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Standard Guide for Safety and Health Requirements Relating to Occupational Exposure to Water-Insoluble Chromates[1]

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INTRODUCTION

This guide is intended to provide guidance in the safe handling of certain chromate compounds that are suspected to be carxcinogenic in man **(1-8)**.[2] Precautions contained herein are believed to protect against possible carcinogenicity, and will also be sufficient to obviate any acute health hazards except where skin hypersensitivity is a factor. Other hazards are considered and discussed.

The time-weighted average (TWA) permissible exposure limit (PEL) specified in this guide are based on studies evaluated by the American Conference of Government Industrial Hygienists (ACGIH) **(9)**. Epidemiological studies of the chromate producing industry have indicated that observed adverse health effects were associated with environmental levels and hygiene procedures considerably less exacting than those recommended here (see Appendix X1).

Hygiene controls and medical surveillance measures have been chosen to protect workers,recognizing that the potential for exposure will vary widely from industry to industry and between one location and another, depending on the compounds handled, scale of operations, kind of process, and physical conditions.

The key to maintaining chromate levels below the PEL is through implementation of cost effective engineering controls augmented as necessary by personal protective equipment, or work practice controls, or both. The choice of methods should depend upon the factors involved in each specific situation.

Biological monitoring is also recommended for lead chromate (see 7.4).

All applicable federal, state, county and local regulations must be complied with when this guide is used.

1. Scope

1.1 This guide covers control procedures for the safe production, storage, transportation, and handling of only the hexavalent chromium compounds found in Table 1 and their various hydrates, and mixtures of coprecipitates of the same regardless of crystalline form.

1.2 This guide is not intended to cover (*a*) such "soluble" chromates as chromates of sodium, potassium, magnesium, or ammonium; (*b*) soluble bichromates; (*c*) chromic acid; (*d*) volatile chromyl compounds; (*e*) any trivalent chromium compound; or (*f*) elemental chromium. Omission of said compounds or classes of compounds should not be construed to mean that they may be handled without due regard to their particular physical, chemical, and toxicological hazards **(9, 10, 11)**.

1.3 The chromate ion, CrO_4^{-2}, depending upon the acidity, complexes to form di-, tri-, and higher polychromates; hence, the chromates listed in Table 1 may contain mixtures of polychromates, depending on the method of isolation and end use.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of whoever uses this standard to consult and*

[1] This guide is under the jurisdiction of ASTM Committee D1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.22 on Health and Safety.

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[2] The boldface numbers in parentheses refer to the references at the end of this guide.

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establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. (For more specific precautionary information see Section 5.)

2. Referenced Documents

2.1 *ANSI Standards:*

Z87.1 Practice for Occupational and Educational Eye and Face Protection[3]

Z88.2 Practices for Respiratory Protection[3]

Z129.1 Precautionary Labeling for Hazardous Industrial Chemicals[3]

2.2 *OSHA Standards:*

29 CFR 1910.20 Access to Records[4]

29 CFR 1910.1200 Hazard Communication[4]

29 CFR 1910.134 Respiratory Protection[4]

29 CFR 1910.1025 Lead[4]

2.3 *NIOSH Publications:*

"Certified Equipment," HEW Publication No. 76-145[4]

"Recommended Industrial Ventilation Guidelines," January 1976, HEW Publication No. 76-162[4]

"Criteria for a Recommended Standard Chromium (VI)," HEW Publication No. 76-129[4]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *exposure area*—buildings and exterior locations where insoluble chromates may be present as airborne particulates in excess of the concentrations specified in 5.1.2, or where there is a likelihood of skin contact with chromate containing dust.

3.1.2 *insoluble*—a relative term to distinguish the low-water solubility of the chromates listed in Table 1 from the much more water-soluble chromates of sodium, potassium, and ammonia. The solubilities of lead chromates and calcium chromate are typical of the lower and upper solubilities of the class (see Section 6).

[3] Available from American National Standards Institute, 1430 Broadway, New York, NY 10018.

[4] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

TABLE 1 Examples of Some Hexavalent Chromium Compounds

Chemical Name	Formula	Color Index Name[A]
Barium chromate	$BaCrO_4$	Pigment Yellow 31
Barium potassium chromate	$BaK_3(CrO_4)_2$	Pigment Yellow 31
Basic copper chromate	$CuCrO_4$ $xCu(OH)_2$	Not listed
Basic cadmium chromate	$Cd_2(OH)_2CrO_4$	Pigment Yellow 44
Basic lead chromate	$PbCrO_4PbO$	Pigment Orange 21
Bismuth basic dichromate	$Bi_2O_3CrO_3$	Pigment Red 103
Calcium chromate	$CaCrO_4$	None assigned
"Chromic chromate" (calcium chromate sinter)	$xCaO\ yCr_2O_3$ $zCrO_3$	Pigment Yellow 33 Not listed
Ferric chromate	$Fe_2(CrO_4)_3$	Pigment Yellow 45
Basic ferric chromate	$Fe(OH)CrO_4$	Pigment Yellow 45
Lead chromate	$PbCrO_4$	Pigment Yellow 34
Lead molybdochromate	$PbCrO_4PbMoO_4$	Pigment Red 104
Potassium zinc chromate	K_2O 4ano·4Cr4O_3	Pigment Yellow 36
Strontium chromate	$SrCrO_4$	Pigment Yellow 32
Zinc chromate	$ZnCrO_4$	Pigment Yellow 36

[A] For Classification, not Toxicology.

4. Significance and Use

4.1 This guide includes chromates that are not readily soluble in water and that have water solubilities (Chromate ION) within the range of the more soluble calcium chromate and the much less soluble lead chromate. The major occupations involving potential exposure to insoluble chromates are in roasting of chromite ore, the manufacture of chromate pigments, the manufacture of coatings containing chromate pigments, and spray painting with these coatings. There is insufficient evidence to conclude that trivalent chromium compounds are carcinogenic.

