JTTEE5 12:542-554

Peer Reviewed

Harmful Risks for Workers in Thermal Spraying: A Review Completed by a Survey in a French Company

Hélène Hériaud-Kraemer, Ghislain Montavon, Sylvaine Hertert, Hervé Robin, and Christian Coddet

(Submitted 2 October 2001; in revised form 22 September 2002)

Thermal spray technologies are implemented in spray booths either manually or automatically. In both cases, workers can be exposed to several potential and real risks. The major risks are to workers' respiratory systems and result from harmful feedstock materials. To the authors' knowledge, very few specific studies have been conducted to assess the significance of these risks. This study describes the major risks encountered and reviews the results of a survey conducted in a French company that uses thermal spray technology on a large scale.

Keywords exposure level, harmful emission, occupational risks, respiratory diseases, thermal spraying, toxicity

1. Introduction

Occupational physicians play an increasingly important role within companies. They survey the health of workers over a certain period of time, which depends mostly on the risks the workers encounter. Physicians study several positions within the plant to determine the potential occupational risks and to establish preventive rules intended to minimize or eliminate risks.

Thermal spraying is a generic term used to describe several surface treatment techniques. A feedstock material (usually powder particles or wires) is melted by an enthalpic source (commonly a flame or a plasma jet exiting from a gun) and simultaneously accelerated by the same source, or by an additional gas flow, toward the surface of a component to be coated. On this surface, the particles impact, flatten, and solidify to form thin lamellae. The deposit is built layer by layer and results from the relative motion of the gun and the part to be coated; usually the gun moves. This relative motion is created either manually (in which a qualified sprayer moves the gun by hand) or automatically by a multi-axis robot or a simpler gun holder that describes predefined trajectories.

Because of the repetitive nature of this technique and the relative difficulty of simultaneously controlling the influent processing parameters, spray facilities most often use automation. However, in many cases thermal spraying is still performed manually, and the worker may be exposed to gases, vapors, dusts, etc., which can induce acute or chronic pulmonary conditions.

Other harmful effects, such as repetitive exposure to noise or radiation, can also generate health problems. Theoretically, even when automatic spray systems are used, the worker can be exposed to the same risks, albeit at a lower level. In each case, it is essential for the sprayers to use individually and collectively adapted protective devices to limit the maximum possible amount of harmful effects caused by exposure. Data available in the literature about the harmful effects of the thermal spray techniques are scarce, and the possible diseases are not extensively described.

The purpose of this article is to list the numerous risks—real and potential—that persist. These risks are relative either to the technique itself or to the nature of the feedstock materials. In addition, this article describes a survey that was conducted in 10 sprayers (chosen from 300 employees) exposed to these risks. They worked in a French company specializing in the repair of turbine engines for aeronautic applications. The company is divided into three major departments: the repair department, to which the 10 sprayers belong; the equipment department; and the engine department. This study focuses on the risks encountered with direct current (dc) plasma torch implementation, but it can still be used as a general guideline for other techniques because powder particles were used as the feedstock.

Hélène Hériaud-Kraemer, Service de médecine du travail, 190 Rue Raoul Briquet, 62 700 Bruay La Buissière, France; and **Ghislain Montavon** and **Christian Coddet,** LERMPS, Université de Technologie de Belfort-Montbéliard, site de Sévenans, 90010 Belfort Cedex, France; and **Sylvaine Hertert,** CRMA, Service medical, 14 Avenue Gay Lussac, Z.A. la clef Saint Pierre, 78996 Elancourt, France; and **Hervé Robin,** Service d'explorations fonctionnelles respiratories, PUPH–CHRU de Lille, Délégation à la Recherche, 2 Avenue Oscar Lambret, 59037 Lille Cedex, France. Contact e-mail: ghislain.montavon@utbm.fr.

2. Major Risk Factors for Workers in Direct Current Plasma Spraying

2.1 Harmful Emission Analysis and Toxicity

2.1.1 Gases and Vapors. The sprayers are exposed to the following chemical hazardous risks:

- gas from the combustion products from flame spraying (mostly CO_2 and CO; H_2O presents no chemical risks to health);

Acronyms	
Institutions	
ACGIH	American Conference of Governmental Industrial Hygienists, www.acgih.org
BMRC	British Medical Research Council, www.mrc.ac.uk
ECCS	European Community of Coal and Steel
INRS	Institut National de Recherche et de Sécurité (French National Institute of Research and Security), www.inrs.fr
NIH	National Institutes of Health, U.S. Department of Health and Human Services, www.nih.gov
NIOSH	National Institute of Occupational Safety and Health, www.cdc.gov/niosh
OSHA	Occupational Safety and Health Administration, U.S. Department of Labor, www.osha.gov
Exposure Levels	
C	Ceiling
PEL	Permissible Exposure Limit
REL	Recommended Exposure Limit
STEL	Short-Term Exposure Limit
TLV	Threshold Limit Value
TWA	Time Weighted Average
Spirometric Test Parameters	
FEV1	(maximum) Forced Expiratory Volume in 1 s
FVC	Forced (expiratory) Vital Capacity
MEF25-75	Maximal Mid-Expiratory Flow
PEF	Peak Expiratory Flow Rate
VC	(expiratory) Vital Capacity
Miscellaneous	
BTPS	Body Temperature Pressure Saturated
ENT	Ear, Nose, and Throat
RADS	Reactive Airway Dysfunction Syndrome

- gas issued from the atmosphere dissociation and recombination from plasma spraying (NO_x, O_3), including the gas exiting from the plasma torch (mostly Ar, H_2, He, and N_2);
- vapors resulting from particle vaporization during their flight within the enthalpic jet. This vaporization phenomenon is especially emphasized when plasma spraying is compared with flame spraying, and particularly when feedstock materials exhibit high vapor pressure, such as chromium oxide or copper-nickel-indium alloy.

For example, Table 1 lists the chemical composition of a high-velocity oxygen fuel (HVOF) flame when natural gas (200 SLPM), mostly methane, is combined with oxygen (400 SLPM) in a CDS gun from Sulzer-Metco (Wohlen, Switzerland), to provide a flame exiting at 3252 K.[1] As indicated, CO_2 and CO are the predominant hazardous species produced.

Due to the high energy level within a plasma jet and air entrapment when the system is run at atmospheric pressure, oxygen and nitrogen dissociation occur, and recombination takes place to form new species, such as NO_x and O_3, as listed in Table 2.

Table 1 Chemical Composition (Molar Fraction) of a High Velocity Oxygen Fuel Flame, After Ref. 1

Processing Parameters	Value
Methane flow rate	200 SLPM
Oxygen flow rate	400 SLPM
Gun	Sulzer-Metco CDS with a 5″ long barrel
Flame temperature at the nozzle exit (calculated)	3252 K
Reaction Products	Molar Fraction
H_2O	0.4037
CO_2	0.1432
O_2	0.0804
N_2	0.0045
H_2	0.0759
CO	0.1327
OH	0.0855
H	0.0420
O	0.0291
NO	0.0030

These gases and vapors can be inhaled by the sprayer. The factors governing the amount of absorbed gases by the pulmonary system, beyond the atmospheric concentration and the exposure duration, are[2]

- solubility of the species in the blood and tissues—an increase of the absorption coefficient of the blood increases the harmful product penetration;
- blood flow;
- pressure gradient of the gases between the alveoli of the lungs and the blood;
- pulmonary ventilation—an increase in ventilation decreases the concentration difference between the inhaled air and the alveolar air; this strongly facilitates the absorption of the soluble gases by blood cells and tissues but has a weak influence on the absorption of insoluble gases by the media.

2.1.2 Dust Particles. Dusts and particles in the atmosphere are inherent to the process. The particles may not spread onto the surface to be coated and rebound, splashing may occur at the point of particle impact and dusts of small dimensions are generated, or the vapors may condense. Because of the high solidification velocity, these particles are very commonly in a metastable state.

After they are inhaled, depending on their average size, dust particles penetrate to varying depths in the tracheobronchial tree. Three major factors affect the particle deposition morphology, respiratory parameters, and physical characteristics of the dust particles.

The tracheobronchial tree is subdivided into three sections (Fig. 1)[2]:

- pharynx;
- trachea (Fig. 2) and the bronchi (including the bronchioles) covered by an epithelial cilia and mucus cells (the cilia are animated by Brownian motion);
- respiratory bronchioles and the pulmonary alveoli (Fig. 3) covered by an epithelium (Fig. 4). This epithelium coexists

Table 2 Mechanisms of Air Component Dissociation and Recombination

Dissociation Mechanisms	Recombination Mechanisms
O_2 energy ($E = h\nu > 0.5$ eV) $\rightarrow$ 2O	O_2 O $\rightarrow O_3$
N_2 energy $\rightarrow$ 2N	N $O_2 \rightarrow NO_2$
	O $NO_2 \rightarrow$ 2NO

with type I and II cells as well as with alveolar macrophages, with engulfed particles deposited in the pulmonary compartment.

