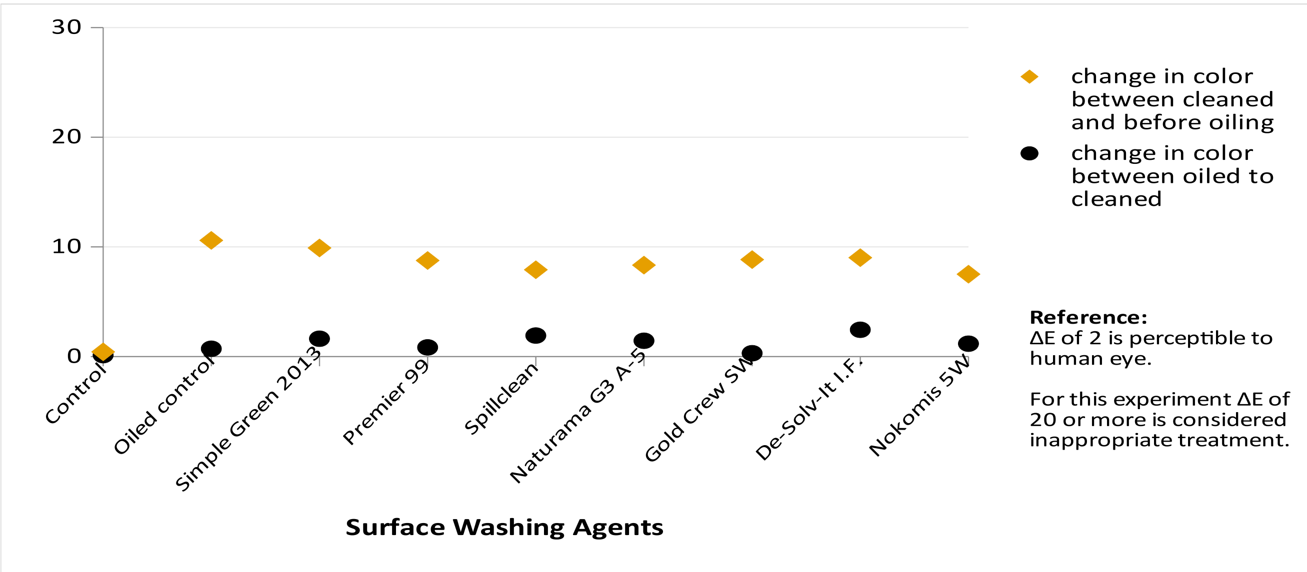


Fig. 18: Color Change (ΔE) after removal of WTI from artificially weathered brick samples

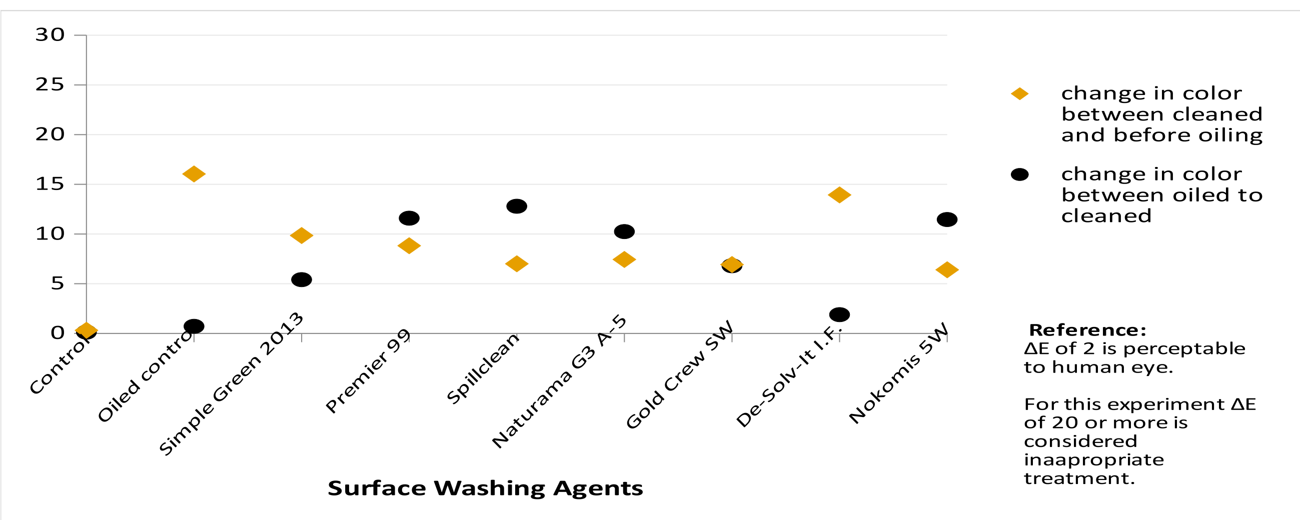


Figure 19. WTI contaminated samples of brick artificially weathered and cleaned with Spillclean compared with the un-oiled and oiled control after the treatment.

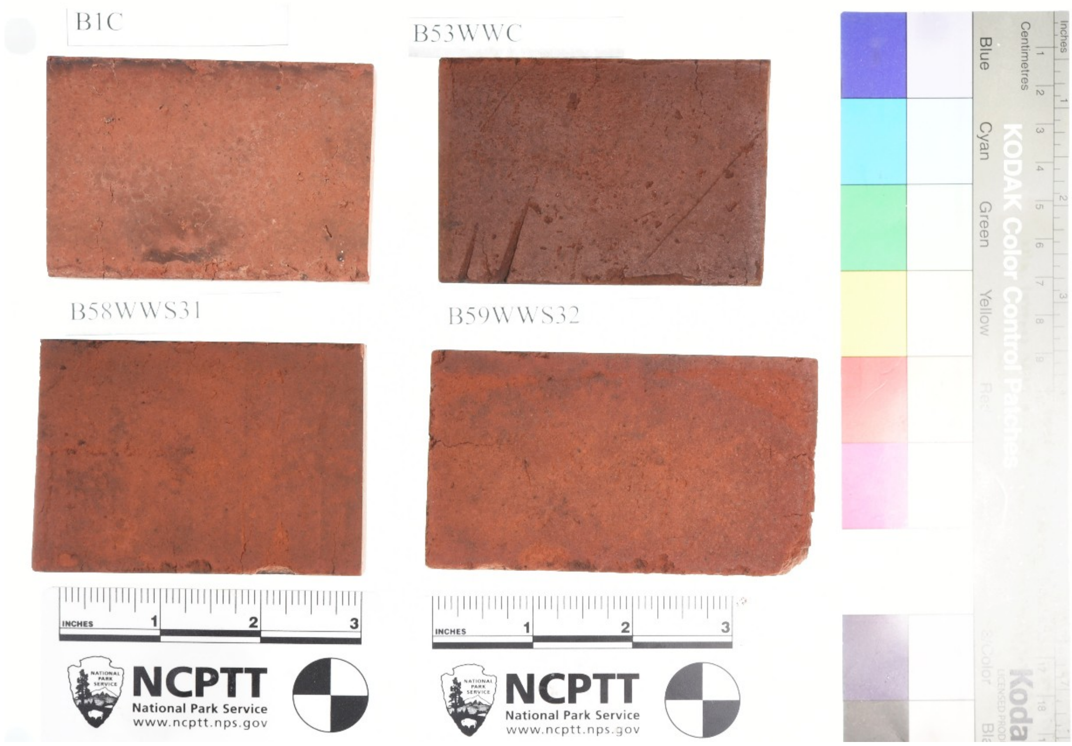
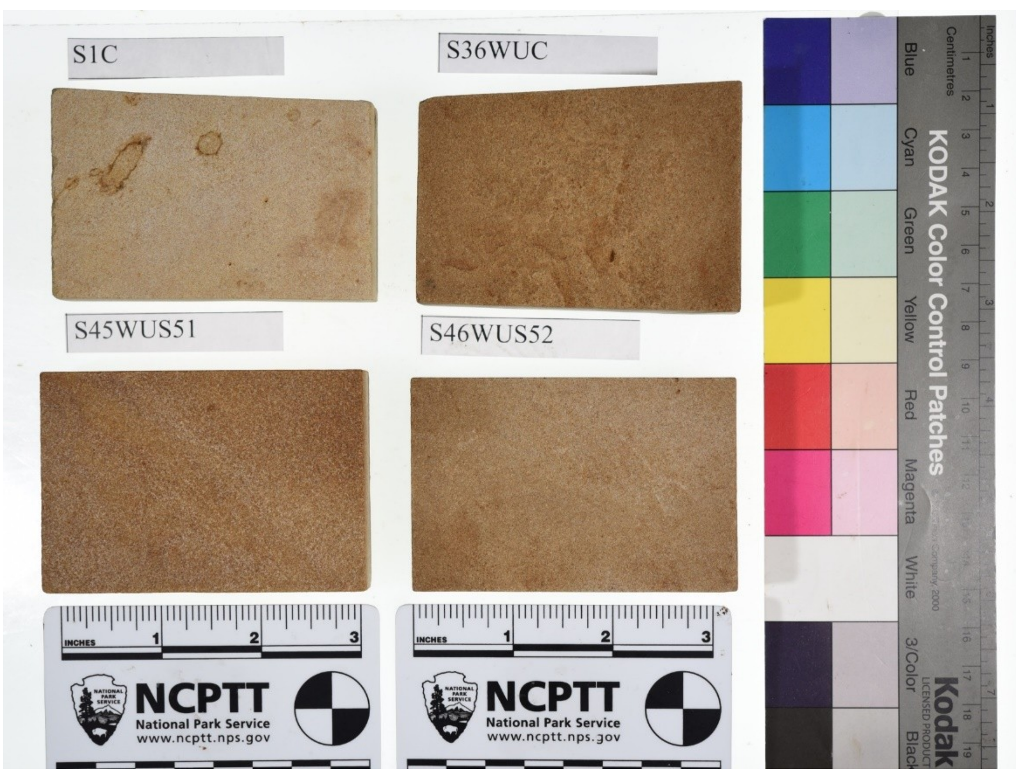


Figure 20. Fresh WTI contaminated samples of sandstone cleaned with Gold Crew SW compared with the un-oiled and oiled control after the treatment.



Sandstone

Fresh WTI contaminated sandstone substrates that were treated with Gold Crew SW (ΔE 8.22, 9.84) and Nokomis 5-W (ΔE 13.48, 9.82) had the lowest color change from the initial to the final stage and the highest color change from the oiled to treated stage with values for Gold Crew SW (ΔE 8.06, 11.77) and Nokomis 5-W (ΔE 10.62, 12.28). For the weathered Sandstone samples the Naturama(ΔE 4.44, 2.81) followed by Gold crew(ΔE 4.79, 4.48) were more successful in having the minimal color change and maximum oil removal with the values Naturama(ΔE 1.99, 2.81) and Gold Crew SW (ΔE 4.36, 2.07)

Fig. 21: Color Change (ΔE) after removal of Fresh WTI from Sandstone Samples

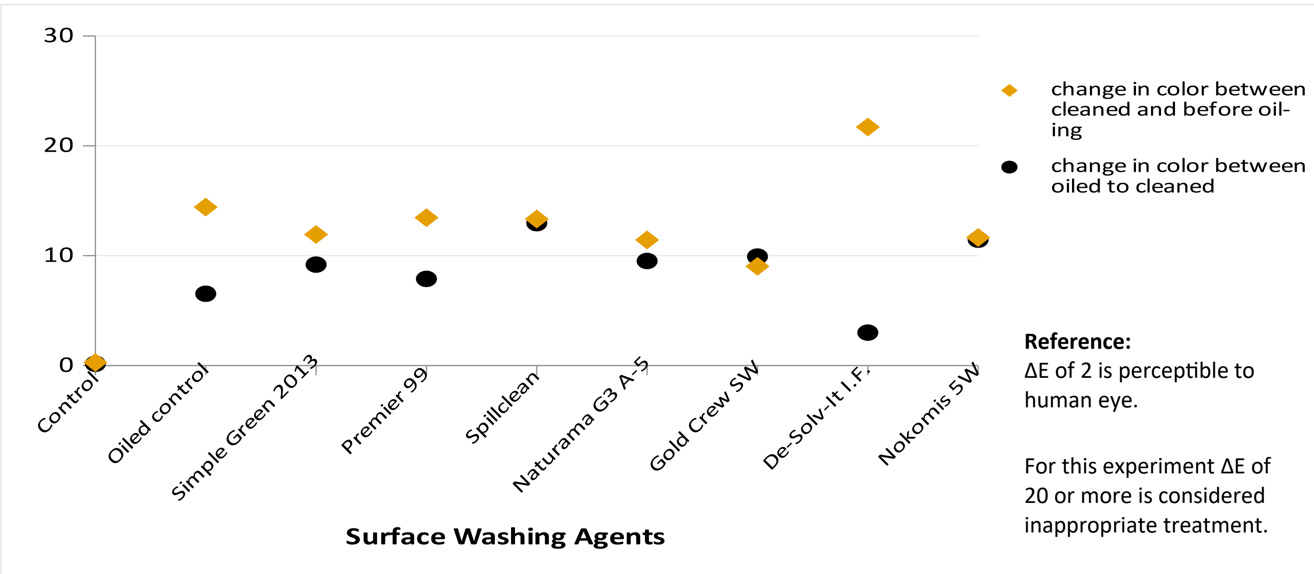
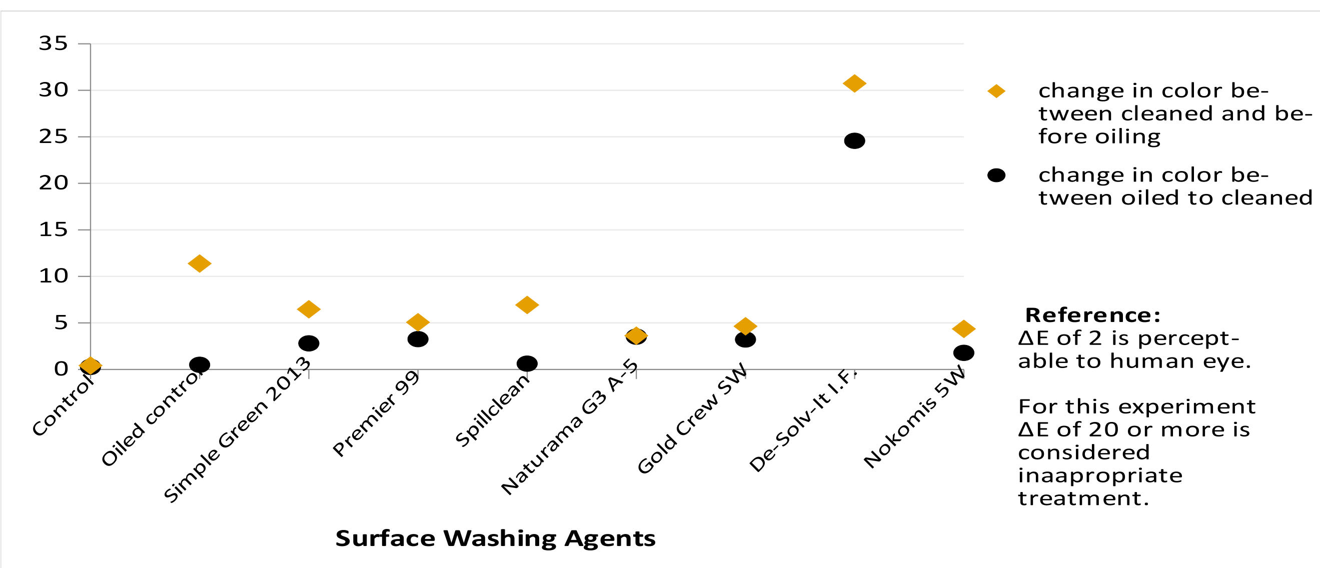


Fig. 22: Color Change (ΔE) after removal of WTI from artificially weathered brick samples



Access western winter blend

As the samples were oiled with diluted bitumen, due to its heavy viscosity it wasn't absorbed by the substrate therefore the color change is measured by the treated with the untreated values.