5. General Requirements

5.1 *Environmental Levels*:

5.1.1 The following guide is designed to protect the health and safety of workers for an 8 to 10-h workday, 40-h workweek, over a working lifetime. The PEL can be met by techniques and controls that reduce employee exposure below the applicable safe limit. These controls must be reliable. Permissible exposure limits are based on the 1985 ACGIH recommended Threshold Limit Values (TLV) for chromates of lead and zinc and for chromite-ore processing **(12)**.[5]

5.1.2 *PEL*—Occupational exposure to any of the compounds listed in Table 1 shall be controlled to a TWA of 0.05 mg/m^3 (as Chromium) for an 8-h workday.

5.1.3 At least one full-shift (80 % of the shift length) personal sample should be taken for each job classification and each work area involving insoluble chromates. These samples shall be representative of a monitored employee's regular daily exposure to insoluble chromates, and may be used to represent the exposure of all employees in that job assignment. One sample may not be sufficient for an adequate characterization. For further guidance and appropriate control objectives see 5.6, 6.2, and 7.3.

5.2 *Medical Surveillance*:

5.2.1 *Examinations*—Individuals who are currently, or who are expected to be employed in exposure areas (see 3.1) shall be given preplacement and annual medical examinations that shall include, but not necessarily be limited to the following:

5.2.1.1 *Work History*, to elicit information on all past exposures to any hexavalent chromium compounds or other toxic substances, particularly those affecting lung function.

5.2.1.2 *Periodic Medical Examination*, consisting of at least the following: Completion of a health history questionnaire with attention given to smoking history, posterior-anterior chest X-ray, complete blood count or red cell count and hemoglobin, and pulmonary function studies (FVC, FEV 1.0 and FEV 1.0/FVC).

5.2.2 Medical examinations shall be made available to workers with symptoms of skin or upper respiratory tract irritation at the time the symptoms are first observed or reported.

5.2.3 *Management*—Proper medical management shall be provided promptly for workers adversely affected by exposure to insoluble chromates. The cause of any excessive exposure

[5] Committee on Industrial Ventilation, *Documentation of TLVs, American Conference of Governmental Industrial Hygienist*, 1985.

shall be sought without delay, and corrective action initiated. A physician shall determine if sensitized individuals should be excluded from jobs with a risk of exposure.

5.2.4 *First Aid*:

5.2.4.1 *Ingestion*—Induce vomiting promptly and obtain prompt medical attention. "Advice to physicians: Administer 500 to 1000 mg ascorbic acid IV as promptly as possible, followed by oral Vitamin C, 5 to 10 g/day until risk of kidney failure has ceased," **(13)**.

5.2.4.2 *Chromium Contamination of Open Wounds*—Flush thoroughly for 15 min with water and seek medical attention.

5.2.4.3 *Eye Irritation*—Flush thoroughly with copious quantities of water for 15 min and seek medical attention.

5.3 *Labeling and Posting*:

5.3.1 *Warning Signs*—In areas where insoluble chromate concentrations in the atmosphere are likely to exceed the standard, appropriate warning signs, barricades, or work practices should be used to restrict access to unauthorized persons. The sign must alert anyone entering the area as to what action should be taken.

5.3.2 *Container Labels*—All containers (bag, barrel, box, can, drum, reaction vessel, storage tanks, but not pipe or pipe lines) should be labeled, tagged, or marked with the following information:

5.3.2.1 *The Identity of the Material(s)*— Identity means any chemical or common name(s), code name or number, or brand name, that is indicated on the material safety data sheet for the chemical.

5.3.2.2 Batch process sheets, batch tickets, operating procedures, or other such written materials are acceptable alternatives to individual labels as long as the appropriate identity is readily accessible to employees.

5.3.2.3 Portable containers for immediate use need not be labeled.

5.3.3 *Material Safety Data Sheet* (*MSDS*)—The MSDS or equivalent is the primary source of the safety and health information. The chemical identification and MSDS for all insoluble chromates used in the workplace must be made readily accessible to all employees. The MSDS in conjunction with the identity on the label and employee training will convey the hazard(s) (both physical and health) determination for the chromate compounds. Information on the MSDS must include:

5.3.3.1 The OSHA PEL and the ACGIH TLV.

5.3.3.2 A statement to that effect if the chromate has been identified as a suspect carcinogen by the National Toxicology Program (NTP), the International Agency for Research on Cancer (IARC), OSHA, or the employer.

5.3.4 *Finished Product Labels*, are the responsibility of the manufacturer based on his knowledge of the end use of his unique products. However, the label should be in agreement with the recommendations of ANSI Z129. Any applicable governmental regulation must be followed.

5.4 *Personal Protective Equipment*:

5.4.1 *Respiratory Protection*—Each employee's personal work environment shall be maintained at a safe exposure level through implementation of cost effective engineering controls, augmented as necessary by personal protective equipment or work practice controls, or both. The choice of method should depend on the factors involved in each specific situation. Two criteria should be used to guide the choice of the control measures. The measure chosen must reduce employee exposure below the applicable safe limit and the control method must be reliable **(14, 15)**. With these two factors met, other factors such as logistics, product quality, economics, morale, housekeeping, and efficiency can then be incorporated into the decision logic for choosing appropriate control measures. Respirators are also required for emergencies and for the performance of nonroutine tests and duties that have the likelihood of exceeding the PEL. Brush or roller application of paints does not normally require respiratory protective equipment for protection from airborne chromates.