In the pharynx, deposition of dust and small particles occurs especially where the respiratory tree abruptly changes direction and where the inhaled air velocity is high. In the trachea and in the bronchial tree, where the inhaled air velocity decreases, the deposition occurs either by impact or by sedimentation.

Finally, in the respiratory bronchioles, where the air velocity is close to zero, deposition occurs by diffusion.[2] The dust particles' size distribution, as well as their morphology, greatly influences the deposition into the respiratory tracts[2]:

- The large particles (average diameters ranging from 5 to 30 μm) are stopped in the pharynx.
- The medium particles (average diameters ranging from 1 to 5 μm) are deposited mostly in the trachea and the bronchi.
- The small particles (average diameters smaller than 1 μm) diffuse into the pulmonary alveoli, from which their harmful effect arises.

2.1.3 Pulmonary Retention Level and Pulmonary Clearance. The pulmonary clearance mechanisms eliminate particles deposited into the tracheobronchial tree. Depending on the level of clearance, the pulmonary retention level can be determined as follows: retention level = deposition level − clearance level.

The pulmonary clearance level describes the capability to reject dust particles outside the tracheobronchial tree[2]:

- The soluble particles are eliminated into the intracellular media.
- The insoluble particles deposited onto the mucus layer in the bronchial tree are transported to the pharynx by the motion the cilia and then expectorated or swallowed. Tobacco, ozone, and NO_x impair the mucus quality and the motion of the cilia and hence modify the inhaled particle clearance.
- The particles that reach the respiratory bronchioles and the pulmonary alveoli devoid of cilia are eliminated by (1) "swallowing up" (the phagocytes merge the particles, absorb them, and digest them), (2) pinocytosis (the inclusion into a cell of a liquid particle forming a vacuole), (3) dissolution and diffusion through the alveolus membranes, or (4) the effect of the pulmonary surfactant, which transports the particles to the cilia where they follow the motion of the mucus.

The pulmonary retention level thus varies as a function of the particle size and the respiratory frequency. Whatever the mode of clearance, the harmful products operate chemically on the organism, which suffers from clamping; the products also operate physically by destroying specific molecular sequences.

2.1.4 Toxicity of Some Metallic Powders. Metallic powders generate two types of disease: the first relates to the nature of the material, and the second is relative to the specificity of thermal spraying.

To the authors' knowledge, no study has been conducted to date to specifically assess the toxicity of the powders commonly used in thermal spraying. For this reason, the following descriptions of diseases and disorders come from the literature and relate to other professions in which workers are exposed to the same materials.

Nickel. Nickel is the most commonly encountered allergen.[2] It can provoke skin diseases such as contact eczema or sensitization dermatitis,[3] and pulmonary diseases such as allergic asthma and pneumoconiosis.[4,5] Moreover, nickel is classified as a potential occupational carcinogen for humans.[5]

Cobalt. Like nickel, cobalt can provoke, when manipulated, skin diseases such as contact eczema and dermatitis,[3] and respiratory irritation or decreased pulmonary function with diffuse nodular fibrosis.[6] It is a potential occupational carcinogen for humans and can interfere with the metabolism of the thyroid hormones.[7]

Copper. Copper can provoke eye irritation and decrease respiratory functions with the appearance of cough and dyspnea. It is classified as a potential occupational carcinogen for humans.[6]

Aluminum. The prolonged inhalation of aluminum may provoke respiratory problems, from a simple cough to an acute pulmonary edema.[5] Some rare cases of pulmonary fibrosis have been reported.[8]

Chromium and Chromium 6. Chromium can provoke skin injury—eczema-type dermatitis—and chronic pulmonary symptoms (i.e., inflammation, asthma, etc.). Oxide chromium (chromium 6) is a carcinogen for humans, very likely after its intracellular reduction into chromium 5.[2,5] It provokes an irritation of the respiratory system and a nasal septum perforation, affects the liver, increases the blood leukocyte level (leukocytosis), irritates the eyes until conjunctivitis occurs, and causes skin ulcers and sensitization dermatitis.

2.1.5 Legislation Regarding Exposure to Harmful Products. Legislation and recommendations define general rules about the exposure of workers to harmful products. Regulations are set by the organizations in charge of health and may vary from one country to another. In France, the Institut National de Recherche et de Sécurité (French National Institute of Research and Security; INRS[1]) is in charge of determining the exposure rules.

Its American counterpart is the Occupational Safety and Health Administration (OSHA) from the Department of Labor (DOL), but several additional associations have also put forth their own recommendations; for example, the National Institute of Occupational Safety and Health (NIOSH) and the American Conference of Governmental Industrial Hygienists (ACGIH).

Several indexes take into account the protection of workers. They define maximal permitted exposures to products and

[1]The INRS operates on behalf of employees and companies under the general Social Security scheme. It is supported by the regional health insurance funds (CRAM) in metropolitan France and general Social Security funds (CGSS) in French overseas administrative departments and provides its competence to other prevention partners, such as occupational physicians and labor inspectorate services.

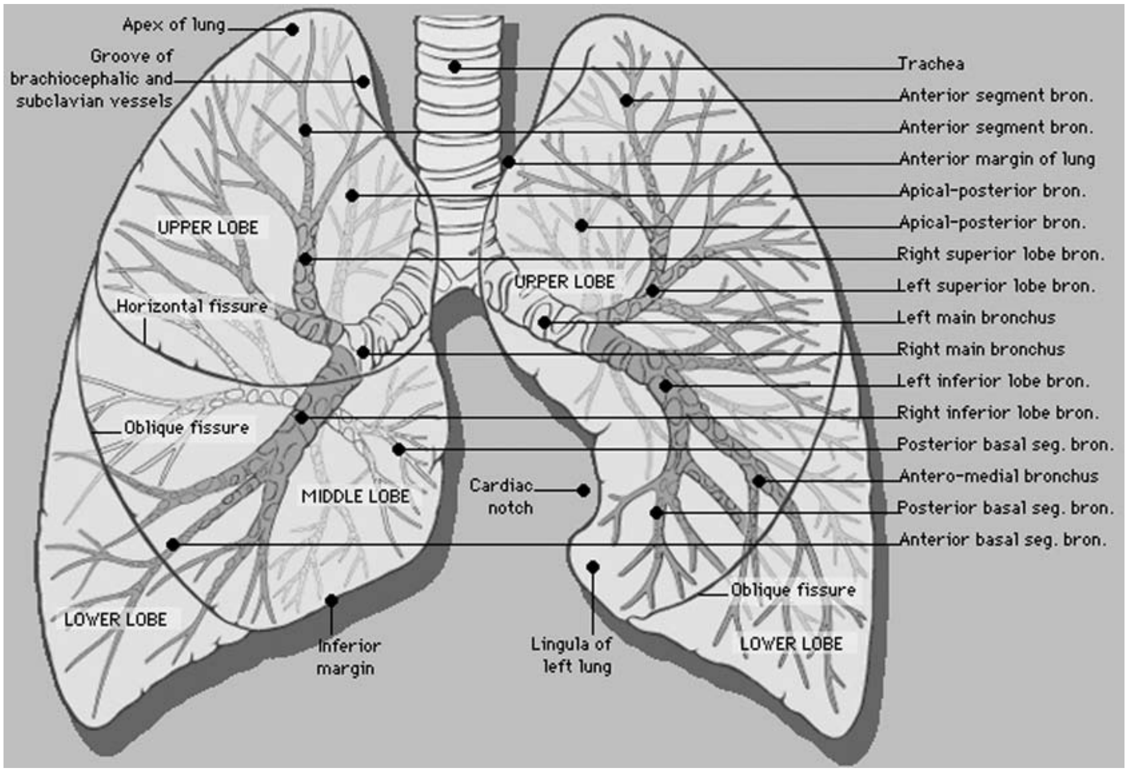


Fig. 1 The tracheobronchial tree, from http://info.med.yale.edu/intmed/cardio/imaging/anatomy/lungs (Credit P.J. Lynch, with the permission of the Yale University School of Medicine, www.info.med.yale.edu)

permanent admitted exposures (Table 3). In fact, these indexes determine several admitted concentrations of a given product in the atmosphere for a given duration of exposure, permanent or not:

- Time Weighted Average (TWA) defines the daily average concentration on the basis of an 8 h day and a 40 h week.
- Recommended Exposure Limit (REL) corresponds to a TWA for a 10 h day shift and a maximum of a 40 h week.
- Threshold Limit Value (TLV) corresponds to a TWA for a work shift of 8 h per day.
- Permissible Exposure Limit (PEL) is the maximum TWA that must not be exceeded during an 8 h per day shift and a maximum of 40 h per week.
- Short-Term Exposure Limit (STEL) is the maximal permitted concentration that cannot be exceeded during 15 min.
- Ceiling (C) defines that maximal concentration limit that must never be exceeded during a work shift.
- Immediately Dangerous to Life and Health concentration (IDLH) is the maximal concentration that represents an immediate danger for life after 30 min exposure.