Concrete

Most of the concrete samples exposed to the AWWB were not cleaned successfully by any SWAs. The values in color change (ΔE) in successful SWAs is higher than 20. The substrates treated by SWA Naturama (ΔE 21.60, 20.43) was able to remove the oil till some extent whereas with De-Solv-it industrial formula (ΔE 27.46, 33.00) the oil dissolved and absorbed by the substrate. Similarly, for the weathered AWWB contaminated samples De-Solv-it industrial formula (ΔE 25.01, 24.51) and Naturama (ΔE 37.54, 42.73) were able to remove some oil.

Fig. 23: Color Change (ΔE) after removal of fresh AWWB from concrete samples

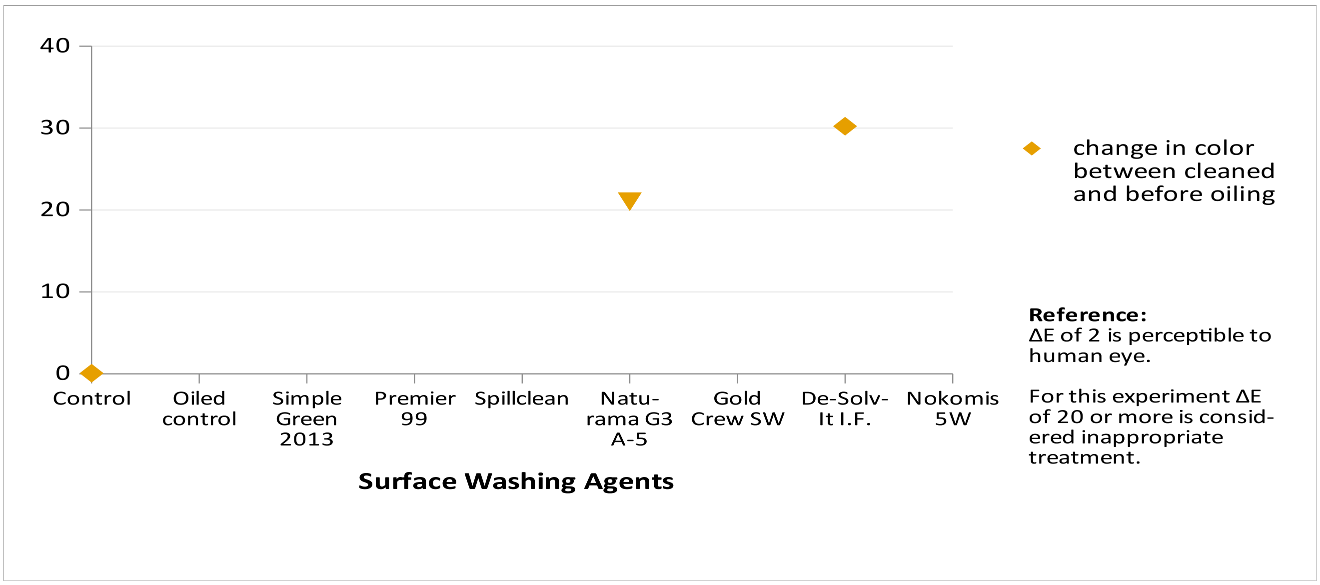


Fig. 24: Color Change (ΔE) after removal of weathered AWWB from concrete samples

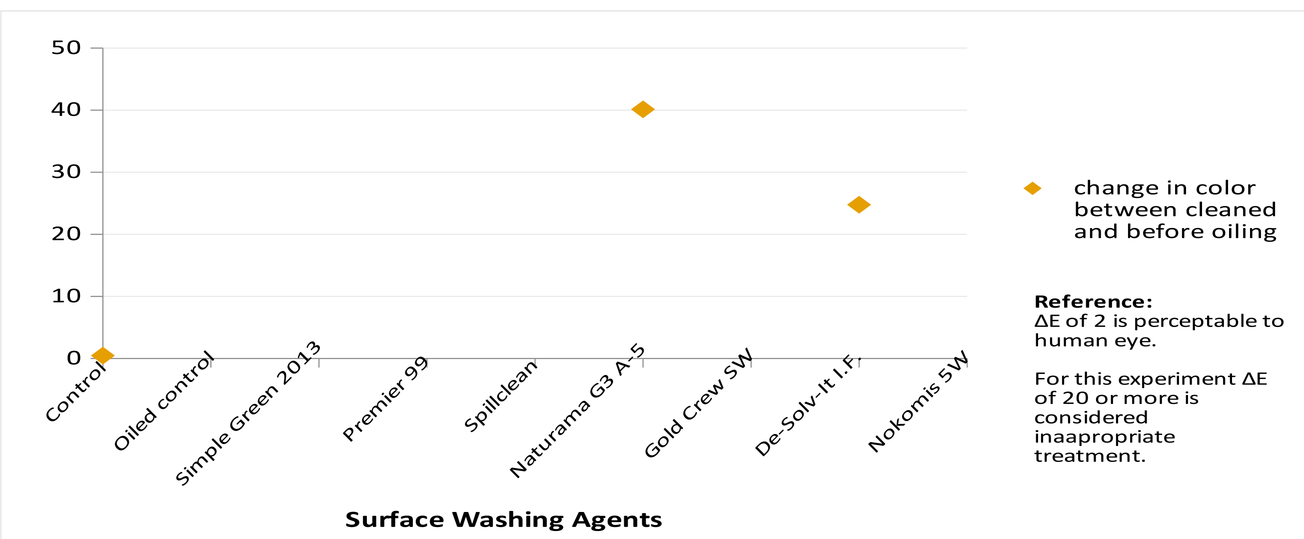


Figure 25. Fresh AWWB contaminated samples of concrete cleaned with Naturama A3 G-5 compared with the un-oiled and oiled control after the treatment.

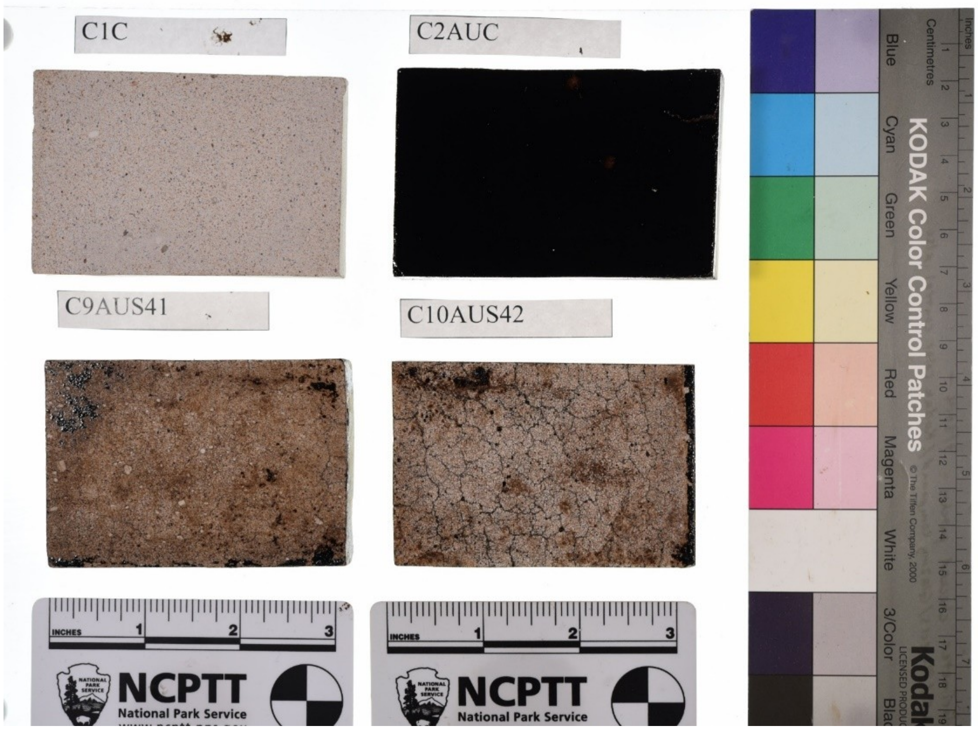
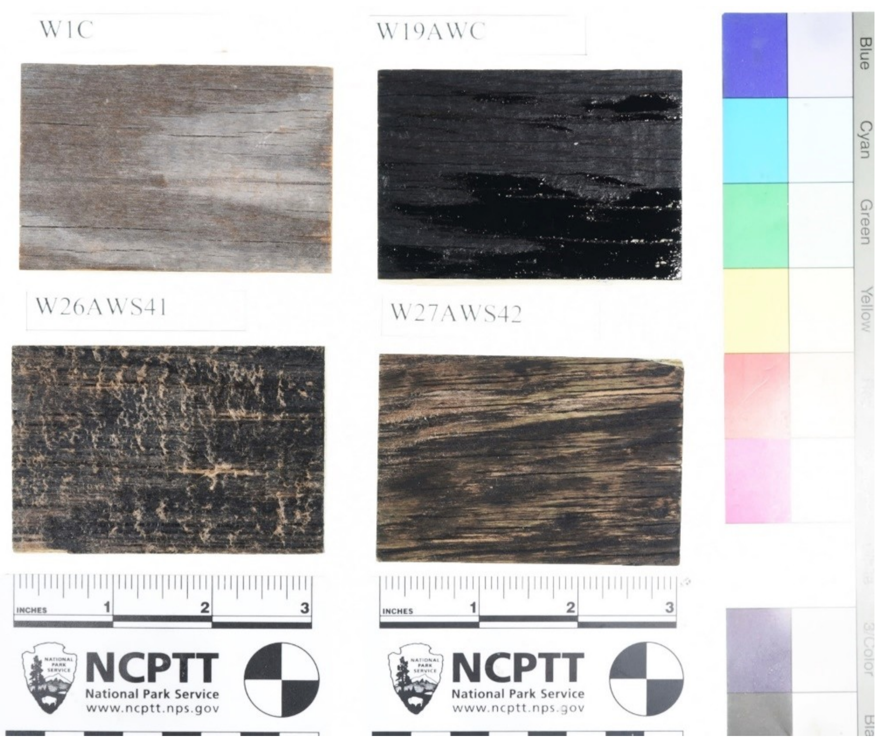


Figure 26. Weathered AWWB contaminated samples of yellow pine cleaned with Naturama G3 A-5 compared with the un-oiled and oiled control after the treatment.



Yellow pine

The color change in yellow pine samples contaminated with fresh AWWB for most of the SWAs was more than 20. The two SWAs which succeeded in removing the AWWB were Naturama(ΔE 11.63, 17.65) and Simple green reformulation (ΔE 21.64, 18.79). The samples exposed to weathered AWWB cleaned by Naturama(ΔE 12.92, 19.06) and Spill clean(ΔE 20.90, 17.22) were able to remove some oil. The color change in Nokomis 5-W (ΔE 16.40) was also lower than 20, although only one sample was measure as the oil persisted on the second one and couldn't be measured.

Fig. 27: Color Change (ΔE) after removal of fresh AWWB from yellow pine samples

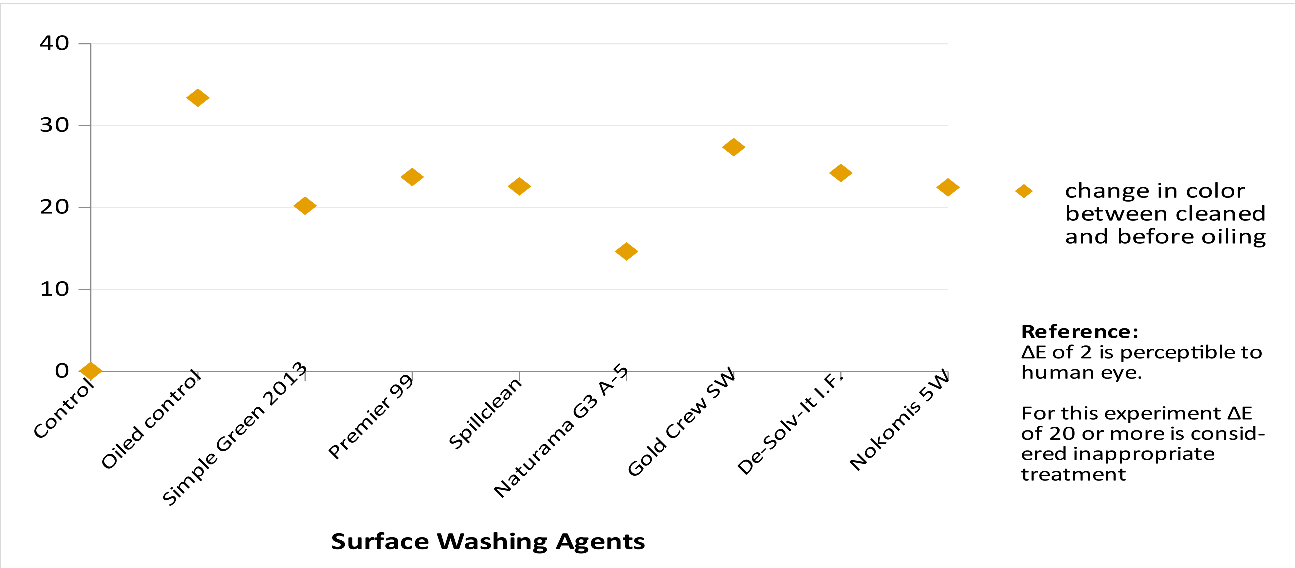
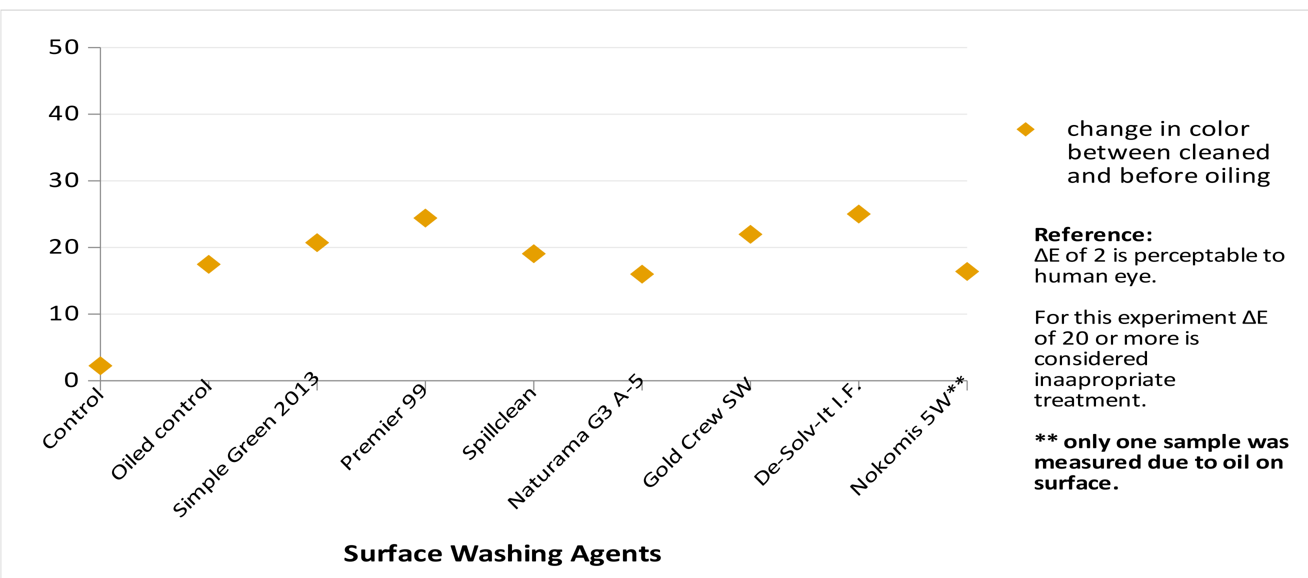


Fig. 28: Color Change (ΔE) after removal of weathered AWWB from yellow pine samples



Brick

In the four substrates the AWWB contaminated brick samples had the best results when cleaned with SWA's. The samples treated with Gold crew SW (ΔE 12.73, 4.76) and Simple green (ΔE 10.52, 11.43) had the best results. Premier 99 (ΔE 4.53) had the lowest color change though only one sample could have been measured. De-solv-it industrial formula (ΔE 10.55, 10.82) had the same results as Simple green reformulation. Naturama (ΔE 5.03, 13.19) and Spillclean (ΔE 14.74, 10.73) were more successful in removing weathered oil. De-solv-it industrial formula (ΔE 11.64, 10.65) was lower than Spillclean though as it decimated the oil, it wasn't considered.