5.4.2 The Respiratory Protection Program must meet the general requirements outlined in OSHA 29 CFR 1910.134 and in ANSI Z88.2-1980, see Ref **(16)**. This program shall include instructions on the proper selection and use, including fit testing, cleaning and maintenance of respirators and air supply devices. The fit test should be performed annually on all negative pressure respirators. Either a quantitative or qualitative test is satisfactory **(14, 15)**. The type of respirator required for protection against known or expected concentration of airborne chromate to be encountered is outlined in Table 2.

5.4.3 *Foot Protection*—Industrial type leather shoes with synthetic soles will provide ample protection under normal operating and good housekeeping conditions. For wet operations during cleanup of spills or when conducting decontamination procedures, rubber or synthetic booties or pullover shoe protection shall be worn, and thoroughly rinsed and dried before reuse. Shoes that are torn or show evidence of inside contamination with chromate shall be disposed of properly.

5.4.4 *Clothing*—Any employee exposed to airborne levels of chromium above the PEL or when the possibility of skin or eye irritation exists, should be supplied with appropriate protective work clothing such as coveralls or similar full-body work clothes. See for example, ANSI Z87.1 for eye and face protection guidelines. Clean work clothing should be supplied at least weekly to employees in these cases. All protective clothing must be removed at the completion of each work shift in the change room provided for this purpose. Employees exposed to chromium above the PEL should shower at the end of the work shift. Employees must not wear or take any of the protective equipment off the work site. Care must be taken to prevent any cross contamination of street clothes.

5.4.5 *Hand Protection*—Suitable gloves to minimize skin contact shall be worn during operations where chromates are handled and may contact skin. Hands should be cleaned after removal of gloves. Gloves showing evidence of internal contamination shall be disposed of or thoroughly cleaned before reuse.

5.4.6 *Inspection*—All personal protective devices shall be inspected regularly and shall be maintained in clean and satisfactory working condition.

5.5 *Appraisal of Employees of Hazards* (*Communications*):

5.5.1 *Education and Training*—All employees who are employed in an exposure area shall be advised of the following according to OSHA 29 CFR 1910.1200:

TABLE 2 Protection Factors for Particulate Filter Respirators

NOTE 1—This table is based on Refs **(17, 18, 19)** and ANSI Z88.2.

Concentrations in Multiples of Permissible Exposure Limits[A]	Face-Piece Pressure	Permissible Respirators
5×	−	Single-use dust
	−	Quarter-mask dust
10×	−	Half-mask dust[B]
	−	Half of quarter mask, fume
	−	Half or quarter mask, high efficiency
	−	Half mask, supplied air demand mode
50×	−	Full-face piece, high efficiency or dust, fume, mist
	−	Full-face piece, supplied air demand mode[C]
	−	Self-contained breathing apparatus (SCBA) demand mode
1000×	+	Powered, high-efficiency, all enclosures[D]
	+	Half mask, supplied air, pressure-demand mode or continuous flow
2000×	+	Full-face piece, hood, helmet, or suit; supplied air; pressure-demand mode or continuous flow
10 000×	+	Full-face piece, SCBA pressure-demand mode
	+	Full-face piece supplied air pressure-demand mode or continuous flow with auxiliary self-contained air supply
Emergency entry into unknown concentrations or firefighting	+	Full-face piece, SCBA pressure demand mode
Escape only[E]	+	Any SCBA
	−	Any self rescuer

[A] Other chemicals, for example, lead may be the controlling factor rather than chromate concentration.

[B] Half-mask and quarter-mask respirators should not be used if the particulate matter causes eye irritation at the use concentration.

[C] Full-face piece, supplied-air respirators should not be used in any atmosphere that is immediately dangerous to life or health unless it is equipped with an auxiliary self-contained air supply that can be operated in the positive-pressure mode.

[D] Recent work by NIOSH would indicate a protection factor of 1000 may not be obtained. Consult your supplier.

[E] In an atmosphere that is immediately dangerous to life or health.

5.5.1.1 Chemical names,[6]

5.5.1.2 Label identification system,

5.5.1.3 Work procedures,

5.5.1.4 Site and government standards,[7]

5.5.1.5 Potential health effects from both acute and chronic exposures,[6]

5.5.1.6 Relevance of medical exams,

5.5.1.7 Protective control measures used and new relevant information,

5.5.1.8 Exposure monitoring programs,

5.5.1.9 Employee responsibility for following procedures and using protective equipment, and

5.5.1.10 Emergency procedures.

5.5.1.11 This information may be communicated and training achieved by any combination of oral or written individual or group methods which achieve understanding. Training should be repeated annually.

5.5.2 *Exposure Records*—Employees have the right to their exposure records and medical records under OSHA 29 CFR 1910.20.

5.6 *Work Practices and Engineering Controls*:

5.6.1 *Housekeeping*—Spills shall be cleaned up promptly by vacuuming, or wet methods, or by absorption methods that will prevent airborne contamination. No dry sweeping shall be performed. Floors, equipment, stains, and other contactable surfaces that may accumulate chromate particulate fallout shall be maintained free of dust that may become airborne. Containers provided for chromate solid waste shall be labeled and covered in accordance with 5.3.2.

5.6.2 *Control of Hazards*:

5.6.2.1 *Engineering Design and Construction*—In the planning and erection of new or modified manufacturing or handling facilities, the principles of industrial hygiene and safety should be systematically applied.

5.6.2.2 *Ventilation*—All operations that release dust, such as opening packages, sampling, taking aliquots, charging vessels, drying, sizing, mixing, discharging (packout), or cleanout shall be provided with appropriately designated local ventilation in accordance with ACGIH recommendations and applicable governmental regulations. Ventilation systems shall be subject to a preventive maintenance inspection program to ensure that hoods, ducts, fans, absorbers, draft controls, filters, alarms, and other components are structurally sound and in good working order. Periodic tests of duct pressures or flows, or both, shall be made to ensure that the ventilation is adequate **(20)**.

