Chapter 9

What are the Health Risks of Occupational Exposure to Adhesive in the Shoe Industry?

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/64936

Abstract

The term "shoe" covers a wide range of products made from various materials. Organic solvents (OS) are components of various products such as the adhesives which are used in many industries. The shoe industry consumes large amounts of adhesives. This chemical risk assessment (CRA) is to validate the hypothesis of decreasing gradient of RA craft enterprises to industrial enterprises through the semi-industrial. The simplified methodology CRA of INRS was applied. For each chemical, a hazard class is assigned based on the sign, and then the potential exposure class is determined according to parameters "quantity and frequency of use". Our RA process is complete with ambient measurements for solvents to which employees are most frequently exposed. Adhesives being constituted as solvent mixture, we have conventionally used an exposure index which is compared with the limit values. The simplified method CRA of INRS was chosen because it is one of the reference methods in RA established from the Kinney model. If these atmospheric samples and toxicology tests were made for the first time in the shoe industry in Sfax, they concerned a sample of companies of the three shoe manufacturing processes preceded by a preliminary RA with post-study and inventory of products handled.

Keywords: risk assessment, chemical risk, shoes manufacturing, organic solvents, adhesive, occupational health

1. Introduction

The term "shoe" covers a wide range of products made from various materials. Boots, shoes, sandals, slippers, clogs, and others are made entirely or in part with leather, rubber, synthetic and plastic, cloth, rope, and wood [1]. Our study deals with the shoe industry, that is to say one based on traditional manufacturing methods. The rubber boots factory (or equivalent synthetic materials), which is one of the branches of the rubber industry, is excluded from this study [1, 2].

Shoes, boots and leather sandals, felt, or other materials have been for century's hand. Quality shoes are still made entirely or partly in this way by craftsmen, but in all industrial countries, today the mass production predominates [2, 3].

Organic solvents (OS) are components of various products such as paints, inks, pesticides, degreasers, solvents, and glues, which are used in many industries [1]. The shoe industry consumes large amounts of adhesives, diluents, and strippers OS bases. Consequently, the employees in this sector are likely to present particular nerve pathologies [2].

2. History of the shoe in the Sfax city

Sfax is an industrial and agricultural pillar of the Tunisian economy [4]. Among its industries, shoemaking is highly developed sector, which employ about 10000 employees or 10% the workforce of the nonagricultural professional environment which 6000 artisans' shoes located in the old city "the Medina."

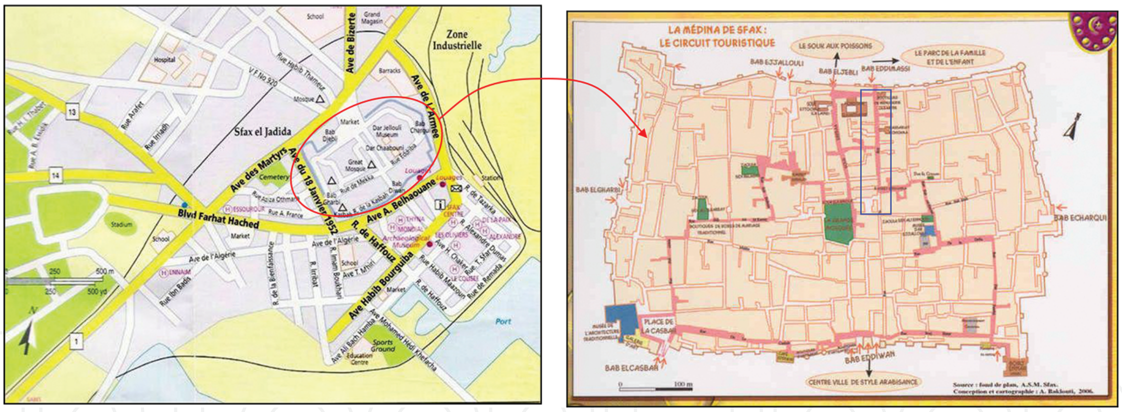

Figure 1. Map of (a) the center of Sfax city and (b) the old town of Sfax.