Fig. 29: Color Change (ΔE) after removal of fresh AWWB from brick samples

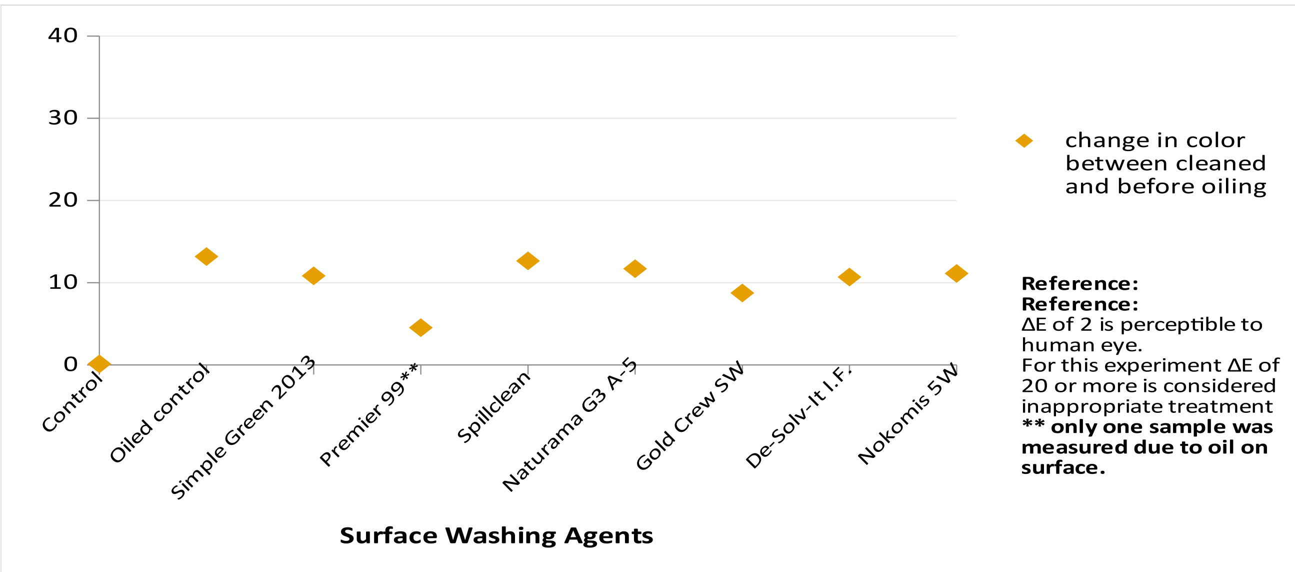
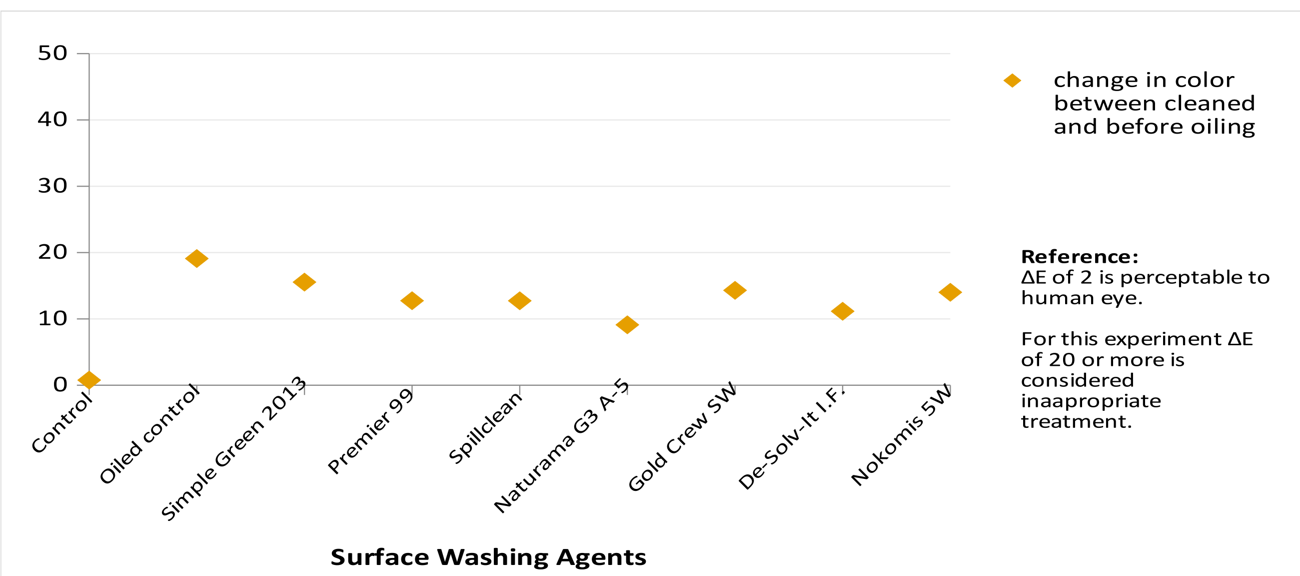


Fig. 30: Color Change (ΔE) after removal of weathered AWWB from brick samples



Sandstone

The sandstone samples treated with fresh AWWB were similar to the concrete. Only a few SWAs were able to remove some oil and the values of color change (ΔE) were higher than 20 for fresh and weathered AWWB. De-Solv-it industrial formula (ΔE 34.53,38.97) and Naturama (ΔE29.28, 47.67) were successful. The removal of weathered oil the lowest color change was observed in De-Solv-it industrial formula (ΔE 20.33,23.74). Only one sample in simple green (ΔE 20.27) had the lowest color change.

Fig. 31: Color Change (ΔE) after removal of fresh AWWB from sandstone samples

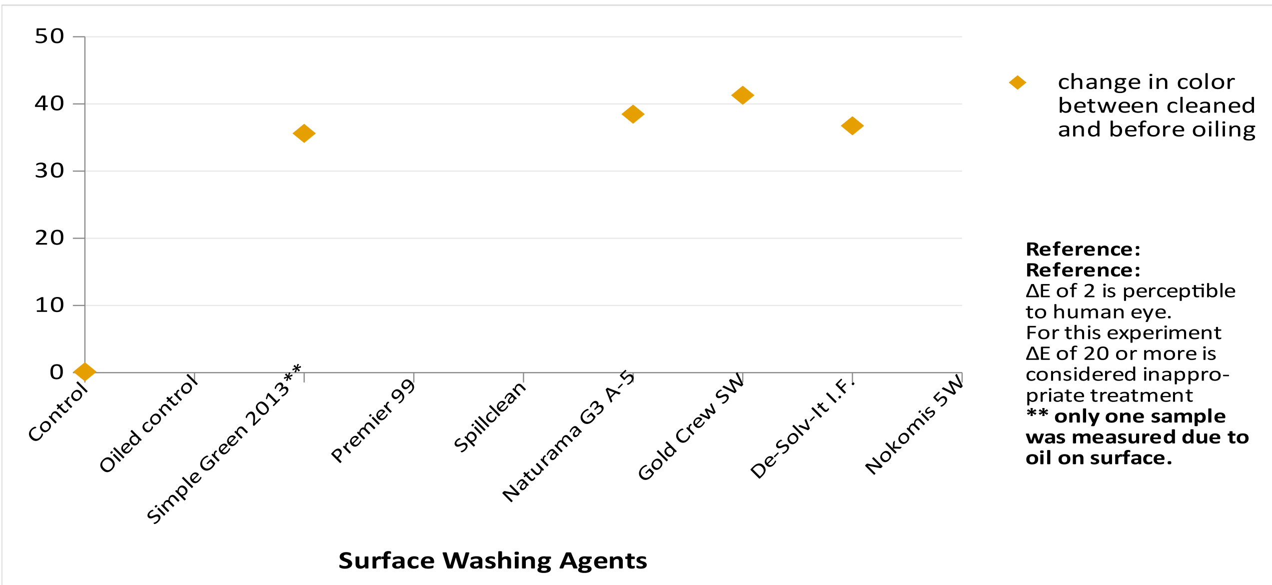
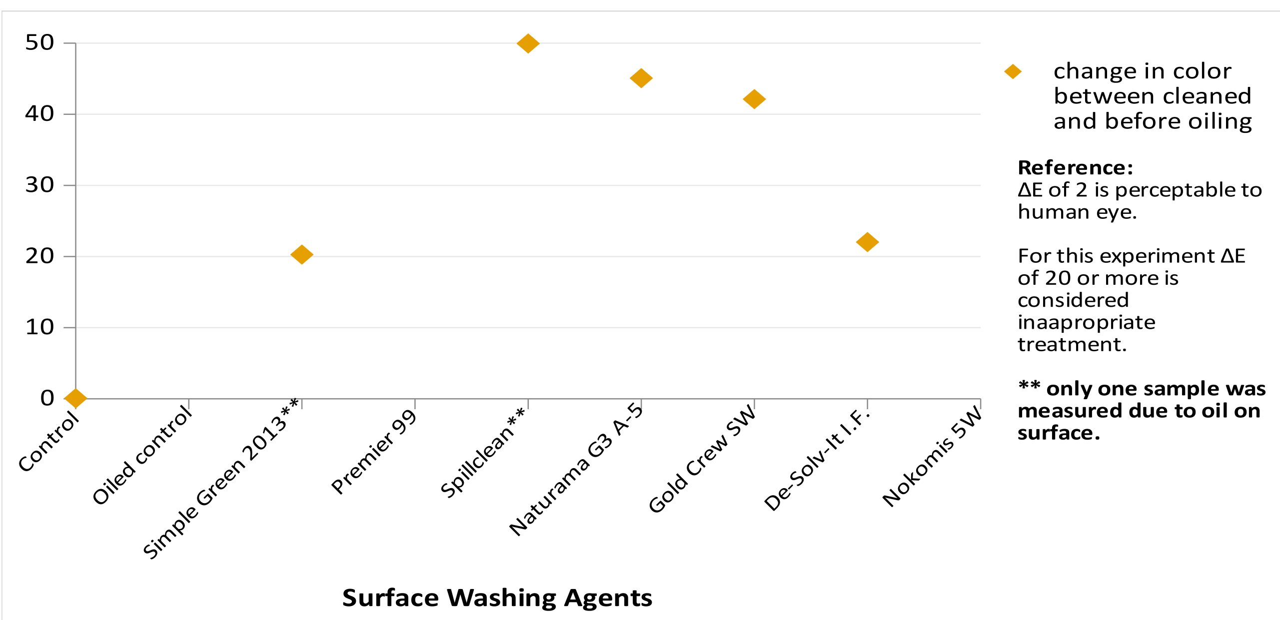


Fig. 32: Color Change (ΔE) after removal of weathered AWWB from sandstone samples



Concluding from the color change (ΔE) observations, samples exposed to WTI were easier to treat and measure than samples exposed to AWWB. When oiled with WTI – Premier 99 performed well on treating concrete, Spillclean and Nokomis 5-W were able to remove oil contamination on Brick and Gold Crew SW on Sandstone. For the yellowpine, there was not one consistent SWA successful to remove WTI oil. Naturama, a surfactant SWA was able to remove some AWWB oil from most of the substrates whereas De-Solv-it industrial formula even with low color change, had dissolved oil which was further absorbed by the substrates. The only other successful SWAs to have cleaned some surface deposition of AWWB oil was Gold Crew SW, Simple green for fresh AWWB and Spill clean for weathered.

Looking at overall color change (ΔE) it was important to also understand the individual shifts in color with the oil exposure for each substrate. In both the cases where samples were contaminated with AWWB and WTI, after the treatment all four substrates showed a negative shift in ΔL reflecting the samples became darker after the treatment. In case of Δa* for fresh WTI contaminated sandstone, all concrete and yellow pine samples exposed to WTI, and majority of concrete, yellow pine, and sandstone exposed to AWWB had a positive change and became redder, whereas artificially weathered samples of sandstone contaminated with WTI and all the brick samples exposed to AWWB and WTI had a negative change making them greener after the treatment. In the case of AWWB. In the case of Δb* yellow pine exposed to WTI and all concrete was found to have the positive change which is shift towards blue, where as the Wood exposed to AWWB, all the brick and sandstone was found to have negative which is making them yellower in color.

Table 3: Successful SWA's for color change (ΔE) in the order of preference

	West Texas Intermediate		Access Western Blend	
	Un-weathered	Weathered	Un-weathered	Weathered Oil**
brick	Spillclean Nokomis 5-W	Nokomis 5-W Spillclean	Gold crew De-Solv-it I.F. Simple green	Naturama G3 A-5 De-Solv-it I.F. Spillclean
concrete	Spillclean Premier 99	Nokomis 5-W Premier 99	Naturama G3 A-5 De-Solv-it I.F.	De-Solv-it I.F. Naturama
wood	Premier 99 Gold crew SW Naturama G3 A5	Spillclean Nokomis 5-W	Naturama G3 A-5 Simple green	Naturama G3 A-5 Spillclean
stone	Gold Crew SW Nokomis 5-W	Naturama G3 A-5 Gold Crew SW	De-Solv-it I.F. Naturama	De-Solv-it I.F.

Gloss

Gloss was another quantitative mean to understand the change in physical properties. Like color change the successful treatment should restore the gloss character and remove maximum oil from the original substrate. All four substrates used for the experiment are matte in character with 0.7 - 3.6 GU for concrete, 0.4 - 5.7 GU for yellow pine, 0.3-3.4 GU for brick, and 0.2 -B0.9 GU for sandstone before the oiling. Apart from several timber and sandstone samples, gloss levels increased in all materials after the contamination with oil followed by treatments.

As AWWB is a high viscosity oil, the samples contaminated with fresh or weathered oil were oilier and glossier as compared to the medium viscosity WTI. In most of the substrates after oiling it was difficult to measure gloss in AWWB. In the case of WTI, apart from Sandstone the fresh WTI samples were observed to be glossier as compared to the artificially weathered samples of concrete, brick and yellow pine.

West Texas Intermediate

Concrete

The gloss change in concrete in fresh WTI was found minimal in Naturama G3 A-5 with1.58 GU and with Goldcrew -SW 1.75GU. The removal of oil was also maximum in both the SWA with negative values 0.52 GU and 0.79 GU, suggesting the samples were less glossy after oil application with respect to after treatment. Similarly, for the weathered samples of concrete Naturama G3 A-5, 1.7 GU and Premier 99 with 1.75 GU and after oil removal negative value of 0.9 GU and 1.52 GU.