5.6.3 *Solid Waste Disposal*—Solid waste containing insoluble chromates that have the potential for becoming airborne shall be stored in labeled and covered containers until disposal in accordance with applicable governmental agency regulations.

5.6.4 *Maintenance*—Equipment and instruments shall be kept in good repair. Pumps, vessels, and lines handling insoluble chromates shall be drained and washed out before repairs are made except where repairs can be made without exceeding the PEL.

5.6.5 *Sanitation*—Washing facilities, emergency showers, eye-flushing fountains, or appropriate washing facilities shall be provided and be easily accessible in areas where there is potential for skin or eye contact with insoluble hexavalent chromium dust or liquids. This equipment shall be frequently inspected, and maintained in good working condition. Contaminated clothing shall be held in containers until removed for decontamination or disposal. Arrangements for laundering or otherwise decontaminating work clothing shall ensure the protection of individuals involved in this work.

5.6.6 *Statistical Control*—Data resulting from air and biological monitoring can be subject to various errors such as

[6] These items should also be included on the Material Safety Data Sheets (MSDS).

[7] *NIOSH Manual of Analytical Methods, 3rd ed.*, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control. National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering; Cincinnati, Ohio, 1990. Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

random sampling device errors, or random analytical errors, or both. These errors can be quantified and their effects minimized by the application of statistically based quality contol programs. Each analytical method should be consulted for appropriate details.

5.6.6.1 Another potential source of large error is due to the random interday and intraday fluctuations in airborne contaminant levels. These fluctuations are generally considered to be log-normal, and may result in erroneous conclusions unless properly considered.

5.6.6.2 An appropriate objective is to control each employee's exposure so that the maximum probability of exposure above the exposure limit is 5 %. A number of references can be used for guidance since this detail is beyond the scope of this practice **(21, 22, 23)**.

5.6.7 *Containers*—All shipping, storage, or in-plant transport containers of insoluble chromates shall be labeled to identify the material.

5.6.8 *Safety* (*Fire and Explosion*):

5.6.8.1 *Fire*—The chromates covered by this practice are nonflammable, but under favorable conditions some may have sufficient solubility in the presence of combustible materials to initiate combustion by local exothermic oxidation.

5.6.8.2 *Explosion*—None of the chromates covered by this practice are explosive even at elevated temperatures. Mixtures of insoluble chromates with readily oxidizable materials may be explosive.

5.7 *Recordkeeping*:

5.7.1 All test results shall be recorded showing location, time and date of sample, and identity of employee in the case of personal or biological sampling. This information shall be retained for at least 30 years, and in the case of personal or biological sampling, results shall be kept for 40 years or at least 30 years after the termination of employment, whichever is longer.

5.7.2 Pertinent medical records, including results of clinical examinations, biological and biochemical analysis, roentgenograms, and dates of treatment or hospitalization, shall be maintained in a secure and confidential manner for at least 30 years after termination of employment.

6. Physical and Chemical Properties

6.1 Selected physical and chemical properties of insoluble chromates are given in Table 3.

7. Monitoring Airborne and Biological Chromates

7.1 *Personnel Monitoring*—Breathing zone samples represent the most accurate measurement of employee exposure to airborne chromates. The sample is taken within a foot of the employee's face, and represents air inhaled by the employee. The sample may be obtained using a personal sampler attached to an individual or by a sampling device held within a foot of the face. An analytical method should be consulted for the necessary details such as collection device, flow rate, and the like.

7.2 *Area Sampling*—This is also known as fixed location sampling and is normally used to determine the maximum potential exposure, or to make a preliminary study of workplace conditions. An example is a continuous monitor.

7.3 *Frequency*—In applying this practice, preliminary investigation of all work operations should be made by an industrial hygienist or other qualified professional for the purposes of designating both frequency and location of air sampling devices and appropriate job assignments to be monitored.

7.4 *Biological Monitoring*—Blood and urinalysis for certain components have long been used for monitoring the effectiveness of programs designed to control worker exposure. Air and blood lead levels should be monitored as required in OSHA 29 CFR 1910.1025. Currently, when lead chromate is used or handled in any manner such that airborne lead levels exceed 30 $\mu g/m^3$, it is essential that a blood-lead monitoring program be undertaken. Monitoring for other biochemical indicators may be useful in certain situations but until better correlation with blood lead levels is established, none are recommended. It is

TABLE 3 Physical and Chemical Properties of Insoluble Chromates

Chromate	Molecular Weight	Particle Density	Melting Point	Solubility in Water,[A] g/100 cm^3	Solubility Product, mol^2/L^2	Solubility in Dilute Acid
Barium potassium	563.52	4.50 (15°C)				
Barium	253.37	4.50 (15°C)		0.00034 (16°C) 0.004 (37°C)	1.6×10^{-10}(18°C)	soluble
Basic cadmium	374.81					
Basic ferric	188.85					
Basic copper	variable compositions					
Basic lead	546.2					
Bismuth basic di-chromate	665.95					
Calcium	156.07			0.75 (37°C)		
Chromic (sinter)	variable compositions			0.13 (37°C) as Cr^{+6}		soluble
Ferric	459.67					
Lead	323.10	6.12 (15°C)	844	5.8×10^{-6}(25°C)		1.77×10^{-14}(18°C) soluble
Lead molybdochromate	variable compositions					
Potassium zinc	819.68					
Strontium	203.63	3.90 (15°C)		0.09 (37°C)		soluble
Zinc	181.37	3.40 (15°C)		0.21 (37°C)		soluble

[A] Solubilities in water at 37°C were calculated on the basis of data given in Heuper, W. C., and Conway, W. D., *Chemical Carcinogenesis and Cancers*, C. C Thomas, Springfield, IL 1964, p. 397.

noted that blood lead levels in excess of 50 µg/100 g of blood require worker removal from the area under the OSHA standard.