Table 4 displays values for several metallic materials. Extensive data for these materials and other chemical products can be found in Ref. 6, 9, and 10. Some significant differences exist between legislative values and recommended values, and some significant differences also exist depending on the country. The maximum exposure levels remain relatively low whatever the material, and limits can easily be reached during a thermal spray operation in two locations and at two moments: in the spray booth during the spray operation if the sprayer does not wear adequate protection (Fig. 5) and outside the thermal spray booth during preparation of the powder feeder if adequate ventilation

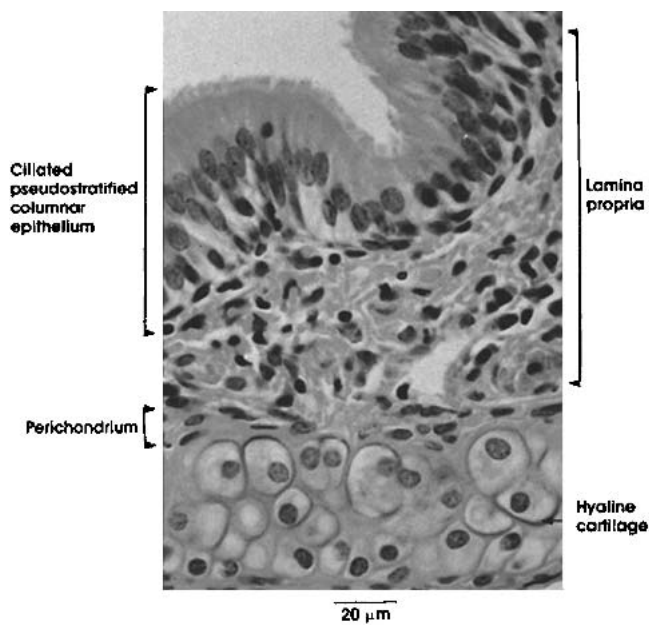


Fig. 2 Trachea, from http://www.vh.org/Providers/Textbooks/MicroscopicAnatomy/Section11/Plate11224.html (Copyright protected by material used with permission of the authors and the University of Iowa's Virtual Hospital, www.vh.org)

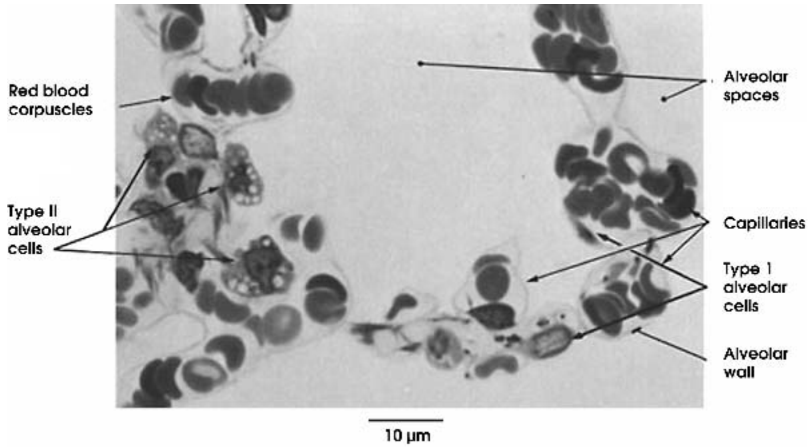


Fig. 3 Alveoli, from http://www.vh.org/Providers/Textbooks/MicroscopicAnatomy/Section11/Plate11230.html (Copyright protected by material used with permission of the authors and the University of Iowa's Virtual Hospital, www.vh.org)

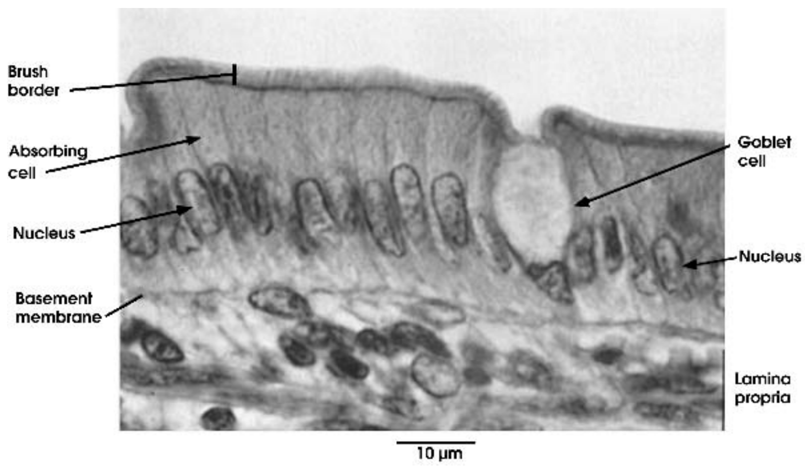


Fig. 4 Epithelium, http://www.vh.org/Providers/Textbooks/MicroscopicAnatomy/Section02/Plate0218.html (Copyright protected by material used with permission of the authors and the University of Iowa's Virtual Hospital, www.vh.org)

Table 3 Several Indexes Describing Permitted Maximal Exposures to Harmful Products

Index	Legislation	Recommendation	
Exposure index	OSHA/INRS	NIOSH	ACGIH
Weekly average concentration	TWA	TWA	TWA
Daily average concentration	PEL/VME	REL	TLV
Maximal limited concentration	STEL/VLE	STEL	STEL
Maximal concentration	C	C	C
Dangerous for life	No index defined	IDLH	No index defined

systems are not installed or if the sprayer does not wear adequate protection. For example, the maximum exposure limit (STEL) is reached with copper for an average value of 43 000 particles of 10 μm diameter per cubic meter, which is a relatively low concentration of particles.

2.1.6 Secondary Diseases Induced by Inhalation of Gas, Vapors, and Dust. The nature of the respiratory attack is a function of the spot of action of the harmful substances. The aqueous solubility of inhaled gases determines their penetration into the respiratory tree. Highly soluble substances are primarily held in the upper parts of the tree where they generate irritation. Moreover, bronchitis lesions can be observed as a result of extended exposure. Insoluble substances such as, nitrogen oxides (NO and NO_2) and phosgene ($COCI_2$) penetrate very deeply into the tracheobronchial tree; deep enough to reach the alveoli.

The location of reaction is primarily determined by the size of the dust particle (Fig. 6). They significantly penetrate into the bronchial tree only if their average diameter is smaller than 5 μm.[11]

External factors also have to be taken into account in the case of exposure. These factors include exposure duration, exposure intensity, atmospheric concentration, ventilation condition, chemical reactivity of the products (with the possible formation of free radicals), alkalinity of the substances, and individual susceptibility of the worker to the product.

Acute Harmful Respiratory Diseases. The symptoms observed in acute harmful effects range from irritation syndrome to pulmonary edema. The inflammatory reaction of the aerial mucous membrane is the common mode of action of numerous

Table 4 PEL, STEL, and Other Indexes for Several Metallic Materials, After Ref. 6, 9, and 10