Fig. 33: Gloss change after removal of fresh WTI from concrete samples

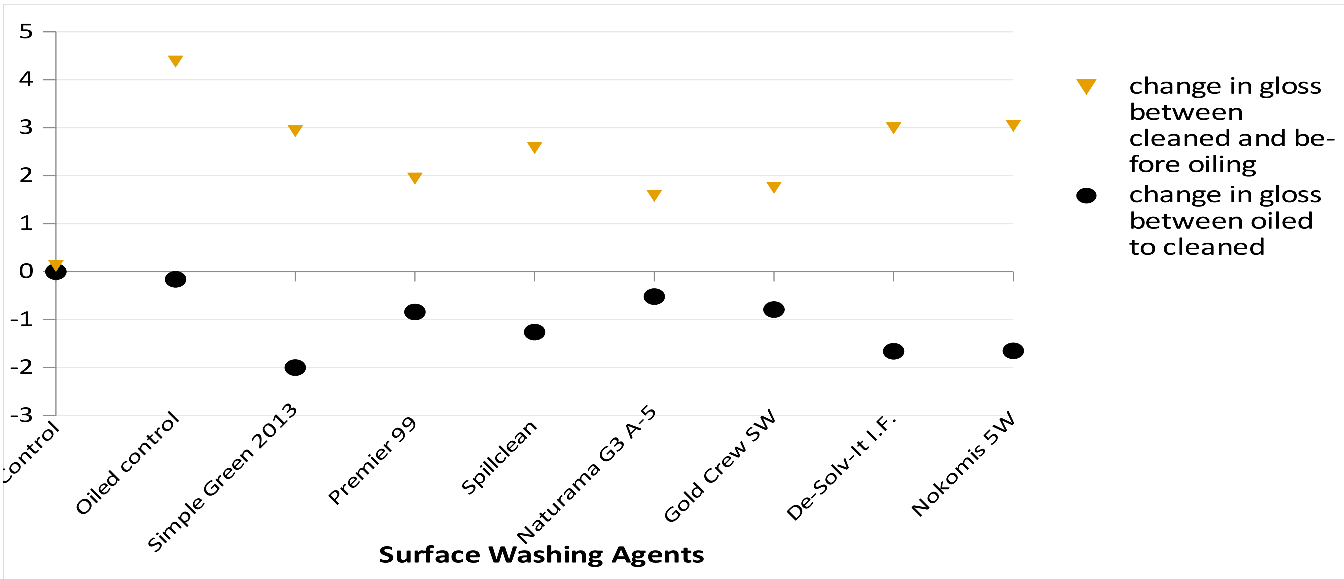
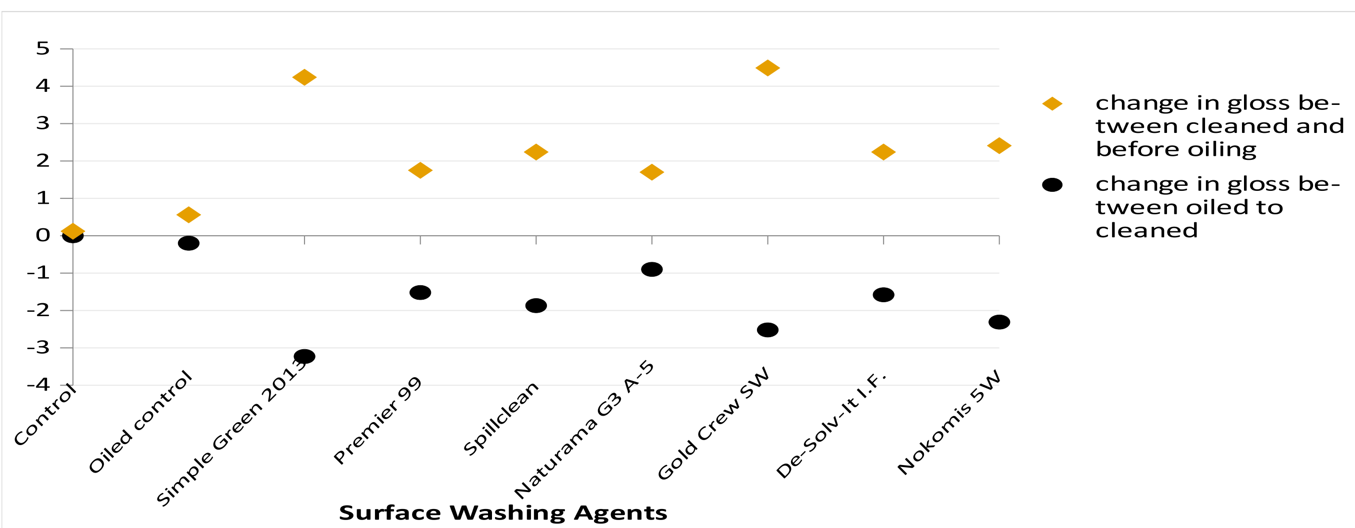


Fig.34: Gloss change after removal of WTI from artificially weathered concrete Samples



Yellow pine

The gloss change in yellow pine from before oiling to after treatment stage was observed to be inconsistent in yellow pine, it was minimal in Nokomis 5W and Naturama G3 A-5 with values 0.25 GU and 0.40 GU, and with maximum oil removal with maximum oil removal Negative value of 0.1 and positive 0.47 GU respectively. In the case of weathered samples, it was observed that the lowest color change was seen in Nokomis as negative 0.29 GU in the same range as the difference in the oiled control as negative 0.26 GU The other two closest SWAs were Gold Crew SW with 0.92 GU and Premier 99 with negative 1.41 GU. The removal of oil was most seen in Nokomis 5W followed by Premier 99 with values negative 0.46 GU and 0.54 GU respectively. The removal of oil from gold crew was not close with negative value 1.23 GU.

Fig. 35: Gloss change after removal of fresh WTI from yellow pine samples

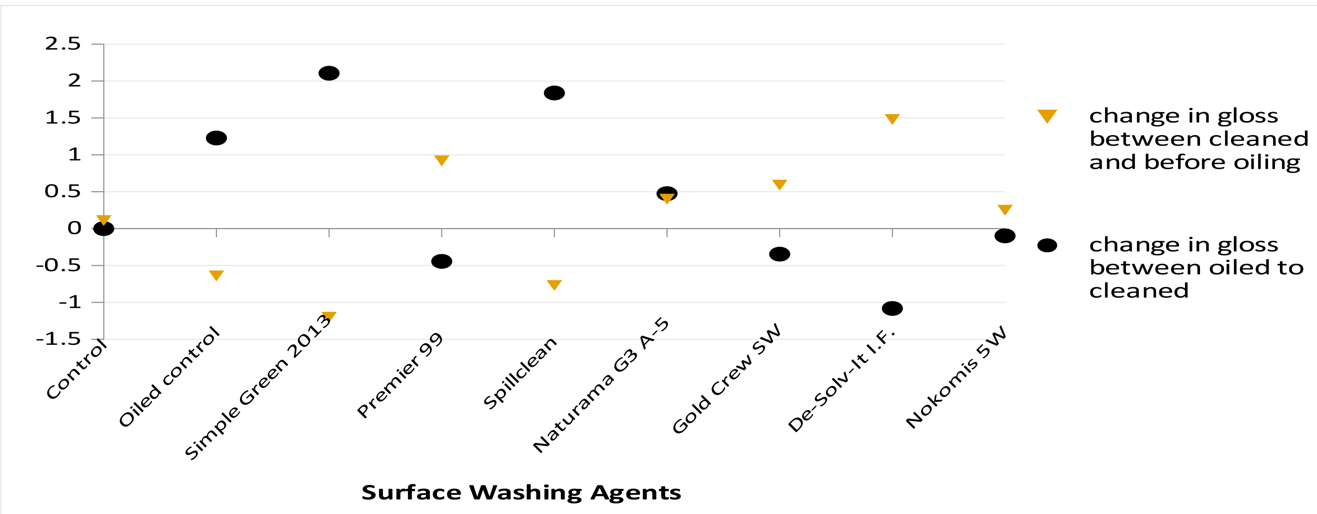
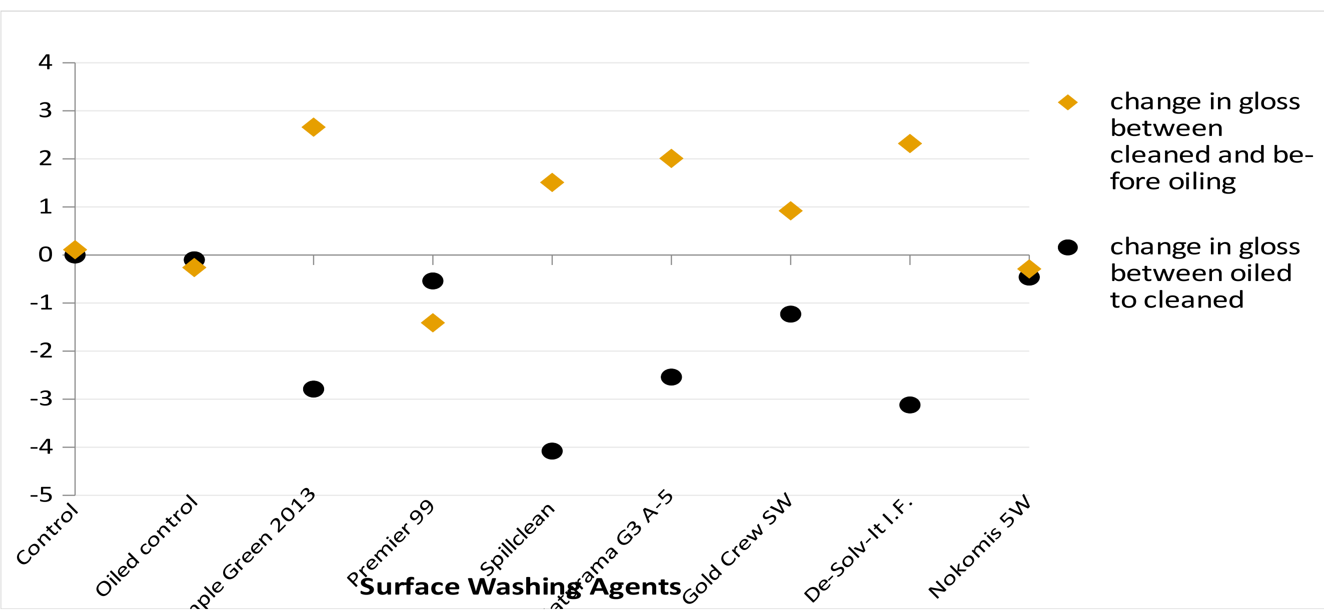


Fig. 36: Gloss change after removal of WTI from artificially weathered yellow pine samples



Brick

In brick samples contaminated with fresh WTI the gloss change was found in De-Solv-It industrial formula was 0.46 GU followed by Simple Green 2013 with 0.68 GU and Spill Clean with 0.87 GU. The maximum removal of oil with 0.30 GU, 0.14GU, and 0.23 GU respectively. Weathered samples when treated with Naturama G3 A-5, De-solv-it industrial formula and Nokomis 5-W showed the lowest gloss change with values 0.22 GU, 0.37 GU, and 0.59 GU respectively. Although maximum oil removal was found in Gold Crew SW, Simple green 2013, followed by Naturama G3 A-5 with negative values 0.35 GU, 0.36 GU, and 0.42 GU respectively.

Fig. 37: Gloss change after removal of fresh WTI from brick samples

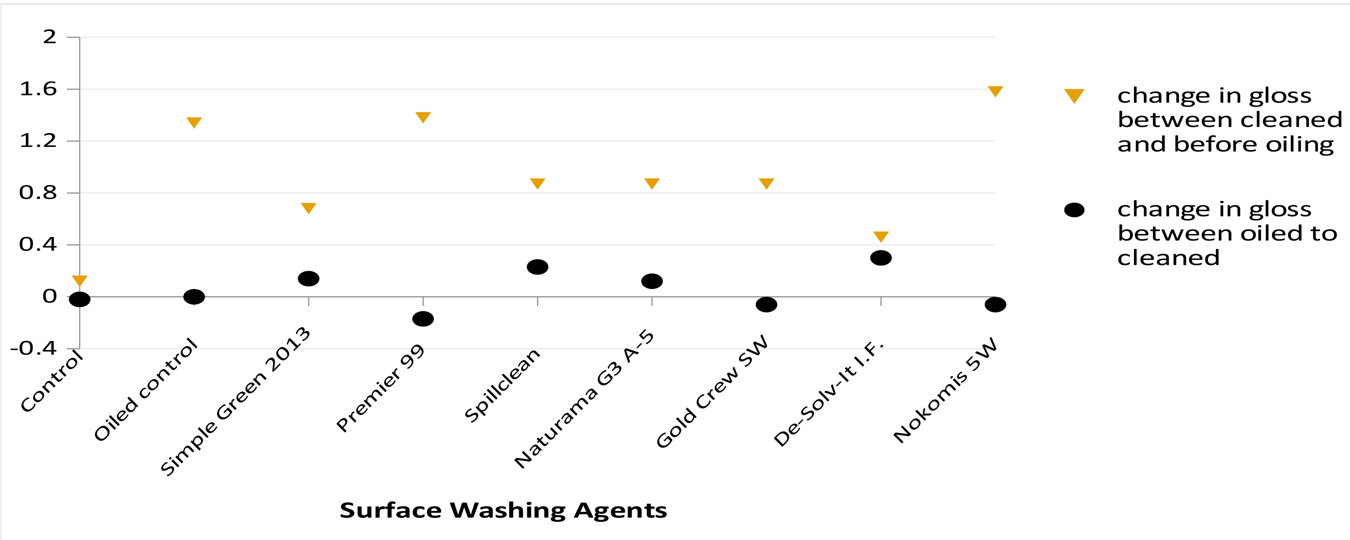
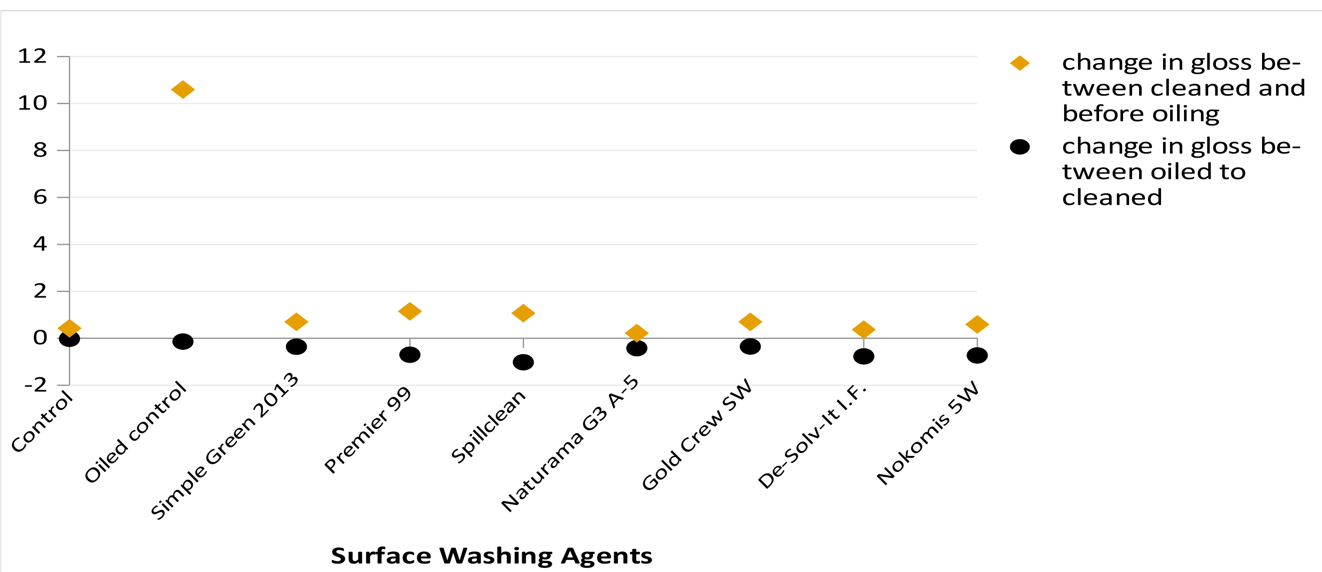


Fig. 38: Gloss change after removal of WTI from artificially weathered brick samples



Sandstone

Sandstone samples exposed to fresh WTI when cleaned with Premier 99 and Nokomis 5-W had the minimum gloss change from the initial stage 0.03 GU and 0.05 GU followed by Simple Green and Naturama G3 A-5 with 0.06 GU each. The oil removal was most in Naturama G3 A-5 at 0.13 followed by Simple green with 0.12 GU and Premier 99 with 0.08 GU. Nokomis 5W the gloss change from after oiling to after treatment stage was observed to be 0. In the weathered samples the gloss change was found to be negative apart from Gold crew SW and Premier 99 with 0.02 GU and 0.03 GU respectively. The oil removal was more in Gold Crew SW as compared to Premier 99 with values 0.08 GU and 0.01GU.

