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THE ANALYSIS OF TOXICITY OF WASTE GASES AFTER SURFACE LASER TREATMENT

There are certain treatment processes in many branches of industry and scientific research during which or due to which hazardous substances are emitted. Special attention must be paid in this respect because the respiratory route enables them to get into the body without our awareness and in the long run they may cause diseases.

This thesis presents the results of experimental research where the presence of selected metals in waste gases after ablative laser treatment was analyzed. The AAS method was used to determine the amounts of Cd, Cr, Pb collected during the laser treatment, little surfaces of aluminum alloy PA7, polypropylene and ceramics covered with paint. The maximum surfaces that can be processed with ablation without exceeding the acceptable concentrations of these metals in the air were determined. The results obtained unequivocally indicate the necessity to conduct research into the harmful effect of the treatment process waste and to apply filtering systems.

Keywords**:** *AAS technique, ablative laser treatment, air pollution, toxicity.*

1. Introduction

The respiratory route is one of the best bio available methods of administering medicines to the body. However, the same application route can also be a way for toxic and hazardous substances to be unconsciously inhaled into the human body. There are, in many branches of industry, and in scientific research, a series of hazardous processing operations during which these gases, aerosols or ashes that contain toxic and hazardous substances are emitted and they affect human health. Not only the workstation staff is at risk but also local communities because these toxic substances get into the atmosphere, soil and water.

The preservation of clean environment (air), health care, ensuring proper conditions for operating machinery and equipment are actions that are not only subject to law but they also create the image of the company.

2. Selected examples of toxic hazard at workplaces

Manufacturers who produce various goods, machines and tools using traditional machining processes or laser technologies as well as electronic equipment manufacturers, plastic things manufacturers, even restoration, engraving or printing houses are obliged to take care of clean air. The extent to which the staff is exposed to the effects of pollutants such as hazardous ashes or gases may vary.

2.1. Metalworking

Metallic elements in minute quantities are necessary for the proper functioning of the human body. However, when the acceptable limits of concentrations in industrial conditions are exceeded, a problem arises. Metals, while penetrating the body through the respiratory tract in the form of ashes (aerosols of solid particles) or smokes (liquid aerosols), cumulate in organs, brain, bones and lead to chronic diseases. Lead, mercury, chromium, iron, zinc, and tin are the examples of metals which disturb metabolism and can have toxic or carcinogenic effects. In category 1 (according to the European Union directive 67/548/EEC), i.e. in the group of metals with proven carcinogenic activity, among other things, the following elements are listed: arsenic and its compounds, beryllium and its compounds, chromium (VI) and its compounds, cadmium and its compounds and nickel salts. The effects of the accumulation of metals can be perceptible after many years of work, even at the retirement age when the symptoms are usually not associated with bad working conditions in the past. Inhalation of fumes given off by aluminum alloys and of zinc coating may cause symptoms similar to influenza. At work-stations, where coolants are used, workers can be exposed to the hazardous effect of water-oil mist. It may contain not only metal elements but may also be contaminated with pathogenic micro-organisms (funguses, bacteria), which, apart from causing respiratory system condition, may result in bacterial infection, allergy or dermatomycosis. The above-mentioned hazard endanger workers in lathe workshops, grinding workshops, cutting work-stations, milling workshops, tool-rooms, smelting workstations, welding shops, etc. Then, the air can contain various metal particles, organic substances or their fractions [1, 2].

2.2. Plastic processing

The production of plastic goods is in fact, interesting because of the possibility of designing product properties such as: shape, colour, strength and other specific features. However, because of their chemical structure, not all plastics are safe for humans. In many cases, the main cause of threat is heat treatment which triggers the emission of hazardous substances. Polyvinyl chloride, after adding plasticizers, dyes, and fillers, becomes an emission source of chloride compounds, benzene, carbon monoxide and aromatic hydrocarbons. These substances cause lesions in the respiratory system, irritations, lungs condition, asthma and neoplasia; they can show a narcotic effect, cause excessive sleepiness or agitation. Another example is commonly used polyurethane adhesives whose vapours and aerosols, when breathed in, can lead to necrosis, and consequently to bacterial infection of pathologically changed tissues, eye damage and hand skin lesions.