Material	PEL (a)	VME (b)	STEL (c)	VLE (d)	REL (e)	TLV (f)	IDLH (g)
Be	2 μg m^{-3}	2 μg m^{-3}	25 μg m^{-3}	N/A(h)	0.5 μg m^{-3}	N/A	4 mg m^{-3}
Ni	1 mg m^{-3}	1 mg m^{-3}	0.30 mg m^{-3}	N/A	15 μg m^{-3}	1 mg m^{-3}	10 mg m^{-3}
Fe	10 mg m^{-3}	N/A	N/A	N/A	N/A	N/A	N/A
Co	0.1 mg m^{-3}	N/A	0.1 mg m^{-3}	N/A	0.05 mg m^{-3}	N/A	20 mg m^{-3}
Mo	15 mg m^{-3}	5 mg m^{-3}	20 mg m^{-3}	10 mg m^{-3}	N/A mg m^{-3}	N/A	5000 mg m^{-3}
Cu	1 mg m^{-3}	1 mg m^{-3}	1 mg m^{-3}	2 mg m^{-3}	1 mg m^{-3}	N/A	100 mg m^{-3}
Al	5 mg m^{-3}	10 mg m^{-3}	15 mg m^{-3}	N/A	10 mg m^{-3}	N/A	N/A
W	N/A	N/A	10 mg m^{-3}	N/A	5 mg m^{-3}	N/A	N/A
Zr	5 mg m^{-3}	N/A	N/A	N/A	5 mg m^{-3}	N/A	50 mg m^{-3}
Cr	1 mg m^{-3}	0.5 mg m^{-3}	15 mg m^{-3}	N/A	0.5 mg m^{-3}	N/A	250 mg m^{-3}
Cr6	0.1 mg m^{-3}	50 μg m^{-3}	30 μg m^{-3}	N/A	1 μg m^{-3}	50 μg m^{-3}	15 mg m^{-3}
Mg	10 mg m^{-3}	10 mg m^{-3}	20 mg m^{-3}	N/A	N/A	N/A	N/A
Ta	5 mg m^{-3}	5 mg m^{-3}	10 mg m^{-3}	N/A	5 mg m^{-3}	N/A	2500 mg m^{-3}
Pb	50 μg m^{-3}	150 μg m^{-3}	50 μg m^{-3}	N/A	50 μg m^{-3}	N/A	100 mg m^{-3}

(a) PEL, Permissible Exposure Limit (OSHA value)
(b) VME, Valeur Moyenne d'Exposition (INRS value, equivalent to OSHA PEL)
(c) STEL, Short-Term Exposure Limit (OSHA value)
(d) VLE, Valeur Limite d'Exposition (INRS value equivalent to OSHA STEL)
(e) REL, Recommended Exposure Limit (NIOSH value)
(f) TLV, Threshold Limit Value (ACGIH value)
(g) IDLH, Immediately Dangerous for Life and Health (NIOSH value)
N/A, Not Available

gases, such as phosgene ($COCL_2$) and ozone (O_3). A delay, ranging from a few minutes to a few hours after exposure, depending on the nature of the gases, precedes the appearance of symptoms. These symptoms disappear when the exposure ceases[11] and are characterized by

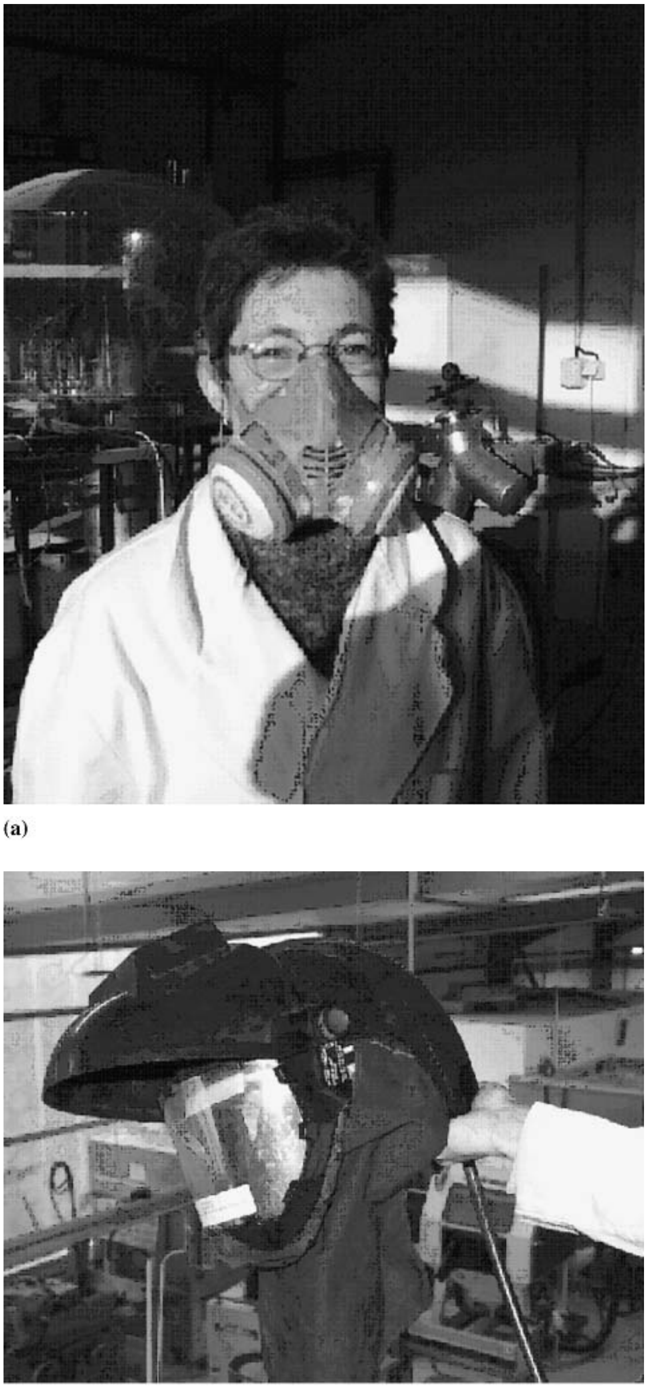
- hoarse, painful, and more or less productive cough;
- sibilant dyspnea;
- some irritation of various mucosa, including that of the eyes (burning, watering), the nose (sneeze, rhinorrhea), the larynx (hoarseness, laryngeal dyspnea), and the stomach (dysphagia, vomiting).

The evolution, however, can be characterized by the appearance of an acute pulmonary lesional edema occurring in the following 24-48 h. The direct aggression of the harmful products on the epithelial alveoli induces an increase of the alveolo-capillary permeability. This permeability makes way for protein-rich liquid in the interstitium and/or in the alveoli. Clinically, coughing, dyspnea, expectoration, and cyanosis can be observed. Auscultation permits detection of rales. The paraclinical checkup reveals a chest x-ray perturbed by irregular pulmonary opacities exhibiting a peri-hilar character. In this case, the victim of such an affliction has to be hospitalized for as least 24 h for complete rest and continuous medical supervision. The evolution is variable because either a complete recovery without any aftereffect, or conversely, degeneration to chronic illness, has been observed.[2,5]

Reactive airway dysfunction syndrome (RADS), described in 1985 by Brooks,[12] can be observed after bronchial hyper-responsiveness persisting for at least three months, even after the total recovery of the acute respiratory lesions. Asthma crises occur in the absence of previous respiratory manifestation and follow a unique massive exposure. It is possible to observe obstructive pulmonary syndrome by spirography. The physiopathology remains relatively unknown, but RADS represents 3-6% of occupational asthma.[12]

Exposure to metallic oxide fumes, among them nickel or aluminum oxides, can set off a disease known as "metal fume fever." This fever appears 4-24 h after exposure and is characterized at first by the appearance of asthenia, nausea, and headache. Then hyperthermia associated with shudders, diffuse myalgia, ENT, and tracheal irritation occurs. The patient experiences a metallic taste in his or her mouth. The maximum clinical symptoms are reached 9-12 h after the exposure. The evolution is favorable because recovery is observed after 24-48 h without any specific treatment.[5]

Chronic Harmful Respiratory Diseases. Two major chronic diseases are encountered: complications of acute edema and chronic bronchitis. Complications of acute edema result from aftereffects of massive exposure, especially to phosgene, ozone, and nitrous vapors. Anatomic lesions generally involve obstructive bronchiolitis. Clinically speaking, obstructive bronchiolitis is characterized by the reappearance of cough, dyspnea, and fever after recovery from the initial edema. The illness appears then as irreversible obstructive respiratory distress. Medical imagery shows multiple and diffuse nodules of various sizes and explicit signs of hyper-inflammation.[2,5] The repetitive inhalation of corrosive or irritant vapors provokes the progressive appearance of a chronic bronchitis called "chemical" bronchitis. This bronchitis can exhibit two distinctive and independent forms: simple chronic bronchitis and obstructive chronic bronchitis.[5] Simple chronic bronchitis involves the attack of medium and large bronchi, whereas obstructive chronic bronchitis involves the smaller bronchi (diameter less than 2 mm). Clinically speaking, simple chronic bronchitis generates a daily productive cough and rhonchus appears during lung auscultation. This attack is reversible. Such diseases, however, can also be due to nicotine addiction. Chronic inflammation combined with irreversible sclerosis induces obstructive chronic bronchitis that initially results in dyspnea after strenuous activity. This dyspnea



(a)

(b)

Fig. 5 Sprayer respiratory protection: **(a)** semi-disposable half face piece mask, **(b)** full face piece respirator

will remain later on, even when the subject is at rest. However, spirography can permit early detection. Obstructive chronic bronchitis is characterized by rhonchus and sibilants.