Fig. 39: Gloss change after removal of fresh WTI from sandstone samples

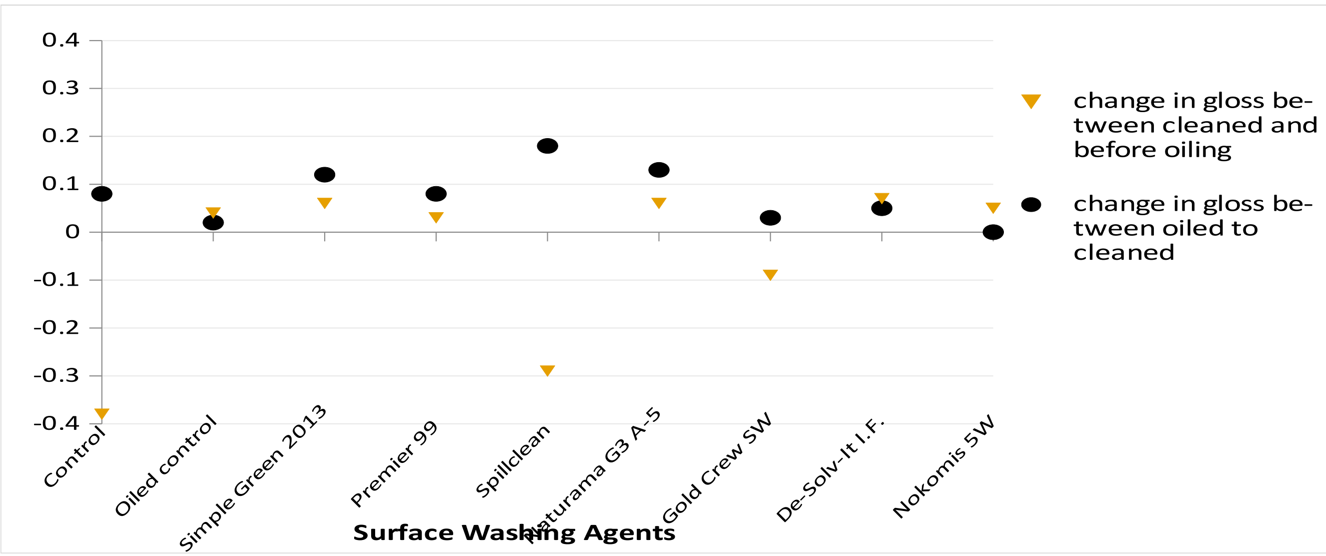
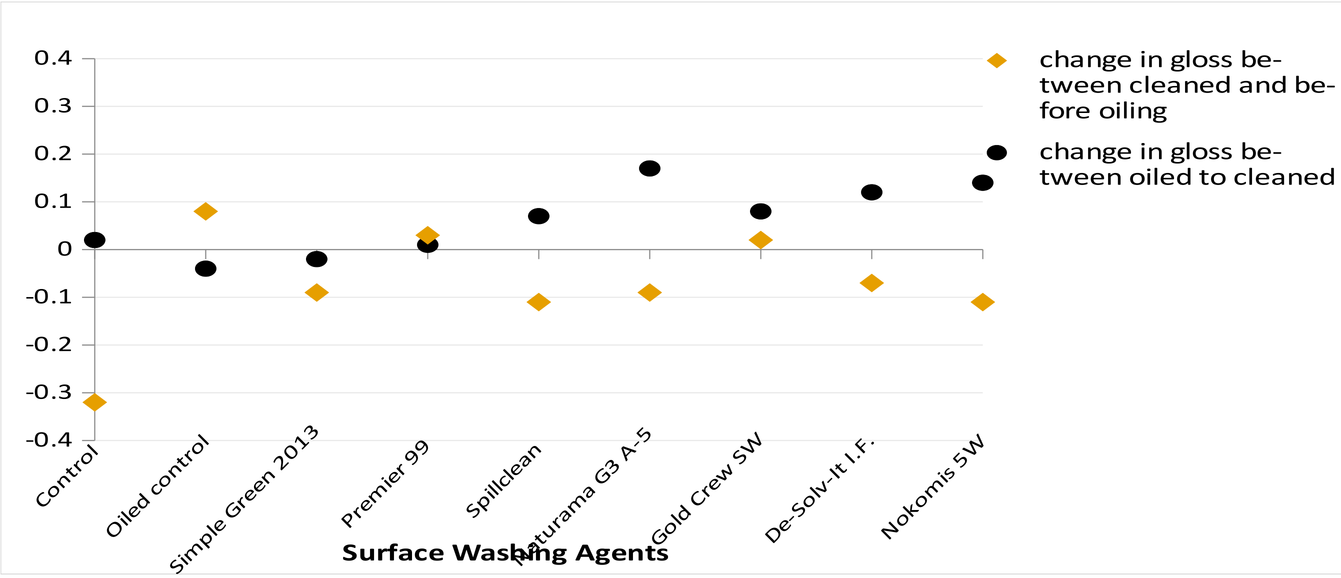


Fig. 40: Gloss change after removal of WTI from artificially weathered sandstone samples



Access western winter blend

Concrete

Like change in color, the gloss change in concrete for fresh and weathered AWWB could not be measured for all the SWAs. The only two SWA's which were able to clean the surface were Naturama G3 A-5 and De-Solv-it industrial formula. In treatment of fresh AWWB the change was measured 3.12 GU and 2.27GU and for weathered the change was measured as 0.97GU and 3.65GU.

Fig. 41: Gloss change after removal of fresh AWWB from concrete samples

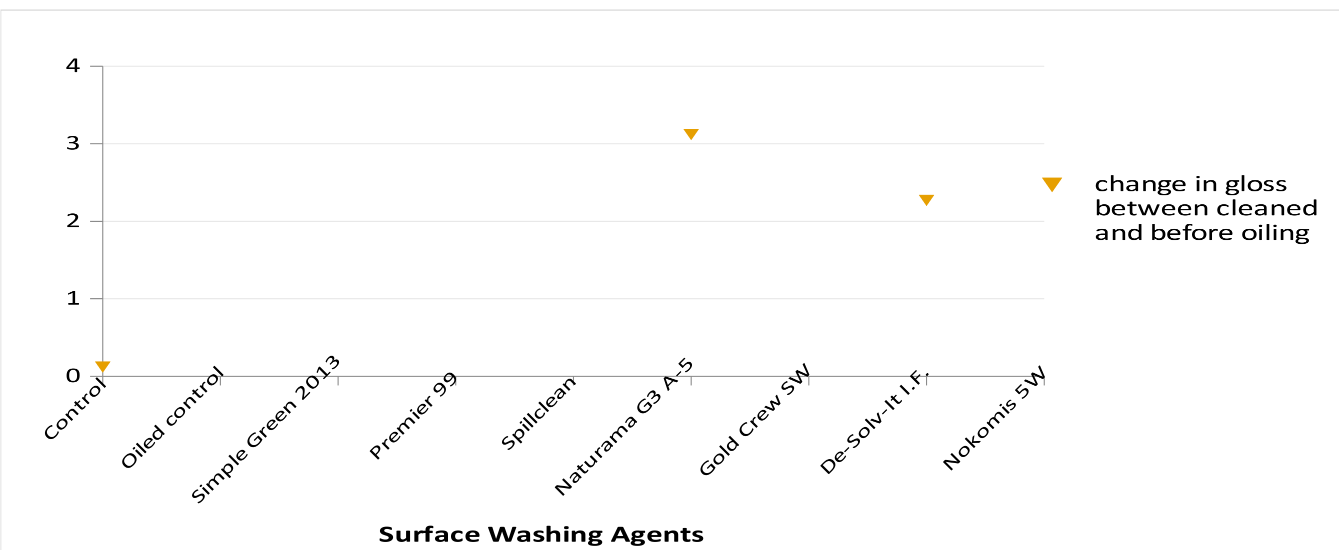
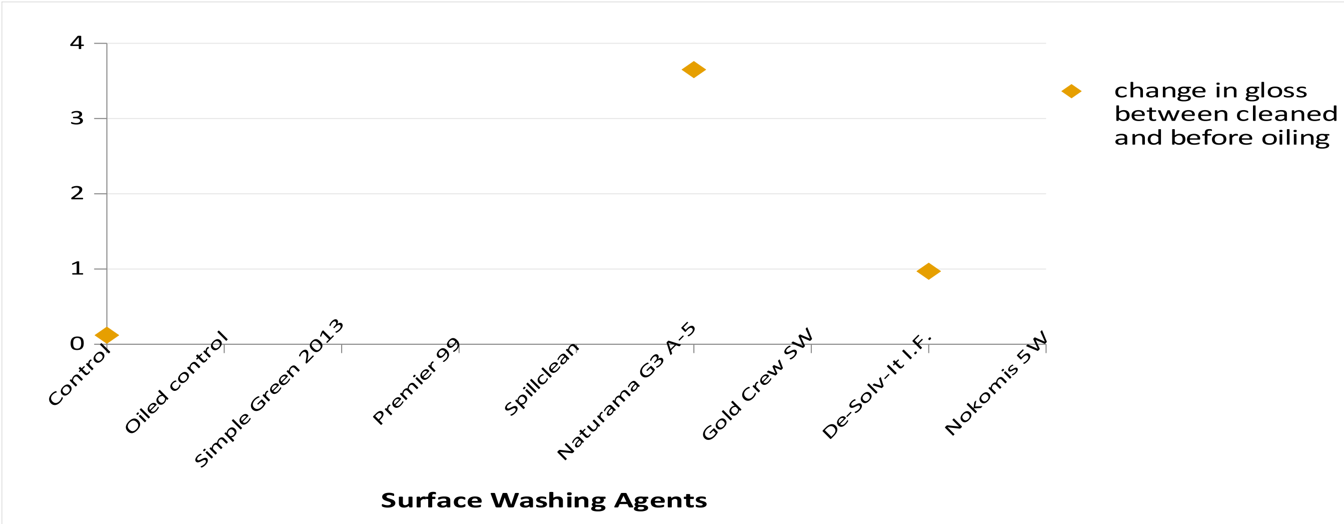


Fig. 42: Gloss change after removal of weathered AWWB from concrete samples



Yellow pine

The gloss change in yellow pine treated with Premier 99 and Naturama G3 A-5 though it is negative was found least with values 0.15 GU and 0.35 GU respectively and for the removal of the weathered oil it is Gold crew SW and Naturama G3 A-5 with values 0.90 GU and negative 0.12

Fig. 43: Gloss change after removal of fresh AWWB from yellow pine samples

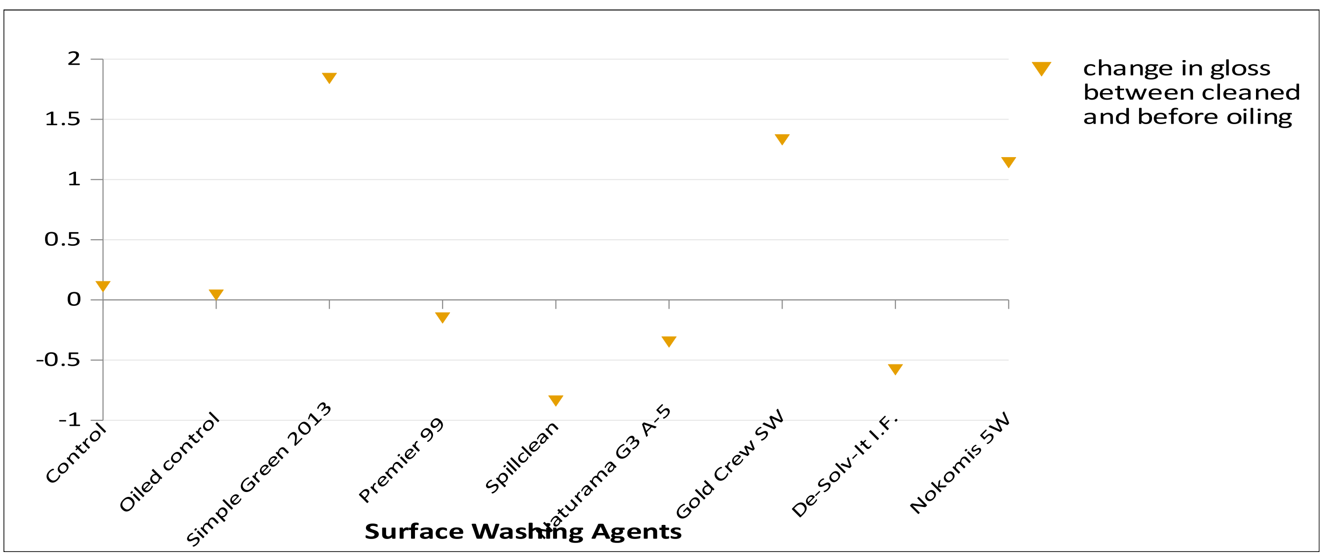
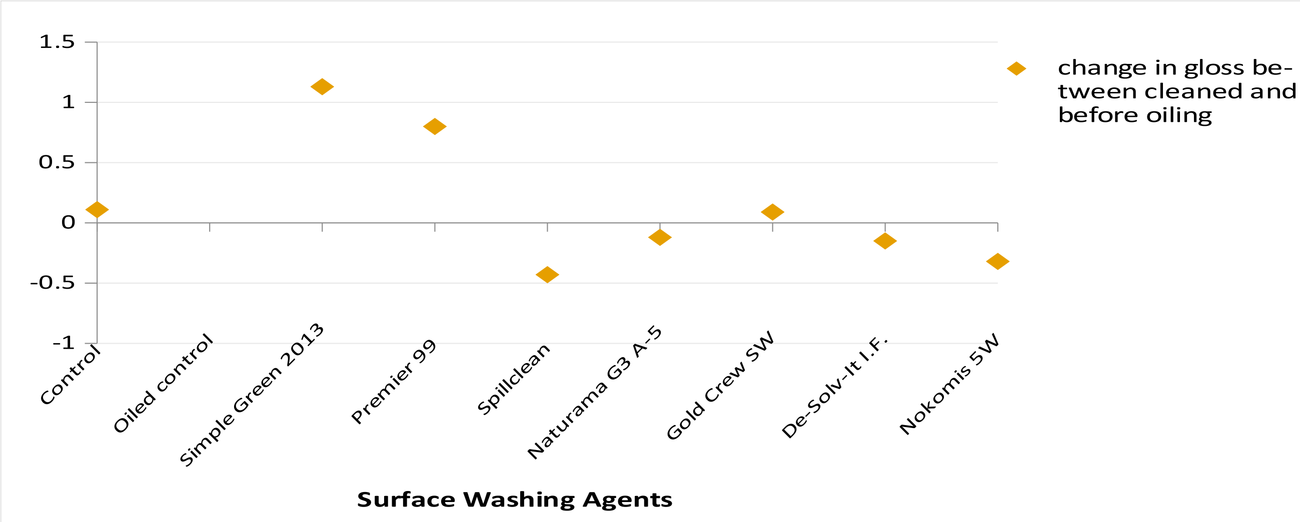


Fig. 44: Gloss change after removal of weathered AWWB from yellow pine samples



Brick

The gloss change in brick was found lowest in Gold crew SW followed by Spill clean and De-Solv-it industrial formula with values 0.12 GU, 0.42 GU and 0.43 GU respectively. Samples contaminated with weathered AWWB when treated with De-solv-it industrial formula, Gold Crew SW, and Naturama G3 A-5 had the lowest gloss change with values 0.16 GU, 0.23 GU, and 0.34 GU respectively.

