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U.S. General Services Administration

Removing Copper/Bronze Stains From Limestone And Marble

Procedure code:

440007S

Source:

Developed For Hspg (Nps - Sero)

Division:

Masonry

Section:

Stonework

Last Modified:

02/28/2017

THE CLEANING OR REMOVAL OF STAINS FROM STONE MAY INVOLVE THE USE OF LIQUIDS, DETERGENTS OR SOLVENTS WHICH MAY RUN OFF ON ADJACENT MATERIAL, DISCOLOR THE MASONRY OR DRIVE THE STAINS DEEPER INTO THE POROUS STONE. USE THE PRODUCTS AND TECHNIQUES DESCRIBED HERE ONLY FOR THE COMBINATIONS OF DIRT/STAIN AND STONE SPECIFIED.

PART 1---GENERAL

1.01 SUMMARY

- A. This procedure includes guidance on removing copper and bronze stains from limestone and marble. Several methods are described.
- B. Copper stains appear as green or muddy-brown discolorations and result from the action of moisture on nearby or embedded bronze, copper and/or brass items.
- C. Safety Precautions:
 - 1. DO NOT save unused portions of stain-removal materials.
 - 2. DO NOT store any chemicals in unmarked containers.
 - 3. EXCELLENT VENTILATION MUST BE PROVIDED WHEREVER ANY SOLVENT IS USED. USE RESPIRATORS WITH SOLVENT FILTERS.
 - 4. No use of organic solvents indoors should be allowed without substantial air movement. Use only spark-proof fans near operations involving flammable liquids.
 - 5. Provide adequate clothing and protective gear where the chemicals are indicated to be dangerous.
 - 6. Have available antidote and accident treatment chemicals where noted.
- D. See 01100-07-S for general project guidelines to be reviewed along with this procedure. These guidelines cover the following sections:

1. Safety Precautions
2. Historic Structures Precautions
3. Submittals
4. Quality Assurance
5. Delivery, Storage and Handling
6. Project/Site Conditions
7. Sequencing and Scheduling
8. General Protection (Surface and Surrounding)

E. These guidelines should be reviewed prior to performing this procedure and should be followed, when applicable, along with recommendations from the Regional Historic Preservation Officer (RHPO).

F. For general information on the characteristics, uses and problems associated with limestone, see 04460-01-S; for marble, see 04455-01-S.

PART 2---PRODUCTS

2.01 MATERIALS

NOTE: Chemical products are sometimes sold under a common name. This usually means that the substance is not as pure as the same chemical sold under its chemical name. The grade of purity of common name substances, however, is usually adequate for stain removal work, and these products should be purchased when available, as they tend to be less expensive. Common names are indicated below by an asterisk (*).

A. For Light-colored Stains:

1. Sodium Hydrogen Citrate ($\text{NaC}_6\text{O}_7\text{H}_7$) - (appears like enlarged salt granules):
 - a. Other chemical or common names include Citrate of soda*.
 - b. Available from chemical supply house, drug store or pharmaceutical supply distributor.
2. Glycerine:
 - a. A sweet syrupy hygroscopic trihydroxy alcohol usually obtained by the saponification of fats and used especially as a solvent and plasticizer.
 - b. Other chemical or common names include Glycerol; Glyceryl hydroxide; Glycyl alcohol; 1,2,3-propanetriol; Propenyl alcohol.
 - c. Potential Hazards: FLAMMABLE.
 - d. Available from chemical supply house, drug store or hardware store.
3. Cotton-wool pads

B. For Sharply-outlined Stains:

1. Sodium Hydrogen Citrate (See 2.01 A.1. above)
2. Crystalline Sodium Thiosulfate - white sal or "hypo" of photographic fixing agent ($\text{Na}_2\text{S}_2\text{O}_3$):
 - a. A hygroscopic crystalline salt used especially as a photographic fixing agent and a reducing or bleaching agent.
 - b. Other chemical or common names include Sodium hydrosulfite; Sodium Hyposulfite; Sodium subsulfite; Antichlor*; Hypo*; Hyposulfite of soda*.
 - c. Potential Hazards: TOXIC; CORROSIVE TO CONCRETE, STEEL, WOOD OR GLASS.
 - d. Available from chemical supply house, dry cleaning supply distributor, drugstore or pharmaceutical supply distributor, photographic supply distributor (not camera shop), or water and sanitation supply distributor.
3. Cotton wadding

C. For Poulticing:

1. Ammonium Chloride - salt-like substance (NH_4Cl):

- a. A white crystalline volatile salt that is used
- b. in dry cells and as an expectorant.:
- c. Other chemical or common names include Ammonium hydrochloride; Chloride of Ammonia*; Hydrochloride of Ammonia*; Muriate of Ammonia*; Sal Ammoniac*.
- d. Potential hazards: TOXIC; CORROSIVE TO FLESH; CORROSIVE TO CONCRETE, STEEL, WOOD OR GLASS.
- e. Available from chemical supply house, dry cleaning supply distributor, drugstore or pharmaceutical supply distributor, or hardware store.

2. Ammonium Hydroxide (NH_5O):

CAUTION: DO NOT MIX AMMONIA WITH CHLORINE BLEACHES, A POISONOUS GAS WILL RESULT! DO NOT USE BLEACH ON BIRD DROPPINGS.