Most production processes of plastic goods require adding other substances such as catalysts, surfactants, pore producing substances, fillers, pigments, plasticizers, antypirenes or oxidants. These are toxic and hazardous substances [1].

2.3. Woodworking and impregnation

Wood as a material is susceptible to the devastating effect of fungi, mould, bacterias and insects, so it is protected with impregnates. Except water impregnates, wood preservative oils are substances with a considerable toxicity level, because of the presence of benzene, phenols and naphthalene. They show carcinogenic effect if they contain anthracene, benzopyrene, arsenic and its compounds, chromium compounds or cyanoorganic compounds. Both the preparation of impregnates and inhalation of fumes or skin and eye contact during their application and drying, are hazardous to humans. Further treatment like wood shaving is also likely to harm people’s health because there may be contaminated wood dust in the air [1].

2.4. Phenol aldehyde resin goods production

Phenol aldehyde resins are widely used to produce a vast scope of goods from frictional and abrasive materials, casting moulds, current – and heat – insulating materials and laminates, to adhesives, paints and lacquers. The resins are modified and mixed with fillers, antisofteners, solvents, lubricants, colours to give them certain properties. Hardened resins are not toxic to humans but during the process of production, especially thermal hardening and moulding, they emit different gaseous substances in big quantities and of various quality and quantity composition [3]. It depends on the kind of actual resin, the hardening conditions and the size of products. Apart from liberated formaldehyde vapours and phenol, which constitute the basic ingredients of a resin, other substances can also be emitted, namely those from the additions, polycyclic aromatic hydrocarbons, ammonia, hydrogen cyanide, chloromethane, benzene, toluene, acetone, methane and other hazardous or carcinogenic chemical compounds. Continuous emissions of the substances listed above always occur when the above mentioned resins are used as the raw material [2].

2.5. Compression - ignition Diesel engine maintenance

Forklift truck drivers, motor vehicle inspection centre workers, bus depot workers, drivers and miners in mines and those who interact with Diesel engines are exposed to the effect of their exhaust fumes. They are a mixture of a few hundred chemical compounds which are the result of incomplete combustion of diesel oil, engine lubricants as well as the additives and impurities contained in them. The unwanted products are emitted to the atmosphere in the form of gases: PAH (Polycyclic Aromatic Hydrocarbons), nitric oxides (NO_x), sulphur (SO_x) and carbon (CO_x) and solid particles: element carbon with chemical compounds organic and inorganic, of different shapes and sizes (nano-elements) adsorbedin its surface. The most hazardous ones - PAH - is easily inhaled through the respiratory route, cumulate in pulmonary alveoluses causing chronic disorders. Prolonged exposures bring about dizziness, tiredness, as well as eye and respiratory tract mucosa irritation. Moreover, they can show cancerogenic activity, mutagenicity and may damage suprarenal body as well as immune and haematopoietic systems [2].

2.6. Asphalt use

Asphalts form naturally or are obtained through crude oil refining. They are raw materials that have found many applications. About 80% of the asphalt world production is used for building road surfaces. It is necessary in the production of insulating materials (waterproof protection, tar papers) as well as a vast range of printing inks and lacquers. The problem here is the exposure to harmful PAH mixtures, sulphur compounds, heavy metals (lead, nickel, cadmium) or phenol, which takes place during either their heating to make them more flexible or while they are liquefied [2].

The above review does not entirely exhaust the topic of hazardous substances in producing processes. Nevertheless, its aim is to signal the necessity to determine the amounts of hazardous substances emitted and their harmfulness with regard to any job environment. Especially because the respiratory route, as mentioned above, is the easiest way for these substances to enter the human body. Table 1. presents a simplified list of chemical substances which can have a negative effect on human body (based on [3,4]).