As in many cities, Sfax had a craft of the shoe. But in addition, Sfax was a shoe industry. The manufacture of the shoes to form Sfax "industrial" dates back to the nineteenth century. It was well structured in the Medina in the shoe area called "Souk Blaghgias." It consists of the main street shoes exhibition: The current street Mongi Slim known under its former name "Street of Bay." Until now, along this road for approximately 300 m shoe shops displaying their products. In the level one called "the Ally" in every store or in the neighboring streets were their own manufacturing facilities.

In 1960, after independence, observers were predicting the rapid decline and disappearance of the craft before the competition of the modern shoe industry. Now, after more than 30 years, this craft, far from having disappeared, has prospered and it feeds today, modern shoes, more than half of the Tunisian market. The artisan district of the boot has grown in the old town of Sfax; we hear all the noise of machines whose artisans are equipped to modernize the sensitive points of their manufacturing (**Figure 1**) [4].

3. Manufacturing processes of the shoe

The realization of a shoe includes several operations. Each step has been mechanized, but the manual production is used as reference. The introduction of new materials has modified manufacturing processes without changing the outline [1, 2].

The manufacture of rods requires sorting and preparation of leather or other materials. The stems are cut with cutters on stitching presses (or burning). The various parties, including the linings, are then "assembled," that is to say, stitched or glued together. Perforation, eyeletting, or making buttonholes are the procedures carried out further.

In the lower part, the outer and inner soles, heels and welts are cut using cutters to moving blades or molding presses. It manufactures heels compressing leather or wooden slats. The assembly is then cut, formed, cleaned, and labeled.

The upper and lower parts of the shoe are then assembled and then stitched, glued, nailed, or screwed together. After that the shoes are shaped and smoothed by means of rollers. The finishing of the shoe includes waxing, staining, spraying, polishing, and packaging.

Among the raw materials used in manufacturing, adhesives, including adhesive solids and liquids and natural adhesive solutions prepared from organic solvents, represent the largest occupational hazards [3].

4. The basic products used in the shoe industry

In the industry of the adhesive and its derivatives, products intended for the manufacture of the shoe are divided into three groups [2, 5–11]:

- Four groups of adhesive,
- Primers, hardeners, and additives,
- Solvents, thinners, and strippers.

4.1. Four groups of adhesive (Table 1)

- The polyurethane (PU) adhesive is used for assembling thermoplastic rubber soles (TR), rubber, polyvinyl chloride (PVC), leathers high in fat or synthetic fabrics requiring the use of high-performance adhesives.

- The polychloroprene adhesives (neoprene) are used for making coatings soles, fast repair, and bonding of natural materials (leather, rubber). They are made from synthetic resins dissolved in ketone solvents.
- The adhesives in aqueous emulsion (latex adhesives or white glues) may be natural or synthetic:
  - Natural latex adhesives are applied by machine gun or by hand. These are contact adhesives to attach soles, stitching, and lining.
  - The synthetic latex adhesives are used for laying the ends and bonding liners.

Products	Composition	Use
Polychloroprene adhesives (neoprene) Implemented by contact with the following: – Coating the two sides to stick, – Respect the drying time (in ways that the two adhesive films release their solvents) – Assembly of parts (pressure) after reactivation	– Solids based on polychloroprene (15–30%) depending on use – *Organic solvents* (mixture): the most used are, by decreasing importance order: * MEK * Gasoline C (up to 30% hexane) * Acetone * Ethyl acetate * Toluene * Cyclohexane * The alcohols and chlorinated hydrocarbons (*little used*)	– Welded shoe soles
The polyurethane adhesives (PU)		
1. based polyurethane elastomers	Polyvinyl chloride Elements (PCV) – Solids of polyurethane elastomers – *Organic solvents*: mixture * Ketones and / or * Overheads	– Contact adhesive which is taken after solvent evaporation
2. Two-component	*Part A:* – Polypol (polyester or polyester) – *Organic solvents* (mixture) : * Ketones and / or * Overheads	Very flexible assemblies The mixture of A with B is carried out at the time of use – The adhesion is after solvent evaporation

Products	Composition	Use
	Part B: – Isocyanate prepolymers (small amount of free isocyanate: Ex diphenylmethane diisocyanate ….)	
Adhesives in aqueous emulsion: latex adhesives or white glues	– Solids (40–60% may be: * Vinyl acetate * polyisoprene * Acrylic polymers * Copolymers: acrylic, isoprene, chlorobutadiene * polyurethane – *Solvents:* * In general: WATER * Optionally and low proportions: – Alcohol – Other solvents	– Installation of liners: manual application by simply coating and touch – Water evaporation Making contact
Hot melt adhesives or "hot melt" *Equipment cadence "very expensive"*	Copolymer Ethylene-vinyl acetate ± possibly: plasticizers or antioxidants	Applying on one of the faces to be bonded by a polymer melt temperature rise

Table 1. The basics products in the shoe manufacturing (part welded) [11].

