

Inventory of the Chemicals and Microenvironment of an Albanian Tannery

Gentiana Shegani

Directorate of Public Health

Albanian University

Berat, Albania

gentashegani@hotmail.com

Abstract— More than 250 different chemicals are used in the production of leather. Workers in tanneries are exposed to these chemicals in various ways: inhalation of airborne substances (gases, dust, vapors, mist, aerosols and fumes), ingestion and skin absorption or contact and through the pores or cut/wounds of unprotected hands, arms and other parts of the body. This study investigated exposure of workers to chemicals in a tannery at full production capacity located in the city of Berat, Albania. The current paper represents a careful investigation of the working process, an inventory, classification and risk assessment of the hazardous chemicals used in each stage in the tannery. Furthermore, this investigation includes the monitoring of some gaseous emissions released at the workplace during leather processing such as ammonia and hydrogen sulfide. There is a good ventilation system and natural airflow in the tannery to reduce bad odors as well as the concentration of airborne pollutants released during the production process. For this reason, indicators of air emissions were within permissible limits. No evidence was found indicating that the tannery workers were at risk of contracting an occupational disease in their workplace. Nevertheless, training of the workers by certified experts is essential in the control of hazardous chemicals.

Keywords— chemicals; inventory; workplace; tannery; worker; occupational health; air emissions.

I. INTRODUCTION

Leather is an exclusive, vastly multi-dimensional, mutually dependent material found all over the world. There are now more than 500,000 people working in this sector around the world, and this number continues to rise every day [1]. Tanneries are one of the emerging sectors for trade and finance affecting the society, environment, and tannery workers [3]. More than 250 chemicals are used in the production of leather. Workers in tanneries are exposed to these chemicals in various ways: Inhalation of airborne substances (gases, dust, vapors, mist, aerosols and fumes), ingestion and skin absorption or contact, generally through the pores or cut/wounds of unprotected hands, arms and body [2]. The impact of such exposure can cause temporary effects such as

dizziness, headaches, irritation of eyes, skin or lungs, allergic reactions, poisoning of the liver, or kidney/nervous system collapse due to a lack of oxygen. Long term illness can also occur such as occupational asthma, ulcers, bronchitis or genetic defects. In some rare cases, even death has occurred [2]. In addition to the adverse effect on the human body, chemicals can also cause fires, corrosion, and damage to structures and electrical installations. They may also have a harmful effect on the surrounding environment when released in an uncontrolled manner [2]. Occupational illnesses are less likely to be detected in developing countries partly as a result of inadequate occupational health services. Developing countries generally also have fewer effective occupational health programs and enforced laws and regulations than in developed countries [4]. This may be a reason why tannery work statistics about occupational diseases are not reported.

In developing countries, the main focus of tanneries revolves around the processing and selling of the finished product. Safe chemical management tends not to be a priority [6]. This is because of a lack of information about the quality, quantity, characteristics and hazards of chemical substances used as well as poor labeling, unknown substances, limited financial and human resources [6]. Occupational Health and Safety (OHAS) is a specialized field that promotes and maintains the physical, mental, and social well-being of workers. It also works to prevent adverse health effects caused by hazardous working processes and conditions [3]. Occupational health and safety are of utmost importance because of the potential adverse effects both on employees and employers [3]. Thus, it is crucial that the existence and implementation of different regulations, directives, and instruments be established to ensure the workers' well being. The objective of the European Chemical Regulations (REACH) is to ensure the safe use and application of chemical substances and preparations (mixtures). For this purpose, all stages in the industrial supply chain have been included in the legal obligations (i.e. producer - downstream user I and the tanner - downstream user II) [5]. According to the International Labor Organization (ILO) constitution, workers should be protected by employers from any kind of sickness, disease, or injury which may arise due to work [3]. A very helpful document is the Chemical Safety Data Sheet (CSDS) that describes the properties and uses

of chemical products or formulation including the identity, chemical and physical properties, health hazard information, precautions for use and safe handling information [7], in order to optimize chemical use and improve workplace health & safety standards [6]. This study investigated exposure of workers to chemicals in a tannery located in the city of Berat working at full production capacity.

The current paper presents a careful observation of the working process, an inventory, classification and risk assessment of the hazardous chemicals used in each stage of production in the tannery. Furthermore, data pertaining to gaseous emissions released at the workplace during leather processing are presented (i.e. ammonia, hydrogen sulfide, parameters of the microclimates such as temperature, humidity and carbon dioxide emissions are also taken into account, to estimate the occupational conditions for workers health and safety). This paper is the first of its kind in reporting chemical management in the Albanian leather industry.

II. MATERIALS AND METHODS

A. Study Area

The study was conducted at a tannery located in a suburban area of Berat (N 40°41' 22.3476" E 19° 58' 34.3236") in a building with great capacity, with surface 860 m².