3. The use of laser beam

Technological development and the implementation of other methods of treatment carry the risk for those workers who are exposed to the hazardous effect of various substances. Laser beam surface treatment is an example of this effect. This is not an entirely new technology, but the construction of modern laser heads allows the treatment e.g. without protective atmospheres or manual controlling of the head movement (energy flow).

Table 1. Substances which have adverse effects on a human body [1-5]

Hazardous substance	**Adverse effects on a human body**	**The highest acceptable concentration of a substance in work environment [mg/m^3]**
Ammonia	Mucosal irritation of respiratory route, eye and skin irritation; necrosis	14,00
Arsenic and its compounds	Skin and lung cancer, nasal septum perforation (occupational disease), damage to peripheral vessels, neuropathy	0,01
Benzene	Anemy which can turn into aplastic anemia, leukemia, fatty degeneration liver, cardiac muscle, suprarenal body	1,60
Chromium (VI) and its compounds	Lung cancer, ulcers, dermatosis, nasal septum perforation (taste and smell loss), asthma, lesions in kidneys, liver, circulatory system	0,10
Hydrogen cyanide	Heart rate disorders and circulatory system, dizzines and headaches, emesis, loss of apetite, body weight loss	5,00
Phenol	Neurosis, liver inflamation, kidney lesions, respiratory system inflamation, unrelenting cough	7,80
Formaldehyde	Irritation of eyes and upper respiratory tract mucosa, contact dermatitis	0,50
Cadmium and its compounds	Cancer, kidneys damage, renal lithiasis, smell loss, emphysema, bones condition	0,01
Methane	Hypoxia, general callousnes	no info
Naphtalene	Optic neuritis, cornea damage, cataract, eye and skin irritation	20,00
Nickel	Lung and paranasal sinuses cancer, asthma and dust disease, respiratory tract irritation, nasal septum elcosis, egzematous dermatitis.	0,25
Lead	Hemoglobin synthesis suppression, eruthrocyte life cycle shortening, disorders of sight and motor coordination, speech and memory impairment, kidney failure, loss of mechanisms resposisble for DNA synthesis and replication suppression	0,05
Polivinyl chloride	Multisymptom syndroms, low temperature hypersensivity, paroxysmal paling of fingers, liver damage, skin and skeleton diseases, neoplasmic changes in liver, lungs, brain, circulatory system and lymphatic system	5,00
Mercury	Depressive moods, memory deterioration, anxiety moods, inflammatory condition in oral cavity, brain damage	0,01
Carbon monoxide	Feeling loss in fingers, memory enfeeblement, dizziness, sleepiness, changes in blood morphology, heart rate and blood pressure disorders	23,00
Nitric oxides	Eye and respiratory tract mucosa inflammation, enamel and dentin damage, effort dysponea, pathologic changes in blood, emphysema	NO –3,50 NO_2 – 0,70
Toluene	Mucosa irritation, conjunctivitis, sore throat; headaches, nervous disorders, changes in blood morphology	100,0
Policyclic Aromatic Hydrocarbons	Lung cancer among workers exposed to inhalation of fumes and ashes from coal-fired furnances, roofers	0,002

Lasers are used for metalworking, i. e. welding, melting and drilling (ruby crystal laser, $Cr^{3+}:Al_2O_3$), pitting, coating, hardening (crystal laser Nd:YAG, $Nd^{3+}:Y_3Al_5O_{12}$) as well as for cutting and welding (molecular gas laser, CO_2:N_2-CO_2-He) [5, 6]. They have also numerous military applications (sights, range-finders, missile and rocket homing quidance, target tracing, bomb fuses). Lasers are now indispensable in the navy (to measure the depth of sea areas), in aviation (in air reconaissance on-board systems, in navigation) and also in surveying (distance measurements, analysis of the geometrical structure of a surface layer) [7, 8].