The hot melt adhesive is a new generation of glue developed in order to reduce the use of solvents. It consists in applying on one of the faces to be bonded by a polymer melt temperature rise. It requires clock equipment which is expensive.

4.2. Primers, hardeners, and additives

- The halogenations operation of TR soles with new functions (rubber look and matt or transparent), must be strictly control any change of model. There are several formulas ready to use (one or two components) for receiving an additive to control the regular application on the soles.
- Catalysts, slow or fast, are used in polyurethane adhesives, polychloroprene or dispersion, as well as direct injection. They provide good resistance to the migration of fat leathers.

4.3. Solvents, thinners, and strippers

Beside adhesives preparations, there are other necessary preparations and complementary type of strippers, thinners, and solvents (**Table 2**).

Preparations	Applications and examples
The cleaning agent	– PU soles: remove traces of mold release agent ; – PCV soles: remove surface plasticizer contained in PCV compounds
The diluents	– Dilute polychloroprene adhesives ; – Clean the machine to glue and brushes, spray guns stained with paint, screens for screen printing ink
The solvents	– Clean the rubber soles, spray guns stained with paint, screens for screen printing ink; – Dilute paints and glues.

Table 2. Other preparations used in the manufacture of shoes [13].

5. Risks of the solvents and the adhesives on the health

According to their properties, the solvents can be used in the manufacture of the shoe, of:

- Degreasing (cleaning soles, textiles…)
- Additives and solvents (paints, varnishes, inks, adhesives…)
- Stripping (removal of paints, varnishes, glues…)

OS hydrocarbons are divided into eight main groups [12–14]. Six families are used in the manufacturing industry adhesives and footwear (**Table 3**).

The intensive use of flammable liquids causes a high risk of fire, and the widespread use of presses and assembling machines has increased also the risk of accidents. The main danger to the health of workers is using toxic solvents, high concentrations of dust in the air, the risks due to ergonomic shortcomings, and noise from machinery.

OS can cause acute and chronic effects on the central nervous system. Benzene, which was once used in adhesives and solvents, has been replaced by toluene, xylene, hexane, methylethylketone (MEK), and methylbutylketone. The n-hexane and MEK can cause peripheral neuropathy and should be replaced by heptane or other solvents [2].

In many factories, there were outbreaks of a disease known as the "paralysis of the shoemaker" and characterized by clinical signs of a form of more or less serious paralysis. This is a flange type of paralysis, located in the upper and/or lower limbs resulting in deep tendon atrophy with areflexia, without altering the superficial or deep sensitivity. From the clinical point of view, this syndrome is due to an inhibition or a functional lesion of the lower motor neurons of the voluntary motor system (pyramidal system). Most often, it leads to a neurological regression with extensive proximodistal functional recovery [1, 2].

Groups of solvents	Applications and examples
Aromatic hydrocarbons	Homologues of benzene (toluene, xylenes, ethylbenzene …) are used as lacquer thinners, adhesives and inks.
Petroleum solvents	Used as solvents in paints, adhesives and coatings: – **Alkanes** such as **hexane (C6H14)**; – **Cycloalkanes**: The most used is **cyclohexane (C_6H_{12})**
Alcohols	Very used as **diluents** inks, resins, varnishes, paints and **glues**. These are excellent dehydrating agents having good degreasing Action Example: **isopropanol** (or isopropyl alcohol).
Ketones	Mainly used as solvent paints, lacquers, varnishes, glues and adhesives. They are sometimes impregnated on wipes for small cleaning. They are good agents drying damp rooms. The most commonly encountered are: **acetone** or **MEK**.
Acetates (esters)	Often mixed with other solvents, for example, in the curing products and halogenation
Halogenated hydrocarbons	Used as diluents **glues**, **adhesives**, paints. Examples: **Trichloroethylene** (degreaser leather, thinner glue) or **dichloromethane** (thinner adhesives and cleaner)

Table 3. The families of solvents used in the manufacture of adhesives and shoes [13, 15].

