CHROMIUM: WORKPLACE EXPOSURE IN ITALY

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WORKPLACE EXPOSURE TO CHROMIUM

Chromium is a naturally occurring element present in soil and in volcanic dust and gases. It is found in the environment in three major states: chromium(0), chromium(III), and chromium(VI). Cr(III) occurs naturally in the environment, while Cr(VI) and Cr(0) are generally produced by industrial processes.

Occupational sources of chromium exposure includes the following:

- Welding of alloys or steel
- Leather tanning
- Chrome electroplating
- Chrome alloy production
- Textile manufacturing
- Paints/pigments
- Photoengraving
- Antifreeze
- Antialgae agents
- Production of high-fidelity magnetic audio tapes
- Wood preservatives
- Agricultural antifungicides
- Porcelain and ceramics manufacturing
- Glassmaking

The entry routes of chromium into the human body are inhalation, ingestion and dermal absorption. Occupational exposure generally occurs through inhalation and dermal contact, whereas the general population is exposed more often by ingestion through chromium content in soil, food, and water.

Rates of chromium uptake from the gastrointestinal tract are relatively low and depend on a number of factors, including valence state (with Cr(VI) more readily absorbed than Cr(III) because it readily

penetrates cell membranes), the chemical form (with organic chromium more readily absorbed than inorganic chromium), the water solubility of the compound and gastrointestinal transit time.
After entering the body, Cr(III) binds directly to a protein in the plasma. while Cr(VI) is rapidly taken up by erythrocytes after absorption and reduced to Cr(III) inside the cell.
Studies on workers in the chromium pigment, chrome-plating and ferrochromium industries also suggest a statistically significant association between worker's exposure to chromium and lung cancer. On the basis of these and other studies, EPA and the International Agency for Research on Cancer (IARC) classified Cr(VI) as a known human carcinogen. On the other hand since no evidence exists to indicate that Cr(III) might cause cancer in animals or humans, it's not classified as a human carcinogen by the National Toxicology Program, EPA, or IARC.

INAIL WORK ACTIVITIES CLASSIFICATION

INAIL - Italian Workers' Compensation Authority - pursues several objectives: the reduction of accidents at work, the insurance of workers involved in risky activities; the re-integration in the labour market and in social life of work accident victims.
All employers are obligated to insure their full-time employees and/or workers with a co-ordinated ongoing collaboration contract hired for activities which the law establishes as risky.
The activities considered as risky are those involving the use of machinery and other types of equipment; those carried out in environments organised for work and services requiring the use of machinery and various types of equipment; those complementary or auxiliary to other risky activities. Furthermore, the law specifically lists a set of activities with an irrefutable presumption of risk for example: building and road works, handling of goods in warehouses, street cleaning and waste collection, private surveillance services, transport, setting up of shows, public events, etc.
Since year 2000 companies are classified according to four sectors in relation on type of activity:

- industry
- craftsmanship
- services
- miscellaneous activities

To each sector correspond a table of the insurance rates (called tariff table). The insurance rates is calculated according to salary and in relation to how risky is the activity carried out. To codify a company according to a suchlike some different production processes are considered as standards of comparison.
So all the activities are divided in ten great groups:

- Agriculture processing. Animal rearing. Fisheries. Foodstuffs

- Chemistry. Plastic and rubber. Paper and poligraphy. Hides and leather.
- Construction: building, hydraulics, roads, transport and distribution lines, pipes. Plant engineering
- Electric energy and communication. Gas and fuels. Water, cold and heat. Nuclear energy.
- Wood and similar products
- Construction: building hydraulics, roads, transport and distribution lines, pipes; plant engineering
- Metal working. Metal processing. Machinery. Means of transport. Equipment transport. Equipment and tools
- Mining. Processing of non-metal materials and rocks. Glass
- Textiles and clothing
- Transport. Loading and unloading. Storage.
- Various activities carried out by industrial enterprises.

Each of them is still further divided into several groups including similar productive compartments and production process.

This system permits to establish premiums and to have general information about similar industrial activities.