2.2. Other Risks

2.2.1 Noise. The abrupt expansion of the plasma jet exiting the spray gun (i.e., velocities ranging from 200-600 m s^{-1} in

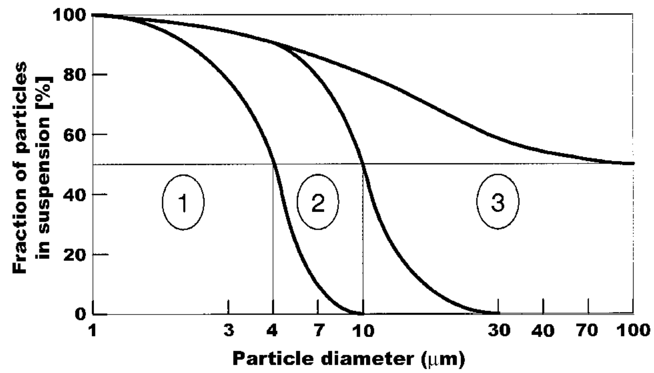


Fig. 6 Spot of action of dust particles depending on their size and on the suspension fraction, after Ref. 6

atmospheric conditions[12]) or the flame (i.e., velocities up to 1800 m s^{-1} for HVOF spraying[13]) generates an acoustic level far higher than the maximal permitted level of 85 dB(A); the level reaches at least 110 dB(A). Two studies,[14] one performed by the center of physical measurements of the regional health insurance funds (CRAM) of Paris, France (Table 5), and the other in the Czech Republic, indicate identical results: at 250 Hz, the noise level in a plasma spray booth exceeds the harmful threshold with a maximum peak intensity around 8000 Hz. This induces serious risk of permanent occupational deafness if no action is taken to protect the sprayers.

2.2.2 Radiation. For plasma spraying in particular, but less so for flame spraying, high-temperature jets generate radiation in a broad range of wavelengths from ultraviolet (UV) to visible and infrared (IR). Dosimeters, held by Czech sprayers, did not reveal harmful alpha, beta, or gamma radiation.[15] However, the emitted radiation represents potential harmful risks, which can cause ocular (Fig. 7) and skin diseases.

The risk of "glass-maker's cataract" has never been reported as a threat to sprayers. The illness begins with a slight opacity in the lower part of the crystalline lens, which progressively extends like a spider's web to the entire lens. This cataract is predominantly induced by IR radiation; UV radiation is stopped by the media located in front of the crystalline lens (Fig. 8). Severe cornea burns also were observed.[15,16]

Visible and near-IR radiation generate an energy density that reaches the retina. When exposed to a luminous source of excessive energy density without any protection, a subject can suffer from a retinal photo-traumatic lesion known as "arc stroke." Functional symptomatology appears at the instant of the exposure or right after it. Sharp pains and a consequent photophobia occur, associated with an intense dazzling feeling, which persists during the palpebral occultation: the patient goes blind for certain period of time. Clinical examination sometimes shows a decrease in the acuteness of the visual field as well as problems with color vision known as dyschromatopsia. If the phototrauma is especially severe, optic atrophy and even lesions in the macula lutea appear. Sometimes, this lesion is irreversible. In most cases, however, the observed symptoms regress after a few days. Blindness can regress totally, partially, or not all.[15,17] Keratoconjunctivitis, or electric ophthalmia, is preceded by a transitory amblyopia after a few hours of latency. The symptomatology is characterized by sharp pains with the feeling of "sand

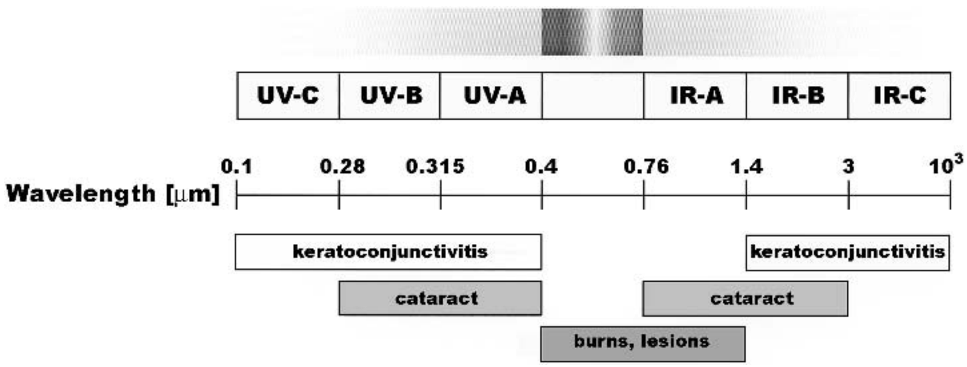


Fig. 7 Major risks encountered by the eye, depending on the wavelength of the emitted radiation

Table 5 Levels of Acoustic Emissions During Plasma Spraying for Various Spray Conditions, After Ref. 14

Spray Conditions	Frequency, Hz	dB									dB (A) global
		63	125	250	500	1000	2000	4000	8000	16 000	
Plasma gun with used electrodes (700 A, 57 V)	At 1.5 m from the gun, inside the spray booth	80	82	84	87	89	98	112	120	114	120
	At 1 m from the spray booth doors, outside	75	72	68	70	72	70	82	84	78	86
Plasma gun with new electrodes (700 A, 69 V)	At 1.5 m from the gun, inside the spray booth	80	82	85	85	94	97	113	114	103	116
	At 1 m from the spray booth doors, outside	80	73	72	73	72	70	80	78	70	84
Ventilation alone	Inside the spray booth										75
Ventilation and air-jets	Inside the spray booth										95

grains" and by an intense photophobia exacerbated by any illumination. Some watering can also occur. Clinical examination reveals palpebral lesions consisting of dermatitis with edema followed by conjunctivitis with blotches and an edema of the cornea with small erosion of the uncovered parts. Recovery occurs after a few days, but recurrence is still possible. UVb radiation can provoke a cataract after only one exposure, contrary to UVa radiation, which requires prolonged exposure. Finally, UV radiation has a photochemical effect on skin that causes an erythema. Burns can be observed.

2.2.3 Thermal Risks. Plasma plumes or flames are directional jets; their thermal effect, caused by extreme energy density and very high temperatures, can be detected as far as 1 m past the exit of the guns. The consequent heat transfers between jets and surrounding atmosphere heat the components to be sprayed. Severe burns by contact with warm parts represent the major risks encountered by the sprayers.

2.2.4 Electric Risks. Electric risks are encountered especially with dc plasma guns for which a high intensity (i.e., a few hundreds of amperes) is used to generate the plasma jet. Proper insulation of the gun and electric devices is absolutely necessary and should be verified frequently, especially when the gun is operated manually by a sprayer.[14]

2.2.5 Risks Associated With the Use of Robots. Robots associated with anti-intrusion security systems on doors are frequently implemented in thermal spray booths. These systems, in terms of security, permit reduction of the exposure of sprayers to numerous risks, but at the same time facilitate the introduction of new risks, quite often because technological sophistication is not understood. The general security rules relative to the use of robots apply for thermal spraying. Numerous national[18] and international standards[19] apply when a robotic system is used.

A robot has no detection capability and a collision is unavoidable when someone or something is along the trajectory. The control device of the system, however, can detect an anomaly in trajectories.

Numerous emergency stops are located on the robot control system, on the robot power delivery system, and near the spray booths. When an anomaly is detected, the system abruptly stops the robot by cutting the power of the servo-controllers.

Practically, four maintenance steps can generate risks of accidents:

- when the robot is brought into service and the system is completed;
- when adjustments are made while the system is running;
- when the sprayer intervenes in the booth during production for a control or to solve a problem occurring in the operating cycle;
- when maintenance must be carried out.

When intervening in the spray booth, the following precautionary measures have to be taken:

- The robot has to be settled in the manual action mode (velocity lower than 250 mm $\cdot$ s^{-1}).
- The robot control system needs to be handled by the operator.
- The operator needs to wear protective devices adapted to the nature of the intervention.
- An emergency exit must always be available for the operator.

The anti-intrusion systems in the robot cell must be checked frequently. These systems consist of physical obstacles (i.e., barriers, doors, etc.), perimetric systems (i.e., nonmaterial

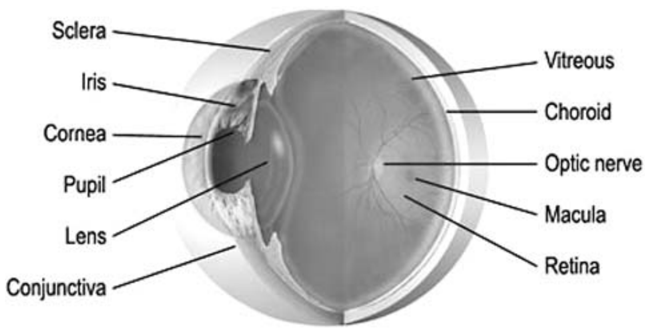


Fig. 8 Anatomy of the eye, from http://www.stlukeseye.com/Anatomy.asp

barriers, optical cells, etc.), or proximetric systems installed on the robot arms.