In the manufacture of shoes and boots, handling and leather processing can cause diseases by exposure to certain chemical substances mentioned above and in tanning and finishing. In addition, various chemicals can produce other diseases. Exposure to toxic solvents contained in adhesives and cleaning products, and to leather dust in the air is of particular concern. The use of benzene can cause thrombocytopenia (decreased number of red blood cells, platelets, and white blood cells in the blood) or pancytopenia. It has been almost eliminated from the footwear industry [3]. It was also found in some shoe factories cases of peripheral neuropathy due to n-hexane content in adhesives. This substance has also been largely replaced by less toxic solvents. Cases of electroencephalographic changes, liver damage, and behavioral alterations due to exposure to solvents have been reported in workers in the shoe industry [3].

6. Occupational chemical risk in shoe industry in Sfax

6.1. Methods

The prevention of occupational risks, particularly chemicals, is based on the risk assessment (RA) according to the specified procedures. Thus, we realized an exposure assessment in making shoes in a sample of volunteer companies (**Table 4**).

This chemical risk assessment (CRA) aims to validate the hypothesis of decreasing gradient of RC craft enterprises to industrial enterprises in passing by semi-industrial. The simplified assessment methodology for chemical risk (SAMCR) of National Institute of Research and Safety (INRS) [15] was applied only for strand "Health." For each chemical, a hazard class (HC) is assigned based on the sign, and then the potential exposure class is determined based on the parameters "amount and frequency of use."

Process	Industrial	Semi-industrial	Artisanal
Number of companies	4	5	9
Equipment used	Mechanization *(workflow)*	Mechanization and manual	Manual
Number of employees	>20	[10–20]	<10
Installation location	IZ	IZ or Medina	Medina

IZ: industrial zone.

Table 4. Business definition.

	Hazard Class	1	2	3	4	4 ou 3
	Pictogram	None	Xi-Irritant	Xn-Harmful	T-Toxic	Not identified Not identified
Unidentified product	Not identified Glue			Xn-Harmful		
	Not identified Solvent			Xn-Harmful	T-Toxic	

Table 5. Hazard classes depending on the labeling [13–15].

The HC was determined only on the labeling. The allocation of HC to a preparation based on the analysis of the pictogram on the packaging (**Table 5**). For preparations of glues or solvents "unidentified" (no information on the composition and/or the manufacturing company), it was decided that the assigned pictogram would be one that represents the greatest health risk and consequently the HC."

Figure 2. Atmospheric sampling (a) "individual" and (b) "stationary."

Solvent	CAS[1]	la France (EU[2]) VEA[5]		USA (ACGIH[3]) TLV-TWA[6]		Germany (MAK[4])		Our Study (Sfax—Tunisia) EAV adopted	
		ppm[7]	mg. m^{-3}	ppm	mg. m^{-3}	ppm	mg. m^{-3}	ppm	mg. m^{-3}
Acetone	67-64-1	500	1210	500	–	500	1200	**500**	**1200**
Cyclohexane	110-82-7	200	700	300	–	200	700	**200**	**700**
n-Hexane	110-54-3	20	72	50	–	50	180	**20**	**72**
Methylethylketone (MEK, 2-butanone)	78-93-3	200	600	200	–	200	600	**200**	**600**
Toluene	108-88-3	50	192	50	–	50	190	**50**	**190**

[1]CAS: Chemical abstract service.
[2]EU: European Union.
[3]ACGIH: American Conference of Governmental Industrial Hygienists.
[4]MAK: Maximum Arbeitsplatz-konzentration.
[5]EAV: Exposure average value calculated over a reference period of 8 hours.
[6]TLV-TWA: Time-weighted average (weighted average values of 8 hours per day and 40 hours per week).
[7]ppm: Parts per million per volume of air.

Table 6. Values of atmospheric exposure limits [17].

