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Applied Occupational and Environmental Hygiene

ISSN: 1047-322X (Print) 1521-0898 (Online) Journal homepage: https://www.tandfonline.com/loi/uaoh20

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To cite this article: Alan K. Fleeger & Jou-Fang Deng (1990) A Case Study of Chromium VI-Induced Skin Ulcerations during a Porcelain Enamel Curing Operation, Applied Occupational and Environmental Hygiene, 5:6, 378-382, DOI: 10.1080/1047322X.1990.10389658

To link to this article: https://doi.org/10.1080/1047322X.1990.10389658

Published online: 25 Feb 2011.

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A Case Study of Chromium VI-Induced Skin Ulcerations During a Porcelain Enamel Curing Operation

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In the facility under study, chromium III-based porcelain enamel paints are applied as a ground coat to kitchen range parts. Following the application, the parts are hooked on small hangers and passed through a curing oven (approximately 1500°F). The employees responsible for handling the hangers (ground-coat line workers) were complaining of skin problems.

The objective of this study was to determine the source of the skin problems. During an initial site investigation, bulk samples were collected for chromium VI and trace metals analyses. Seven workers reporting skin problems were examined. A yellowish discoloration of the hands accompanied with ulcerations of the hands and forearms were observed on each of the workers. The bulk samples showed chromium VI levels ranging from 0.1 to 2.4 micrograms per milligram (μg/mg) of sample. Trace metals analysis detected 19 additional metals.

Following the repair of the curing oven coils to prevent emission of open flames, no new cases developed. During the follow-up investigation, bulk samples showed chromium VI levels ranging from 0.3 to 4.4 μg/mg of sample. Trace metal analysis detected 24 additional metals. In addition, a medical symptom questionnaire identified ten chromium ulceration cases. Among the ten cases, eight were ground-coat line workers. The questionnaire indicated that the ground-coat line workers were seven times more likely to develop the ulcers than other workers in the Enamel Department.

Prior to the follow-up investigation, it was theorized that the open flames were contributing to the production of chromium VI. However, the bulk concentrations of chromium VI following the curing oven repair were practically identical to those collected prior to the repair. It was determined that the open flames in the oven caused the chromium VI to be more readily available on the hooks through improper curing of the enamels which created sharp edges on the hooks, cutting the workers' hands, thus affording the chromium VI a direct route of entry beneath the skin. Recommendations are made for oven maintenance and personal protection. Fleeger, A.K.; Deng, J-F.: A Case Study of Chromium VI-Induced Skin Ulcerations During a Porcelain Enamel Curing Operation. Appl. Occup. Environ. Hyg. 5:378–382; 1990.

Background

The National Institute for Occupational Safety and Health (NIOSH) received a request for a health hazard evaluation to investigate the source of skin problems in the Enamel Department of a facility engaged in the manufacturing of consumer gas and electric ranges.

The facility is divided into many different departments, all of which are responsible for some aspect of the range production process. The Enamel Department is primarily responsible for painting the individual range parts prior to their final construction. Porcelain enamel paints are applied to the range parts by either a dipping or flow-coat process. The porcelain enamels are trivalent chromium based. However, oxidizers are added to the enamels, creating a potential for the formulation of hexavalent chromium. Following the application of the paint, the parts enter a drying oven (approximately 400°F) and a reinforcing ground coat is applied. The parts are then hung on small hooks and enter the curing oven (approximately 1500°F).

The ground-coat line workers, responsible for hanging the parts on small hooks prior to entering the curing oven, originally reported the skin problems. The first reported case occurred around January 1988. Most of the ground-coat line workers do not wear protective gloves when handling the hooks. The gloves reportedly reduce dexterity. The workers are paid on an incentive basis, causing them to handle a large quantity of hooks during the shift.

Management reported that prior to January 1988 there were no reported skin problems in the Enamel Department. They also stated that no changes were made in the process when the skin problems began to occur. However, in March 1988, open flames were detected in the curing oven, causing a greater number of product defects. When the flames contacted the enameled surface, they burned off small patches of enamel from the parts. In addition, it was reported that the flames caused sharp edges to form on the hooks which cut the employees' hands as the hooks were handled. The objective of this study was to determine the source of the skin problems in the Enamel Department.