B. Observations of the Workplace

Experimental data for all hazardous chemicals was gathered from March 2013 to November 2014. A detailed report of all chemicals was prepared at each working stage; the responsible personnel and the owner were interviewed about their handling procedures, personal protective equipment (PPE), etc. Chemical products lists and material safety data sheets (MSDS) were collected from the tannery as well as the labels of the chemical manufacturers. The potential risk of all chemicals, including the CAS numbers (Chemical Abstracts Service) as harmful or irritant was assessed using the MSDS and the ECHA Website (European Chemicals Agency). The monitoring of the indoor microclimate indicators such as CO₂, NH₃, H₂S, C₂H₅OH were carried out by short-term detector tubes (MSA/ Auer; SIGMA-ALDRICH). Temperature and Relative Humidity were measured with a Temp & Humidity Meter DT- 83. The obtained data were subjected to descriptive statistical analyses (95%confidence limit) using Microsoft Excel to determine the minimum, maximum, mean, standard deviation, threshold and coefficient of variation.

III. RESULTS AND DISCUSSION

Fig. 1 presents a flow diagram of the leather processing. During the tanning process "wet – blue leather" at least 323 kg of chemicals (lime, salts, enzymes, acids) are used per 1 ton of hides. The inventory of chemicals used in the working process and the effect of each chemical are presented in

Tables 1, 2, and 3. In pre-processing, hides are received and Sodium Chloride is applied on the flesh side of the skins/hides. Sodium chloride may dehydrate the worker's skin [4]. After pre-processing, the beam house process begins with the soaking stage in which the preserved raw hides regain their normal water contents, using Sodium Sulphide, different enzymes and liquid soap. Hair removal/liming is done to remove the epidermis, hair and skin appendices, applying lime, Sodium Sulphide, Sodium Sulphidrate, degreasing agents, and enzymes to achieve the alkaline condition. This condition destroys the epidermal keratin. Occupational risk in tanneries is related to the frequent and prolonged exposure of the workers to chemicals as well as to hot and humid environmental conditions and various machinery/equipment. Workers are exposed to hazardous chemicals by absorbing them through their skin, inhalation, and ingestion [4]. Unwanted flesh is removed with the help of fleshing machines after the liming process [11]. Workers at the beam house process are exposed to these harmful chemicals which irritate their skin and eyes. These chemicals are known to be corrosive and are classified as toxic and hazardous waste [12]. Furthermore, the chemicals can pose a safety risk and a health hazard for workers during the handling, transferring, storage, and disposal of chemical waste stages [2]. In the pre- tanning section, de-liming, bating and pickling processes are applied to the hides. They are delimed using Ammonium Sulphate, Sodium Hydrogen Sulphite, degreasing and deliming agents, and enzymes. The skins are then washed. Bating is done for further purification of hides [11]. Enzymatic treatment using protease and lipase enzymes remove excess hair and degrade proteins. The pickling treatment treats the skin with acids and salts to bring it to desired pH level [11], enabling chromium tannins to enter the hide [10]. In this process, Sodium Chloride, Sodium Hydrogen Sulphite, bleaching agent, formic acid and sulphuric acid are used. Workers at the pre- tanning section are exposed to different chemicals which are harmful if swallowed, dangerous for the respiratory tract by inhalation, skin and eye irritants, corrosive and can cause burns [12]. In the tanning process, Basic Chrome Sulphate is used as the main tanning agent. The process of chromium tanning is based on the cross-linkage of trivalent chromium ions with free carboxyl groups in the collagen [10], protecting the leather from enzymatic degradation, enhancing the strength and increasing its resistance to heat, hydrolysis and microbial degradation [4]. Biobase Cro. is added to fixate the chromium and the Sodium Formate as a buffering agent to increase the pH. The chromium – tanned hide contains Cr³⁺ about 2-3% of dry weight. . Wet blue, i.e. the raw hide after the chrome – tanning process, has about 40% of dry matter [10]. Fat liquors and anti mould agent are added to the tanning section, too. The chemicals used in this stage are classified as eye and skin irritants, and are also harmful if inhaled [12].

