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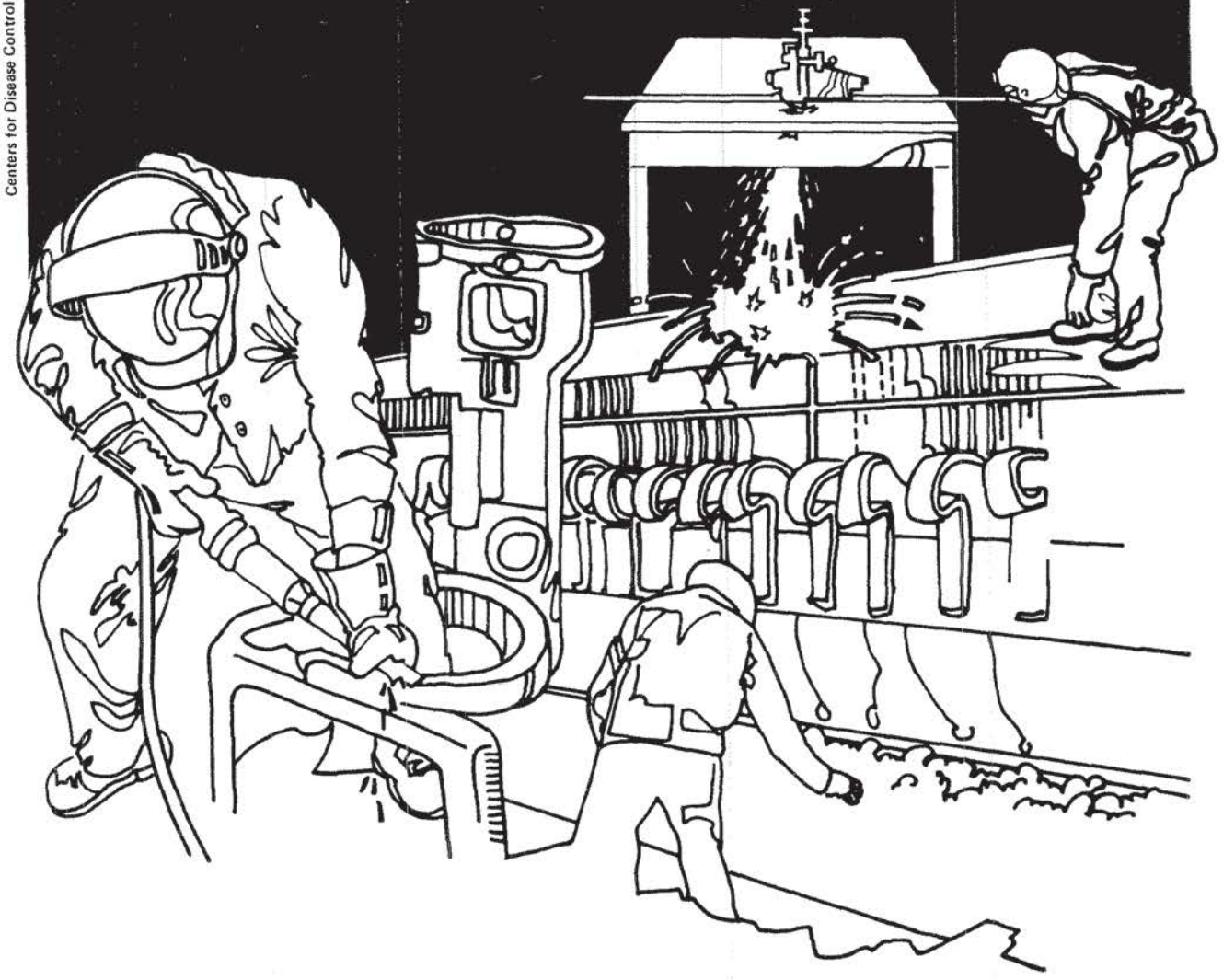

Health Hazard Evaluation Report

HETA 81-171-880
CYANOTYPE PRINTING IN
AN ARTIST'S WORKSHOP
BUCYRUS, OHIO

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

HETA 81-171-880
May 1981
Cyanotype Printing in
an Artist's Workshop
Bucyrus, Ohio

NIOSH INVESTIGATOR:
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I. SUMMARY

On February 9-10, 1981, the National Institute for Occupational Safety and Health (NIOSH) conducted a health hazard evaluation at the home studio of an artist engaged in the cyanotype printing process. The artist reported mucous membrane irritation, burning and itching sensation on her arms, face and hands; facial and finger edema, difficulty focusing eyes, sore mouth and anus, headache and nausea, which were temporally associated with the cyanotype printing process itself, or contact with fabrics which had undergone the cyanotype process. The artist had not performed the process for 18 months. However, she continued to report symptoms when utilizing fabrics which had been previously treated.

