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Assessment of Hazardous Chemicals Risk in Fur Industry in Lithuania

Birutė Vaitelytė, Jolanta Dvarionienė
Institute of Environmental Engineering, Kaunas University of Technology

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The article describes the research on the possibilities of hazardous chemicals replacement with less hazardous substances. This issue has become of special importance to industrial companies after the adoption of the REACH Regulation. The article examines fur industry and traditional chemicals used in it, namely, sodium dichromate, formaldehyde, and naphthalene. Because of their properties these chemicals are pretending to be included in the REACH Regulation lists of the authorised chemicals. The risks of quasi-materials to the workplaces and the environment have been studied. This research has also looked for the alternatives to hazardous chemicals and has conducted their risk assessment. The analyzed chemicals have been compared with their alternatives with a view of disclosing specific risk reduction.
Key words: *hazardous chemicals, chemicals risk assessment, fur industry.*

1. Introduction

A variety of legal acts on regulating chemicals has encouraged the need for a single and unanimous regulation. A draft project on chemicals regulation was submitted to the European Union (EU) institutions in 2003 (Bajoraitienė A. 2009). The European Parliament and Council Regulation 1907-2006 on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) was adopted in 2006. In a chemical sector the REACH Regulation replaced approximately forty legal acts valid until then and concentrated all legal regulations in one document.

The REACH Regulation aims at ensuring a high level of human health and environment, including chemicals hazard assessment of the alternative methods of promotion The new European Union chemicals policy provides for a single chemical registration and evaluation system, as well as the authorization of the supply to the market and use of the substances of very high concern (carcinogens, mutagens, toxic for reproduction, etc.). The goal of authorization is to ensure good functionality of the internal market, whilst appropriately controlling high concern chemicals and the risk of gradual replacement of these substances with suitable alternative substances or technologies where it is economically and technically reasonable (REACH in brief 2004).

The authorized chemical substances will be included in REACH Annex XIV (a list of authorized chemicals). The following chemical substances may be included in Annex XIV: carcinogens, mutagens and reproductive toxic chemicals of category 1 and 2, persistent bio accumulative and toxic chemicals as well as very persistent and very bio accumulative ones. Chemicals causing similar concern can make a serious negative impact on human health or the environment, their impact having been proved by the research.

In the risk management of chemical substances and preparations, the goal of industrial enterprises is to choose chemicals appropriately and to ensure the safe organization of the selected materials use. Having selected a specific substance or preparation for testing, the requirements of the usage, storage, and release into the environment of a substance or preparation should be complied with. The requirements include preventive measures in the workplace, the limit values for chemical substances in

the workplace air, emissions to air, water, waste management, or technical performance requirements (REACH regulation 2009).

Fur industry which uses natural resources and water is heavily polluting industry (Dvarioniene J., Stasiskiene Z. 2007). It is necessary to evaluate not only the impact of usual emissions and concentrations to the environment, but also the use of certain chemicals, for example, pesticides, surfactants and organic solvents, (The Human Society of the United States 2009)

Large quantities of various chemicals (up to 500 kg of chemicals per ton of raw skins) are used in the fur skins industry (Information document on best available techniques for leather industry 2003). Their storage, transportation and usage are essential requisites. According to the best available techniques (BAT), it is recommended to use chemicals in a safe and prudent way in order to avoid polluting the natural environment. Chemicals such as: formaldehyde, naphthalene, and sodium dichromate used in the fur industry are carcinogenic and toxic to people.

2. Methodology

2.1. Questionnaire survey of chemicals used in fur industry

Six Lithuanian fur companies were surveyed. To establish the distribution of hazardous chemicals, questionnaires containing specific questions were sent to them. Respondents were free to choose whether to respond to the questionnaire or not.

2.2. Assessment of risks posed by chemicals in a workplace

The methodology based on the "COSHH grounds" (COSHH guide 2002) was applied to the evaluation of the risk of chemical substances used in the workplace Depending on the hazard to health, according to the COSHH method chemical substances and preparations include the risk groups from the "A" to "E"(Tables 1 and 2). When a wide variety of chemicals is used, first of all the risks caused by them are to be assessed, then they are to be attributed to hazard groups, and any possible impacts on the health and environment have to be taken into account.