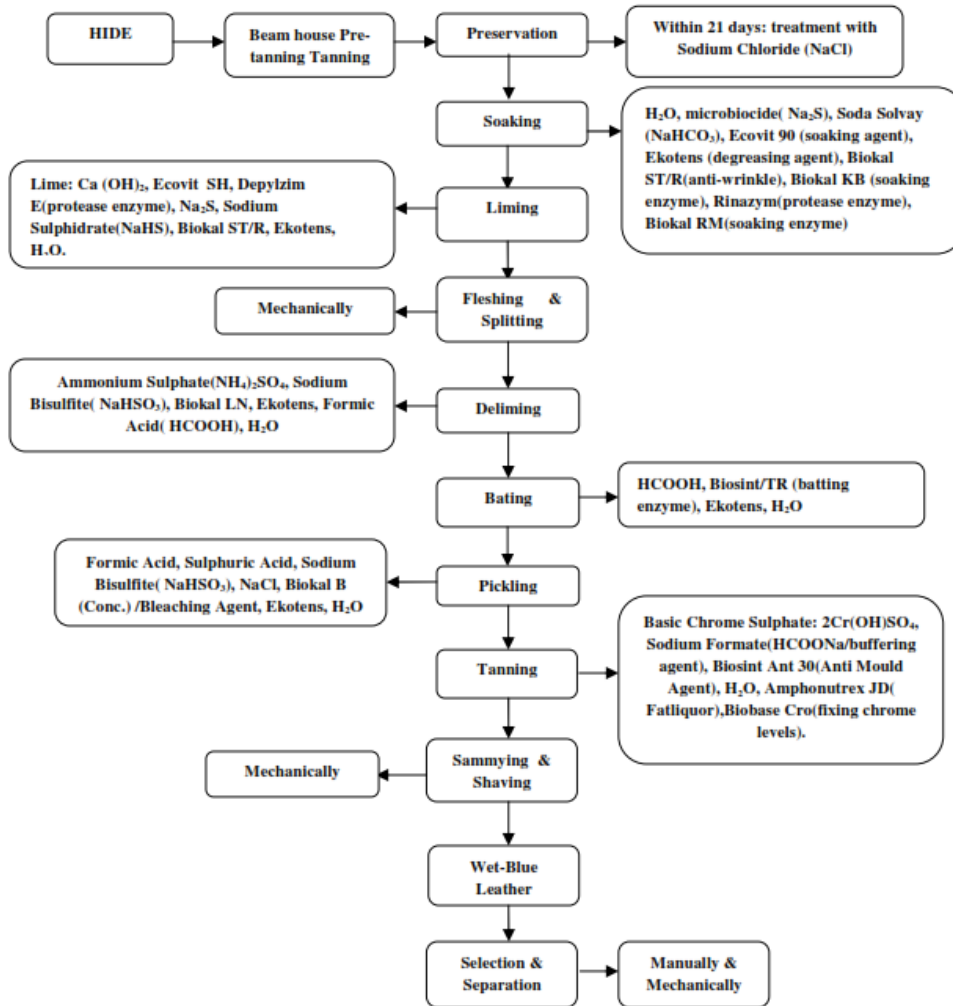


Fig. 1. Flowchart of the "Wet-Blue" Leather Manufacturing Process

TABLE I. Inventory of the Chemicals in the Beam House Process in the Tannery

Process Operation Beam house	Product Name	Name of Chemical (Formula)	CAS No.	Physical Form	Usage of Chemical Quantity%	Risk Phrases Hazard Statement	Safety Phrases	Comply with CLP	PPE
Preservation	Sodium Chloride	NaCl	7647-14-5	Crystalline (white)	50 % of raw material	H319- Eye Irrit.2 H373-Stomach (prolonged & repeated exposure)	S24/S25 Avoid contact with eye/skin	Yes	Gloves Goggles Apron Safety boots
Soaking	Sodium Sulphide (Antibacterial agent)	Na ₂ S(oxidized, Poison, soluble water, strong alkaline solution)	1313-82-2	Thin yellow flakes(solid)	0.15% & 0.1% 2 times	T; R24-toxic/skin Xn; R22/harmful if swallowed C; R34-burns R31-produces toxic gas N; R50;-very toxic to aquatic fauna Seveso substance(9) GHS06 GHS09 GHS05 Dgr	(S1/S2)/locked up & keep out the reach of the Children S26 S36/37/39-PPE eye/face S45 S61-avoid release to the env.	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Soda Solvay (Sodium Hydrogen Carbonate)	NaHCO ₃	144-55-8	Crystalline or fine powder (white)	0.1%	H315-skin irrit.2 H319-eye irrit.2A H332-acute tox.4/harmful if inhaled H335-resp.irrit.GHS07 Wng	S36/37/39-PPE eye/face	Yes	Gloves Cotton mask Goggles Safety boots
	Ecovit 90(Special Soaking Agent)	Not applicable	-	Powder (white)	0.8%	R36-Eye irrit. (Xi)	S22-Do not breathe dust;S26-Rinse immediately/eye S60-don't empty/drains/hazardous waste	Yes	Cotton mask Gloves Goggles Safety boots

Soaking	Ekotens (Degreasing agent with strong emulsifying action)	Isodecanol-Ethoxylated (contain)	-	Liquid	0.1%	R22-Harmful if swallowed R41-Risk of serious damage/eye Xn- Harmful	S26-eye/rinse immediately S29-don't empty into drains S36/39-wear PPE eye/face S60-hazardous waste	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Biokal ST/R(auxiliary liming, anti-wrinkle agent)	Methylamine of Sodium Hydroxide(contain)	-	Liquid	0.3%	R11/F-Highly flammable R34-causes burns C-Corrosive	S3/S9-Keep in cool and dry place S26/36/37/39/45 Rinse/eye; PPE-eye/face S60-Hazardous waste	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Biokal KB (traditional enzymatic soaking agent)	Not applicable	-	Powder	0.2%	R36/Xi-Eye/ irrit.	S22-Do not breathe S26-Eye/rinse immediately S29/S60-Do not empty into drains/hazardous waste	Yes	Goggles Gloves Cotton mask Safety boots
	Rinazym (concentrated enzymatic soaking agent)	Protease	-	Powder (white)	0.11%	R42/Xn-May cause sensitization by inhalation	S22-Do not breathe dust S36-Wear PPE S29/S60- Do not empty into the drains- Hazardous waste	Yes	Cotton mask Goggles Gloves Apron Safety boots
	Biokal RM(soaking enzyme)	Protease	-	Powder	0.05%	R36/38-Irrit. Eyes & skin. (Xi)	S22-Don't breathe dust; S26/Contact with eyes, rinse immediately& seek medical advice. S29- Do not empty into the drains	Yes	Gloves Apron Cotton mask Safety boots
Liming	Lime	Calcium dihydroxide Ca(OH) ₂	1305-62-0	Powder (white)	1% & 1.5% (2 times)	H315-Skin irrit. 2 H318-Eye dam. 1 H335-Respiratory tract/Inhalation GHS07 GHS05 Dgr C-Corrosive	S36/37/39- Wear suitable protective clothes; PPE eye/face (optional)	Yes	Goggles Cotton mask Gloves Apron
	Ecovit SH(liming accelerator)	Not applicable	-	Powder (white)	1%	R36/38-Irrit. Eyes & skin. (Xi)	S26/Contact with eyes, rinse immediately& seek medical advice.S29-Don't empty into drains.S37-Wear suitable gloves.S60-Hazardous waste	Yes	Gloves Cotton mask Goggles Apron Safety boots
	Sodium Sulphide (Antibacterial agent)	Na ₂ S(oxidized, Poison, soluble water, strong alkaline solution)	1313-82-2	Thin yellow flakes(solid)	1.5% (2 times)	T; R24-toxic/skin Xn; R22/harmful if swallowed C; R34-burns R31-produces toxic gas N; R50;-very toxic to aquatic fauna Seveso substance(9i) GHS06 GHS09 GHS05 Dgr	(S1/S2)locked up & keep out the reach of the Children S26 S36/37/39-PPE eye/face S45 S61-avoid release to the env.	Yes	Goggles Cotton mask Gloves Apron Safety Boots