Chromium Toxicology

Chromium is a major industrial chemical widely used in anodizing, plating, pigment production, and alloy, battery, and match manufacturing.[1] The most extensive use of chromium is in electroplating. Many household appliances are chrome-plated. In addition, many enamels applied to metal products contain chrome pigments. The chrome enamel prevents corrosion caused by acids, corrosive waters, high temperatures, and atmospheric conditions.

In 1974, NIOSH estimated that approximately 175,000 workers were potentially exposed to chromium.[2] The chief exposure to hazardous chromium substances in industry is believed to be to an acid-soluble, water-insoluble, chromate-chromite mixture, produced in the preparation of chromate.[3]

The principal toxicological reaction sites from industrial exposures to chromium are the skin, larynx, lung, and upper respiratory tract. The harmful effects of chromium include carcinogenicity, skin sensitization, and skin and mucosal ulcerations. The harmful effects are heavily dependent on the valence state of the chromium. Divalent chromium is of minor importance in industrial exposures because it readily oxidizes to the trivalent state. The tetravalent and pentavalent forms are essentially unstable and are used as intermediates in chemical production. Trivalent and hexavalent chromium are the only compounds known to be significantly associated with human disease. With specific regard to skin ulcerations, trivalent chromium is poorly absorbed through the skin. Normally, trivalent chromium does not cause skin ulcers unless it is oxidized to a hexavalent state, which can easily penetrate the skin.[4] Hexavalent chromium can have a corrosive, necrotizing effect on living tissue, forming ulcerations known as chromium holes.

Chromium-induced skin ulcerations and perforations of the nasal septum have been well documented since the 1930s.[1,5,6] Ulcerations generally occur on exposed areas of the body, chiefly the hands, forearms, and feet. They may develop more readily if there is a break in the skin, such as at the site of an insect bite or other injury. The ulcerations are round and deeply penetrating, with a clean-cut central crater, 2–5 mm in diameter, whose base is covered with exudate or a tenacious crust. Once developed, the ulcer is slow to heal, and if exposure continues, it may persist for many months. The healing process usually leads to scar formation.

Evaluation Design and Methods

Based on the information obtained during the preliminary telephone conversations and the initial walk-through evaluation, it appeared that the problem was a direct skin contact phenomenon. The reported symptoms were apparently limited to the ground-coat line workers in the Enamel Department.

During the initial survey on June 29, 1988, bulk samples from the curing oven and two hooks were collected for water-soluble chromium VI and trace metals analyses. The bulk samples and scrapings from the hangers were analyzed for hexavalent chromium following NIOSH Method 7600.[7] The sample residues were dissolved and further analyzed for trace metal by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The results were reported as average percent by weight for each element. The limits of quantitation (LOQ) were 0.01 μg/mg of sample for soluble hexavalent chromium and 0.01 percent (0.01% is equivalent to 0.1 μg/mg) for trace metals.

During the return visit (September 26–27, 1988) which followed the repair of the curing oven coils, bulk samples were again collected from the curing oven and the two hooks to be analyzed for hexavalent chromium and trace