Table 1. Hazard assessment in accordance with the R-phrases: chemicals affecting inhalation (COSHH guide2002)

A (minimum risk)	**B**	**C**	**D**	**E (the highest risks)**
R36, R36/38, R38 and all substances that don‘t have R-phrases in group B-E.	R20, R20/21, R20/21/22, R20/22, R21, R21/22, R22, R67.	R23, R23/24, R23/24/25, R23/25, R24, R24/25, R25, R34, R35, R36/37, R36/37/38, R37, R37/38, R41, R43, R48/20, R48/20/21, R48/20/21/22, R48/20/22, R48/21, R48/21/22, R48/22.	R26, R26/27, R26/27/28, R26/28, R28, R27, R27/28, Carc. cat 3, R40, R48/23, R48/23/24, R48/23/25, R48/24, R48/24/25, R48/25, R60, R61, R62, R63.	Mut. Cat 3, R68, R42, R42/43, R45, R46, R49.

Table 2. Hazard assessment in accordance with the R-phrases: chemicals affecting contact with skin and eyes (COSHH guide2002)

S	
R20, R20/21, R20/21/22, R21/22, R24, R23/24, R23/24/25, R24/25, R27, R26/27, R26/27/28, R26/27, R34, R35,R36, R36/37, R36/38, R36/37/38.	R38, R37/38, R41, R43, R42/43, R48/21, R48/20/21/22,R48/21/22, R48/24, R48/23/24, R48/23/24/25, R48/24/25.

The impact of the workplace on worker depends on both the quantity of chemicals used and mobility of the latter. Other important factors are: conditions of use and implementation of the risk-reduction measures. Information about the chemicals and the volatility (or) dust can be taken directly from the safety data sheets. The temperature at which the process is going on should be also considered.

Linking a chemical hazard group with the information on the quantity and mobility, the degree of risk is determined. The figures in the matrix indicate a degree of risk (1 - low risk, 4 - very high risk) (Table 3). The higher degree of risk, the tighter control of the applicable approach on the protection of the workers should be taken. If you have already applied the recommended or even more severe risk removal and/or reduction measures, and the appropriate control tools, the risk may be considered acceptable.

Table 3. Evaluation matrix of the risk factors affecting the workplaces (COSHH guide 2002)

Quantity of used chemical	Low volatility or dustiness	Medium volatility	Medium dust	High dustiness or volatility
Hazard group A				
Small	1	1	1	1
Medium	1	1	1	2
Large	1	1	2	2
Hazard group B				
Small	1	1	1	1
Medium	1	2	2	2
Large	1	2	3	3
Hazard group C				
Small	1	2	1	2
Medium	2	3	3	3
Large	2	4	4	4
Hazard group D				
Small	2	3	2	3
Average	3	4	4	4
Big	3	4	4	4
Hazard group E				
4				

The control approach is applied in the presence of a risk degree of 1. General ventilation and good farming practices for chemicals handling are applied in case of a risk degree of 2. Engineering measures - at a risk degree of 3. Special measures are applied at a risk degree of 4.

2.3. Assessment of chemicals risk to the environment

The objective of the risk assessment of chemicals to the environment is to identify chemical substances that have or may have a significant impact on the environment (toxic effects of ozone depletion, greenhouse effect, etc). There are no standard methods of evaluation and documentation at a company level. Therefore, the environmental risk assessment method referred to in this research is based on the survey (Baltic Environmental Forum). Information required for the environmental risk assessment has to be collected on each of the environmental hazardous substance and each process separately.

Table 4. Matrix of the material used to define the level of risk (Baltic Environmental Forum)

Risk factor	Persistence	Biological accumulati	Aquatic toxicity	Chronic toxicity to vertebrates	Mobility	Amount	Quantity mobility leading	Emission properties of indirect	Risk index
Very high (5)									
Large (4)									
Medium (3)									
Low (2)									
Very low (1)									
Points (weight)									

A completed matrix helps determine the risk associated with specific substances and tested samplers for a specific process and degree. Evaluation of the results can be individually assessed for each of the 8 risk factors, attributing the percentage value in accordance with their importance to this specific process. The initial assessment score (1-5) can be multiplied by the percentage of the gate and thus the rating points are obtained. If these points are added together, a digital value of a risk index is obtained. (Table 4). Having compared the risk indices of various chemicals used in the activities, they may be set according to their importance factors, and in this way the actions to be taken first can be decided.