Liming	Ekotens (Degreasing agent with strong emulsifying action)	Isodecanol-Ethoxylated (contain)	-	Liquid	0.1%	R22-Harmful if swallowed R41-Risk of serious damage/eye Xn- Harmful	S26-eye/rinse immediately S29-don't empty into drains S36/39-wear PPE eye/face S60-hazardous waste	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Biokal ST/R(auxiliary anti-wrinkle agent)	Methylamine of Sodium Hydroxide(contain)	-	Liquid	0.5%	R11/F-Highly flammable R34-causes burns C-Corrosive	S3/S9-Keep in cool and dry place S26/36/37/39/45 Rinse/eye; PPE-eye/face S60-Hazardous waste	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Sodium Hydrogen sulphide	NaHS	16721-80-5	Yellow flakes(solid)	0.5%	EUHO31-acid /toxic gas EUHO71-Corrosive/respiratory tract H290- Met.Corr.1 H301-Acute Tox.3 H314-Skin Corr.1B H318-Eye Dam.1 H400-Aquatic Acute1; GHS02 GHS06 GHS09 GHS05 Dgr C-Corrosive T-Toxic Xi-Irritant	S3/S9/S15-Keep away/heat S26/36/37/39/45 Rinse/eye; PPE-eye/face S29/S60-Do not empty into drains/hazardous Waste	Yes	Goggles Gloves Cotton mask Apron Safety boots
	Depilzym E (enzymatic unhairing agent)	Protease	-	Powder(white)	0.05% (2 times)	R42-May cause sensitization by inhalation Xn-Harmful	S22-Do not breathe dust S36/S45-Wear PPE S60-Hazardous waste	Yes	Cotton mask Goggles Gloves Apron Safety boots

TABLE II. inventory of the chemicals in the pre-tanning section

Process Operation Pre-tanning	Product Name	Name of Chemical (Formula)	CAS No.	Physical Form	Usage of Chemical Quantity%	Risk Phrases Hazard Statement	Safety Phrases	Comply with CLP	PPE
Deliming	Ammonium Sulphate (fertilizer)	(NH ₄) ₂ SO ₄	7783-20-2	Crystalline (white)	0.4%;0.5% & 0.5% (3 times)	H315-Skin Irrit.2 H319-Eye Irrit.1 H335-Resp.Irrit. GHS07 GHS09 Wng	S24/S25 Avoid contact with eye/skin S3/S9-Keep in cool and dry place S26/36/37/39/45 Rinse/eye; PPE-eye/face	Yes	Gloves Goggles Apron Cotton mask Safety boots
	Sodium Hydrogen sulphite	NaHSO ₃	7631-90-5	Crystalline or powder(white)	0.2%	H301-Acute Tox.3 H302-Acute Tox.4 H314-Skin Corr.1C H318-Eye Dam.1 3Xn-HarmfulR22-Harmful if swallowed;R31-acid/tox.gas GHS07-Wng GHS05-Dgr;C-Corrosive;	S2-Keep out of the children S25-Avoid contact with eyes S46-Seek medical advice immediately	Yes	Goggles Gloves Apron Cotton mask Safety boots

Delimiting	Ekotens (Degreasing agent with strong emulsifying action)	Isodecanol-Ethoxylated (contain)	-	Liquid	0.1% & 0.2% (2times)	No Seveso Substance R22-Harmful if swallowed R41-Risk of serious damage/eye Xn- Harmful	S26-Eye/rinse immediately S29-Don't empty into drains S36/39-Wear PPE eye/face S60-Hazardous waste	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Biokal LN (delimiting agent at low developing of nitrogen)	Not applicable	-	Powder (white)	0.2%; 0.8% & 0.8% (3 times)	R36/-Eye Irrit. R38-Skin Irrit. (X)-Irritant	S26/S28-Eye/Skin /rinse immediately S37/S39- Wear suitable PPE eye/face/skin	Yes	Goggles Gloves Apron Cotton mask Safety boots
	Formic acid or (methanoic acid)	HCOOH	64-18-6	Liquid (clear, colorless; pungent odor)	0.3%	H226-Flam.Liq.3 H314-Skin Corr.1A H318-Eye Dam.1 R23/ R24/R25-Tox. By inhalation, skin and if swallowed. R34/R35/R36/R38-Irrit. Eye/skin/inhalat. R40/R43-skin sensitisation T, C, Xi	S23-Do not breathe gas S26- Avoid contact with eye/skin S36/S37/S39-Wear suitable PPE Eye/skin/face S45-Seek medical advice immediately	Yes	Goggles Cotton mask Gloves Apron Safety boots