In recent years, lasers have found their use in conservation of art works. Dirt accumulations, repaints and previous layers are removed from canvas, sculptures, buildings and other concrete or ceramic constructions where impulse laser beam is used to evaporate accumulated foreign material. Modern heads allow effective control of the treatment speed, beam focusing to a diameter of a few micrometers, which gives the possibility of high accuracy of the treatment. The possibility of choosing the radiation length enhances effectiveness and makes it possible not to disturb deeper layers and antique grounds [9].

Laser cleaning can be used to remove varnish coating and prepare the surface for next lacquering as well as to remove residues and grease before adhesion [10, 11]. Mobile heads clean elements from organic layer and coating of rust [9, 12, 13].

The examples described above indicate the increasing use of this technology in renovation and revitalization of metal, ceramic, concrete, linen etc. products.

4. The AAS analysis of waste gases after laser treatment – experiment investigation

The operations of cleaning with the use of mobile or stationary laser heads can be a source for its pollution. To answer the question about what substances can be in the inhaled air during the laser treatment, an experiment was carried out. Air samples were taken from the laser working space and analyzed in terms of quality and quantity with the use of ASS technology.

Atomic absorption spectrometry (AAS) is a known analytic technique which allows the determination of chemical elements (especially metals) in liquid, solid and gaseous samples. The measurement principle is based on the phenomenon of absorption of radiation (energy) of specific wave length by free metal atoms. The absorbance measurement is made here (proportional to the number of absorbing atoms) and this is the basis for calculating the concentration of the examined element in relation to the absorbance of patterns of concentrations (calibration curve) [14].

In Poland, for instance, metals and their compounds and so called metalloids (semi metallic elements: arsenic, selenium, tellurium) constitute a considerable group of hazardous factors. The most important metals in working environment are lead, cadmium, chromium, cobalt, iron, zinc, copper and nickel [15, 16].

Thus the presence of chromium, cadmium and lead was determined in the experiment. The samples were prepared in the following way:

1. As a base surface cleaned with laser beam – a plate of the dimensions: 95?250 mm (0,02375 m^2), made of:
   a) Aluminum alloy PA7,
   b) Plastic material (polypropylene - PP),
   c) Ceramic without glaze, covered with a layer of black spray (graphitti).
2. A solution of 1 M nitric acid was prepared (in accordance with [15, 16]) and a set of three Dreschl's washing kettles connected in series, each with 50 cm^3 of solution, in order to

maximize the amount of absorbed substances and to minimize the pollutants invading the atmosphere (to obtain reliable results).

3. A laser treatment of the prepared surfaces was performed, each time the air vacuumed from the treatment area was put through the set of the washing kettles. The treatment was performed in one pass of a fiber laser beam of wave length λ=1,07 μm and energy density Q=7?33 J/cm^2. The 500 W power laser head was fitted relative to the moving sample (stand description in [10]) in such a way that a steady speed rate of the material with regard to the stream of energy was ensured; the assumed speed was 115 mm/min, at 50% laser power applied. Three solutions containing products (pollutants) evaporated from treated surfaces were obtained.

Fig.1 presents the stand prepared for the experiment.

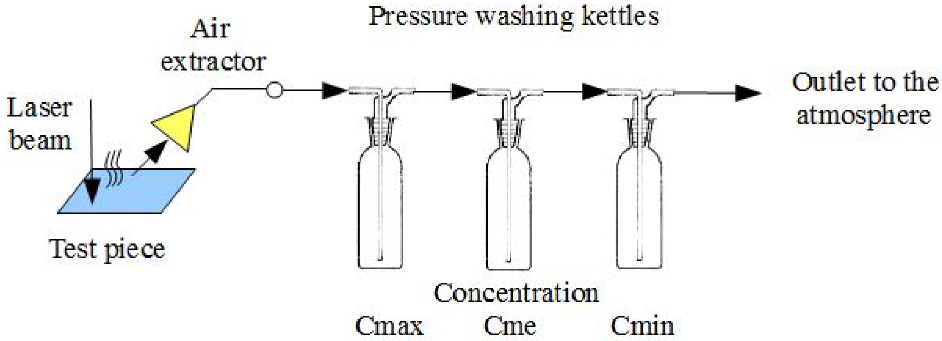

Fig. 1. The diagram of the stand for waste gas absorption

Fig.2 presents the treatment of the examined materials, the photographs show changes on the surface caused by laser impulse.