8. Analytical Test Methods

8.1 National Institute for Occupational Safety and Health, (NIOSH) published the following methods:[7] 7024; 7200; 7300; 7600; 7604; 8005; and 8310. These methods should be consulted for advantages and disadvantages. (Such as separating CR III from CR VI).

8.2 Any analytical procedure that has been shown to possess equivalent or better sensitivity, reproducibility, and accuracy may be used to determine whether environmental levels are within the recommended standards.

9. Keywords

9.1 chromium; chromium based pigments; chromium compounds; exposure; health; hexavalent chromium; insoluble chromium; safety

APPENDIX

(Nonmandatory Information)

X1. EPIDEMIOLOGY AND TOXICOLOGY

X1.1 General

X1.1.1 This appendix is restricted to discussion of the epidemiology and toxicology of insoluble chromates as defined in Section 1. For a more thorough understanding, the original articles should be consulted.

X1.2 Early Studies

X1.2.1 Although chrome dermatitis, skin ulcers, and nasal septum perforations were reported as early as 1827 in Scotland and in 1933 in the United States, indications that chromates of some kind were a possible cause of bronchogenic carcinomas observed in chromate-producing plants first appeared in the German literature during the 1930s **(1, 2, 24, 25, 26, 27)**. Following evidence in 1945, that a similar situation might be developing in the United States, the chromates industry sponsored literature and case studies that culminated in reports by Machle and Gregorius, by Baetjer, and by the U.S. Public Health Service **(28, 29, 30, 31)**. These reports were in substantial agreement that the causative agents were associated with the lime-roasting phase of the production process. By this time, it was clear that most of the dermatitis, sensitization, and ulceration effects were due to exposures to chromic acid and the soluble chromates and causative agents. It is noted, lead chromate compounds have *not* been associated with sensitization or ulceration.

X1.2.2 The carcinogenicity of calcium chromate and sintered and roasted ore (containing calcium chromato chromite, misnamed "chromic chromate") was confirmed by animal studies: by Heuper in 1958 and 1959, Baetjer in 1959, and Payne in 1960 **(32, 33, 34, 35, 36)**.

X1.3 Oral Toxicity and Metabolism

X1.3.1 Insoluble chromates, at rates dependent on their solubility, are either eliminated unchanged in the feces or reduced to trivalent chromium that is bound to protein **(37)**. Rates of the later have three components with half-lives of 0.5, 5.9, and 83.4 days.

X1.3.2 Obviously, the oral toxicity of insoluble chromates is dependent on the nature of the cation, especially in the cases of lead chromate. A lethal dose, in man, of lead chromate as low as 50 mg/kg was reported by Gleason, but Harrold found this compound was poorly absorbed by paint workers **(29, 38)**. Gross found that rats and mice tolerate 1 % zinc chromate in their feed **(39)**. Kennedy summarized the toxicity of lead chromates **(40)**. The size of the dose required to produce effects varies considerably between pigments. The most adverse effects result from the availability of the lead cation.

X1.3.3 In most studies the compounds were administered by intravenous injection, a procedure considered irrelevant for the purpose at hand. At least for the more soluble of the chromate pigments, it is expected that excessive oral ingestion will result, as with the injected soluble chromates, in acute or chronic renal damage or failure, or both. Hunder found, for example, that 0.02 g/kg of potassium dichromate (as 2 % solution) was fatal to a monkey, producing acute renal lesions **(41)**. Tandon reported elevated chromium levels in the urines of pigment handlers in Indian paint factories **(42)**. Toxicity by the oral route has not been reported to be an occupational hazard.

X1.4 Skin and Eye Irritation

X1.4.1 The dermal irritancy and skin-sensitizing properties of the soluble chromates are well known and fully documented **(43, 44)**. Less is known about the action of the insoluble chromates in these regards. However, since several of the chromate pigments have some limited solubility in moisture and therefore in perspiration, allergic skin reactions can occur in sensitized individuals. Walsh is of the opinion that once chromate sensitivity becomes established, there is apparently no "hardening" or increased tolerance to further exposures **(45)**. Both Fisher and Engle have observed dermatitis in workers exposed to pain containing zinc chromate **(46, 47)**. Calnan made a study of so called "cement dermatitis" and concluded that the presence of chromates was a possible cause **(47)**. It seems likely, that any chromate present in cement would be largely in the form of calcium salt. Similarly, as reported by Fregert and Shelly, the chromium alleged to be a possible causative agent in dermatitis from welding fumes may be in the hexavalent form **(48, 49)**. In any event, there is reason to believe that the more soluble chromate pigments may be

causative agents for contact dermatitis, particularly among sensitized or allergic individuals.

X1.4.2 Insoluble chromates should be regarded as possible eye irritants, due to their irritancy as particulates. No reports of special studies of the effects of insoluble chromates on the eye have been found. Although skin ulcers and nasal-septum perforations are unusually associated with excessive exposure to soluble chromates, dichromates, and chromic acid, some chromate pigments are sufficiently soluble to make it unwise to rule them out as causative agents.

X1.5 Respiratory Tract Irritation

X1.5.1 It has been shown that inhalation of soluble chromates can cause a variety of adverse respiratory reactions such as bronchitis, laryngitis, bronchogenic asthma, rhinorrhea tracheitis, pharyngitis, and emphysema **(1, 44)**. No reports establishing airborne insoluble chromates as the cause of these effects have been found.