2.2.6 Risks Associated With the Manipulation of Heavy Loads. The major risk encountered by the sprayer is lumbago caused by the manipulation of heavy loads when installing the parts to be sprayed onto the part holders.

2.2.7 Explosiveness of Powders. Numerous feedstock powders are in an unsteady thermodynamic state. Input of energy provided by an ignition source (i.e., thermal, electric, etc.) can induce an evolution of the system toward a more stable state with the release of an enthalpy of reaction. The explosiveness thus defines the explosive character of a powder.

Some powders can react explosively, especially with components of the surrounding atmosphere such as water vapor or oxygen. Another example is the formation of hydrogen in presence of water.

Methane or acetylene can also be released by the fermentation of organic materials. Finally, magnesium and zirconium are known to be reactive with carbon dioxide. Aluminum and titanium are reactive with chlorine.

Several parameters influence the explosive character of a given powder. Among the most critical factors appear to be the concentration of particles in the atmosphere (a critical concentration can be defined for each type of powder), their shapes and sizes (small irregular particles are more prone to explosion than are large and spherical particles), temperature, pressure, and hygrometry, and nature of the ignition source.

To limit the risks, the possible ignition sources (such as flames, electrostatic charges, etc.) have to be avoided. In addition, the local accumulation of powder particles in hazardous areas (spray booth, spray vacuum chamber, etc.) has to be limited by frequent cleanings and appropriate ventilation.

2.2.8 Pyrophoricity of Powders. Pyrophoricity is defined as the spontaneous inflammation of a powder in air and at ambient temperature. Pyrophoricity differs from the autogenous ignition by the absence of temperature increase. The mechanisms driving pyrophoricity remain relatively unknown.

With the notable exception of precious metals (e.g., gold, silver, etc.), the metallic powders, whatever their nature, are subjected to pyrophoricity from the moment that their sizes are sufficiently small (a few micrometers). In such a way, the predominant factors favorable to pyrophoricity are the size and the shape of the particles, their specific surface (with an important potential risk once the specific surface reaches the critical value of 1 $m^2\ g^{-1}$), and oxidation enthalpy.

To limit the risks, the use of spherical powder particles, when possible, is highly recommended.

The presence of water vapor in the storage room must be limited, the room should be kept as dry as possible. Frequent cleanings of spray booths must limit the accumulation of fine particles. In the most critical cases, encountered especially with titanium powders, inhibition treatments can be performed (but they induce a significant additional cost to the manufacturing of the feedstock), or specific storage containers under a neutral atmosphere of argon, for example, can be used.

3. Case Study: Survey and Analysis of Potential and Real Risks to Sprayers in a French Company

3.1 The Company

3.1.1 General Facts. The company for which this survey was performed was created in 1950 by the merging of three companies specializing in aeronautics and piston engine manufacturing. At the end of the 1970s, this company joined a larger industrial consortium and developed its thermal spray facilities. Since then, the company has become integral to the industrial strategy of the group to which it belongs.

The major activity of the company is to repair aeronautic components for civil (80% of the global turnover) and military (more than 5% of the global turnover) aviation. Its customers are other subsidiaries of the company (more than 80%) and civil and military organizations (approximately 10%) worldwide.

Three hundred people (approximately 200 workers, 50 technicians, and 50 executives and engineers) participate in the activities of the company and generate an annual turnover of approximately US $36 billion (i.e., approximately 38.5 billion €); this annual turnover has increased constantly over the years.

The company is located at the periphery of an important French city, permitting direct accesses to major airports, railroad stations, and freight dispatching centers.

3.1.2 Organization of the Company. The company's activities are divided into three major areas: repair of components, equipment, and engines. Each area has its own technical department, and the general scheduling of the production and supplying are provided by a common logistics department. The Quality Control Department is in charge of the quality, and the company is certified JAR145, FAR145, ISO9002, etc. The Quality Control Departments primary task is to maintain these certifications. Its secondary task is to ensure an irreproachable quality to each component produced. The department implements intensive nondestructive testing and uses specific testing benches. The other departments are nonoperational services.

3.1.3 The Thermal Spray Workshop. This workshop is part of the repair department and is outfitted with flame, plasma, and electric arc spray guns installed either on six-axis robots or run manually by sprayers. These facilities apply abradable coatings, thermal barrier coatings, and various other types of deposits (either of metallic, ceramic, or organic nature) onto the engine components to be refitted.

The survey described in this article relates to this thermal spray workshop.

Components to be Sprayed. The components to be sprayed are delivered and stocked onto specific shelves inside the workshop for the smallest components, or onto pallets outside the workshop for the largest components. Their size varies from 25 mm to 1.2 m, whereas their weight varies from a few grams to 200 kg. The larger components are manipulated using hoists.

Sprayers. Nine sprayers work in the workshop in two teams: the first team works from 6:15 am to 2:15 pm, and the second team works from 2:15 pm to 10:15 pm, from Monday to Friday.

Spray Facilities. The workshop is outfitted with three spray booths (ranging from 60 to 75 m^3); two booths are fitted with robots, and the other booth is dedicated to manual spray operation.

Feedstock. The feedstock powders are stored in specific containers. In 1998, 6 metric tons were used and manually manipulated by sprayers when feeding the powder feeders. Particle size distribution ranges from approximately 5 to 100 μm.

3.2 Medico-Technical Prevention and Safety Measures

3.2.1 Collective Prevention. Several collective systems are installed to protect sprayers from potential and real encountered risks.

Ventilation. The workshop is outfitted with ventilation hatches located in the ceiling. The automated spray booths are connected to dry filtering systems. An external company is employed to clean the spray booth and to clean and maintain the dry filtering system; they also verify the efficiency of the filtering systems annually. The manual spray booth is connected to a wet filtering system. The particle dust collector is cleaned every 3 months, and the mud is recycled. Depressions are generated in the spray booths to keep the possible leaks at the lowest possible level. The system extracts 6000 $m^3 h^{-1}$ in each booth.

Noise. Noise emission is reduced by covering the spray booth walls and doors with 15 cm thick soundproof materials.

Gas Storage. Gas containers are stored outside the building in a dedicated area.

The tightness of the gas delivery lines is verified once a year, and each spray booth and spray controller is outfitted with hydrogen leak sensors.

Miscellaneous. The electric cabinets are controlled and grounded once a year by a specialized external company. The same procedure is applied to the robots. Moreover, a control of the external wasters is conducted following the ISO14001 standard.

3.2.2 Individual Prevention

Gas, Vapors, Dusts. The protective equipment used by manual sprayers are semidisposable masks (3M, St. Paul, MN)—6000 series, full face, low-maintenance respirators with P3-type filters. When cleaning the spray booths or filters, the workers wear semidisposable half face masks outfitted with an expiratory valve (3M, no. 9925).[20]

Noise. Silicone custom-made earplugs are used constantly by sprayers in the workshop. These plugs are outfitted with a specific filter permitting a sound attenuation, following ISO 4869-1 and -2 standard measurement protocols[21,22] between 27.4 and 36.9 dB, depending on the frequency, as listed in Table 6. Soundproof muffs are used by sprayers when they enter the spray booth. In the spray booth, the sprayers use a helmet to complement the custom-made plugs.

Table 6 Sound Attenuation Provided by Silicone Custom-Made Earplugs Worn by Sprayers in the Workshop (Measurement Performed Following ISO 4869-1[21] and 4869-2[22] Standards

Frequency, Hz	Average Attenuation, dB (A)
63	27.4
125	29.4
250	28.2
500	28.1
1000	29.7
2000	31.5
4000	36.9
8000	31.5

3.3 Risks Submitted to Medical Supervision

3.3.1 Noise. To assess diseases related to the inner ear, an audiogram is performed annually for each member of the spray team. The frequency of these checkups is defined by the occupational physician, depending on the level of exposure of the workers. The French Department of Labor (i.e., Ministère de l'Emploi et de la Solidarité[2]), following the L231.2 regulation,[3] [23] specifies, however, the general frame of the responsibility of the occupational physician.

3.3.2 Shift Work. Shift work induces sleeping troubles and can provoke tiredness and digestive problems. In France, shift workers are submitted to a specific medical supervision.