a) b) c)

Fig. 2. Laser material treatment: a) aluminum alloy (PA7), b) plastic (PP), c) ceramic with graphitti

5. Results

Collected solutions with maximum, medium and minimal concentrations were analyzed in AAS[1]. The results obtained were given in Tables 2?4.

[1] AAS was made in the Department of Inorganic and Analytical Chemistry of Rzeszow University of Technology from samples prepared using a GBC Savant AA apparatus and provided by the authors

Table 2. Concentration values of chromium in samples

Kind of element	Sample No.	Aluminium alloy (PA7)		Plastic (PP)		Ceramic with graphitti	
		Concen-tration [μg/cm³]	Average absorbance	Concen-tration [μg/cm³]	Average absorbance	Concen-tration [μg/cm³]	Average absorbance
Chro-mium Sensiti-vity 0,05 ppm	Sample I C_{max}	No data	0,0054	0,221	0,0080	No data	0,0049
	Sample II C_{med}	No data	0,0049	0,490	0,0092	No data	0,0044
	Sample III C_{min}	0,07	0,0067	0,929	0,0111	No data	0,0034

Table 3. Concentration values of cadmium in samples

Kind of elemen t	Sample No.	Aluminium alloy (PA7)		Plastic (PP)		Ceramic with graphitti	
		Concen-tration [μg/cm³]	Average absorbance	Concen-tration [μg/cm³]	Average absorbance	Concen-tration [μg/cm³]	Average absorbance
Cad-mium Sensiti-vity 0,009 ppm	Sample I C_{max}	0,007	0,0032	0,004	0,0018	0,027	0,0129
	Sample II C_{med}	0,004	0,0020	0,000	-0,0001	0,013	0,0065
	Sample III C_{min}	0,004	0,0020	0,000	-0,0004	0,008	0,0041

Table 4. Concentration values of lead in samples

Kind of elemen t	Sample No.	Aluminium alloy (PA7)		Plastic (PP)		Ceramic with graphitti	
		Concen-tration [μg/cm³]	Average absorbance	Concen-tration [μg/cm³]	Average absorbance	Concen-tration [μg/cm³]	Average absorbance
Lead Sensiti -vity 0,05 ppm	Sample I C_{max}	0,000	-0,0001	0,000	-0,0001	0,075	0,0046
	Sample II C_{med}	0,024	0,0014	0,000	-0,0005	0,021	0,0013
	Sample III C_{min}	0,001	0,0001	0,000	0,0000	0,000	-0,0007

With the assumption that each washing kettle contained 50 cm³ of nitric acid, with the data from Tab.2?4, the entire content of pollution in waste gases was calculated from the relation:

$$m_{Me} = \left(C_{max} + C_{me} + C_{min}\right) \cdot V_p \quad (1)$$

where:

m_{Me} – the weight of metal absorbed during the process of material treatment [?g],

C_x – the concentration of a given metal in subsequent washing kettles (maximum, medium, minimum), [?g/cm³],

V_p – the volume of washing kettle (V_p = 50 cm³).

The results of the calculation were presented in Table 5:

Table 5. Total content of examined metals in solutions

Element	Processed material		
	Aluminium alloy (PA7)	Plastic (PP)	Ceramic with graphitti
Chromium [μg]	3,50	82	0,00
Cadmium [μg]	0,75	0,20	2,40
Lead [μg]	1,25	0,00	4,8

The results obtained are in agreement only for the surface adopted for the experiment (95x250 mm – 0,02375 m^2). In practice the treatment is carried out on much larger surfaces.