	Biosint TR (Conc. Enzymatic bating agent)	Not applicable	-	Powder (white)	0.025%	R36/38-Eye & skin irrit. H319-Eye irrit. H335-Resp.Inhal.	S22-Don't breathe dust S26-Avoid contact with eye/skin S29- Don't empty into drains	Yes	Goggles Gloves Cotton mask Apron Safety boots
--	---	----------------	---	----------------	--------	---	---	-----	---

Pickling	Formic acid or (methanoic acid)	HCOOH	64-18-6	Liquid (clear, colorless; pungent odor)	0.3%	H226-Flam.Liq.3 H314-Skin Corr.1A H318-Eye Dam.1 R23/ R24/R25-Tox. By inhalation, skin and if swallowed. R34/R35/R36/R38-Irrit. Eye/skin/inhalat. R40/R43-skin sensitisation T, C, Xi	S23-Do not breathe gas S26- Avoid contact with eye/skin S36/S37/S39-Wear suitable PPE Eye/skin/face S45-Seek medical advice immediately	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Ekotens (Degreasing agent with strong emulsifying action)	Isodecanol-Ethoxylated (contain)	-	Liquid	0.1%	R22-Harmful if swallowed R41-Risk of serious damage/eye Xn- Harmful	S26-Eye/rinse immediately S29-Don't empty into drains S36/39-Wear PPE eye/face S60-Hazardous waste	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Sodium Chloride	NaCl	7647-14-5	Crystalline (white)	5%	H319- Eye Irrit.2 H373-Stomach (prolonged & repeated exposure)	S24/S25 Avoid contact with eye/skin	Yes	Goggles Gloves Apron Safety boots
	Sodium Hydrogen sulphite	NaHSO ₃	7631-90-5	Crystalline or powder(white)	0.1%	H301-Acute Tox.3 H302-Acute Tox.4 H314-Skin Corr.1C H318-Eye Dam.1 3Xn-Harmful/R22-Harmful if swallowed;R31-acid/tox.gas GHS07-Wng GHS05-Dgr;C-Corrosive;No	S2-Keep out of the children S25-Avoid contact with eyes S46-Seek medical advice immediately	Yes	Goggles Gloves Apron Cotton mask Safety boots

Pickling	Biokal B(Conc. Bleaching agent)	NaClO (contain sodium hypochlorite)	7681-52-9	Powder (white)	0.2%	Seveso Substance H270-Ox. Gas 1 H314-Skin Corr. 1B H318-Eye Dam. 1 H335-Resp. Inhal. H400-Aquatic Acute 1; R31-acid/tox. gas R34-causes burns R50-Tox. to aqua. organ. Seveso Substance (9i) GHS09 GHS05 GHS07 Dgr	(S1/S2)/locked up & keep out the reach of the Children S28-Skin/rinse immediately S45-Seek medical advice S50-Do not mix S61-Avoid release to env.	Yes	Goggles Gloves Apron Cotton mask Safety boots
	Formic acid or (methanoic acid)	HCOOH	64-18-6	Liquid (clear, colorless; pungent odor)	0.5%	H226-Flam. Liq. 3 H314-Skin Corr. 1A H318-Eye Dam. 1 R23/ R24/R25-Tox. By inhalation, skin and if swallowed. R34/R35/R36/R38-Irrit. Eye/skin/inhalat. R40/R43-skin sensitisation T, C, Xi	S23-Do not breathe gas S26-Avoid contact with eye/skin S36/S37/S39-Wear suitable PPE Eye/skin/face S45-Seek medical advice immediately	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Sulphuric acid	H ₂ SO ₄	7664-93-9	Liquid (heavy ;colorless)	1.3%	H290-Met. Corr. 1 H314-Skin Corr. 1A H318-Eye Dam. 1 H335- Lung Irrit. R35-C-Corrosive GHS07 GHS05 Dgr	S1/S2- locked up & keep out the reach of the Children S26-Avoid contact with eye/skin S30-Never add water S45-Seek medical advice immediately	Yes	Goggles Cotton mask Gloves Apron Safety boots