X1.5.2 *Epidemiologic Studies*:

X1.5.2.1 Machle and Gregorius made the first epidemiologic study of the U.S. chromate industry **(28)**. They examined the incidence rates of lung cancer in seven chromate producing plants and found consistently high mortality ratios in six of these plants.

X1.5.2.2 Baetjer, limiting her study to two production plants in Baltimore, found a similar elevation in mortality ratio **(29, 30)**. Both Machle and Baetjer studied plants that used a lime-roasting process. One plant examined by Machle did not use alkaline oxidation of chromite and had no deaths from lung cancer in 1853 man-years of exposure.

X1.5.2.3 Mancuso and Heuper investigated an Ohio chromate-producing plant using the lime-roasting process and found a marked increase in lung cancer cases beyond that found in control groups **(50)**.

X1.5.2.4 A thorough review of the chromate-producing industry in the United States was undertaken by the U.S. Public Health Service in 1948 and was published in 1953 **(2, 51)**. This report concluded: “Some factor, not present in the comparison group, is responsible for the greater prevalence and earlier production of bronchogenic carcinoma in chromate workers.”

X1.5.2.5 In 1951, Bidstrup reported on her study of the British chromate-producing industry where the lime process was used **(52)**. Her results were limited in significance because she found only one case of lung cancer in 724 workers. In 1956, Bidstrup and Case demonstrated that from 1949 to 1955 in three bi-chromate producing factories in Great Britain there existed a statistically significant increase in mortality due to carcinoma of the lung **(53)**.

X1.5.2.6 Alderson, Rappan, and Bidstrup in 1981 showed in a follow-up study of 2715 men who had worked for at least one year at the three chromate-producing factories in Britain between 1948 and 1977, that the relative risk of lung cancer for those men employed at the one factory still in operation, had decreased from over three before plant modification to about 1.8, in those who had worked only since plant modification (this included the elimination of lime in 1961) **(54)**.

X1.5.2.7 In 1966, Taylor reported on a study of 1212 workers representing three plants and 70 % of the U.S. chromate-producing capacity **(55)**. These plants used the lime process. He found a nine-fold increase in deaths from lung cancer.

X1.5.2.8 Enterline, in 1974, reanalyzed the data from Taylor’s study for 1941 to 1960 and found, again, the nine-fold increase in deaths from lung cancer **(56)**. In addition, he also found a slight excess in deaths from cancer of the digestive system.

X1.5.2.9 In 1979, Hill and Ferguson investigated the impact of changes in production technology at a Baltimore plant using “probability window analysis” **(57)**. These authors found that the successive decline in bronchiogenic carcinomas among the successive cohorts of those persons entering risk in the ten year periods, 1932 to 1941, 1942 to 1951, 1952 to 1961, and 1962 to 1971 was highly significant. No further cases occurred in a subsequent period 1972 to 1977 and there have been no observed cases of bronchogenic carcinoma among workers entering risk during the twenty year period 1958 to 1977. The results suggest that the risk of lung cancer in chromate-production workers has been reduced by improvements in the process and by consequent reduction of exposure to chromium materials.

X1.5.2.10 Although the number of cases is sometimes too low to permit valid conclusions and most exposures have been mixed, there is accumulating epidemiological evidence that calcium chromate and sintered lime roast containing calcium chromato-chromite are lung cancer causative or promoting (genotoxic or epigenetic) agents in chromate-producing plants using the lime process **(57)**.

X1.5.2.11 The earliest epidemiological study of a chromate pigment-producing plant was reported by Gross in 1943 **(26)**. In a German factory, there were seven deaths from lung cancer in fewer than 50 workers. Lead, zinc, potassium, and barium chromates were among the pigments produced. Potassium dichromate was used as a raw material.

X1.5.2.12 In 1975, Langaard and Norseth reported an increase in bronchogenic cancer in a Scandinavian chromate pigment-producing plant **(3)**. Unfortunately, the subgroup studied is small. Only 24 men worked more than three years and of these, three had bronchogenic cancer and two of these were smokers. In 1983, Langaard and Vigander reported the results of a follow-up study on the same group of workers **(21)**. Three more cases of lung cancer were found. The observed/expected ratio of 44 was the same as in 1972. Five of the six lung cancer patients smoked and all had been exposed to zinc chromate.

X1.5.2.13 Davies compared the incidence of lung cancer mortality among English workers at two manufacturing sites who were exposed to both zinc and lead chromate with another site that only manufactured lead chromate **(8, 58)**. There was no excess lung cancer mortality among workers with chromate exposures rated as “low” nor among those exposed only to lead chromates at all exposure levels. Workers with mixed exposures in the “medium to high” category to both lead and zinc chromate had a marked excess of lung cancer deaths. In the author’s opinion, the results suggest that the manufacturer of zinc chromate may involve a lung cancer hazard.

X1.5.2.14 In 1981, Hagauenor, and others performed a prospective study of mortality in a chrome-pigment manufacturing plant in France **(59)**. They studied 251 workers who had been exposed for at least six months during 1958 and 1977 and had been involved in the manufacture of both lead and zinc chromate. The relative standardized risk of bronchogenic cancer was 6.41. Also, it was noted that 10 of the 11 cases of bronchogenic carcinoma were smokers and five had previously had a history of lead poisoning.

X1.5.2.15 In 1982, Sheffet, and others performed an epidemiological study of mortality in a pigment plant in Newark, NJ that utilized both lead and zinc pigments **(60)**. The study population comprised two cohorts, one containing 1296 white and the second 650 non-white male employees who worked at the plant between January 1940 and December 1969 for longer than one month. A statistically significant, relative risk of 1.6 for lung cancer among white male employees was found. A relative risk of 1.9 was noted for individuals employed for at least two years who were "moderately" exposed to chromates. An increased incidence of lung cancer among non-whites and stomach and pancreatic cancers among the total cohorts was also evident but these are *not* statistically significant.