- a. A weakly basic compound that is formed when ammonia dissolves in water and that exists only in solution.
- b. Other chemical or common names include Ammonia water*; Aqua ammonia*; Household ammonia*.
- c. Potential hazards: TOXIC; MAY IRRITATE THE EYES.
- d. Available from chemical supply house, grocery store or pharmaceutical supply distributor, or hardware store.

NOTE: TRADITIONAL USAGE OF AMMONIA DIRECT OR IN A PASTE WITH WHITING IS ONLY SUCCESSFUL ON LIGHT STAINING.

3. Ethylene diamine-tetra-acetic acid (EDTA):

- 1. EDTA is chelating agent used to remove metallic stains from masonry.
- 2. Chelating agents are molecules that coordinate metal ions together. The metal ions in the stain attach themselves to the chelating agent to form either a soluble or insoluble metal complex that can then be removed.
- 3. Available from chemical supply house.
- 4. It is available as an acid or in the form of its more soluble sodium salts. It is known to be used as a preservative. Its most important use, however, is in the removal of unwanted metal ions from water, as in the manufacturing of agricultural chemical sprays.

4. Appropriate filler such as Attapulgit clay, talc, diatomite, or ground or powdered chalk

D. Mineral water

E. Distilled water

F. Accessible source of clean, potable water, soap and towels for washing and rinsing in case of emergencies associated with the use of chemicals

2.02 EQUIPMENT

- A. Glass or ceramic container for mixing the solution
- B. Bowl for mixing chalk paste
- C. Wooden utensil for stirring the ingredients
- D. Wood scrapers or plastic spatula
- E. Plastic sheets
- F. Clean dry towels for blotting the area after treatment
- G. Masking tape
- H. Rubber gloves to prevent skin irritation

I. Glass plates to cover pads

J. Weights

PART 3---EXECUTION

3.01 EXAMINATION

- A. Examine the masonry surface CAREFULLY to determine the cause of staining to ensure the required treatment is determined before proceeding with any cleaning operation.

3.02 PREPARATION

- A. Protection: Provide adequate wash solutions (i.e. water, soap and towels) before starting the job.
- B. Surface Preparation: If possible, remove the sources of moisture to prevent further oxidation of the metal. Where the source of the stain is an embedded anchor, tie, or other device, the only non-destructive remedy is to eliminate the moisture at its source.

3.03 ERECTION/INSTALLATION/APPLICATION

NOTE: DO NOT TRY MORE THAN ONE TREATMENT ON A GIVEN AREA UNLESS THE CHEMICALS USED FROM PRIOR TREATMENT HAVE BEEN WASHED AWAY.

- A. For Light-Colored Stains: Apply an active agent with cotton-wool pads:
1. Thoroughly cleanse the area to be treated with mineral water.
 2. Put on the rubber gloves to avoid contact with the chemicals to be used and to avoid unnecessary skin irritation.
 3. Prepare a 15% aqueous solution of sodium hydrogen citrate with some glycerine (to deter evaporation) in the appropriate container.
 4. Dampen the cotton-wool pads in the solution and apply them to the area to be treated.
 5. Cover the pads with the glass plates.
 6. Apply weights on top of the glass plates to insure close contact between the pads and the stained stone.
 7. Allow the pads to set 3-4 days, before removing them.
 8. Remove all the equipment including the pads, thoroughly rinse with mineral water and allow to dry.
 9. If there is residual staining, repeat the process to achieve the desired level of cleanliness.
- B. For Sharply-outlined Stains: Apply an active agent with cotton wadding:
1. Rinse the area to be treated with distilled water.
 2. . Put on the rubber gloves to avoid unnecessary skin irritation.
 3. Mix a 15% aqueous solution of sodium hydrogen citrate in the glass or ceramic container.
 4. Form a paste of ground chalk and distilled water.
 5. Soak the cotton wadding in the sodium hydrogen citrate solution and apply them to the stained area.
 6. Spread the chalk paste over the cotton wadding.
 7. Sprinkle the crystalline sodium thiosulfate over the paste.
 8. Allow the chemicals to act on the stain for one hour.
 9. Remove all of the materials with a wood or plastic spatula.
 10. Thoroughly cleanse the area with mineral water and allow to dry.
 11. If there is residual staining, repeat the process to achieve the desired level of cleanliness.

-OR-

- C. Apply a poultice of ammonium chloride, ammonium hydroxide, EDTA, and attapulgate clay (see also 04455-02-R

for additional guidance on poulticing).

1. Prepare the poultice mixture:
 - a. Add 70 g of ammonium chloride to 570 ml of ammonium hydroxide; Add water to make the volume 1 liter.
 - b. Add 37 g of EDTA to the ammonia water.
 - c. Add attapulgate clay to form a soft paste.
2. Pre-wet the stain with clean water to prevent too deep a penetration of the chemical cleaning agent.
3. Apply the poultice mixture to the stained surface in layers no more than 1/4 inch thick.
4. Cover the poultice with sheets of plastic taped against the wall in order to prevent too quick of an evaporation.
5. Re-wet the poultice as needed and leave to dry for several days.
6. When the paste has dried, remove it with a wood or plastic spatula.
7. Thoroughly rinse the area with clean, clear water in order to remove any chemical residue and allow to dry.
8. Repeat this process as often as necessary to satisfactorily lift or lighten the stain.

Last Reviewed: 2018-10-25