TABLE III. Inventory of the Chemicals in the Tanning Section

Process Operation	Product Name	Name of Chemical (Formula)	CAS No.	Physical Form	Usage of Chemical Quantity%	Risk Phrases Hazard Statement	Safety Phrases	Comply with CLP	PPE
Tanning	Basic Chrome Sulphate	2Cr(OH)SO ₄	10101-53-8	Powder (bright green)	4.5% (2 times)	R22/harmful if swallowed R36-Eye irrit. R38/R43-skin sensitization	S3/S9/S15-Keep in cool & Dry place, away from heat; S24/S25-Avoid contact with Eye/Skin S36/37/39-PPE eye/face S61-avoid release to the env.	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Sodium Formate (Buffering Agent; increase pH)	HCOONa	141-53-7	Granular (white deliquescent)	0.5%	H315-Skin Irrit. 2 H319-Eye Irrit. 2 H335- Resp. Inhalat. GHS07 Wng	S36/37/39-PPE eye/face S45 S24/S25-Avoid contact with Eye/Skin	Yes	Goggles Cotton mask Gloves Apron Safety boots
	Amphonutrex JD (all purpose fatliquor)	Donor of Formal aldehydes (isotiazolone Max. 10%)	-	Liquid	0.05%	R36-Eye irrit. R38-Skin Irrit.	S24/S25-Avoid contact with Eye/Skin S26-Eye/rinse immediately S29-Don't empty into drains.	Yes	Goggles Cotton mask Gloves Apron Safety Boots
	Biosint ANT 30 (anti mould agent, biocide)	Benzothiazol-2-ylthio)methyl thiocyanate, Alcohol C11-13 ethoxylated	-	Powder (white)	0.2%	H330- Fatal if inhaled; H318-Serious eye dam. H410- Very tox./ aqua. Life. H302- Harm. if swallowed; H315-Skin irrit. H317-May cause allergic skin reac. Xn, C, T.	S22-Don't breathe dust S24/S25-Avoid contact with Eye/Skin S26-Eye/rinse immediately S45-Seek medical advice immediately S36/S37/S39-Wear suit. PPE	Yes	Goggles Cotton mask Gloves Apron Safety boots

	Biobase Cro(stably fixing high chrome levels)	Not applicable	-	Powder (white)	0.4%	R36/38-Eye & skin Irrit. H319-Eye irrit. H335-Resp.Inhal.	S22-Don't breathe dust S24/S25-Avoid contact with Eye/Skin S36/37/39-Wear suit,PPE S29-Do not empty into drains	Yes	Cotton mask Gloves Apron Safety boots
--	---	----------------	---	----------------	------	---	--	-----	--

TABLE IV. Statistical Data of Air Emissions in the Tannery

Parameters	Minimum	Maximum	Mean	Median	Standard Deviation	Coefficient of Variation	Threshold X + 2S
Temperature(°C)	10	29.5	21.3	21.25	4.377	0.205	30.05
Relative Humidity RH (%)	61.8	78	69.816	70	4.839	0.069	79.494
Carbon Dioxide CO ₂ (mg/m ³)	1830	5490	3263.5	3294	969.63	0.297	5202.76
Ammonia gas NH ₃ (mg/m ³)	0.35	8.4	2.485	2.1	1.776	0.714	6.037
Hydrogen Sulphide H ₂ S gas (mg/m ³)	0.14	14.1	2.213	1.41	3.365	1.52	8.943
Ethanol (mg/m ³)	361	855	619.48	570	165.63	0.267	950.74

Sammying, the process of reducing water content and shaving off the pickled hides is carried out manually and mechanically. Personal protective equipment such as goggles, gloves, cotton masks, aprons and safety boots are required to be used by workers. The workers must always use a plastic apron and safety boots while working. In some cases they don't regularly use the gloves and cotton masks, nor do they use protective goggles. Hazardous risks and the probability of chemicals causing harm are reflected in an internationally-accepted system of risk phrases (R- Phrases) and safety phrases (S-Phrases). R-Phrases refer to health effects on humans and environmental effects. S-Phrases give guidance for the safe handling of dangerous chemicals and preparations [6]. Occupational risk in tanneries is mainly related to the frequent and prolonged exposure of workers to chemicals as well as to hot and humid environmental conditions and machinery equipment [4]. Table 4. shows the statistical data of air emissions in the tannery. Workers are exposed to hazardous chemicals through skin absorption, inhalation and ingestion. During the working process, chemicals emit fumes, mist, vapors and dust thereby exposing workers to airborne chemical pollutants [4]. There should be sufficient airflow to capture the dust or vapor before it disperses into the workplace. For dust, airflow above 1 m/s will generally be needed; for vapors, airflows above 0.5 m/s will generally be needed [6]. Data on different parameters of the microclimate such as the range and mean are presented respectively in Fig. 2, Fig.3 and Fig. 4.

During 2013, Temperature ranged from 18- 29.5°C with a mean value of 22.84°C. In terms of the 2014 work area, the temperature ranged from 10- 25°C with a mean value of 18.46°C.