3. Research results

3.1. Use and prevalence of preparations with formaldehyde, naphthalene, and dichromate

As mentioned above, to obtain the information about formaldehyde, naphthalene and sodium dichromate used in fur industry, the survey has been conducted among fur producers of Lithuania. Out of 6 companies inquired, 4 have sent their replies, while 2 enterprises have given no response.

The survey results show that the substances studied in this research are used by all fur producers. Companies that use products containing formaldehyde, naphthalene, and dichromate have indicated 3 products containing exploratory materials: technical formalin, sodium dichromate; naphthalene.

Technical formalin contains >37% of pure formaldehyde(IHCP, Formaldehyde 2003), sodium dichromate contains 100% of sodium dichromate(IHCP, Sodium dichromate 2005) and naphthalene has 100% of naphthalene(IHCP, Naphthalene 2003). Based on the information provided by the companies, 50.7 tons (technical formalin - 1.1 tons, sodium dichromate - 47.8 t, naphthalene - 1.8 t) of the above-mentioned preparations were used in 2008.

3.2. Materials in this study

To find out what chemicals are currently used by Lithuanian fur enterprises, one fur company was chosen for the study. . The company produces fur products of sheep and various small animals. In 2008 the company processed 60,000 units of semi-manufactured products, 10,000 pieces of furs of various small animals, and 4,800 units of sheepskins. Fur production is recognised not only in Lithuania but also abroad, products are exported to Italy (65%), Finland (15%), Denmark (5%) and other EU countries (7%). Only 8% of the production is sold in Lithuania.

3.2.1 Choice of materials

Choice of materials in the company inquired is determined by:

- Customer requirements for materials to be used in production.
- Customer requirements for fur skins. In this case the company receives customer's requirements for the quality and colour of the fur. The company chooses the chemicals to be taken into account in the price-quality ratio.

Having compiled and analyzed the list of chemical substances and preparations in the analyzed company, the hazardous substances were selected for the study. The list of hazardous substances and preparations in that company is not complete since there is no information about the chemicals used in the workplace, the residues of the product, etc. The priority is given to the most hazardous chemicals: sodium dichromate, naphthalene, and formaldehyde.

3.2.2. Risk assessment of chemicals in the workplace

To determine the risks associated with the use of chemicals and their impact on the health of workers, the assessment of sodium dichromate, formaldehyde, and naphthalene has been carried out in the workplace on the basis of the methodology.

Chemicals selected for the study are classified as dangerous to human health. Since the impact on inhalation and access to skin are very important in the workplace, all chemicals used in hazardous components are to be analyzed. Preparations and their hazardous substances as their constituents are assigned into risk groups from the "A" (lowest risk) to "E" (most hazardous) in accordance with the Tables.

Table5. Dangerous products and components of hazardous materials

Name	Ingredients	CAS No.	Hazard symbol letter	R-phrases	Hazard group
Formalin	formaldehyde	50-00-0	T	R 10 23/24/25, 34, 40, 43	D/S
	methyl alcohol	67-56-1	T	R23/24/25-39/23/24/25	C/S
Sodium dichromate	sodium dichromate	91-20-3	T+, N	R45-46-60-61-8-21--34-42/43-48/23-50/53	E/S
Naphthalene	naphthalene	10588-01-9	N	R36, 40, 48/22, 48/23, 63	D/S

Table 5 shows that sodium dichromate from the highest risk group is present in the workplace. Other studied substances are assigned to group "D". All chemicals are included in the medium and high hazard groups. The chemicals classified as belonging to "A" and "B" hazard groups are not analyzed since there is no substances which would be assigned to these groups. Preparations or chemicals used in the workplace can cause the following harmful effects: they can be toxic if ingested, highly toxic if inhaled, can cause cancer and inheritable genetic damage; can be harmful for fertility and to unborn child.

Description of the quantities of chemicals used in the workplace. The quantity of chemicals used at the workplace is evaluated since their impact

on workers depends on the quantity of chemicals and their mobility.