Thus, the maximum surface of given material was determined whose treatment will yield the "boundary" amount of a particular pollutant (metal) – compared to the values of given elements found in literature [3, 4]. For calculation the following relation was used:

$$S_{max} = \frac{C_{norm}}{\frac{m_{Me}}{S_{obr}}} \qquad (2)$$

where:

S_{max} – maximum, within the norm, surface of material treatment, calculated for 1 m^3 of polluted air, [m^2/m^3],

C_{norm} – the highest acceptable concentration of a given metal in working environment [3, 4], expressed in [?g/m^3],

m_{Me} – the weight of metal, absorbed during the process of material treatment – according to tab. 4, [?g],

S_{obr} – the material surface subjected to laser treatment (S_{obr} = 0,02375 m^2).

The results of the calculation were presented in Table 6.

Table 6. Maximal surface of treatment [m^2] when the acceptable values of metal concentration in the air are not exceeded - the maximum boundary value

Processed material	Maximum surface of treatment [m^2]*		
	Cr	**Cd**	**Pb**
Aluminium alloy (PA7)	0,68	0,32	0,95
Plastic (PP)	0,03	1,19	No data
Ceramic with graphitti	No data	0,10	0,25

* for the examined metals, in relation to the unit of polluted air [1 m^3]

6. Conclusions

Many harmful elements can not be completely eliminated from the working environment as they posses positive properties as well. In the case of metals, good thermal and electrical conductivity, satisfactory mechanical properties and usefulness for different methods of forming (forging, rolling, casting) are the features making them indispensable for manufacturing goods. In this context, the priority is to effectively protect workers against the harmful effect of substances which come out during processing, provide the appropriate protective equipment and make use of ventilating and filtering appliances work-stands are fitted with.

A professional literature review shows that industrial work-stands should be of a concern as excessive emission of hazardous substances may occur there. These substances can, mostly imperceptibly, cumulate in the human body causing serious health problems. In order to verify the occurrence of these hazards, some labels were marked Cr and Pb (disadvantageous for the human body and possible to occur at the work-stand). The experimental analysis carried out proves the occurrence of these metals in the examined media. The results unequivocally show that in the examined group of three materials, the highest content of Chromium is in a plastic - polypropylene. Referring to the maximum concentration allowed by the norms ([3, 4]) it can be noticed that in the group of materials containing Chromium, the safest material is an aluminum alloy (PA7), which is due to the maximum surface of treatment and compliance with the norms. In the case of Cadmium, it is polypropylene and in the group of materials containing lead it is again an aluminum alloy (PA7).

Keeping in mind the considerable environment pollution, efforts should be made to develop research into the harmfulness of waste gases because of the real danger they pose to the workers of the industrial sector of material treatment.

The ASS method can be used, among other things, as a technique appropriate for the routine labeling of elements contained in the work-stand air.

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АНАЛИЗ ТОКСИЧНОСТИ ГАЗОВ ПОСЛЕ ЛАЗЕРНОЙ ОБРАБОТКИ ПОВЕРХНОСТНОГО СЛОЯ

Во многих отраслях промышленности наблюдаются эмиссии токсических веществ. Эта проблема заслуживает особого внимания, так как большинство токсинов попадает в организм человека дыхательным путем, а негативные для здоровья последствия могут появиться лишь через много лет.

В работе представлены результаты экпериментальных исследований, проведенных для описания эмиссии токсинов при лазерной обработке поверхности ПА7, ПП и керамики. Определены концентрации избранных элементов, попадающих в воздух в результате лазерной абляции. Подтверждено, что допустимые концентрации значительно превышены на значительно меньших образцах, чем действительные поверхности обрабатываемых лазером. В дальнейшем необходимо применение профессиональных фильтров для исключения этой угрозы.

***Ключевые слова**: технология ААС, абляционная лазерная обработка, загрязнение воздуха, токсичность.*