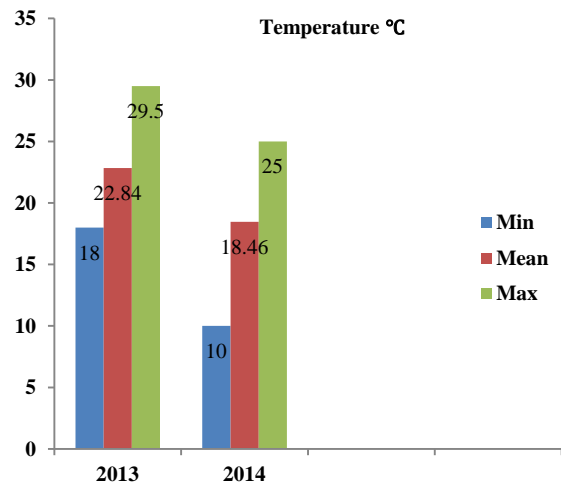


Fig. 2. Comparison of the Min. Mean, Max. of the Temperature values 2013 -2014

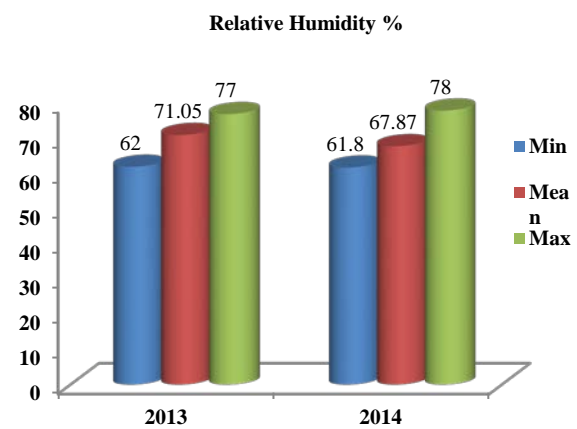


Fig. 3. Comparison between the Min. Mean, Max. Values of the Relative Humidity 2013 - 2014

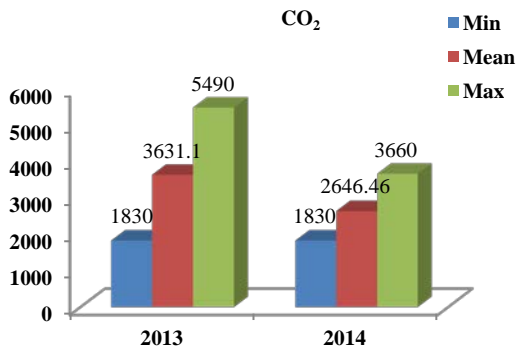


Fig. 4. Minimum, Mean, Maximum values of CO₂ 2013 - 2014

Relative Humidity values ranged from 62% – 77%, with a mean value of 71.05% during 2013, and within a range from 61.8% to 78%, with a mean value of 67.87% during 2014. These parameters are affected by several factors including weather conditions, vapors, and mists that are released into the working area. CO₂ values ranged from 1830 to 5490mg/m³, with a mean value of 3631.1mg/m³ during 2013. CO₂ values ranged from 1830 to 3660 mg/m³, and the mean value was recorded as 2646.46 mg/m³ during 2014. The figures show lower CO₂ values, Temperature and Relative Humidity during 2014 compared to 2013. This fact explains the use of local exhaust ventilation at the work area and the natural airflow, due to the installation of the air filtration system and the great capacity of the building.

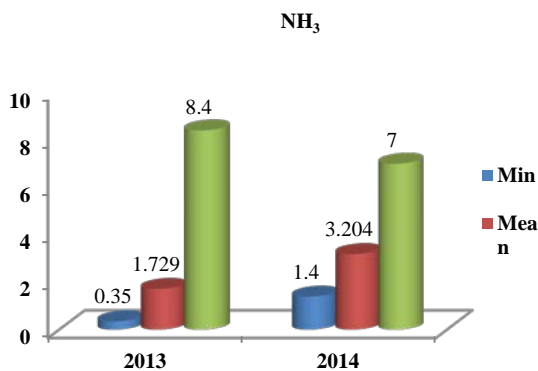


Fig. 5. Minimum, Mean, Maximum values of NH₃ between 2013 - 2014

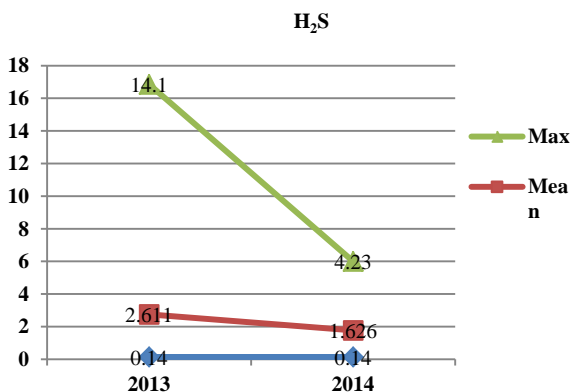


Fig. 6. Minimum, Mean, Maximum values of H₂S between 2013-2014

Fig. 5 shows the range of Ammonia gas values from 0.35mg/m³ to 8.4 mg/m³, with a mean value of 1.729 mg/m³ during 2013, and from 1.4mg/m³ to 7mg/m³, and a mean value of 3.204 mg/m³ during 2014. Values of NH₃ emissions in the tannery are within the Short- Term Exposure Limit 20mg/m³ [8]. Ammonia is a byproduct that is released during leather processing. It is harmful if inhaled and it may cause burns or serious eye damage in higher levels [14]. Hydrogen sulphide is heavier than air and may travel along the ground. The primary route of exposure is inhalation. Absorption through the skin is minimal. H₂S is a highly flammable gas and gas/air mixture that can be explosive. Its health effects can vary depending on the level and duration of exposure. Low concentrations irritate the eyes, nose, throat and respiratory system [9]. In this paper, H₂S values ranged from 0.14mg/m³ to 14.1mg/m³, with a mean value of 2.611mg/m³ during 2013 and from 0.14mg/m³ to 4.23mg/m³, with a mean value of 1.626 mg/m³ during 2014. The maximum value of H₂S illustrated in Fig. 6. during 2013 exceeded the prescribed limit 10mg/m³ [13]. This is most likely due to the lack of local exhausted ventilation during this year compared to 2014, when there was an air filtration system installed within the tannery.