Fig. 45: Gloss change after removal of fresh AWWB from brick samples

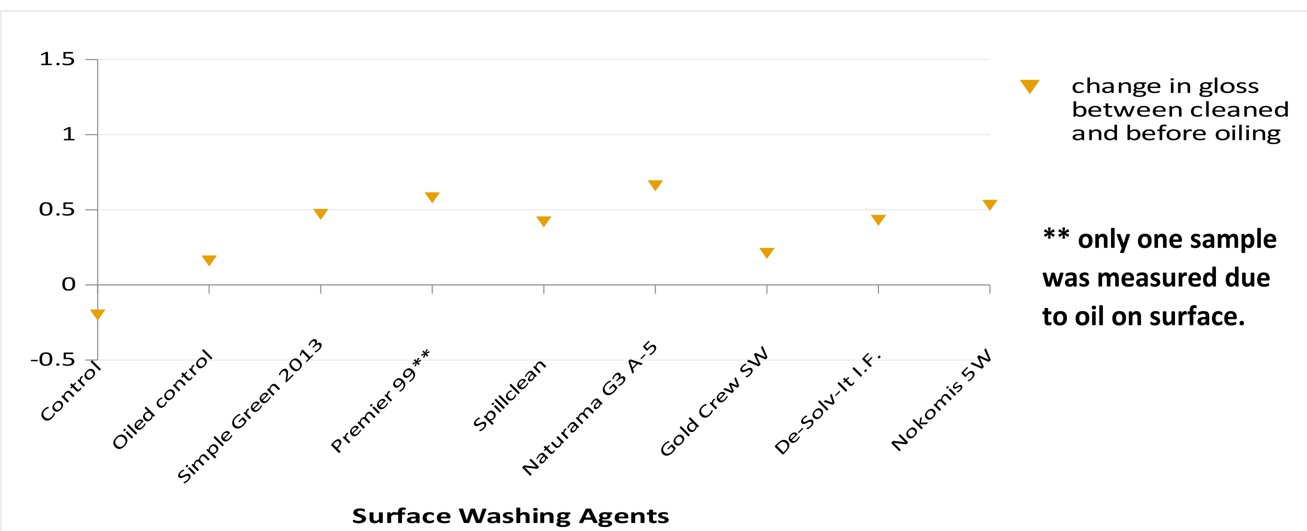
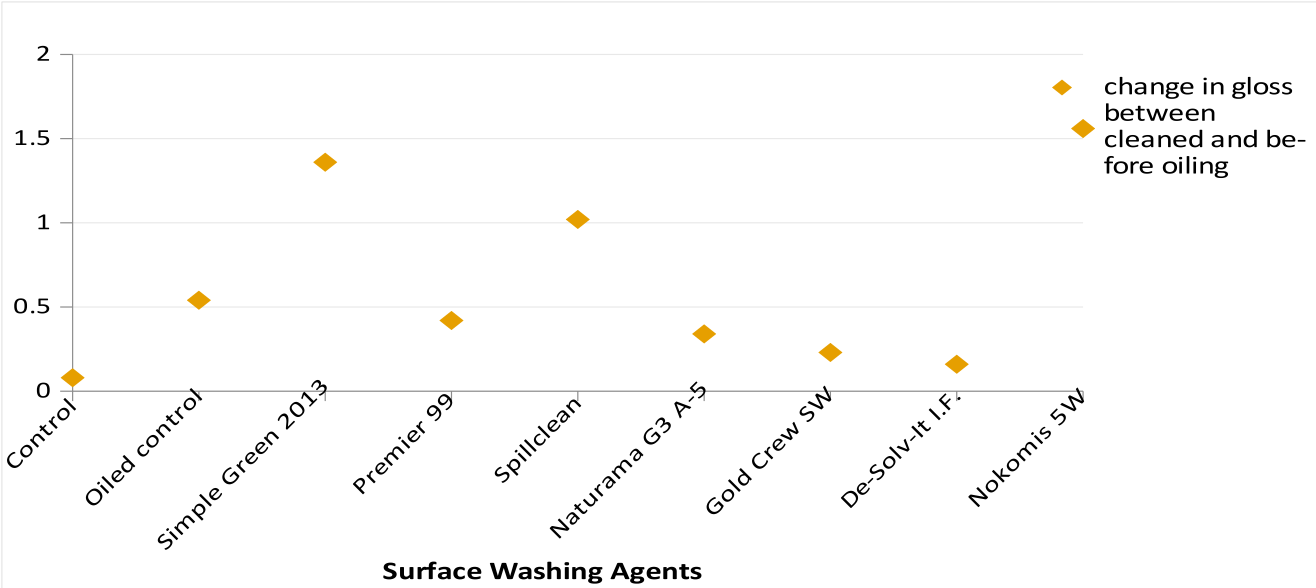


Fig. 46: Gloss change after removal of weathered AWWB from brick samples



<u>Sandstone</u>

Similar to color change, all the sandstone samples contaminated with AWWB couldn't be cleaned with the SWA and only a few could be measured. In case of fresh oil contamination Naturama G3 A-5 was found to be the lowest with 0.05 GU and De-Solv-it industrial formula 0.13 GU. In case of weathered oil, the lowest gloss change was found in De-Solv-it industrial formula and Gold Crew SW with 0.040 GU and 0.06 GU respectively. Although Simple green has the lowest change in gloss for fresh and weathered which is 0.04 GU and 0.02 GU, only one sample was cleaned enough to be measured.

Fig. 47: Gloss change after removal of fresh AWWB from sandstone samples

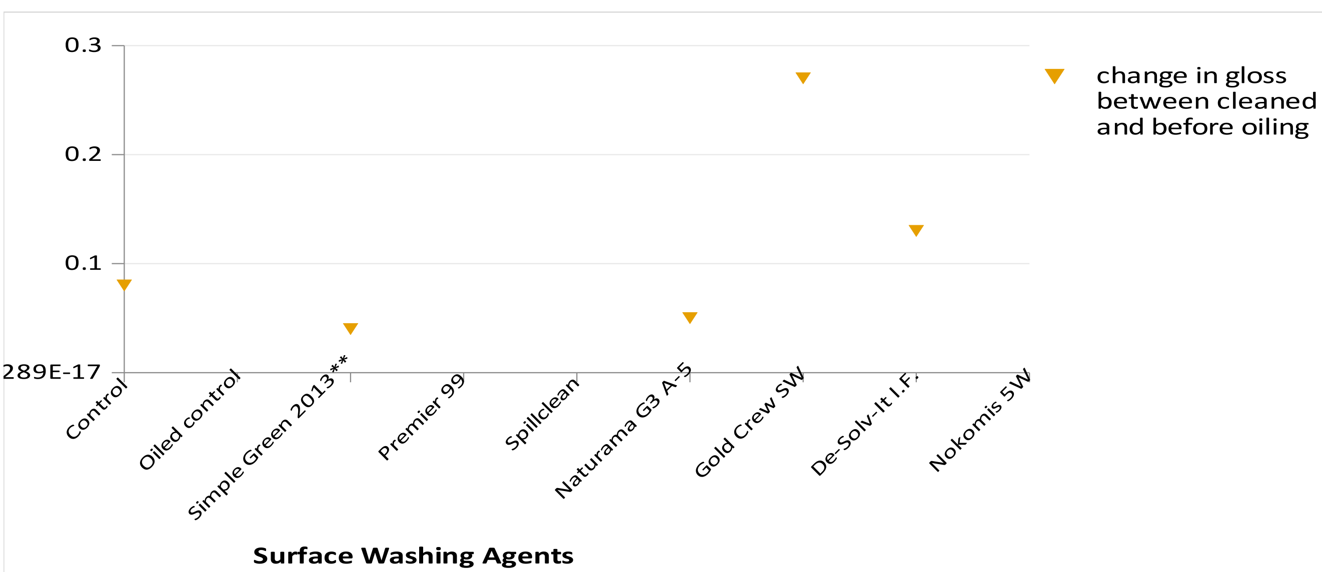
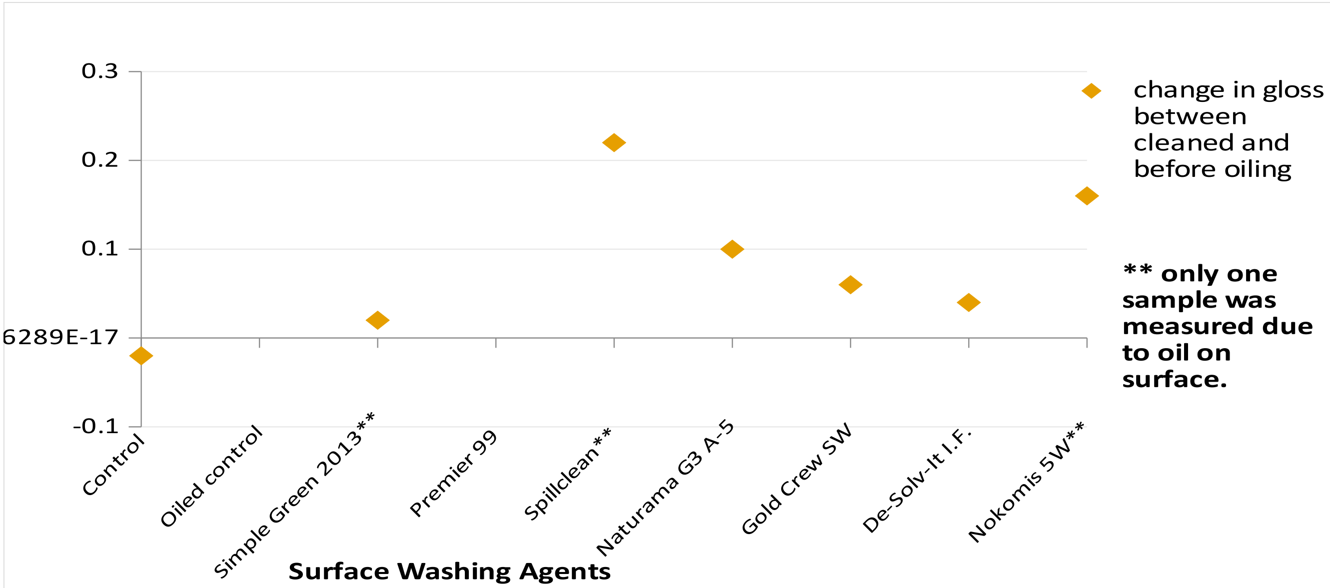


Fig. 48: Gloss change after removal of weathered AWWB from sandstone samples



When exposed to WTI in fresh and weathered conditions, most of the substrates performed well with Naturama G3 A-5, Premier 99, and Nokomis 5W. The change in gloss units in fresh application of WTI in concrete ranged between 1.6-4.38 GU, and in brick between 0.5 to 1.6 GU. In case of weathered samples contaminated with WTI the concrete samples ranged between 0.6 – 4.25 GU, brick between 0.2 – 1.15 GU. It was noticed for timber and sandstone samples treated for WTI the values were negative. For fresh WTI the yellow pine values ranged between- 1.2 to 1.5 GU and for sandstone -0.29 to 0.07 GU. Similarly for weathered samples yellow pine the values ranged between -1.4 to 2.0, and for sandstone it ranged from - 0.32 to 0.08 GU.

In case of AWWB – Naturama G3 A-5, De-Solv-it industrial formula and Gold Crew SW were found successful. The gloss change in Concrete was really high in both conditions for Naturama G3 A-5 in both and De-Solv-it industrial formula in fresh application with measurements ranging between 2.27-3.65 GU. In case of bricks the gloss change was found less as compared to the contamination by WTI, the values ranged between 0.2 – 0.7 GU for both the conditions. Only a few SWAs were successful for sandstone and the values ranged between 0.02 – 0.27 GU in both exposures. Similar to yellow pine exposed to WTI, the values were negative after the treatment for most SWA's ranging from -0.84 to 1.84 GU for fresh and for weathered -0.43 to 1.13 GU.

Table 4: Successful SWA's for gloss change

	West Texas Intermediate		Access Western Blend	
	Un-weathered	Weathered	Un-weathered	Weathered Oil**

brick	De-Solv-it I.F. Simple Green 2013 Spillclean	Naturama G3 A-5 De-Solv-it I.F. Nokomis 5-W	Gold crew SW Spillclean De-Solv-it I.F.	De-Solv-it I.F. Gold crew SW Naturama G3 A-5
concrete	Naturama G3 A-5 Gold Crew SW Premier 99	Naturama G3 A-5 Premier 99	De-Solv-it I.F. Naturama G3 A-5	De-Solv-it I.F. Naturama G3 A-5
wood	Nokomis 5-W Naturama G3 A-5	Nokomis 5-W Gold crew SW Premier 99	Premier 99 Naturama G3 A-5	Gold Crew SW Naturama G3 A-5
stone	Premier 99 Naturama G3 A-5 Simple Green Reformulation Nokomis 5-W	Gold Crew SW Premier 99	Naturama G3 A-5 De-Solv-it I.F.	De-Solv-it I.F. Gold Crew SW Naturama G3 A-5

Mass

Two surrogate materials were oiled together for each condition. An average of 2.5gm fresh AWWB was applied on concrete and yellow pine and 1.26gm on brick and sandstone. Brick absorbed fresh WTI the most with an average of age of 4.6gm, followed by yellow pine with an average of 2.76gm, sandstone with 0.7 gm and the least was concrete with 0.5gm approximately. In case of weathered AWWB approximately 1.2 gm was applied to concrete, yellow pine and sandstone. The brick absorbed more oil and the average was around 2.2gm. After weathering of the surrogate samples contaminated with WTI the concrete samples saw an overall mass loss around 0.1gm, yellow pine a weight gain of 1.7gm, sandstone a gain of 0.6gm and brick maximum gain of 4.1 gram from before oiling stage.

West Texas Intermediate

The lowest mass gain in concrete exposed with WTI was found in Nokomis 5W with 0.718gm and maximum oil removal from the oiled stage followed by Spillclean at 2.045gm and Gold crew SW at 2.234gm. In case of artificially weathered samples of concrete the lowest is spill clean with a gain of 0.165gm followed by Naturama G3 A-5 0.811gm, and Gold crew SW 1.048gms. As compared to spillclean, Naturama G3 A-5 and Goldcrew performed better at removing oil. In case of fresh WTI on yellow pine Spillclean has the lowest gain of 1.565gm and Naturama G3 A-5 at 1.821gm. For the weathered samples as well spillclean had the lowest gain of 0.483gm followed by Nokomis 5W 0.811gms and Naturama G3 A-5 with 0.845gms. In case of Brick, Simple green reformulation and Premier 99 had the lowest gain after the treatments 3.833gms and 3.985gms respectively. In case of the weathered samples of the brick Simple green and Gold crew SW are lowest with mass change of 3.615gms and

3.75gms respectively. It is followed by Premier 99 with a gain of 4.684gm. Sandstone samples contaminated with fresh WTI when treated with Simple green reformulation, spillclean and Gold Crew SW had the lowest mass change with values 0.523gm, 0.698 gm, and 0.699gm respectively. Oiled sandstone samples when weathered and treated with Simple green reformulation, spillclean and Premier 99 had the least mass change and maximum removal of oil with values 0.456gm, 0.515gm and 0.571gm.

Access western winter blend

The concrete samples when exposed to fresh AWWB had the lowest mass change with Nokomis 5W and Gold crew SW with values 0.058gm and 0.066gm. The cleaned samples of Naturama G3 A5 had maximum mass gain of 5.344gm as compared to De-solv-it industrial formula 4.586gms. In case of the weathered AWWB contaminated samples of concrete, when treated with Spillclean, Gold crew SW followed by Naturama G3 A-5 had the lowest mass gain 0.782gm, 0.804 gm, and 0.948 gm. The mass gain of De-solv-it was maximum of 3.579gm. The timber samples when exposed to fresh AWWB had the lowest mass gain when treated with Simple green reformulation, Nokomis 5W, and Gold crew SW with mass gain 1.089gm, 1.251gm, and 1.853gms. The yellow pine samples when treated with Naturama G3 SW and Gold Crew SW had the lowest weight gain of 0.265gm and 0.320gm. Brick samples when exposed to fresh AWWB when treated with Simple green had a mass loss of 0.077gm. Apart from this one example the lowest gain was found in Premier 99, Gold Crew SW, and Naturama G3 A-5 with 0.907gm, 1.898gm, and 2.050gm. Similar to fresh AWWB the weathered brick samples had the lowest mass gain with Naturama G3 A-5, Gold Crew SW and Premier 99 with values 2.944gm, 3.230 gm, and 3.520 gm. In case of fresh application of AWWB on Sandstone, Gold crew had the least mass gain with 0.240 gm followed by Simple green with 0.432gm and Naturama G3 A-5 with 0.451gm. De-solv-it industrial formula had the maximum mass gain with 1.745 gms. IN case of weathered samples of sandstone treated with Simple green reformulation there was a mass loss of 0.027gm. On samples treated by Gold Crew SW and Naturama G3 A-5 there was a mass gain of 0.294gm and 0.331gm respectively. The mass gain for De-Solv-it industrial formula was 0.362gm.

In conclusion the Spillclean, Simple green 2013 and Gold Crew SW were found more successful in terms of lowest mass gain on samples contaminated with WTI. For AWWB samples cleaned with Gold Crew SW and Naturama G3 A-5 had the least mass gain on the substrates.

Table 5: Successful SWA's for mass change

	West Texas Intermediate		Access Western Blend	
	Un-weathered	Weathered	Un-weathered	Weathered Oil**
brick	Simple Green 2013 Premier 99	Simple Green 2013 Gold Crew SW Premier 99	Premier 99 Gold crew SW Naturama G3 A-5	Naturama G3 A-5 Gold crew SW Premier 99
concrete	Nokomis 5W Spillclean	Spillclean Naturama G3 A-5	Nokomis 5W Gold crew SW	Spillclean, Gold Crew SW

	Gold Crew SW	Gold Crew SW		Naturama G3 A-5
wood	Spillclean Naturama G3 A-5	Spillclean Nokomis 5-W Naturama G3 A-5	Simple green 2013 Nokomis 5W Gold crew SW	Naturama G3 A-5 Gold Crew SW
stone	Simple Green 2013 Spillclean Gold Crew SW	Simple Green 2013 Spillclean Premier99	Gold Crew SW Simple green 2013 Naturama G3 A-5	Gold Crew SW Naturama G3 A-5 Spillclean De-Solv-it I.F.