3.3.3 Respiratory Supervision

Introduction. This survey focused on the respiratory supervision of the sprayers because they are exposed to vapors and dust during their activities. The sprayers are thus subjected to potential respiratory risks. One third of the studied subjects are workers operating manual spray guns. The others rarely manipulate these guns and are more often assigned to the automatic systems. In this case, in particular, they are in charge of feeding the powder feeders, a task completed without wearing any respiratory protection. They are also in charge of loading and unloading the components to be sprayed inside the spray booths, which they enter also without wearing any respiratory protection. For these reasons, it was especially interesting to evaluate any potential bronchopulmonary impact on these subjects. For this study, the workers were subjected to a questionnaire and a spirometric study.

Studied Subjects. The studied population consisted of nine men whose biometric characteristics were the following: age, 35.0 ± 8.2 years; weight, 78.0 ± 14.4 kg; height, 174.0 ± 6.6 cm. The average length of service at the exposed positions is 9.60 ± 4.96 years. Nicotine addiction affected six subjects, with an average daily consumption of 4.40 ± 6.89 cigarettes. The survey was accomplished with subjects working from 2:15 to 10:15 pm.

[2]www.emploi-solidarité.gouv.fr/index.asp.

[3]Regulation defined in the labor act No. 82-1097, 23 December 1982, published in the "Journal Officiel" of the French Republic, 26 December 1982, complemented by the labor act No. 91-1414, 31 December 1991, published in the "Journal Officiel" of the French Republic, 7 January 1992.

Table 7 Spirometric Data at D1, D1 2h, and D4

D1

	Observed		Observed/Predicted	
Monday, 2:15 pm	**Average Value**	**Standard Deviation**	**Average Value**	**Standard Deviation**
VC (a)	4.47	0.75	0.94	0.06
FVC (b)	4.59	0.89	0.96	0.08
FEV1 (c)	3.83	0.80	0.97	0.09
FEV1/FVC	0.83	0.06	1.01	0.07
PEF (d)	8.25	0.96	0.88	0.11
MEF25 (e)	7.26	1.20	0.91	0.16
MEF50 (f)	4.96	1.33	0.95	0.22
MEF75 (g)	1.89	0.63	0.81	0.21
MEF25-75 (h)	4.76	1.14	1.04	0.23

D1 2 h

	Observed		Observed/Predicted	
Monday, 4:15 pm	**Average Value**	**Standard Deviation**	**Average Value**	**Standard Deviation**
VC	4.54	0.82	0.95	0.07
FVC	4.52	0.80	0.95	0.07
FEV1	3.87	0.77	0.97	0.08
FEV1/FVC	0.85	0.05	1.03	0.07
PEF	8.25	1.64	0.88	0.17
MEF25	7.60	1.60	0.95	0.19
MEF50	4.89	1.27	0.94	0.19
MEF75	2.05	0.77	0.87	0.23
MEF25-75	4.86	1.20	1.06	0.21

D4

	Observed		Observed/Predicted	
Thursday, 2:15 pm	**Average Value**	**Standard Deviation**	**Average Value**	**Standard Deviation**
VC	4.57	0.83	0.96	0.07
FVC	4.59	0.89	0.96	0.08
FEV1	3.85	0.80	0.97	0.09
FEV1/FVC	0.84	0.06	1.01	0.08
PEF	8.56	1.23	0.91	0.10
MEF25	7.56	1.50	0.94	0.17
MEF50	4.75	1.38	0.91	0.23
MEF75	1.88	0.69	0.81	0.23
MEF25-75	4.68	1.17	1.02	0.23

(a) VC, (expiratory) vital capacity, l
(b) FVC, forced (expiratory) vital capacity, l
(c) FEV1, forced expiratory volume in one second, l
(d) PEF, peak expiratory flow rate total, ls^{-1}
(e) MEF25, forced expiratory flow rate at the point that is 25% from the beginning of the FVC, ls^{-1}
(f) MEF50, forced expiratory flow rate at the point that is 50% from the beginning of the FVC, ls^{-1}
(g) MEF75, forced expiratory flow rate at the point that is 75% from the beginning of the FVC, ls^{-1}
(h) MEF25-75, maximal mid-expiratory flow rate, ls^{-1}
Note: The differences between D1, D1 2 h, and D4 were not significant at $p < 0.05$.

Experimental Protocols. The questionnaire used for this study was derived from a questionnaire established by the British Medical Research Council (BMRC)[4] in a simplified form. The questionnaire was oriented toward professional experience and respiratory disease. It relates to functional symptomatologies and the possibility of chronic bronchitis or asthma.[24-26] A functional respiratory test using spirometry (Fig. 9) was conducted for each subject. The first measurement was performed at the beginning of the work shift of the first day of the week (D1). Another measurement was made on the same day 2 h later (D1 + 2 h). Finally, a third measurement was made on the fourth day of the working week (D4) in the middle of the work shift (i.e., at 6:00 pm). The measurements (i.e., flow-volume curve) were performed using a Microspiro HI-501 spirometer from Essilor International (Saint Maur des Fosses, France).

The tests were carried out when the subject was upright, and the better of three consecutive measurements was taken into account; the two other measurements were discarded from the study. The parameters studied were as follows:

- (expiratory) vital capacity (in liters; VC), which is the maximum volume of gas that can be expired from the lungs during a relaxed expiration from a position of full inspiration;
- forced (expiratory) vital capacity (in liters; FVC), which corresponds to the maximum volume of air exhaled as rapidly, forcefully, and completely as possible from the point of maximum inhalation;

[4]www.mrc.ac.uk.

Fig. 9 Spirometric test

- forced expiratory volume in 1 s (in liters per second; FEV1), which describes the maximum exhaled flow rate measured over 1 s on forced expiration starting from full inflation of the lungs;
- FEV1/FCV ratio;
- peak expiratory flow rate (in liters per second; PEF), which is the greatest flow rate that can be sustained for 10 ms on forced expiration starting from full inflation of the lungs;
- forced expiratory flows at 25%, 50%, and 75% from the FVC (in liters), MEF25, MEF50, and MEF75, respectively;
- maximal mid-expiratory flow rate (in liters per second; MEF25-75), which is the average flow rate between the 25% level and 75% level of the observed FVC. This parameter is also known as the MEF25-75.

The measured values are expressed in body temperature pressure saturated (BTPS) units and compared with the predicted values from the European Community of Coal and Steel (ECCS)[5] standards.

[5]During its 40 years of existence, ECCS research has supported the efforts of the coal and steel industry by increasing research efficiency, enabling the coal and steel industry jointly to tackle large projects that could not have been carried out by individual companies, and creating through the Member States a network of researchers through which there is an effective exchange of information related to multi-partner multinational projects.

These values are considered as pathologic when they are lower than 80% compared to the reference values.[27]

Results. From the answers collected from the questionnaire, functional pulmonary problems were detected for two sprayers who were smokers; they experienced early morning expectoration. These signs, however, do not correspond to the chronic bronchitis symptoms. Dyspnea appearing from rapid walking was found also in three sprayers; two of them were smokers. The third subject had pulmonary tuberculosis in 1978 that was cured by selected treatments. This subject was not discarded from supervision. Without any incidence that affected the respiratory function, and because of a failure of the disposable respiratory masks that induced accidental inhalation of powder particles, two subjects suffered a few years ago from slight pharyngeal burns.

The analysis of the questionnaire was completed by study of the systematic annual pulmonary radiography, which revealed no disorder for any of the subjects.

The results revealed that the subjects showed no spirometric disorders; the observed compared with the theoretical value ratios were higher than 80% for each of the studied average parameters. The same analyses performed for each subject (data not shown) did not reveal any disorders; the ratios were always higher than 80%.

Nevertheless, the analysis of the individual cases clearly indicates a tendency toward a decrease of the FVC, FEV1, and MEF25-75 values between D1 and D1 + 2 h. However, the observed variations are approximately 10 and 300 ml, which can be considered as negligible in a first approximation.

At D4, several measured values could reflect the effect of accumulated exposure during the working week. However, once again in this case, the calculated average ratios were higher than 80%, which allowed us to conclude that no significant spirometric disorder existed.

The student *t*-test performed on the results at D1, D1 + 2 h, and D4 did not reveal any significant statistical difference for $p < 0.05$.

Analysis. This study was performed on a small group of subjects. This does not allow an epidemiological approach of the question, and the results cannot be generalized, but they remain of prime interest from the medical point of view.

The spirometric data at D1 result from the cumulated variations during the previous years, months, and days, but also from the possible recovery after two days of non-exposure (D1 corresponds to Monday, first day of the working week). In such a way, if the results collected at D1 are considered to be the result of a possible chronic effect, there is no argument to conclude the influence of the exposure.