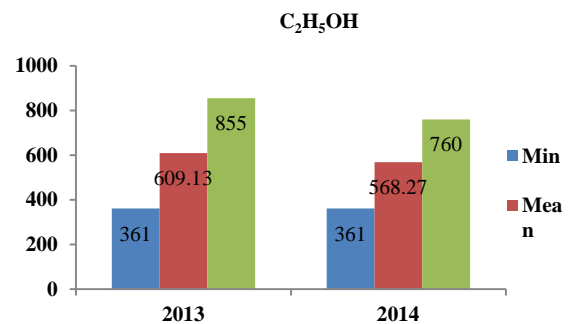


Fig. 7. Minimum, Mean, Maximum of C₂H₅OH during 2013– 2014

Fig.7. shows Ethanol values that ranged from 361mg/m³ to 855 mg/m³, with a mean value of 609.13 mg/m³ during 2013 and from 361mg /m³ to 760mg/m³, with a mean value of 568.27mg/m³ during 2014. This proves that there did exist a better ventilation system in the working area of the tannery. Ethanol is flammable, a skin and eye irritant, and hazardous in case of inhalation [16]. Its values were within the limit [13], although Ethyl Alcohol is not classified as a carcinogen following occupational exposure [17].

IV. CONCLUSION

This paper provides a detailed scheme of the working process and a comprehensive inventory of all chemicals used in leather processing up to the “wet-blue” stage. This study argues that the workers’ health can be affected by the working conditions and hazardous chemicals used in a tannery, so it presents data illustrating that precautions should be taken to ensure a safer working environment. There is a good ventilation system and natural airflow in the tannery

described in this study to reduce the bad odors and the concentration of airborne pollutants released during the leather manufacturing process. This is why all indicators of air emissions were within the permissible limits. There was no external evidence or symptoms of occupational diseases among the workers of the tannery. Training of the workers by experts is essential in the control of chemical hazards. They should be aware of the possible health risks caused by the chemicals, care, and use of PPE.

REFERENCES

- [1] S. Biswas, T. Rahman, "The effect of working place on worker's health in a tannery in Bangladesh", *Advances in Anthropology*, vol.3, no.1, pp.46-53, February 2013.
- [2] IUE-11 "Document for occupational health and safety in the use of chemicals in tanneries" Document OSH, pp.1-7, updated 2008. M
- [3] A.R. Sarker, "Occupational health and safety (OHAS) crisis in tanneries of Bangladesh: is this the violation of labour rights?", *European Journal of Business and Management*, vol.6, no.16, pp.165-169, 2014.
- [4] S. A. Febriana, F. Jungbauer, H. Soebono, P. J. Coenraads, "Inventory of the chemicals and the exposure of the workers' skin to these at two leather factories in Indonesia", *Int. Arch. Occup. Environ. Health*, DOI 10.1007/s00420-011-0700-1, 22 September 2011.
- [5] Tegewa, "The leather tanner and REACH", Guidance for the leather industry on fulfilling its REACH obligations, version 1.1, issued: June 2011.
- [6] J. Miller, M. Tischer, C. Vosseler, "Chemical management guide", Pilot Project Chemical Safety, GTZ, Bonn, May 2002. <http://www.gtz.de>
- [7] "Guidelines for the preparation of a chemical register", (Use and standard of exposure of chemicals hazardous to health Regulations, Ministry of Human Resources, Malaysia, 2000. <http://library.unisel.edu.my/equip-unisel/>
- [8] "Ammonia in workplace atmospheres", <https://www.osha.gov/dts/sltc/methods/>
- [9] "OSHA fact sheet: Hydrogen Sulphide", https://www.osha.gov/OshDoc/data_Hurricane_Facts/
- [10] "Description of the tanning process", http://en.wikipedia.org/wiki/Tanning#Beamhouse_operations
- [11] V. Dandira, K. Mugwindri, T. Chikuku, "A cleaner production exercise of a leather manufacturing company: a zimbabwean experience", *Int. Journal of Scientific & Technology Research*, vol.1, issue 11, December 2012.
- [12] European Chemicals Agency (ECHA), <http://echa.europa.eu/>
- [13] Institute of Public Health, "State Inspectorate Manual", Tirana, Albania, pp.54 – 59, 1998, unpublished.
- [14] Materials Safety Data Sheet "Ammonia air gas" <https://www.airgas.com/msds/001003.pdf>
- [15] Materials Safety Data Sheet "Hydrogen Sulphide", June 2014, <http://www.praxair.com/~media/North%20America>
- [16] Materials Safety Data Sheet "Ethanol", version 2.0, pp.1-9, issued May 2012. <http://www.ncpalcohols.com/MSDS/>
- [17] G. Shegani, "Study on some pollutants in the leather industry: a case study in Albania", *Int. Journal of Sciences: Basic and Applied Research (IJSBAR)*, vol. 14, no.1, pp.115 – 124, March 2014.