TABLE I. Trace Metal and Chromium VI Bulk Sample Analysis—June 29, 1988

Analyte	Sample: Number One Coupler Curing Oven (μg/mg of sample)	Number Two Coupler Curing Oven (μg/mg of sample)	Hook (μg/mg of sample)	Analyte	Sample: Number One Coupler Curing Oven (μg/mg of sample)	Number Two Coupler Curing Oven (μg/mg of sample)	Hook (μg/mg of sample)
Gold	ND*	ND	ND	Sodium	47.5	43.0	ND
Aluminum	28.4	67.1	19.1	Nickel	23.3	16.0	8.8
Arsenic	ND	ND	ND	Phosphorus	0.1	0.3	0.8
Barium	0.2	0.3	1.0	Lead	0.8	0.7	0.1
Beryllium	ND	ND	ND	Platinum	ND	ND	ND
Calcium	12.2	12.1	43.0	Antimony	ND	ND	ND
Cadmium	ND	ND	ND	Selenium	0.5	0.5	ND
Cobalt	0.4	0.3	1.6	Strontium	ND	ND	ND
Chromium	44.3	37.0	6.7	Tellurium	ND	ND	ND
Copper	1.1	1.2	4.6	Titanium	2.4	3.5	0.6
Iron	37.2	33.2	5.7	Thallium	ND	ND	ND
Lanthanum	ND	ND	ND	Vanadium	ND	ND	ND
Lithium	2.7	1.9	ND	Yttrium	ND	ND	ND
Magnesium	9.4	23.2	1.0	Zinc	ND	0.2	0.1
Manganese	1.4	1.5	2.1	Zirconium	1.0	1.1	ND
Molybdenum	0.7	0.4	ND	Chromium VI	2.4	1.3	0.1

*ND = Nondetected

TABLE II. Trace Metal and Chromium VI Bulk Sample Analysis—September 27, 1988

	Sample			
Analyte	Number One Coupler Curing Oven (μg/mg of sample)	Number Two Coupler Curing Oven (μg/mg of sample)	Hook 1 (μg/mg of sample)	Hook 2
Aluminum	42.0	33.0	35.0	7.5
Arsenic	0.8	0.3	0.4	0.8
Barium	0.4	1.1	0.9	0.1
Beryllium	ND[A]	ND	ND	ND
Calcium	17.0	27.0	31.0	4.0
Cadmium	0.03	ND	ND	0.01
Cobalt	0.3	0.9	1.7	0.1
Chromium	63.0	34.0	79.0	49.0
Copper	1.8	3.9	4.5	0.6
Iron	26.0	50.0	64.0	10.0
Lithium	3.0	3.5	1.8	2.9
Magnesium	15.0	1.2	0.8	2.4
Manganese	2.0	6.2	5.3	0.5
Molybdenum	0.4	0.06	0.1	0.5
Sodium	68.0	88.0	110.0	45.0
Nickel	14.0	130.0	140.0	7.2
Phosphorous	0.4	0.2	0.2	0.2
Lead	0.9	0.08	0.08	0.7
Platinum	ND	ND	ND	ND
Selenium	1.5	ND	ND	0.1
Silver	0.02	ND	ND	0.01
Tin	ND	ND	ND	ND
Tellurium	ND	ND	ND	ND
Titanium	4.7	7.2	6.1	0.9
Thallium	ND	ND	ND	ND
Tungsten	ND	ND	ND	ND
Vanadium	0.07	0.03	ND	0.01
Yttrium	0.02	0.08	0.1	ND
Zinc	1.0	3.3	2.5	0.2
Zirconium	1.0	12.0	2.7	0.5
Chromium VI	2.6	NA[B]	0.3	4.4

[A]ND = Nondetected [B]NA = Not analyzed

metals. In addition, personal breathing zone (PBZ) samples and area air samples were collected for hexavalent chromium and trace metals at the ground-coat line. The air samples for chromium VI were collected with 5-μm pore size, tared, polyvinyl chloride filters connected via Tygon® tubing to battery-powered pumps operating at a flow rate of 1.0 L/min. The sample filters were analyzed for chromium VI by visible spectroscopy according to NIOSH Method 7600.[7] The limit of detection (LOD) was 0.3 μg per sample. The LOQ was 0.76 μg per sample. The air samples for trace metals were collected on 0.8-μm pore size cellulose ester membrane filters connected via Tygon tubing to a battery-powered pump at a flow rate of 1.0 L/min. The sample filters were analyzed via NIOSH Method 7300 using a scanning inductively coupled plasma emission spectrometer.[7] The LOD varied according to the 30 individual analytes.