Surface Roughness: 3-D Profilometry

Spc, Arithmetic mean peak curvature

The *Spc* parameter indicates the roundness or rigidity of peaks on the sample surface, smaller values represent rounder peaks and higher values represent pointed peaks.

West Texas Intermediate

In case of fresh WTI contaminated samples of concrete, yellow pine, and sandstone the *spc* values increased on an average of 0.031/mm, 0.013/mm, and 0.245/mm making the samples more pointed. In case of brick there was a decrease in *spc* values, making the surface rounder with an average decrease of 0.035/mm. With the artificially weathered samples an increase in *spc* was observed in concrete and yellow pine with average values of 0.033/mm and 0.404/mm, whereas there was a decrease, and the peaks of brick and sandstone became rounder with values 0.054/mm and 0.009/mm.

After the treatment for both fresh and weathered samples of concrete, and most of the brick samples there was a decrease in the peaks indicating the surface became rounder, whereas for yellow pine and sandstone there was an increase in peaks. The two SWAs which had the least change while removing the fresh oil from concrete were Spillclean and Naturama G3 A-5. For yellow pine, the SWAs which had the least impact were De-Solv-it industrial formula, Spillclean, and Gold crew SW. Nokomis 5W, Gold Crew SW and Naturama G3 A-5 were more successful on brick. Sandstone had the least impact with the use of Nokomis, Gold Crew SW, and Premier 99.

The artificially weathered samples of concrete were least affected by Gold Crew SW, Naturama G3 A-5, and Spill clean. For yellow pine the successful samples were De-Solv-it Industrial Formula, Spillclean, and Gold Crew SW. The SWAs which had the least change while removing the oil on brick were Simple Green, Gold Crew SW, Premier 99, and Naturama G3 A-5. For the sandstone samples the least changed was noticed in Nokomis 5-W where the peaks were rounder followed by the SWAs which had much more pointed peaks which were Spillclean and De-Solv-it Industrial formula.

Access Western Winter Blend

In case of AWWB, *spc* increased to a great extant on few of the freshly oiled brick and sandstone samples to 30 to 80 times its original value. The same increased pattern was there in the weathered AWWB oiled samples and pointed peaks, in concrete an average of 54.173/mm increase from unoiled state, yellow pine 24.810/mm, sandstone 47.370/mm, and brick due to its highly porous structure it was 0.733/mm.

After the treatment in all sour surrogate materials in both the application of oils there was an increase in *spc* values, proving the increase in peaks after repeated agitation. In the freshly oiled samples of concrete the least impact was seen on De-Solv-it industrial formula treated samples, Naturama G3 A-5 and Premier 99. In yellow pine De-Solv-it industrial formula and Gold Crew SW were followed by Simple green 2013 and Premier 99. In removing freshly applied AWWB on Brick Gold Crew SW, Nokomis 5W, Spillclean, and De-Solv-it Industrial formula were equivalently successful. Like Concrete, De-solv-it Industrial formula and Naturama G3 A-5 were most successful on Sandstone followed by Gold Crew SW.

In case of the weathered oil application on concrete, the same SWAs as the freshly applied were successful along with Spillclean. For the yellow pine, the *spc* was lowest for Spillclean, De-Solv-it I.F., and Goldcrew SW. The change in *spc* values for brick was 0 for Premier 99, followed by Simple Green, Gold Crew SW and Spillclean. Similar to the freshly applied AWWB on Sandstone, the successful SWAs were De-solv-it Industrial formula, Naturama G3 A-5, and Gold Crew SW.

Spd, Density of peaks

Spd is the density of peaks or the number of peaks per unit area, measured in $1/mm^2$. Larger the number means more number of peaks per unit area.

West Texas Intermediate

After the samples of concrete, yellow pine, and sandstone were exposed to fresh application of WTI oil, the *spd* values increased to an average of 0.271/mm, 0.816/mm and 0.533/mm peaks per unit. Similar to *spc* values, the *spd* values for brick decreased to 0.106/mm on an average indicating lesser peaks. In case of the weathered samples of WTI, the number of peaks for concrete and brick decreased to an average of 0.163/mm and 0.203/mm. Whereas the values increased for yellow pine and sandstone to 0.532/mm and 0.081/mm. Comparing the *spd* values for the weathered and the un-weathered samples indicated that the weathering process reduced the peaks further.

When freshly oiled concrete was treated most of the successful SWAs reduced the number of peaks, which were Premier 99, De-Solv-it Industrial formula, Naturama G3 A-5 and Spillclean. In case of yellow pine the number of peaks reduced drastically and the best performing chemical were De-Solv-it

Industrial formula, Spillclean, and Premier 99. Brick had a similar change the successful treatment and there was an increase in peaks by Nokomis 5W, and Naturama G3 A-5. For Sandstone after the treatment there was an increase in peaks and the successful ones were Nokomis 5W, Premier 99 and Gold Crew SW.

The weathered samples of concrete after the treatment had lesser peaks, and the least decrease was found in samples treated by Simple green, Premier 99, and De-Solv-it Industrial formula. Similar to the unweathered samples of yellow pine, the weathered samples had drastic decrease in their peaks, and the lowest were observed in Naturama G3 A-5, Simple green, Spill clean, and premier 99. In case of brick the peaks reduced and were the least in Nokomis 5W and Premier 99 and Gold Crew. In case of spillclean the peaks had increased for the brick. The number of peaks increased in Sandstone in Spillclean and Gold Crew SWand only in one case it reduced which was in Nokomis 5W. The increase in peaks in unweathered and weathered Sandstone is probably due to the agitation and loosing of its particles.

Access Western Winter Blend

In case of AWWB in both fresh and weathered oil application there was a decrease in peaks, as the AWWB oil flattened the surface while reaching every valley. In fresh oil application on brick and sandstone there was a decrease of 0.893/mm and 6.273/mm peaks per unit area. In the weathered oil the least decrease in peaks was found in brick with values 0.284/mm, followed by timber with 1.789/mm and concrete 3.024/mm. Like fresh application, sandstone in weathered oil application had a high decrease of 6.505/mm peaks on an average.

After cleaning the fresh oil from concrete the least increase was found in Spillclean, Naturama G3 A-5 and De-Solv-it Industrial formula. In yellow pine there was a decrease in peaks in most of the SWAs and the lowest decrease was observed in Gold Crew SW, Nokomis 5W and Simple Green 2013. For brick after the treatment the number of peaks increased apart from Nokomis 5W which was followed by an increase in Gold Crew SW and Naturama G3 A-5. In case of Sandstone there was an increase after the treatment apart from Simple green with the lowest and decrease in the peaks followed by De-Solv -it and Naturama G3 A5.

The weathered oil treated concrete had an increase in peaks in most of the SWAs and the lowest increase was found in Premier 99 which was followed by decrease in peaks by Naturama G3 A-5. The yellow pine had a similar reduction of peaks like in other oiled conditions with WTI and AWWB, the lowest decrease was seen in Naturama G3 A-5, followed by Premier 99 and Simple green. Most of the samples of brick when treated had an increase in peaks apart from Premier 99 which had the lowest and followed by Gold Crew SW and Simple Green. The peaks increased in all treated samples of Sandstone the lowest increase was found in De-Solv-it Industrial formula, Simple Green followed by Naturama G3 A-5.

Sdr, Developed interfacial area ratio

Sdr, as expressed in percentage is the additional surface area contributed by the texture as compared its its planar area.

It quantifies the flatness of the surface, which made it clear that after oil application the values became closer to 0, stating the oil flattened the surface. This was also noticed after every treatment on AWWB the the oil residue re-mobilized and the surface was flat. The concrete, brick and sandstone surfaces are most flat, evidenced by *Sdr* values closer to 0. Nominal shifts were noticed predominantly in yellow pine as after the treatment the fibres in the yellow pine started detaching and it added to its *sdr* value.

Table 6: Successful SWA's for Surface roughness profile for WTI contaminated substrates.

	Un-weathered			Weathered		
Surface Roughness Profile	*Spc* 1/mm	*Spd* 1/mm	*Sdr* (%)	*Spc* 1/mm	*Spd* 1/mm	*Sdr* (%)
brick	Nokomis 5-W Gold Crew SW Naturama G3 A-5	Nokomis 5W Naturama G3 A-5 Gold Crew SW Spillclean	Premier 99 Simple Green Nokomis 5W Gold Crew SW	Simple Green Gold Crew SW Premier 99 Naturama G3 A-5	Nokomis 5W Premier 99 Gold Crew SW Spillclean	Simple Green Naturama G3 A-5 Gold Crew SW De-solv-it I.F.
concrete	Spillclean Naturama G3 A-5	Premier 99 De-Solv-it I.F.	Premier 99 Gold Crew SW	Gold Crew SW Naturama	Simple green 2013 Premier 99	Simple green 2013 Gold Crew

	Nokomis 5W Simple Green 2013	Naturama G3 A-5 Spillclean	Spillclean Simple Green 2013	G3 A-5 Spillclean De-solv-it I.F.	De-Solv-it I.F.	SW Spillclean
wood	De-Solv-it I.F. Spillclean Gold crew	De-Solv-it I.F. Spillclean Premier 99.	Gold Crew SW Spillclean Nokomis 5-W De-Solv-it I.F.	De-Solv-it I.F. Spillclean Gold crew SW	Naturama G3 A-5 Simple green 2013 Spill clean Premier 99	Spillclean Gold crew SW Naturama G3 A-5 De-solv-it I.F.
stone	Nokomis 5-W Gold Crew SW Premier 99	Nokomis 5-W Premier 99 Gold Crew SW	Naturama G3 A-5 Spillclean De-Solv-it I.F. Gold Crew SW	Nokomis 5-W Spillclean De-Solv-it I.F. Gold Crew SW	Nokomis 5-W Spillclean Gold Crew SW	De-Solv-it I.F. Spillclean Gold Crew SW Nokomis 5-W

Table 7: Successful SWA's for Surface roughness profile for AWWB contaminated substrates.

	Un-weathered			Weathered Oil**		
Surface Roughness Profile	*Spc* 1/mm	*Spd* 1/mm	*Sdr* (%)	*Spc* 1/mm	*Spd* 1/mm	*Sdr* (%)
brick	Gold Crew SW Nokomis 5W Spillclean De-Solv-it I.F.	Nokomis 5W Gold Crew SW Naturama G3 A-5	Naturama G3 A-5 De-solv-it I.F. Gold Crew SW Spillclean	Premier99 Simple Green, Gold Crew SW, Spillclean	Premier 99 Gold Crew SW Simple Green 2013	Naturama G3 A-5 Gold Crew SW Spillclean Simple Green 2013
concrete	De-solv-it I.F. Naturama G3 A-5	Spillclean Naturama G3 A-5 De-solv-it	De-solv-it I.F. Naturama G3 A-5	De-solv-it I.F. Naturama G3 A5	Premier 99 Naturama G3 A-5	De-solv-it I.F. Naturama G3 A-5

	Premier 99	I.F.	Premier 99	Spillclean Premier 99		Spillclean Premier 99
wood	De-solv-it I.F. Gold Crew SW Simple green 2013 Premier 99	Gold Crew SW Nokomis 5W Simple green	Simple green 2013 Premier 99 Gold Crew SW Spillclean	Spillclean De-solv-it I.F. Goldcrew SW	Naturama G3 A-5 Premier 99 Simple green 2013	Gold Crew SW Spillclean Simple green 2013
stone	De-Solv-it I.F. Naturama G3 A-5 Gold Crew SW	Simple Green 2013 De-Solv-it I.F. Naturama G3 A-5	Naturama G3 A-5 De-Solv-it I.F. Premier 99 Gold Crew SW	De-Solv-it I.F. Naturama G3 A-5 Gold Crew SW Simple Green 2013	De-Solv-it I.F. Simple Green 2013 Naturama G3 A-5	De-Solv-it I.F. Simple Green 2013 Naturama G3 A-5

Water Vapor Transmission

In each of the sample set, the unoiled control let the water vapour passed through it easily. The slowest water vapour transmission was observed in the oiled control. In each of the scenarios only one sample of the successful SWA's was used to test for the WVT.

Access Western Winter Blend

Although in the case of fresh AWWB on concrete the fastest water vapor transmission was found in the case of De-Solv-it I.F. which was followed by Naturama G3 A-5 and then the Un-oiled control.

Fig. 49: Rate of Water Vapor Transmission (24 hrs): Fresh Access Western Winter Blend on Concrete.

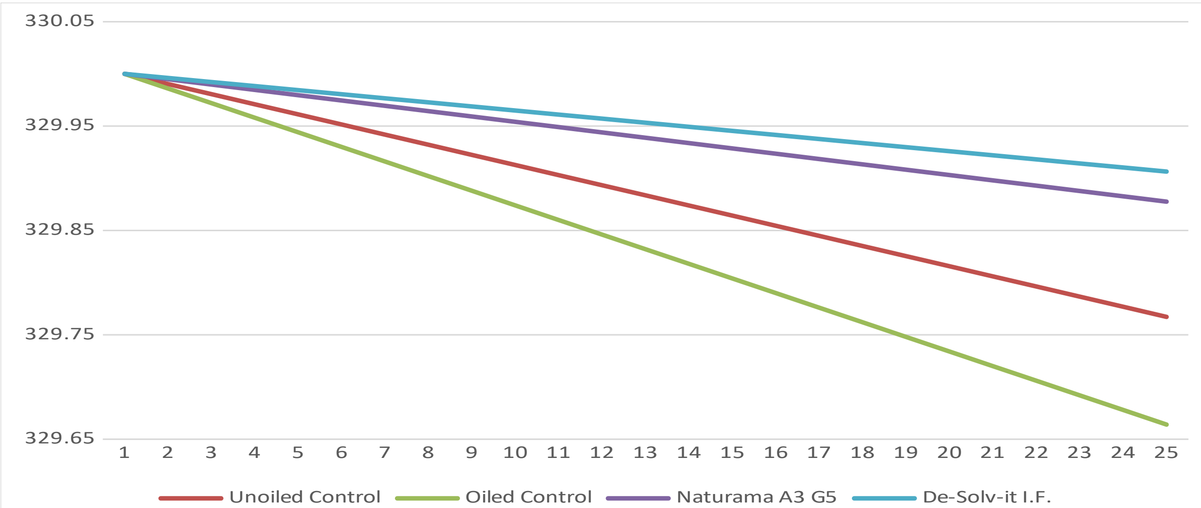
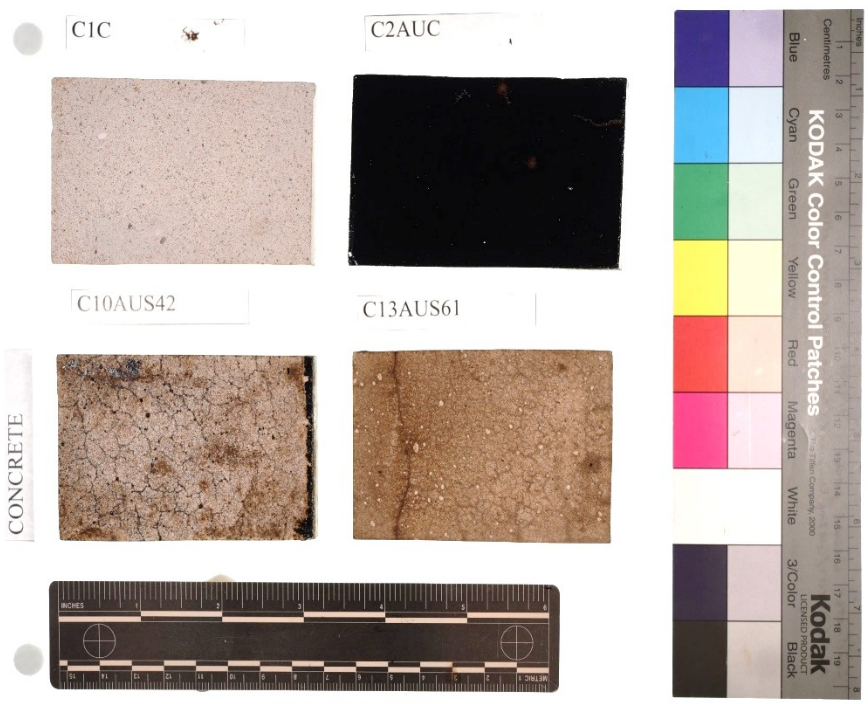


Fig. 50: The treated samples of Naturama G3 A-5 (bottom left) and De-Solv-it I.F.(bottom right) along with oiled control(top right) and unoiled control(top left) used for the WVT for fresh AWWB.