- *Unidentified glue:* The glue most dangerous to a symbol "Xn-Harmful" [5, 11] for the health and attributed HC is "3." Thus, any unidentified glue the symbol "Xn-Harmful" and "3" class was assigned.
- *Unidentified solvent (solvents, thinners, and strippers):* Two hypotheses "HC" were individualized [11, 13–15]:

- Let the symbol "T-Toxic" and class "4," the highest existing level;
- Let the symbol "Xn-Harmful" and "3" class more realistic for the majority of solvents.

Solvents	Identification	Chemical substance	Use	Nature	Pictogram	Hazard class
Acetone		Acetone		Ketones	Xi-Irritant	**2**
Alcohol	Isopropyl alcohol (IPA)	Isopropyl alcohol	Paint solvent	Alcohol	Xn-Harmful	**3**
Asouplex	Stripper	Acetone MEK +	Soften the "strong against Calorex"	Ketones	Xi-Irritant	**2**
Stripper		Methylene chloride (2%) in MEK	Washing, sole preparation (PU, PVC)		Xn-Harmful	**3**
Desmodur	DESMODUR RC	TDI (5%) in Ethyl acetate	Diluent PU glue		Xi-Irritant	**2**
Durcisseur	DESMODUR RC				Xi-Irritant	**2**
Diluent	Solvent mixture	Toluene (100%)	Thinner neoprene glue	Aromatic hydrocarbons	Xn-Harmful	**3**
PA	IPA			Alcohol	Xi-Irritant	**2**
Halogenation product		98% Ethyl acetate	Surface preparation sole	Acetates	Xi-Irritant	**2**
Flexibility	ASOUPLEX			Ketones	Xi-Irritant	**2**
Supersouple	ASOUPLEX			Ketones	Xi-Irritant	**2**
Tucosolve	Stripper	MEK, AE, Cyclohexane			Xn-Harmful	**3**
Bidonplaste ***Elaste*** ***Special ink*** ***Solvent not defined***	**Not identified**	Solvent mixture			**Xn-Harmful** or **T-Toxic**	**3** or **4**

Table 7. Inventory preparations "solvent" used in the footwear industry and hazard class.

Our approach to RA is complete, and ambient measurements [16] (**Figure 2**) for solvents (acetone, cyclohexane, n-hexane, MEK, toluene) to which employees are more frequently exposed are taken.

Adhesives being constituted as solvent mixture, an exposure index (I.exp) was used and compared with the limit values (**Table 6**) [17, 18]:

$$I.exp = C1 / EAV1 + C2 / EAV2 \ldots + Cn / EAVn \quad (1)$$

Cn and EAVn are respectively the concentration and the average value of n pollutants exposure.

If I.exp is greater than 1, the limit value is considered outdated. Calculated from stationary sampling, this index is called pollution index (I.pol).

6.2. CRA

However much the manufacturing process, the inventory of solvent borne formulations showed HC "2" and "3". When the unidentified preparations, they were classified "3" or "4" (**Table 7**). For the 23 identified glue preparations, HC ranges from "1" to "3" (**Table 8**).

The potential risk score (PRS) process "industrial" 2 in case of danger class puts 13 chemical preparations to examine with high priority, including five of solvent preparations. For the HC "3," PRS do not exceed "10000," while with the hazard class "4" three of five solvent borne preparations pass a PRS 100000.

The situation of distinction for a process "semi-industrial" does not arise since we did not detect unidentified preparations. The preparations to consider with high priority are 2 solvents and 5 adhesives unidentified.

In the "artisanal" process, we have identified eight chemical preparations to examine with high priority: two solvents borne preparations and six adhesives.