On June 29, 1988, private interviews and brief physical examinations were conducted on the seven workers who were reported to have skin problems. During the September 26–27, 1988, follow-up survey, a questionnaire was administered to 74 of the 78 workers in the Enamel Department. Participation in the survey was voluntary. The questionnaire asked for information regarding skin ulcerations, job history, demographics, hand washing, glove use, and barrier cream application. Workers reporting a skin ulceration after January 1, 1988, were given a brief physical examination. The physician examined the skin for active skin ulcerations and for hyperpigmentation or scar formations resulting from previous ulcers. The data collected by the questionnaire were analyzed by Chi-square analyses.

Results

Table I presents the bulk sample results for water soluble chromium VI and trace metals collected on June 29, 1988. Quantifiable levels (LOQ of 0.01 μg/mg of sample) of water soluble chromium VI were detected in each of the three samples collected. Chromium VI levels ranged from 0.1 to 2.4 μg/mg of sample. The highest chromium VI level was collected in number 1 coupler in the curing oven. Trace metals were detected in 19 of the 31 tested analytes.

Table II presents the bulk sample results for chromium VI and trace metals collected on September 27, 1988. Quantifiable levels (LOQ of 0.3 μg/mg of sample) of chromium VI were detected in two of the four samples collected. The highest chromium VI level was in a bulk sample of scrapings from the two hooks collected on the floor of the ground coat line. Trace metals were detected in 24 of the 30 tested analytes.

Five air samples collected at the ground coat line, September 27, 1988, were all reported below the analytical LOQ for chromium VI. One personal breathing zone sample detected a trace amount of chromium VI (0.4 μg/sample) which is between the analytical LOD and LOQ and, therefore, cannot be reported as an accurate exposure concentration.

Five air samples, collected at the ground coat line for trace metal analysis on September 27, 1988, were nondetected for 29 of the 30 tested analytes. Small quantities of iron were detected in each of the five samples, ranging in concentration from 2.5 to 5.0 $\mu g/m^3$ of air. These concentrations are well below the American Conference of Governmental Industrial Hygienists (ACGIH) recommended Threshold Limit Value (TLV) for iron oxide of 5 mg/m^3. NIOSH has not established a Recommended Exposure Limit for iron oxide; therefore, the ACGIH TLV is recommended.

Employee interviews and physical examinations on June 29, 1988, revealed seven workers with a localized yellowish discoloration of the hands, accompanied by a burning sensation and "punched-out" ulcerations (3 mm in diameter) and "chaffing" on the hands and forearms. One of the seven workers also had multiple ulcerations and scarring with increased pigmentation over the left subaxillary region. This particular worker placed bundles of hooks under his arm so he would not have to bend over as often to retrieve hooks. The ulcerations were compatible with those seen in workers exposed to hexavalent chromium.

Workers who reported a chromium ulcer on the upper extremities, armpits, or abdomen after January 1, 1988, were considered cases. By this definition, ten cases were identified during the period of January 1 to September 27, 1988. The overall attack rate was 14 percent (10/74). Among the ten cases, eight were hangers or hookers (hook handlers). Hangers and hookers (combined) were at a greater risk for developing ulcerations [Rate Ratio (RR) = 12.44; 95% confidence interval (CI) = 2.90–53.35] than workers with other job classifications. After controlling for age, sex, and frequency of handwashing, the hangers or hookers remained seven times more likely to develop ulcers than the other workers in the Enamel Department.

Discussion/Conclusion

Based on the observations made during the initial site visit on June 29, 1988, NIOSH investigators determined that the ground-coat line workers developed chromium ulcers as a result of their employment. The observed symptoms were the result of a direct skin contact phenomenon and were diagnosed to be chromium VI induced. No new cases were reported after the initial visit.

These findings left the following two questions unanswered:

1. Why were no new cases found after June 29, 1988?
2. What originally caused the ulcerations to develop in March 1988?

To address the question as to why no new cases occurred after June 29, 1989, a comparison was made between the concentration of chromium VI in the bulk samples. The analytical results from the initial (0.09 to 2.4 μg/mg) and follow-up (0.3 to 4.4 μg/mg) evaluations revealed that the chromium VI levels were slightly higher during the follow-up investigation. Prior to the follow-up investigation, it was suspected that that the chromium VI levels would be higher during the initial site visit when the skin problems existed, but this was not the case.