Environmental air samples, wipe samples, and vacuum samples of surface areas were obtained from the artist's workshop. One of the chemicals used in the cyanotype process is potassium dichromate. Spot tests (wipe samples) for chromium VI (Cr VI) indicated lingering contamination of Cr VI in several areas in the artist's workshop. Analytical results for the environmental air samples, vacuum samples and bulk samples of treated fabrics were below the limits of detection for chromium VI.

Based on the data gathered in this investigation, NIOSH determined that a health hazard did exist in the artists workshop at the time of the investigation. Chromium VI which was detected in the workshop, is a well documented sensitizer. The artist's symptoms were consistent with the known primary irritant and sensitization effects of Chromium VI. Recommendations for decontamination of the area are included in this report.

Keywords: SIC 7332, chromium VI, potassium dichromate, cyanotype printing process, hazards in the arts, blueprinting.

II. INTRODUCTION

On January 21, 1981, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation from an artist in Bucyrus, Ohio. The artist makes handmade quilts in her residence. She was concerned about potential exposures to toxic chemicals during a cyanotype printing process which she had pursued in her basement workshop. The artist reported mucous membrane irritation; burning and itching sensations on her arms, face and hands; facial and finger edema, difficulty focusing eyes, sore mouth and anus, headache and nausea, which were temporally associated with the cyanotype printing process itself or contact with fabrics which had undergone the cyanotype process. The artist had not performed the process since the summer of 1979. However, she continued to report symptoms when utilizing fabrics which had been previously treated. She was also concerned about potential contamination of her work area and residence.

III. BACKGROUND

The cyanotype, often referred to as the "blueprint" or "ferroprussiate" process, is a negative/positive process that yields a blue image on a white background from a negative transparency. The cyanotype process utilizes ferric ammonium citrate, potassium ferricyanide and potassium dichromate. The first two chemicals are sensitizers; the potassium dichromate is optional; it is used to fix the color and prevent fading.

The artist learned of the cyanotype process through an article which had been published in a popular magazine. She used it to transfer photographic prints to fabric. The instructions were:

> Dissolve 1 ounce of ferric ammonium citrate in 1/2 cup water; mix 1/2 ounce of potassium ferricyanide with 1/2 cup water, stirring until dissolved, then mix the chemicals together in a bowl. Wet a paintbrush with water, then cover each piece of fabric with the sensitizer solution. Hang the pieces to dry. Next, place the fabric in a sandwich arrangement of glass, fabric (painted side up), then a clear, high-contrast Kodalith photographic negative with emulsion (dull) side down. Place a second piece of glass on top of the negative and expose the entire package outside in direct sunlight. Expose for 10-30 minutes until the fabric has turned dark blue. After prints have been exposed, rinse fabric in lukewarm water until every trace of the chartreuse color has gone. Dry fabric inside, on a flat surface. The instructions state that the cyanotype print is sensitive to light, and may fade over time. Therefore, one teaspoon of potassium dichromate mixed in one quart of water was proposed as a fixer for the color. The fresh print is dipped in potassium dichromate solution until the blue darkens somewhat. Then, the chemical is rinsed out and the print is laid on a towel to dry.

The instructions also stated that the process "requires the use of dangerous chemicals which must be handled with care and kept out of the reach of children. Wear rubber gloves as you work." No other warnings were included

in the article. The artist followed the above directions; she mixed the chemicals at a workbench, and performed the potassium dichromate rinse in a bowl in a washbasin in her basement. She then rinsed the fabrics in 5 gallons of room-temperature water, wearing rubber gloves at all times when chemicals and solutions were handled.