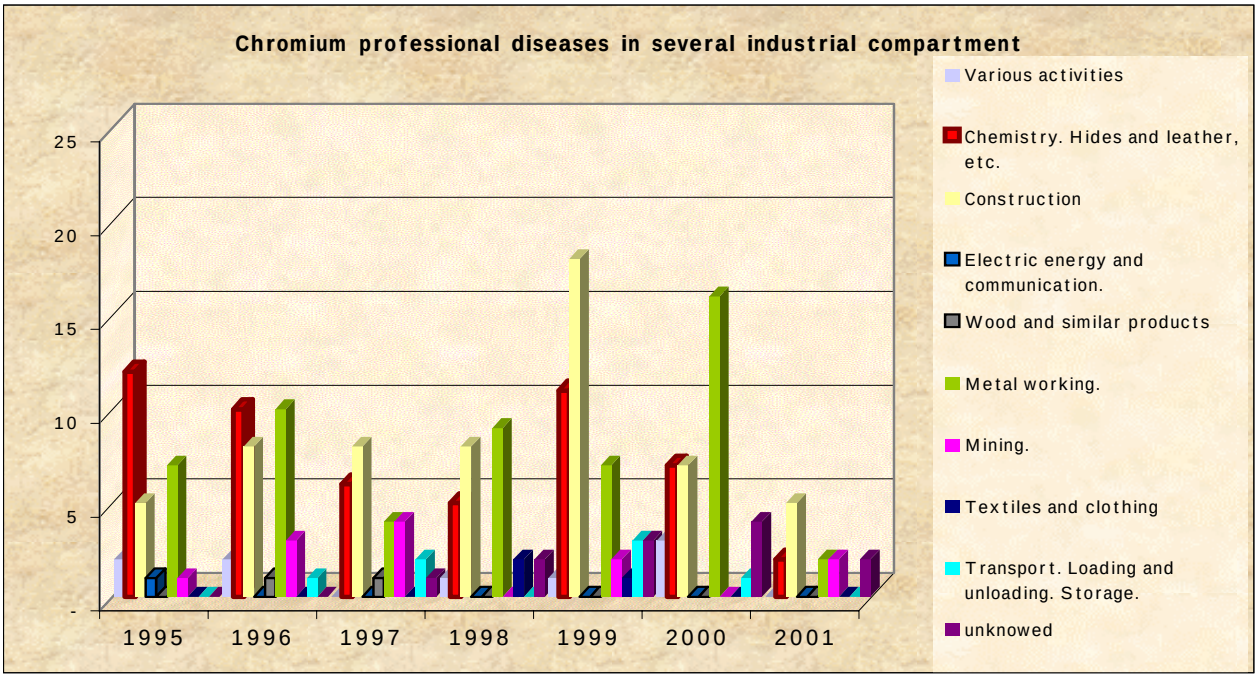
Professional diseases data are available querying INAIL database.

PROFESSIONAL DISEASES DATA

Statistical data of the professional diseases from Cr(III) and Cr(VI) from 1995 to 2001 have been taken into account.

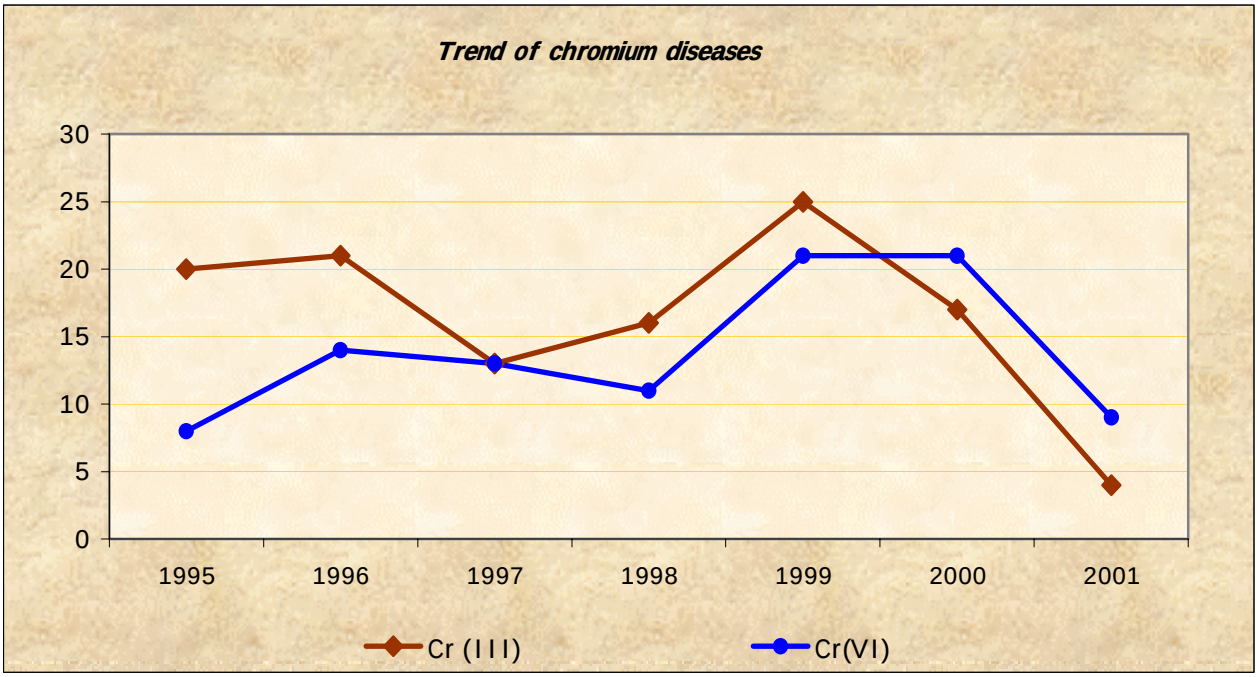
Data are divided according to the ten great groups of Inail tariff and graphic 1 shows trend of professional diseases in these several industrial compartments.