X1.5.2.16 In 1976, Equitable Environmental Health, Inc. completed a study of mortality of employees in three U.S. chromate-pigment manufacturing plants **(61)**. Analysis of the deaths gave inconclusive results, but the data did suggest that prolonged excess inhalation of chromate pigment could cause lung cancer. In 1983, a five year follow-up study was completed **(62)**. The follow-up showed that in the one plant having exposure only to lead chromate pigment, there was no statistically significant excess of lung cancer deaths. The author concluded that "the study, therefore, did not produce evidence supporting any association between lead chromate and lung cancer." There was a statistically significant increase in lung cancer deaths in the plants producing both lead and zinc chromate and the author concluded that "although the numbers are small, this updated follow-up supports the hypothesis that zinc chromate increases the risk of lung cancer." However, the number of lung cancer deaths among persons exposed only to lead chromate was too small to draw definitive conclusions.

X1.5.2.17 A study done by Frentzel-Beyme, and others, of five factories in the Netherlands and West Germany with a total of 1921 employees all producing zinc and lead chromate showed a moderate but consistent increased risk of lung and respiratory tract cancer at four of the five factories. A multicentric European epidemiological study investigated the lung cancer mortality of workers employed in chromate pigment factories **(63)**. Other studies of the occurrence of lung cancer in workers producing chromium pigments were reported by Langard in 1983 **(64)** and a publication by Satoh in 1981 described an epidemiological study of workers engaged in the manufacturer of chromium compounds **(65)**.

X1.5.2.18 The American Conference of Government Industrial Hygienists (ACGIH) has designated chromates of lead and zinc as industrial substances suspect of carcinogenic potential for men with a TLV of 0.05 mg/M ^{3}.

X1.5.2.19 The International Agency for Research on Cancer (IARC) has prepared a review on chromium and chromium compounds as part of its monograph on the evaluation of carcinogenic risk of chemicals on humans **(66)**. The conclusion is as follows:" There is sufficient evidence of respiratory carcinogenicity in men occupationally exposed during chromate production. Data on lung cancer risk in other chromium associated occupations and for cancer at other sites are insufficient. The epidemiological data do not allow an evaluation of relative contributions to carcinogenic risk of metallic chromium, chromium (III), chromium (IV), or soluble versus insoluble chromium compounds."

X1.5.2.20 A recent review of the known toxic effects of lead chromate by J. Morgan concluded that "In past reviews, toxic properties that are characteristic of certain lead compounds and certain hexavalent lead chromate compounds and of processes in which they occur, have been erroneously attributed to lead chromate pigments and the processes in which they have been manufactured and used," **(40)**. Past reviews did not recognize the dissimilar physical, chemical, and toxic properties of lead chromate pigments as compared to the general classes of lead compounds and hexavalent chromium compounds.

X1.5.2.21 Lung cancer has been unequivocally associated with the process of producing soluble chromates from chromite ore. This observation was made in a period of time when dust concentrations were exceedingly high compared to the present OSHA standard for chromic acid and chromates. In the manufacture of lead chromate pigments, the dust composition is different from that in chromite or processing. Even during past decades when dust concentrations were high, the lung cancer incidents have failed to reveal a clear-cut relationship between exposure and disease. J. Morgan concluded that compliance with the current OSHA chromate standard in past decades of pigment manufacture and use would have been adequate to protect the health of exposed workers.

X1.5.2.22 A retrospective mortality study of 4215 male employees at 10 automobile factories, with special consideration to spray painters, was reported by Chiazzi **(67)**. He reported a proportionate mortality ratio (PMR) of 1.3 for 278 combined cancers of the upper respiratory tract and lungs among all white male workers. The number of such cases was not significantly higher than the expected number. The standardized mortality ratio (SMR) for spray painters was 1.26 versus 1.34 for employees with no spray paint exposure. No information was given as to the exposure level or smoking habits of the cohorts under study.

X1.5.2.23 A proportionate mortality study of aircraft spray painters was reported by N. Dalager **(68)**. The study (of workers who worked at least 3 months) reported a significant excess of cancer (PMR 1.36) particularly of the respiratory tract (1.84) among workers who use spray paints containing zinc chromate. However, the study did not specify the many other chemicals present in the paints, or smoking in the presence of the paints, or smoking histories or the fact that many of these workers had previously worked in other unknown occupations.

X1.5.2.24 A National Paint and Coatings Association (NPCA) sponsored a mortality study in 1981 of production workers in the paint and coatings manufacturing industry **(69)**. This study showed a reduced standardized mortality ratio

(SMR) for malignant neoplasms from all causes. However, the pigment cohort group did show some elevation for certain types of cancers. This could possibly be due to the small numbers of deaths involved. A follow-up study examined the pigment cohort group and indicated that the relative risk of having cancer in relation to the entire study cohort was not elevated **(70, 71)**.

X1.6 Animal Carcinogenesis

X1.6.1 A large number of animal tests have been made using insoluble chromates. These have for the most part involved implants, or intromuscular, intrapleural, and subcutaneous injections. While local sarcomas and occasional distant tumors have been obtained by these methods in a variety of species, the significance of many studies is doubtful either because the incidence rates are low or the increase over controls is not large.