IV. EVALUATION CRITERIA

Ferric ammonium citrate and potassium ferricyanide are chemicals possessing relatively low orders of toxicity. Potassium dichromate ($K_2Cr_2O_7$), however, is a highly toxic compound. Potassium dichromate contains hexavalent chromium (Cr VI) in a soluble form. Chromic acid mists and chromate dusts (chromium VI materials) are severe irritants of the naso-pharynx, larynx, lungs and skin.[1]

Chromium VI materials have been implicated as responsible for such effects as ulcerated nasal mucosa, perforated nasal septum, rhinitis, nosebleed, perforated eardrums, pulmonary edema, kidney damage, epigastric pain, erosion and discoloration of the teeth, primary irritant dermatitis, sensitization dermatitis, and skin ulceration.[2] Sensitization dermatitis, with varying degrees of eczema, has been reported numerous times and is the most common manifestation of chromium toxicity, affecting not only industrial workers, but also the general population.

Parkhurst[3] reported the case of a woman employed in blueprint production using a process where a 1% potassium dichromate solution was used as a fixative. A 0.5% potassium dichromate solution applied to the right thigh of the woman caused a local sensation of burning and itching. Twelve hours later, there was a follicular erythematopapular dermatitis where the solution had been applied. A similar application was made to the left thigh with resultant burning and itching. It was noted that an application of aqueous saturated solution of sodium bisulfite ($NaHSO_3$) prevented the development of a dermatitis in this area, presumably by reducing the hexavalent chromium to the trivalent state.

Jaeger and Pilloni[4] demonstrated that workers with cement eczema were sensitive to potassium dichromate. They patch-tested 32 patients with cement eczema and 168 patients with eczema from other causes. Thirty (94%) of those with cement eczema gave positive patch tests with aqueous 0.5% solutions of potassium dichromate, while only 5% of the other eczema patients exhibited positive reactions from the dichromate.

Kaaber and Vien[5] administered a tablet containing 7.1 milligrams of potassium dichromate or a placebo to 31 chromate allergic patients. The dermatitis of 11 of the 31 patients flared after the ingestion of chromate, but not the placebo. Three patients had equivocal reactions to both tablets. The dermatitis worsened in two patients following ingestion of the placebo, but not after the chromate tablet. Several patients also had eruption in

areas which had been affected several years previously, or on old chromate patch test sites. Eruptions were also observed at secondary sites, such as elbow folds, sides of the neck, or inner aspects of the thighs, in a few patients.

Denton, et al.[6] patch-tested a patient with "strong specific hypersensitivity to potassium dichromate" with 1) a 50 ppm aqueous solution of potassium dichromate, 2) a filtrate containing 1 ppm water-soluble hexavalent chromium from American Portland Cement, and 3) a filtrate containing 4 ppm water-soluble hexavalent chromium for American Portland Cement. The patient repeatedly had erythematous, edematous, and papulovesicular reactions. He did not react to distilled water.

The NIOSH recommended standard for non-carcinogenic chromium VI (potassium dichromate) is 25 micrograms per cubic meter of air (25 ug/M^3) as an 8-hour time-weighted average.

V. STUDY DESIGN AND RESULTS

On February 9-10, 1981 the NIOSH industrial hygienist made a site visit to the workshop of the artist. Discussions with her included her medical history, work practices, and procedures involved in the cyanotype process.

The artist reported that she had first begun the cyanotype process in June 1978. She noticed a tingling in her hands and skin during the measurement of chemicals, and acute flareups of symptoms each time she engaged in the process. She discontinued use of the process in the summer of 1979. The symptoms, however, would recur from time to time. By careful observation the artist was able to link her symptoms to contact with materials which were directly or indirectly involved in the cyanotype process. The symptoms abated when she was away from home, providing she did not bring any of the treated cloth with her. The symptoms were most severe during hand stitching of the fabric into a quilt, during which time there was extensive skin contact with the cloth and some oral contact due to threading of needles, knotting of threads, etc. Occasional accidental needle pricks to the fingers also occurred, and thus, offered another potential route of exposure.