Glues	Identification	Chemical substances	Use	Nature	Pictogram	Hazard class
110/Textile glue	Rubber 110F	Natural rubber, hexane, petroleum resin	Provisional or final bonding of leather fabric (handcrafted process)	Polychloroprene	Xn-Harmful	**3**
420	Ceylanprène 420	Polycholoroprène, cyclohexane, hexane, MEK, Resin (phenol, phenol terpene), Toluene	Bonding the leather	Polychloroprene	Xn-Harmful	**3**
425S	Ceylanprène 425	Polycholoroprène, cyclohexane, hexane, MEK, Resin (phenol, phenol terpene), Toluene	Bonding the leather	Polychloroprene	Xn-Harmful	**3**
715			Bonding the	Polychloroprene	Xn-Harmful	**3**

Glues	Identification	Chemical substances	Use	Nature	Pictogram	Hazard class
			leather			
945			Bonding the leather	Polychloroprene	Xn-Harmful	**3**
C3			Bonding the leather	Polychloroprene	Xn-Harmful	**3**
C4			Bonding the leather	Polychloroprene	Xn-Harmful	**3**
Calorex	Calorex	Polycholoroprène, cyclohexane, hexane, MEK, Resin (phenol, phenol terpene) on a ribbon	Polyester fabric coated with an adhesive	Polychloroprene	No	**1**
CD11			Gluing soles	Polyurethane	Xi-Irritant	**2**
CN13			Bonding the leather	Polychloroprene	Xn-Harmful	**3**
White glue	Glue "Latex"	Synthetic or natural rubber in an aqueous phase	For bonding wood heel	Aqueous emulsion	No	**1**
Yellow glue	Neoprene glue			Polychloroprene	Xn-Harmful	**3**
Colle neoprene	Neoprene glue			Polychloroprene	Xn-Harmful	**3**
Vinyl glue	Ex: R10	Polymer of vinyl acetate, acrylic polymer, water	Manufacture of the shoe	Aqueous emulsion	No	**1**
D1			Gluing soles	Polyurethane	Xi-Irritant	**2**
Forestali/ICF			Gluing soles	Polyurethane	Xi-Irritant	**2**
Plastipole	Polyurethane glue		Gluing soles	Polyurethane	Xi-Irritant	**2**
Polyurethane	Polyurethane glue		Gluing soles	Polyurethane	Xi-Irritant	**2**
Could	Polyurethane glue		Gluing soles	Polyurethane	Xi-Irritant	**2**
Tucoplast	Polyurethane glue		Gluing soles	Polyurethane	Xi-Irritant	**2**
UF43	Plestiprene	Polyurethane,	Gluing	Polyurethane	Xi-Irritant	**2**

Glues	Identification	Chemical substances	Use	Nature	Pictogram	Hazard class
	UF43	ethyl acetate, acetone, MEK, Toluene	soles			
Colle geant ***Precision without glue***	**NOT IDENTIFIED**	**Solvent mixture**			**Xn-Harmful**	**3**

Table 8. Inventory preparations “glues” used in the footwear industry and hazard class.

6.3. Atmospheric measurements

Measurements of atmospheric concentrations (**Table 9**) show high levels especially in companies with semi-industrial process and type 1 craft.

Process		**Business**	**Number of workstation**	**Personal sampling**			**Atmosphere sampling**			
				Exposure index*			**Pollution index****			
				Not	**Scope**	**Average**	**Not**	**Scope**	**Average**	
Industrial		Industrial 1	5	3	0.3–1.1	0.7	2	0.5–0.8	0.6	
		Industrial 2	2	1	–	1.8	1	–	0.3	
		Industrial 3	5	4	0.9–9.4	3.7	1	–	0.8	
		Industrial 4	5	4	0.8–19.8	6.8	1	–	0.0	
Semi-industrial		Semi-industrial 1	5	3	0.4–1.2	0.7	2	0.0–0.3	0.1	
		Semi-industrial 2	5	4	0.5–2.0	1.0	1	–	0.4	
		Semi-industrial 3	4	2	0.2–2.5	1.3	2	0.2–0.4	0.3	
		Semi-industrial 4	5	4	0.9–2.4	1.7	1	–	0.1	
		Semi-industrial 5	4	1	–	5.6	3	4.3–8.8	6.8	
Artisanal	**Type 1**	Craft 1	2	1	–	0.1	1	–	0.4	
		Craft 2	1	/			1	–	0.7	
		Craft 3	1	/			1	–	0.8	
		Craft 4	3	2	0.4–1.7	1.1	1	–	1.6	
		Craft 5	2	1	–	1.5	1	–	0.9	
		Craft 6	2	2	1.6–3.4	2.5	/			
		Craft 7	2	1	–	6.4	1	–	5.1	
		Type 2		Craft 8	1	/			1	−0.5
Craft 9	1	/			1	–	0.6			
Total = 33						**Total = 22**				

Table 9. Atmospheric exposure of employees by industrial trial.