The same conclusion comes from the comparison of the results between D1 and D1 + 2 h, for which significant differences could be interpreted as the effects of a severe respiratory malfunction.

Finally, the same conclusion also comes from the comparison of the results between D1 and D4, for which significant differences could reflect the effect of a weekly exposure.

The effectiveness of respiratory protection is clearly demonstrated from the spirometric analysis. The result of these investigations agrees with the answers given by the subjects on the questionnaire, medical supervision, and radiological analysis.

However, this conclusion has to be balanced by the fact that the accumulated average exposure of the subjects remains rela-

Peer Reviewed

tively short (9 years) and that a small effect on the spirometric tests could be hidden by a training phenomenon that results from repetitive tasks.

4. Conclusion

The role of occupational medicine is of prime importance in prevention. In fact, the number of sprayers in the company remains relatively small but is continuously increasing. This does not allow us to conclude the absence of effects of feedstock used on the pulmonary function of the exposed subjects; the occupational physician is too closely involved for a proper view of the cumulative effects of the several materials. The physician must remain vigilant to ensure a rigorous medical supervision of these subjects.

The potential risks encountered in thermal spraying may still be significant because they were mainly studied through data available in literature and a survey conducted in only one company. To identify more precisely the reality of the respiratory risks, a study on a larger scale should be undertaken. However, the question remains about whether it is pertinent to carry out such an epidemiological study because the reality of the risks is not obvious. To try to answer such a question, the protocol developed in this survey should be extended to other companies using thermal spray technologies.

References

1. Y.M. Yang: "Modélisation Mathématique d'un Système de Projection Thermique à la Flamme de Type HVOF: Application à L'élaboration de Revêtements Protecteurs," (Mathematical Modeling of a HVOF Type Thermal Spray System: Application to the Manufacturing of Protective Coatings), Ph.D. Thesis, Université de Franche-Comté, France, 1996 (in French).
2. R. Lauwerys: *Toxicologie Industrielle et Intoxications Professionnelles* (Industrial Toxicology and Occupational Intoxications), Editions Masson, Paris, France, 1992 (in French).
3. J.M. Haguenoer and D. Furon: *Toxicologie et Hygiène Industrielles* (Toxicology and Occupational Hygiene), Vol. 2, LaVoiser, Paris, France, 2000, pp. 275-321 (in French).
4. N. Rosenberg, X. Rousselin, and P. Gervais: "Allergie Respiratoire Professionnelle au Nickel" (Occupational Respiratory Allergy to Nickel), *Documents pour le Médecin du Travail*, 1989, *38*(2), pp. 143-46 (in French).
5. F. Testud: *Pathologie Toxique en Milieu du Travail* (Hazardous Disease in Occupational Activities), Editions ESKA, Paris, France, 1998, pp. 112-54 (in French).
6. Anon: *NIOSH Pocket Guide to Chemical Hazards for Nickel Metal and Other Compounds,* NIOSH Publications, (as Ni at www.cdc.gov/niosh/npg/ngpd0445.htm).
7. B. Swennen, J.P. Buchet, D. Stanescu, D. Lison, and R. Lauwerys: "Epidemiological Survey of Workers Exposed to Cobalt Oxides, Cobalt Salts and Cobalt Metal," *Brit. J. Ind. Med.*, 1993, *50*(9), pp. 835-42.
8. N. Rosenberg: "Asthme, Alvéolite, Fibrose Pulmonaire dans L'industrie de L'aluminium et de Ses Sels," (Asthma, Alveolitis, Pulmonary Fibrosis in the Industry of Aluminum and Its Salts), *Documents pour le Médecin du Travail*, *46*(2), 1991, pp. 107-12 (in French).
9. Anon: "Valeurs Limites d'Exposition Professionnelle aux Agents Chimiques en France," (Occupational Exposure Limit Levels to Chemical Products in France), Cahier de Notes Documentaires, *Hygiène et sécurité au Travail*, Pub. INRS, Paris, France, 1999, *174*(1), pp. 59-77 (in French).
10. Hazardous Chemical Database (at ull. chemistry.uakron.edu/erd/).
11. B. Nemery: "Principes de Toxicologie Pulmonaire" (Pulmonary Toxicology Principles) in *Encyclopédie Médico-Chirurgicale-Pneumologie, 6*(019-A-38), 1994, pp. 1-8 (in French).
12. R. Bolot, C. Coddet, and M. Imbert: "On the Use of a Low-Reynolds Extension to the Chen-Kim k-ε Model to Predict Thermal Exchanges in the Case of an Impinging Plasma Jet," *Int. J. Heat Mass Transfer*, 2001, *44*(6), pp. 1095-106.
13. R. Bolot, M.P. Planche, and C. Coddet: "Modeling of the Natural Gas HVOF Process" in *Thermal Spray 2001: New Surfaces for the New Millennium,* C.C. Berndt, K.A. Khor, and E.F. Lugscheider, ed., ASM International, Materials Park, OH, 2001, pp. 911-16.
14. Anon: *Note Technique sur la Métallisation par Projection Plasma, Risques et Prévention* (Technical Memorandum on Plasma Spraying, Risks and Prevention), Institut National de la Recherche sur la Santé/CRAM Ile de France, Paris, France, 1993 (in French).
15. G. Hee, I. Balty, A. Mayer, D. Courant, and M. Lievre: "Les Lasers, Risques et Prévention" (Lasers, Risks and Prevention), *Cahier de Notes Documentaires, Hygiène et Sécurité au Travail*, INRS, Paris, France, *173*(4), 1998, pp. 445-63 (in French).
16. C. Coddet, G. Barbezat, P. Fauchais, and G. Montavon: "La Projection Thermique et les Revêtements épais" (Thermal Spraying and Thick Coatings) in *Revêtements et Traitements de Surface: Fonctionnalités, Durabilité, Procédés,* S. Audisio, M. Caillet, A. Galerie, and H. Mazille, ed., Presses Polytechniques et Universitaires Romandes, Lausanne, Switzerland, 1999, pp. 467-93 (in French).
17. H. Desoille, J. Scherrer, and R. Truhaut: *Précis de Médecine du Travail* (Occupational Medicine Handbook), Editions Masson, Paris, France, 1980, pp. 696-97 and 856-57 (in French).
18. Anon: AFNOR NF EN 775 Standard, "Robots Manipulateurs Industriels—Sécurité" (Industrial Robots—Safety), AFNOR, La Plaine Saint Denis, France, 1993 (in French).
19. Anon: ISO 10218 Standard, "Manipulating Industrial Robots —Safety," ISO, Genève, Switzerland, 1992.
20. P. Hure: "Les Appareils de Protection Respiratoire" (Protective Respiratory Apparatus), *La Ligne Prévention,* INRS, Paris, France, No. ED780, 1998 (in French).
21. ISO 4869-1 Standard, "Acoustics—Hearing Protectors, Part 1: Subjective Method for the Measurement of Sound Attenuation," 1990.
22. ISO 4869-2 Standard, "Acoustics—Hearing Protectors, Part 2: Estimation of Effective A-Weighted Sound Pressure Levels When Hearing Protectors Are Worn," ISO, Genève, Switzerland, 1994.
23. Anon: L231.2 Regulation From the French Ministry of Labor, Paris, France at www.afaqap.org/jpsadh/article_I231.htm
24. F.J. Chicou, S. Pedrizet, and J. Rochemaure: "Les Grandes Règles du Questionnaire épidémiologique" (The Major Rules of the Epidemiological Questionnaire), *Revue Française des Maladies Respiratoires*, 1977, *5,* pp. 37-44 (in French).
25. G. Letourneau, F. Turcotte, C. Lapointe, C. Boulenguez, M. Romon, and P. Frimat: "Utilisation Sérielle d'un Questionnaire Respiratoire Normalisé et de la Spirométrie Auprès de Travailleurs Exposés aux Irritants Respiratoires" (Use of a Normalized Respiratory Function Investigation in Workers Exposed to Respiratory Irritants), *Archives de Maladies Professionnelles*, 1987, *48*(5), pp. 369-74 (in French).
26. G. Debaisieux: "Enquête Respiratoire dans une Usine D'engrais Ammonitrés" (Respiratory Survey in Company Producing Ammonia-Nitrated Fertilizers), M.D. Thesis, Université de Lille, France, 1987 (in French).
27. A. Pedrix, *Guide Pratique D'exploration FonctionnelleRespiratoire–Utilisation en Milieu Professionnel* (Practical Guidebook of Functional Respiratory Investigation–Use on Occupational Environment), Editions Masson, Paris, France, 1994 (in French).