Data shows that chemical, building and metallurgic industries are the most important for diseases related to chromium.



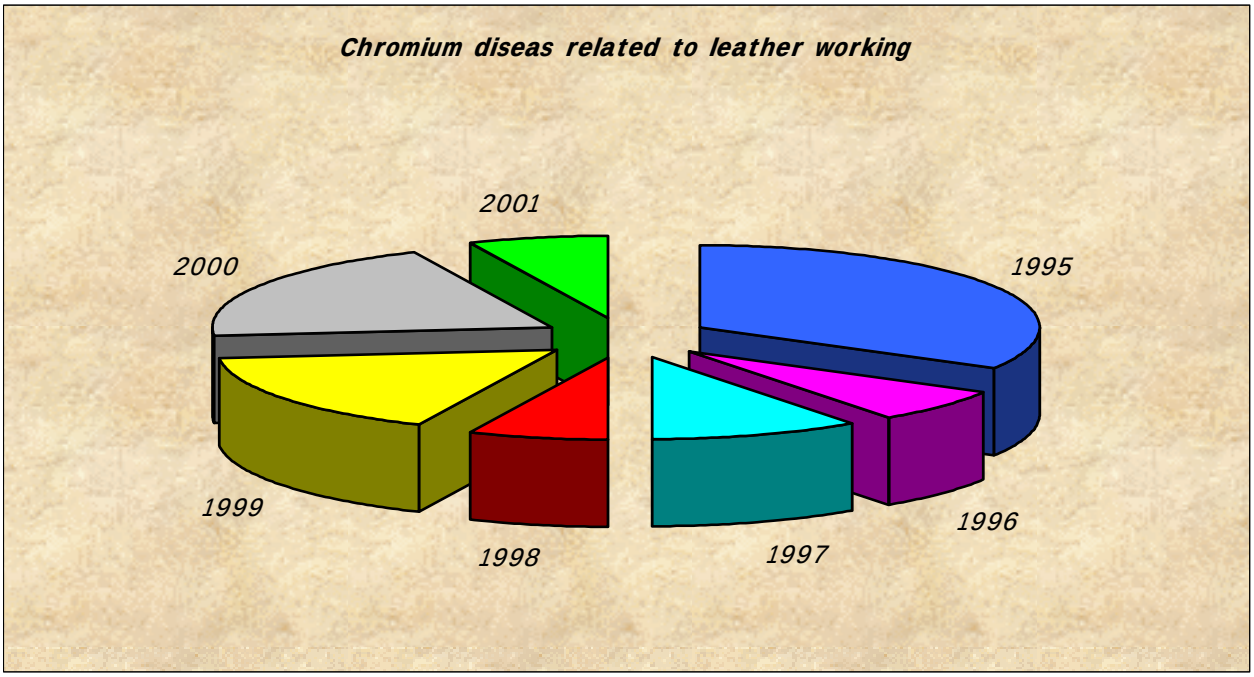
Graphic 1: Chromium diseases in several industrial compartment in last seven years

During 1995-1998 Cr (III) related diseases are more than Cr(VI), instead in the last years diseases from Cr(VI) are in a greater number (graphic 2).



Graphic 2: Cr(III) and Cr(VI) diseases in Italy in last seven years

It is evident that a great number of diseases are related to industrial compartment that includes leather working. Graphic 3 shows the trend of chromium diseases in leather industry in last seven years.