The industrial hygienist sampled the work and ancilliary areas in the basement for contamination with Cr VI compounds. Figure 1 is a schematic diagram of the basement. 100 cm^2 blocks of surface area were wiped with a Whatman smear tab which had been dampened with distilled water. A few drops of 0.5 normal sulfuric acid was added to the smear tab, followed by a few drops of diphenylcarbazide solution. In the presence of Cr VI the smear tab turns to a violet shade. Table I indicates the results of the smear sampling. This qualitative spot test indicated lingering contamination of Cr VI at the workbench where chemicals had been mixed; the boards on which the fabric was placed during exposure to the sun; the glass used to sandwich the fabric; and the bottom panel of a cabinet located above the washbasin where the fabric was fixed in the potassium dichromate solution.

General area air samples for Cr VI were obtained. Surface areas (each 100 cm^2) in diverse sections of the workshop and basement were "vacuumed" using a tygon tube attached to a small two-stage plastic cassette containing a PVC filter with a Gast suction-type pump to collect the sample. Table II indicates the results of the air and vacuum sampling.

The analytical method used for the air and vacuum samples for Cr VI was NIOSH Method P & CAM 169. It has a limit of detection equivalent to 2 ug/sample (2 micrograms per sample). The results of the air and "vacuum" sampling for Cr VI indicated that Cr VI was not present on these samples at levels which could be detected. Seven bulk samples of fabric were submitted for analysis for Cr VI. These samples were also analyzed by NIOSH Method P & CAM 169, which is intended for Cr VI in air and may not be entirely suitable for the bulk samples to which it was applied.

The limit of detection for the fabric samples which were submitted is 0.01 ug Cr VI per 1 mg of sample (the equivalent of 10 parts per million). Table III indicates the results. Chromium VI was not found to be present in detectable amounts in the fabric samples which were submitted.

Detector tubes were employed to evaluate the presence of oxides of nitrogen and formaldehyde in the basement with negative results. Carbon monoxide levels in the basement averaged 1 ppm. Several fabric samples were obtained for laboratory analysis.

An experimental decontamination of one of the boards on which treated fabrics had been placed was implemented. Potassium dichromate is insoluble in alcohol. Its solubility in cold water (0^oC) is 4.9 gm/100 cc. Its solubility in hot water (100^oC) is 102 gm/100 cc. A board which had a positive spot test for Cr VI was placed under hot tap water for 5 minutes. Post examination with the spot test indicated no color change and, therefore, no detectable Cr VI.

Since the process had been discontinued 1 1/2 years prior to sampling, it is not surprising that areas subject to normal cleaning did not demonstrate detectable levels of Cr VI. The spot test with a wet smear tab, however, indicated some lingering contamination of Cr VI at the workbench, washbasin, and on implements used in the process.

In summary, Cr VI is a well documented sensitizer. Sensitization to chemicals can, and does occur at levels which may be below limits of detection. The artist's symptoms are consistent with the known primary irritant and sensitization effects of CR VI.

VI. RECOMMENDATIONS

1. Discontinue work with the cyanotype process, or discontinue use of potassium dichromate as a fixer.

2. Decontaminate the basement with a hot soapy water solution paying special attention to the chemical workbench area, overhead ducts located near the chemical workbench, and the cabinet above the washbasin.

3. Wash all fabrics, involved directly or indirectly in the process, thoroughly with hot water.

4. If symptoms persist following decontamination of work areas and fabrics, consult a dermatologist or allergist regarding the advisability of skin patch-testing for sensitivity to chromates and other substances involved in the process.

5. Avoid other sources of chromates, i.e., certain tanned leathers, color pigments, etc.

VII. REFERENCES

1. Proctor, N. and J. Hughes, Chemical Hazards in the Workplace. J.B. Lippincott Company, Philadelphia, PA, 1978.

2. "Criteria for a Recommended Standard - Occupational Exposure to Chromium" (VI). DHHS (NIOSH) Publication No. 76-129, 1975.

3. Parkhurst, H.J., "Dermatitis Industrialis in a Blue Print Worker Due to Chromium Compounds." Archives of Dermatology and Syphilology, Vol. 12, pp. 253-256, 1925.

4. Jaeger, H. and E. Pelloni, "Skin Test to Dichromates, Positive with Cement Eczema." Dermatologica 100:207-16, 1950.

5. Kaaber, K. and J. Vien, "The Significance of Chromate Ingestion in Patients Allergic to Chromate." Acta Dermatoven (Stockholm) 57:321-323, 1977.