The calculation of the quantities of hazardous substances is based on the maximum concentration in the product indicated in the safety data sheets. Sodium dichromate in accordance with the quantity (9,120 kg) is estimated as 3, naphthalene (498 kg) as 2, and formaldehyde (187.6 kg) as 2.

The mobility of material is assessed according to their boiling temperature, given that the process takes place at the temperature of 20 ^{0}C . The results of the evaluation on the basis of the boiling temperature of sodium dichromate (> 400 ^{0}C) is 1(IUCLID, Sodium dichromate 2005), naphthalene (218 ^{0}C) – 1(IUCLID, Naphthalene 2000), and formaldehyde (- 19.2 ^{0}C) – 3(IUCLID, Formaldehyde 2000).

In view of the chemicals hazard group, and the evaluation of the quantity and mobility of the used materials, the degree of risk is determined according to the Table. The figures in the matrix indicate the degree of risk (1 - low risk, 4 - very high) and an applicable control.

Comparison with the recommended control approaches

As Table 6 shows the company's risk reduction measures are not as strict as required by the COSHH methodology. Having evaluated the market of these chemicals and a potential impact on workers, the methodology recommends the use of these substances in closed systems which have only limited openness.

Table 6. Comparison with the recommended control approaches

Material	Recommended control method	Recommended for the risk of exposure by inhalation, the reduction	Existing risk reduction measures
Sodium dichromate	4	Ensure good ventilation by using local exhaust ventilation and good overall traction, if it is not enough - respiratory protection. Special measures	Ventilation, workers using respirators
Formaldehyde	3		
Methyl alcohol	3		
Naphthalene	2		

To clarify a potential impact on the environment of preparations containing sodium dichromate and naphthalene formalin, the synoptic environmental risk assessment has been conducted in accordance with the methodology.

3.2.3. Risk assessment of analyzed materials to the environment

Toxicity of sodium dichromate causes a high risk to the aquatic environment and vertebrates, as well as its quantity and mobility do. Naphthalene is hazardous for its toxicity to the aquatic environment and vertebrates because of its bioaccumulation and persistence. Formaldehyde is hazardous for its mobility and endurance, aquatic toxicity and chronic toxicity vertebrates. Having combined all the 8 points (Fig.1) of the risk factors assessment, an environmental risk index is obtained which is 4.00 to sodium dichromate, 3.75 to naphthalene and 3.45 to formaldehyde.

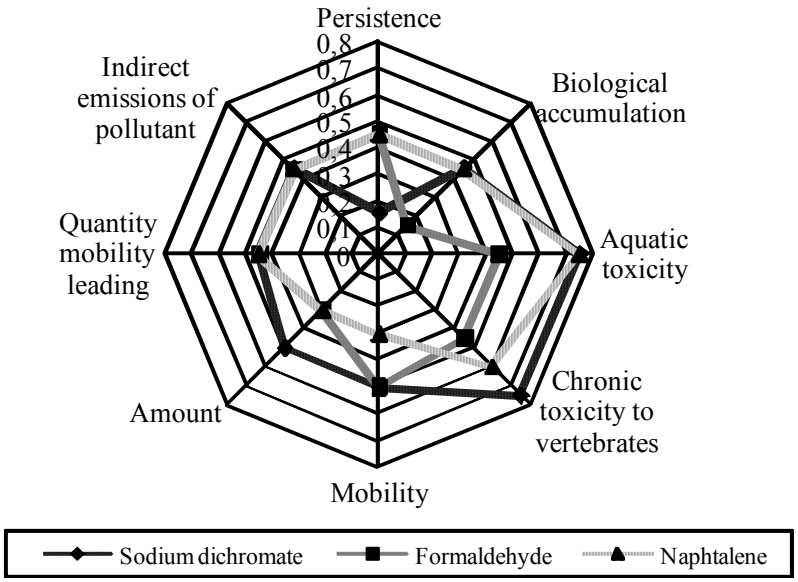

Fig.1. Risk factors of sodium dichromate, formaldehyde, naphthalene

3.3. Alternatives to hazardous chemicals

3.3.1. Reasons for the choice of alternatives

Search for the alternatives to the products containing sodium dichromate, formaldehyde and naphthalene has been encouraged by higher quality and environmental requirements for the production received from EU purchasers. For this reason, an interest has grown in the studies of chemicals that are used by other fur companies. The alternatives have been found to the previously used substances: sodium dichromate-chromic hydroxide is replaced with sulphate, naphthalene - with Skinman Soft (propan-2-ol-based), formaldehyde - with copper salt (copper sulphate pentahydrate).