X1.6.1.1 Heuper obtained an increase in tumors in rats with muscular implants of chromite-ore lime roast, calcium chromite, and sintered calcium chromate, but not with barium chromate **(32, 33)**. Payne obtained sarcomas in mice with intramuscular implants of calcium chromate and sintered calcium chromate **(35)**. He also implanted calcium chromate intramuscularly and intrapleurally in rats and obtained local sarcomas. Subcutaneous injections into the nape of the neck of mice gave equivocal results with the same compounds **(36)**. Heuper made intratracheal instillation in rats using calcium chromate, strontium chromate, and zinc chromate with negative results. Mice and rats were subjected by Baetjer to inhalation of a dust consisting of both soluble and insoluble chromates with negative results **(72)**. Intratracheal injection as well as intravenous injections in mice of zinc potassium chromate and of barium chromate gave negative results.

X1.6.1.2 Steffee and Baetjer were unsuccessful in producing significant tumors in rabbits, guinea pigs, rats, or mice by intratracheal injections of lime roast, zinc potassium chromate, lead chromates, or leached lime roast **(73)**.

X1.6.1.3 Using arachis oil as the vehicle, Roe obtained significant numbers of local sarcomas in rats with calcium chromate **(74)**.

X1.6.1.4 In 1966, Heuper reported on the formation of a high percentage of injection site cancers in rats from injection of "chromic chromate", sintered calcium chromate, calcium chromate, strontium chromate, and zinc yellow **(75)**. A low yield was obtained with barium and lead chromates. Laskin obtained interesting results by intrabronchial implantation of leached lime-roast residue and calcium chromate in cholesterol **(76)**. He obtained a low yield of squamous cells in subjected rats and hamsters in long-term inhalation of calcium chromate dust and obtained laryngeal hyperplasia and a few squamous tumors, the significance of which is doubtful.

X1.6.1.5 In 1971, Nettesheim reported a low yield of lung tumors and no bronchiogenic tumors in mice inhaling 13 mg/m^3 of calcium chromate **(77)**. The increase over controls was 6/2 for 136 male mice and 8/2 for 136 female mice. Nettesheim also subjected hamsters to 15 weekly intratracheal injections of calcium chromate and found deterioration of the alveoli.

X1.6.1.6 In 1965, Heuper and Conway concluded that the relative carcinogenic potency of the chromium compounds depends upon their solubility in water and is greatest for these compounds of medium solubility that are gradually dissolved in the body **(78)**. This enables them to exert a prolonged action. This view of the importance of solubility is supported by Clayson in 1962 **(79)**.

X1.6.1.7 A study by Levy, in 1975, used the intrabronchial pellet implantation technique with a range of chromium containing materials normally found in a chromate producing industry **(80)**. The study showed that bronchial carcinomas could be formed in the rat lung in the presence of some chromium containing materials.

X1.6.1.8 The technique developed by Laskin **(81)** is referred to as the intrabronchial pellet implantation in which a metal pellet or basket containing the material under test is surgically implanted into the left inferior bronchiole of the rat **(82)**. The metal pellet acts as a framework in and around where the test material is suspended. A1983 study performed by Levy at Aston University in England has made some significant findings from this technique **(83)**. They are as follows: Zinc chromate (low solubility) gave a significant number (5 out of 100) of bronchial carcinomas when compared to the expected number. Another zinc chromate (Norge composition) gave 3 out of 100 bronchial carcinomas and this was just not statistically significant. No bronchial carcinomas (0 out of 100) were seen in the control group containing only cholesterol, and bronchial carcinomas were seen in the two positive control groups (methylcholanthrene and calcium chromate, the number of tumors was 22 out of 48 and 25 out of 100, respectively). Barium chromate had 0 bronchial carcinomas (1 out of 100 for pure lead chromate, primrose chrome yellow, LD chrome yellow, medium chrome yellow, and 0 out of 100 for molybdate chrome yellow). The authors conclude "These and other results suggest that lead chromate pigments are non-carcinogenic, or at most have an extremely low carcinogenic potential." The authors also conclude, "The results of the chromate pigment materials examined in this study, taken together with previous animal studies can be used to explain the reported lung cancer risk to chromate pigment workers. Where the workers in this industry tend to be exposed to both zinc and lead chromate, this present study strongly supports the hypothesis that lead chromate is non-carcinogenic, or at most has an extremely low carcinogenic potential. This is consistent with the findings of Davies **(8, 58)**. It is recognized that this technique does not simulate human exposure in that it is an extremely harsh treatment with respect to the constancy of contact of each test agent with target tissue, and the duration of contact, the chronic irritation caused by some of the materials.

X1.6.1.9 In 1981, Petrilli and De Flora concluded that chromium mutagenicity is exclusively due to the hexavalent ion which appears to induce errors in DNA reproduction **(18)**. All the trivalent chromium materials tested were non-toxic and non-mutagenic even in very high concentrations. They also showed that the mutagenicity of hexavalent chromium could be decreased or eliminated by various chemicals and metabolites such as human gastric juice. This suggests possible detoxification orally, the blood through stream, or other enzyme routes.

The liver is most effective in reducing the mutagenicity of chromium (IV) compounds. Levy and coworkers reported in 1986 on the investigation of the potential carcinogenicity of a range of chromium containing materials on rat lung **(84)**.

X1.7 Teratogenicity Endpoint

X1.7.1 Teratogenicity

X1.7.1.1 No reports on the teratogenicity of insoluble chromates were found.

X1.8 Summary

X1.8.1 Although both epidemiologic and animal studies of chromate pigments and process residues leaves much to be desired and do not offer definitive proof that any of the suspect compounds are carcinogenic, a number of epidemiological reports indicate that industrial exposure during insoluble chromate manufacture at levels well in excess of the current OSHA PEL or TLV is associated with an increase in lung cancer. The most likely causative agents appear to be certain chromates of limited solubility.

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