6. Denton, C.R., M.S. Keenan, and D.J. Birmingham, "The Chromium Content of Cement and Its Significance in Cement Dermatitis." J. Invest. Dermatol. 23:189-92, 1954.

VIII. AUTHORSHIP AND ACKNOWLEDGEMENTS

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IX. DISTRIBUTION AND AVAILABILITY

Copies of this report will be available from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226 for 90 days. Thereafter, copies will be available from the National Technical Information Service (NTIS), Springfield, Virginia. Information concerning its availability through NTIS can be obtained from the NIOSH Publications Office at the above Cincinnati address.

Copies of this report have been sent to:

1. The artist
2. NIOSH Region V
3. OSHA Region V

TABLE I

Spot Test for Chromium VI Using Whatman Smear Tabs
to Wipe 100 cm^2 Blocks of Surface Areas

Cyanotype Printing in an Artist's Workshop
Bucyrus, Ohio
HETA 81-171
February 10, 1981

LOCATION	TEST RESULTS
Lower right corner of formica-coated fiberboard used in cyanotype process	+
Upper left corner of formica-coated fiberboard used in cyanotype process	+
Center of formica-coated fiberboard used in cyanotype process	+
Pass through above workbench	+
Top of vent ductwork above workbench	+
Glass divider used in cyanotype process (both sides)	+
Second glass divider used in cyanotype process (both sides)	+
Second formica-coated fiberboard used in cyanotype process	+
Door in storage cabinet	-
Floor, directly in front of workbench	-
Floor, 3 feet in front of workbench	-
Top of water heater	-
Brown paper covering on workbench	-
Wall directly behind washbasin	-
Underside of cabinet, directly above washbasin (northhand basin)	+
Underside of cabinet, directly above washbasin (southhand basin)	+
Front of cabinet above washbasin	+
Table next to washbasin	-
Clear plastic-covered drying bench	-
Yellow plastic-covered drying bench	-
Storage cabinet, 1st shelf	-
Storage cabinet, 2nd shelf	-
Storage cabinet, 3rd shelf	-
Storage cabinet, 4th shelf	-
Storage cabinet, 5th (top) shelf	-
Clothespin used to hang fabric while drying	-
2nd Clothespin used to hang fabric while drying	-
Carpet - center of Room 3	-
Carpet - at bottom of stairs	-
Fully-prepared cyanotype print - swipe of fabric	-
Fully-prepared cyanotype print - direct application of reagents	-

TABLE II

Air and Vacuum Sampling for Chromium VI

Cyanotype Printing in an Artist's Workshop
Bucyrus, Ohio
HETA 81-171
February 10, 1981

Location of Sample	Type of Sample	Air Volume or Surface Area	Concentration
Above workbench	Air	8.1 M^3*	ND**
Above workbench	Air	8.1 M^3	ND
Lower left corner of formica-coated fiberboard	Vacuum	100 cm^2***	ND
Center of workbench on brown paper	Vacuum	100 cm^2	ND
On pass through above workbench	Vacuum	100 cm^2	ND
Floor, beneath workbench	Vacuum	100 cm^2	ND
Bottom of cabinet above washbasin	Vacuum	100 cm^2	ND
Floor, beneath washbasin	Vacuum	100 cm^2	ND
Interior of south sink in washbasin	Vacuum	100 cm^2	ND
Threshold between Rooms 2 and 3 in basement	Vacuum	100 cm^2	ND
Center of lowest stair on stairway leading to 1st floor	Vacuum	100 cm^2	ND
3rd shelf of storage cabinet	Vacuum	100 cm^2	ND

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* M^3 = Cubic meter of air
** ND = Below detectable limits(limit of detection is 0.01 micrograms of Chromium VI per sample)
*** cm^2 = Square centimeter