Graphic 3: Chromium diseases in leather industry

In Italy leather tanning and silk treating activities are very important and their products are exported in all the world.

TANNING PROCESS

Leather is made from animal skins or hides which have been chemically treated to preserve quality and natural beauty. The chemical procedure used to prepare raw animal hides for use is called "tanning." A piece of hide or skin which has been tanned produces a strong, flexible leather which is able to resist decay and spoilage.

The tanning process consist in several steps:

- *Curing* : a process which involves salting and/or drying the hide once it's been stripped from the animal. Hides can be cured in two ways:

  Wet-Salting is done by salting the hide and then piling many skins together until they form a moist bunch. They are then left to cure for one month, so that the salt can completely be absorbed into the skin.

  Brine-curing is more common than wet-salting, as it's considered a faster, easier method. During brine curing, hides are positioned carefully in vats and smothered with a mixture of

salt and disinfectant. After 10-16 hours, the skins are completely cured and ready to move on to the next stage.

- *Soaking*: after curing the hides are soaked in water for several hours to several days. The water helps to rid the skin of salt, dirt, debris, blood and excess animal fats.
- *Flesh removal* : animal hides are moved through a machine which strips the flesh from the surface of the hide.
- *Hair removal*: hides are transported to a large vat, where they are immersed in a mixture of lime and water, which loosens the hair from the skin. Liming is a process by which the bonds between the fibrils are partly broken and also part of interfibrillar skin matter takes out. After this process the skin is very alkaline (pH 13-14).
- *Scudding*: stray hairs and fat which were missed by machine, are removed from the hide with a plastic tool or dull knife in this process
- *Deliming*: hides are delimited in a vat of acid, to neutralise the alkaline skin, carbon dioxide and ammonium salts are used. This process is essential before the tanning process begins, otherwise the acidic tanning agents would harden up the grain fibres.
- *Tanning*: This process makes the skin much more resistant to deterioration, more flexible, and durable when exposed to water. There are two types of tanning: vegetable and mineral. The mineral is performed on skins which will be used for softer, stretcher leathers, such as those found in purses, bags, briefcases, shoes, gloves, boots, jackets, pants, and sandals.

  Vegetable tanning

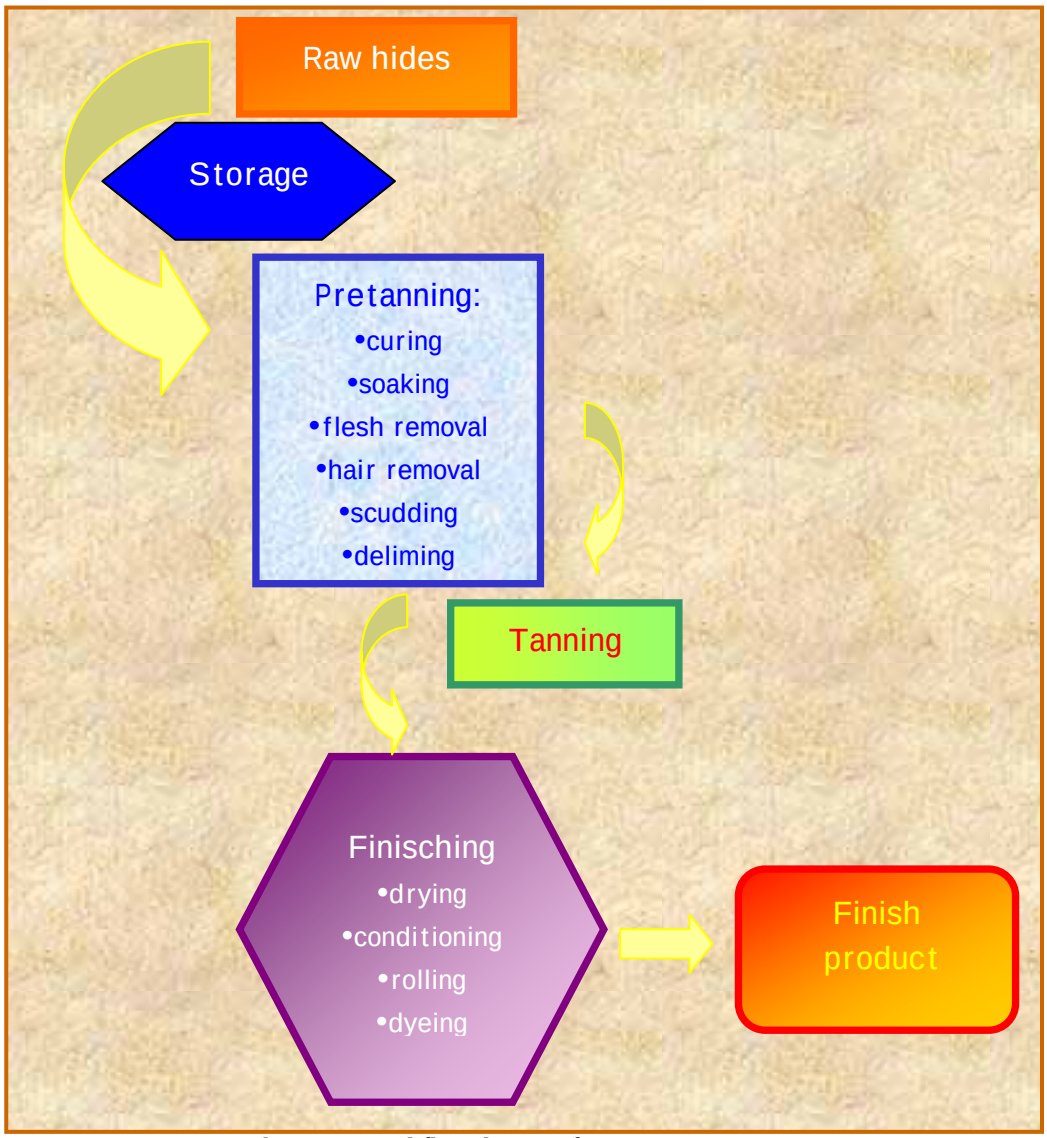
  Skins are suspended into large pots or vessels containing the vegetable tannins derived from wood, roots, bark, leaves, and fruits of various plants, such as oak, chestnut, hemlock, and willow trees. Periodically the skins are exposed to increasing concentration of the tannin solutions.