Stages of production	Sources of pollution
1. Individual sizing	Solvent vapor:
Post "UPPER PART MAKER"	– Glue container in use
	– Piece glued
	– Materials used for coating (pre-sizing operation)
2. The preparation of surfaces prior	– Clean and degrease the parts to be assembled (brush, cloth)
to bonding	– Washing of soles
Post "SOLE MAKER"	– Halogenation: Treatment of some soles (rubber)
3. Drying	Objects are placed in general on fixed or movable shelves near collages positions
4. Finish	– Cleaning after bonding to remove excess glue
	(solvent-soaked rag)
	– Coloring and application of polish (usually by spraying)
5. Cleaning equipment	Brushes and accessories: With solvents
6. Fractionation and storage	Adhesives wholesale packaging: A transfer in small containers used in gluing
"Decanting" preparations	station

Table 10. The steps of the shoe manufacturing (the welded Technique) and sources of pollution [11].

Exceedances of I.exp and/or I.pol are noted for exhibitors' positions including the upper part makers, smelters and finishing (**Table 10**) within three manufacturing processes (**Table 11**).

All measurements in different companies show that exposure to OS varied from one process to another and from one position to another (**Table 12**). The average atmospheric concentrations of hexane are particularly high, especially with the exposure average value (EAV) which overruns the position of the upper part maker, the sole maker, and finishing in all production processes except the process artisan type 2. The other solvents (acetone, cyclohexane, MEK, and toluene) are relatively high without exceeding the EAV.

6.4. Comments and discussion

Despite significant exposures to solvent-based preparations, an almost total lack of use of personal protective equipment such as gloves, masks, and goggles by the manipulators of the adhesives formulations and/or solvents was noted. The equipment of rooms by adequate ventilation is not rated very often, while the Tunisian regulations require companies to preserve human capital and implement a preventive political.

Process	Post working		Number of workstation	Personal sampling Exposure Index			Atmosphere sampling Pollution Index		
				levies	scope	average	levies	scope	average
Industrial		**Chopped off**	1	/			1	-	0.0
		Quilting	1	/			1	-	0.8
		Upper part maker	4	3	0.9 to 19.8	8.4	1	-	0.5
		Sole maker	7	5	0.3 to 3.5	1.5	2	0,3 - 0,8	0.5
		Finish	3	3	0.9 to 1.8	1.2	/		
		Serigraphy *(Woman)*	1	1	-	9.4	/		
Semi-industrial		**Upper part maker**	8	4	0.5 to 2.5	1.6	4	0.1 to 7.2	2.5
		Sole makers	12	10	0.2 to 5.6	1.8	2	0.2 to 8.8	4.5
		Finish	3	/			3	0.3 to 4.3	1.7
Artisanal	**Type 1**	**Upper part maker**	5	2	0.1 to 1.6	0.9	3	0.9 to 5.1	2.5
		Sole makers	8	5	0.4 to 6.4	2.7	3	0,4 - 0,7	0.6
	Type 2	**Upper part maker / Sole makers**	2	/			2	0.5 to 06	0.6
				Total = 33			**Total = 22**		

Type 1: The positions of Upper part maker and Sole maker are separated (made by different people)
Type 2: One confused post, in two Upper part maker and Sole maker

Table 11. Average atmospheric concentrations of solvents assayed.