TABLE III

Chromium VI Analysis of Bulk Fabric Samples

Cyanotype Printing in an Artist's Workshop
Bucyrus, Ohio
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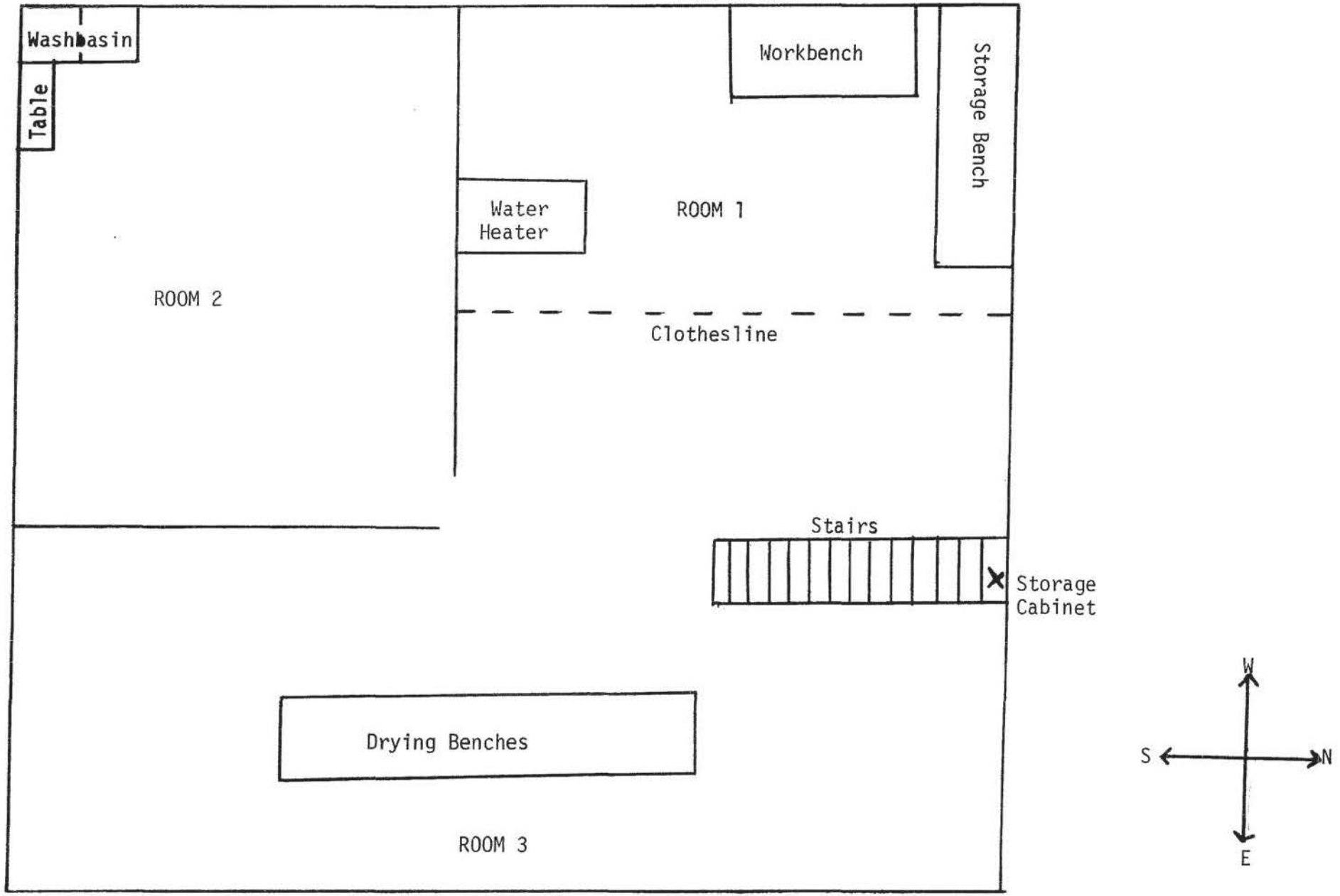
Bulk Sample Description	Results
Fabric A - Untreated fabric which had been stored with treated fabric	ND*
Fabric B - Cyanotype print and cotton batting	ND
Fabric C - Cotton batting sewn into a cyanotype quilt - batting was then removed and reused	ND
Fabric D - A cyanotype print	ND
Fabric E - Cloth which was untreated, but was stored with treated cloth and caused a skin reaction	ND
Fabric F - Untreated fabric	ND
Fabric G - A yarn sample	ND

* ND = Below detectable limits (limit of detection is 0.01 micrograms of Chromium VI per sample).

FIGURE 1

Schematic Diagram of Artist's Workshop

Cyanotype Printing in an Artist's Workshop
HETA 81-171



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