  Mineral tanning

  Mineral or Chrome tannins are used in leather production by treating the skins with chromium sulfate. The tanning process draws collagen fibres together and creates crosslinks between them. These crosslinks on a molecular and fibre level make the skin much more resistant.

  As in vegetable tanned leather the degree of control defines the quality and type of leather produced.
- *Finishing*: Different process can fallow depending on the desired product. The hides could be dye, run through a machine, to make it stronger (rolling), could be buffed and

sandpapered to remove imperfections. Also waxes, pigments, dyes, glazes, oils and other solutions could be added to make the it more appealing to the buyer. The finish applied determines how the end product looks in terms of shine, colour, and texture.



Graphic 4: General flow diagram for tanning process

CHROMIUM SAMPLING PROCEDURES AND ANALYTICAL METHODS

The basis of analytical methods for analysis of Cr(VI) is its complexation with 1,5-diphenylcarbazide (DPC) and measurement of the resulting violet chromium complex, after acid extraction of the Cr(VI) from the sample.

In *NIOSH 9101* method, used for estimation of soluble Chromium content in settled dust, a specific reagent kit is used to estimate colour development.

NIOSH 7600 involves acid extraction of Cr(VI) and determination of the final complex by visible adsorption spectrometry (UV-VIS) at 540 nm. For a 200 L air sample the working range is 0.001 to 5 mg/m^3. Insoluble chromates can be extracted in alkaline buffer. Interference due from reducing agents, that could convert the Cr(VI) to Cr(III) using acidic extraction medium, is minimised from alkaline extraction.

In *NIOSH 7604***,** specific for Cr(VI), ion chromatography (IC) is used. It is free from interference from cations of metals and interference from reducing agents are eliminated from alkaline extraction.

Similar procedures are *NIOSH 7605* and *OSHA ID-215***,** methods used for air samples analysis. In the second one Cr(VI) is separated from other compounds using IC, reacts with the DPC in a postcolumn and is measured by UV-VIS at 540 nm. The qualitative and quantitative detection limit are $1.0*10^{-3}$ µg/m^3 and $3.0*10^{-3}$ µg/m^3 as Cr(VI) for a 960-L air volume. *OSHA ID-215* supersedes *OSHA ID-103* in which analysis is conducted by differential pulse polarography (DPP).

NIOSH 7703 is used for determination of soluble Cr(VI) by field-portable spectrophotometry, after solid phase extraction. Its working range is 0.05 to 1000 µg/m^3 for a 200 to 500 L air sample.

MDHS method 61 is another field method but no isolation step of Cr(VI) is involved..

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