Process		Post working	Sampling	Acetone (mg/m³)		n-Hexane (mg/m³)		methylethylketone (mg/m³)		Cyclohaxane (mg/m³)		Toluene (mg/m³)	
				scope	average	scope	average	scope	average	scope	average	scope	average
Industrial		Chopped off	1	-	0.0	-	0.0	-	0.0	-	0.0	-	0.0
		Quilting	1	-	0.0	-	36.8	-	0.0	-	160.5	-	6.8
		Upper part makers	4	0.0 to 1652.0	413.0	28.1 to 975.0	300.1	0.0 to 2656.9	776.6	0.0 to 183.8	66.8	13.6 to 321.0	103.5
		Sole makers	7	0.0 to 3077.3	439.6	14.3 to 139.3	51.9	0.0 to 121.4	17.3	0.0 to 72.1	21.2	00 to 71.9	21.3
		Finish	3	-	0.0	53.8 to 86.6	66.8	0.0 to 165.3	108.7	0.0 to 34.2	12.9	56 to 43.7	20.8
		Serigraphy	1	-	0.0	-	401.8	-	1090.8	-	1281.1	-	38.6
Semi-industrial		**Upper part makers**	8	0.0 to 114.3	16.1	0.0 to 204.0	57.4	0.0 to 509.5	113.4	-	118.5	4.4 to 500.0	106.6
		Sole makers	12	0.0 to 989.1	222.0	0.0 to 214.1	58.6	0.0 to 622.5	134.2	-	94.0	4.0 to 615.9	121.6
		Finish	3	0.0 to 474.3	158.1	0.0 to 116.0	43.8	0.0 to 350.3	136.2	-	3.9	10.3 to 329.0	130.4
Artisanal	**Type 1**	**Upper part makers**	5	0.0 to 217.6	43.5	0.0 to 112.8	52.9	0.0 to 334.5	124.0	-	111.5	7.8 to 480.0	138.5
		Sole makers	8	-	0.0	3.3 to 147.3	58.6	0.0 to 442.5	150.8	-	112.2	0.4 to 578.1	115.0
	Type 2	**Ipper part makers /Sole makers**	2	0.0 to 43.4	21.7	21.6 to 27.2	24.4	-	0.0	-	26.6	27.7 to 35.9	31.8
			Total = 55										

Type 1: The positions of Upper part maker and Sole maker are separated (made by different people)
Type 2: One confused post, in two Upper part maker and Sole maker

Table 12. Average atmospheric concentrations of solvents assayed.

The natural ventilation has been the main alternative ventilation: Some kind of artisans 2 working doors open because they have no other coming from vents (without windows), while others worked closed doors because of their irregular position (no statement to the National Case Social Security and/or cohabitation a group of craftsmen in a building intended for habitation and not commercial and industrial travailing each for its own account).

Semi-industrial footwear companies are craft enterprises working on a large scale with some mechanization, which paid their employees the number of parts produced per day (upper part makers and sole makers). They correspond to industrial companies that should be in IZ [19]. Another feature in this type of business is the presence of women in age mount positions rods and finishing [20]. Shoes manufacturing companies are increasing in the region with an extension to the new IZ south of the city of Sfax. The semi-industrial companies continue to invade Medina and especially the houses which are in most cases protected historical monuments.

The SAMCR of INRS was chosen because it is one of the reference methods in RA established from the Kinney model (mathematical model) [21].

If these atmospheric samples and toxicology tests were made for the first time in the shoe industry in Sfax, they concerned a sample of companies of the three shoes manufacturing processes (industrial, semi-industrial, and artisanal) preceded by a preliminary RA with a job and a study inventory of products handled.

Interest carcinogenic characteristics of certain preparations and especially their potential toxicity for reproduction must be taken, as a female presence in the shoe manufacturing sector increasingly important and cases of couple infertility [22] have been highlighted.

7. Conclusion

Identification and CRA are important steps in this process of prevention in the shoe industry. This detection was to (i) highlight the chemical preparations that are really harmful. This could be achieved by the inventory and prioritization of chemical preparations; and (ii) identify the nature of the manipulated chemical preparations. This identification was made by labeling of preparations. After this step, the semi-industrial process CRA is most at risk followed the industrial process and finally that of the artisanal process. When the study of exposure to workplace needs to know not only the average exposure over the EAV, but also to identify the polluting phases to determine the short-term exposure over the TLV.

Apart from the strengthening of health and safety measures in the shoe industry, two actions are to be undertaken in parallel: (i) the substitution of certain solvents by others in the manufacture of glues and derivatives seems necessary while maintaining the preparations use properties and (ii) a change in the Tunisian regulations on hygiene and safety, in particular, is necessary to mandate the RA in business.

Acknowledgements

This study was partly funded and supported by Sfax University. We are grateful to the director and staff of the adhesive company SIFCOL for their cooperation. We are also indebted to the workers who participated voluntarily in the study.

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