The lower chromium VI analytical results from samples obtained during the follow-up evaluation were thought possibly to be attributed to the different extraction techniques used for the two sample sets. Deionized water was used in the initial analysis to extract the chromium VI, whereas sodium hydroxide and sodium carbonate were used in the subsequent analysis. However, the analytical chemist suggested that this difference would not affect the sample results. Therefore, the following rationale was used in deciding that the two separate extraction methods did not affect the chromium VI sample results:

1. A comparison of the sample results collected from the two evaluations in the curing oven, number one coupler, reveals that they are practically identical (2.4 μg/mg and 2.6 μg/mg).
2. A comparison of the total chromium results collected from the two evaluations in the curing oven, number one coupler (where both analyses were conducted under similar conditions according to NIOSH Method 7300), reveals that they are consistent (44 μg/mg and 63 μg/mg).
3. When referencing Tables I and II, it is noted that the trace metals detected from the number one coupler in the curing oven are consistent throughout.

Next, process changes that may have caused the symptoms to develop were investigated. Discussions with both management and employees revealed that nothing different was added to the paint mixtures when the problems began to occur. A review of the paints and additives for the previous two-year period confirmed this. Nothing was noted that would have dramatically changed the consistency of the paints. Also, the employees stated that their work practices had not changed during the period. Most of the employees had worked on the line for several years prior to having any work-related skin problems.

At this point in the evaluation, efforts were focused on the time frame of when the symptoms began to occur. It was determined from the medical questionnaire that the skin problems actually began to occur in March 1988, when the hook handling employees noticed a yellowish discoloration on the hooks, which rubbed off onto their hands and other exposed areas that came into direct contact with the hooks.

About this time, the company noticed a greater number of part defects exiting the curing oven. As a result of the increased number of defects, an inspection of the curing oven was conducted. This inspection detected open flames present in the oven, resulting from tiny holes in the heating coils. As a result, the flames were causing "burn-off" on the parts which came into contact with the flames. Several employees also mentioned that the hooks used to hang the parts were developing very sharp edges and were cutting their hands. Further investigation revealed that the hooks were being used to hang smaller parts on the conveyor prior to receiving the ground coat application. Therefore, the hooks were also receiving a direct application of the ground coat and developed an excess layer of enamel.

To reduce the increased number of part defects, the company repaired the tiny holes in the oven coils during the last weekend in June. Following the repair of the oven, the employees noticed that the hooks were no longer discolored. Also, the part defect ratio was reduced drastically. Finally, the employees reported that the hooks no longer had sharp edges and that their skin problems began to clear.

Based on the prior information, it is evident that repair of the oven coils not only reduced the part defect ratio but also resolved the skin problems on the ground coat line. It was concluded that the open flames were causing an improper curing of the paint, thus making the chromium VI more readily available on the hooks. In addition, the sharp edges that developed on the hooks, in combination with the normal mechanical friction that existed when the employees placed a great number of hooks in their hands or any other exposed area of the body, resulted in skin abrasions that allowed the chromium VI a direct route of entry beneath the skin surface to cause the ulcerations.

Recommendations

Based upon these findings, the following recommendations were made:

1. Quarterly maintenance should be conducted to inspect the curing oven coils for leaks.
2. A mechanism should be developed to clean the hooks after they exit the curing oven.
3. The workers should wear protective gloves to minimize the potential for skin exposures.
4. Should the problems occur again (i.e., discoloration of the hooks), it is recommended that the workers apply a ten percent ascorbic solution or ointment, which has been shown effective in preventing as well as treating the chromium ulcers, to any body area with potential equipment or part contact until the oven can be repaired.[8–15]

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Received 7/11/89; review decision 10/6/89; revision 11/22/89; accepted 12/21/89