In weathered AWWB the fastest water vapor transfer was through Naturama G3 A-5 followed by unoiled control and then oiled control. The De-solv-it I.F. had the lowest transmission rate suggesting that the SWA dissolved the oil and added to substrate reducing the water vapor transmission capabilities of the concrete.

Fig. 51: Rate of Water Vapor Transmission (24 hrs): Weathered Access Western Winter Blend on Concrete.

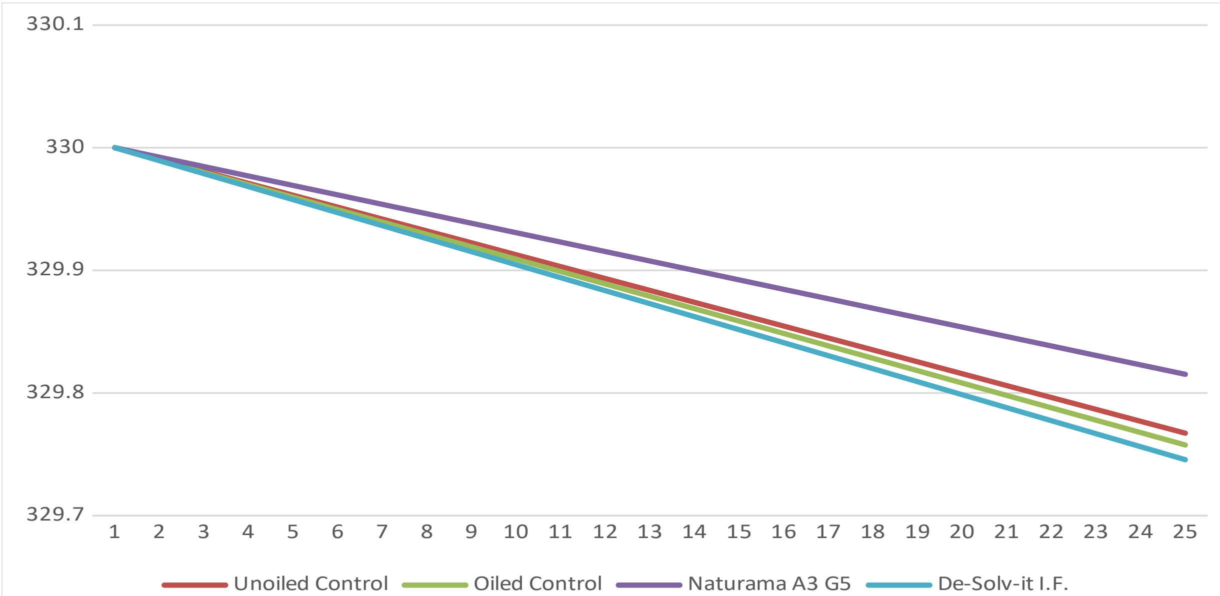
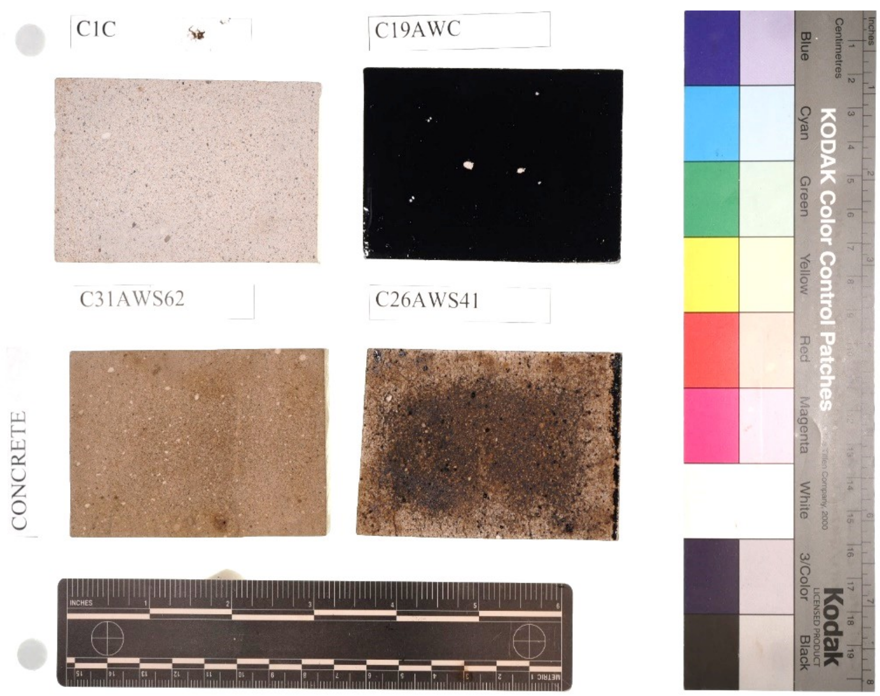


Fig. 52: The treated samples of Naturama G3 A-5 (bottom right) and De-Solv-it I.F.(bottom left) along with oiled control(top right) and unoiled control(top left) used for the WVT for weathered AWWB.



In the case of application of fresh AWWB on sandstone, the fasted water vapor transmission was found through unoiled control, followed by Naturama G3 A-5, De-Solv-it I.F. and then Simple green 2013. Simple green had only one successfully cleaned sandstone substrate out of the two duplicates.

Fig. 53: Rate of Water Vapor Transmission (24 hrs): Fresh Access Western Winter Blend on Sandstone

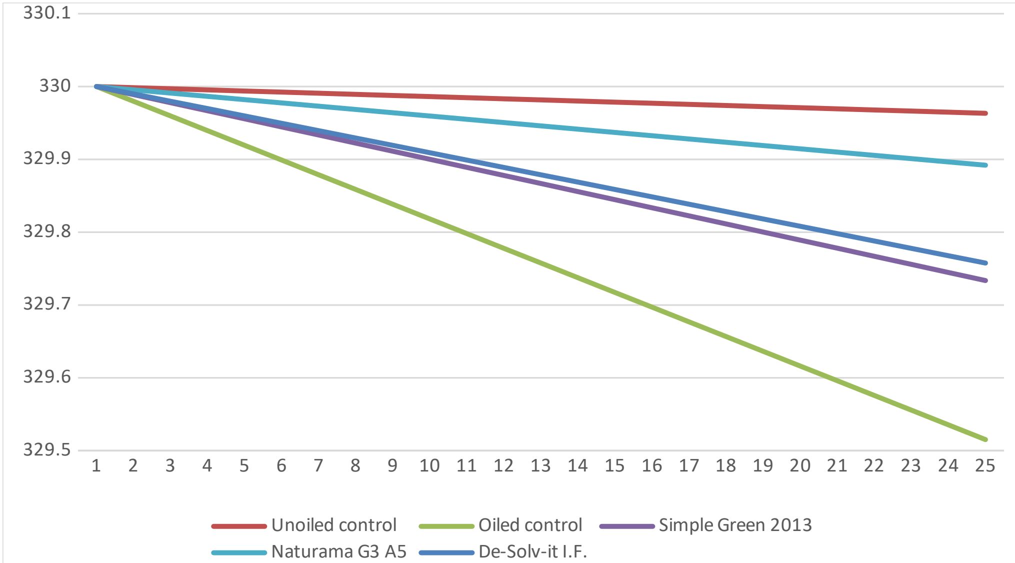
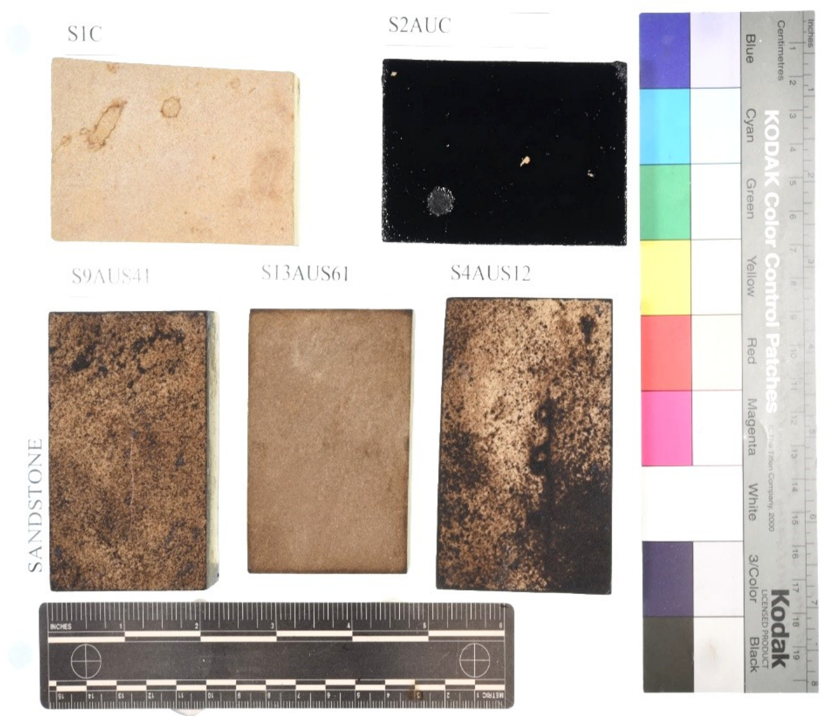


Fig. 54: The treated samples of Naturama G3 A-5 (bottom left) and De-Solv-it I.F.(bottom middle) and Simple Green 2013 (bottom right) along with oiled control(top right) and unoiled control(top left) used for the WVT for fresh AWWB.



7. Statistician’s analysis

As observed in the analysis one single treatment wouldn’t be best at restoring all parameters across the substrates and the oiling conditions. The analysis was described in three parts – first on substrates, second on oiling and last on the SWAs over the cleaning stages.

It was observed through the thorough analysis that yellow pine had the most color change (ΔE) and brick had the least. Concrete and Sandstone had similar change. Overall, the substrates lost the *l** parameter for light to dark, showing the samples became darker after the treatments. In SWA's it was noticed that the maximum color change happened across De-Solv-it industrial formula and the least change with Naturama G3 A-5. Concrete had the most increase in gloss whereas for sandstone it was minimal. Yellow pine and brick had a small increase. In case of mass, it increased after each treatment instead of reducing. Brick gained most of the weight followed by concrete and yellow pine. Sandstone gained the least mass. In surface roughness, the largest change in *spc* was noticed in concrete and least on brick. The *spd* had the decreased on yellow pine whereas it increased tremendously on sandstone. *Sdr* had the largest increase on yellow pine and concrete.

The samples contaminated with fresh WTI became lighter in color after the treatment whereas the weathered samples became darker. Concrete and sandstone had the most color change with fresh WTI as compared to weathered. Brick and pine had no difference. Brick and concrete had larger color change with weathered WTI. Brick samples exposed to weathered AWWB became greener and bluer as compared to unweathered. Weathered WTI oil had larger increase in gloss through out the treatments as compared to unweathered on brick, yellow pine and most on concrete. The samples oiled with WTI had more mass gain as compared to samples oiled with AWWB. The substrates exposed to WTI also had overall higher weight gain highest on concrete. AWWB oil led to higher *spc* as compared to WTI. *Spd* had a small gain on AWWB and small loss for WTI exposed samples. There was a loss of *sdr* noticed on AWWB but there was a little change on WTI. There was a small gain on pine samples.

After treatment with most of the SWAs the materials became lighter however De-solve it industrial formula made the samples darker. Nokomis 5W and Spillclean made brick lighter, Naturama G3 A-5 on concrete and Premier 99 and Nokomis on sandstone and yellow pine. Spillclean made brick redder. Most of the treatments had little effect on concrete and sandstone apart from De-Solv-it I.F. All the SWAs made yellow pine redder with Gold Crew SW and Simple green the highest. Spillclean and Naturama G3 A-5 made the brick yellower, Nokomis 5W on concrete. Most of the SWAs had the least impact on sandstone and Nokomis 5W had none. De-Solv-it industrial formula made yellow pine bluer and Goldcrew SW and Nokomis 5W made them yellow. Overall Nokomis 5W and Spillclean had the lowest change on brick, Primier 99 and Spillclean on concrete, Naturama G3 A-5 on sandstone and Premier 99 on yellow pine.

De-Solv-it industrial formula and Naturama G3 A-5 had the least impact on gloss for brick, Naturama G3 A-5 and Premier 99 on concrete and Nokomis 5W no change on yellowpine. Sandstone had very small impact on gloss.Premier 99 and Nokomis 5W had the least on weathered WTI samples.Samples treated with De-Solv-it industrial formula had the most gain in mass on all substrates as compared to other SWAs. Spillclean and Nokomis 5W had higher than average gain on brick where as Spillclean and Premier 99 had no change. Concrete was least impacted by Nokomis 5W, Gold Crew SW and Spillclean.

Concluded with one single treatment cannot be suggested to best restore all the parameters in all the situations. The two poultice stages might not be needed, the only difference was noticed in *spc* after the second treatment although, the change in *spd* and *sdr* was noticed after the first poultice. Poultice cleaning after spray agitated changed some color measures (*b** and *l*)* but didn't affect *a** after either of the poultice steps. Gloss increased after spray agitate and second poultice treatment especially for concrete. There was a mass gain after each cleaning stage.

Naturama G3 A-5(apart from pine) and Spillclean seemed to perform well across most of the parameters.

8. Conclusion

The takeaways from the Phase I and II were the success of the ethoxylated alcohol based SWA while removing the oil.

Concrete substrates contaminated by WTI were best removed by premier 99 across color, gloss and in surface roughness profile with least change in number of peaks on the sample. The color change was seen best in Spillclean on unweathered samples and Nokomis 5W on the weathered samples. ln the case of AWWB the only two SWAs that were able to remove oil to some extant were De-Solv-it industrial formula and Naturama G3 A-5. The success of the two SWAs was visible across each parameter baring mass for De-Solv-it.

Yellow pine substrates were cleaned with Naturama G3 A-5 had the most success on WTI unweathered and both conditions in AWWB. Premier 99 was particularly successful with the weathered samples of yellow pine. Spillclean was another SWA which was successful on the weathered samples although the change in gloss post oiling to after treatment wasn't much. The surface roughness was most affected on this substrate as the top layer softened after the poultice treatment the fibers started detaching from the surface.

Brick substrates that were treated by Spillclean and Nokomis 5W had the least amount of color change along with maximum oil removal on the WTI contaminated samples. The lowest gloss change was also found in the two SWAs along with De-Solv-it industrial formula. In case of surface roughness – Nokomis 5W performed well across the three parameters, although Spill clean performed well only for *spd.* AWWB exposed brick samples in the fresh oil application were best removed by Gold Crew SW, it performed well in all four parameters. After which De-Solv-it performed well across – color, mass, and surface roughness, it increased the mass of the substrate after the treatments. In case of the weathered oil Naturama G3 A-5 performed the best in removing oil for color, gloss and mass. It was followed by De-Solv-it I.F. though the success was seen only in color and gloss parameters.

On sandstone contaminated with fresh WTI, Nokomis 5W performed best over color, gloss and surface roughness. Goldcrew SW performed well across all parameters although there was a decrease in gloss as compared to the other SWAs. For weathered samples Gold Crew SW gave better results across color, gloss and surface roughness. In case of AWWB it was difficult to remove oil with any SWA. De-Solv-it I.F. dissolved the oil in the substrate and removed the oil and had the least color change although the values were higher that 20. Apart from De-Solv-it the other successful SWA considered was Naturama G3 A-5, as it performed well in all the parameters.

Naturama G3 A-5 performed well across all substrates and oiling conditions.

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