Table 7. Dangerous products and components of hazardous materials

Name	Ingredients	CAS No.	Hazard symbol letter	R-phrases	Hazard group
Chromium hydroxide - sulphate	chromium hydroxide -sulphate	12336-95-7	C;	R 34	C/S
	sodium sulphate	7757-82-6	Xi	R: 36	C/S
Copper salt	copper sulphate pentahydrate	7758-99-8	Xn; N;	R22 R50 R53	B/S
Skinman Soft	propan-2-ol	67-63-0	F; Xi;	R11R36	C/S
	quaternary ammonium compounds, chlorides	68424-85-1	Xn; C; N;	R22 R34 R50	C/S

3.3.2. Risk assessment of alternatives in the workplace

New alternatives are used in the same workplace where the above-described preparations were used.

Table 7 indicates that the alternatives no longer use components containing toxic properties. Chromium hydroxide - barium and skinman soft are used for preparing tanning solution, and copper salt is applied to refining processes. The limits of the alternatives to be used per year are as follows: chromium hydroxide - sulphate -~ 9580 kg / year, soft skinman - ~ 560 kg / year, while copper salt - ~ 480 kg / year.

Preparations used in the workplace can be harmful if swallowed, they can be irritating to eyes, very toxic to aquatic organisms, may cause long-term adverse changes in aquatic ecosystems.

Description of the quantities of alternatives used in the workplace. Since the impact of the workplace on workers depends on the quantity of chemicals used and their mobility, the evaluation of the quantity of material used at the workplace was carried out. The calculation of quantities was based on the maximum concentration of the product indicated in the safety data sheets. Chromium hydroxide - sulphate (6706 kg) – 3(IHCP, chromium hydroxide - sulphate 2004), propan-2-ol (558.6 kg) – 2 (IHCP, propan-2-ol 2003), copper sulphate pentahydrate (480 kg) – 2(IHCP, copper sulphate pentahydrate2003).

Material mobility was assessed according to the boiling temperature of these materials, given that the process is at a temperature of 20 0^C. The evaluation results based on the boiling point are as follows: chromium hydroxide - sulphate (> 900 0^C) - 1(IUCLID, chromium hydroxide - sulphate 2000), propan-2-ol (82.3 0 ^{C}) – 2(IUCLID, propan-2-ol 2000), copper sulphate pentahydrate (150 0^C) – 2(IUCLID copper sulphate pentahydrate2000).

In view of the chemical hazard group and the evaluation of the quantity and mobility of the used materials, the degree of risk is determined according to the Table. The figures in the matrix indicate a degree of risk (1 - low risk, 4 - very high) and the applicable control approach (Table 8).

According to the obtained evaluation results, the risk reduction measures used in the company are not as strict as required by the COSHH methodology. The methodology recommends using these substances in enclosed systems where local exhaust ventilation is not sufficient.

Table 8. Comparison with the recommended control approaches

Material	Recommended control method	Recommended for the risk of exposure by inhalation, the reduction	Existing risk reduction measures
Chromium hydroxide -sulphate	2	Ensure good ventilation by using local exhaust ventilation and good overall traction, if it is not enough - respiratory protection.	Ventilation, workers using respirators
Sodium sulphate	2		
Copper sulphate - pentahydrate	1		
Propan-2-ol	3		
Quaternary ammonium compounds, chlorides	2		

3.3.3. Risk assessment of alternatives to the environment

To ascertain a possible impact of alternatives on the environment, the synoptic environmental risk assessment has been conducted in accordance with the methodology. The following chemicals are selected for further environmental risk assessment of the alternatives: chromium hydroxide-sulphate because of its higher concentration (> 70%) compared to the sodium sulphate concentration (<30%), copper sulphate pentahydrate because of its concentration of 100%, propan-2-ol, since it has a higher concentration (> 99.75%) than the concentration of quaternary ammonium compounds (<0.25%).

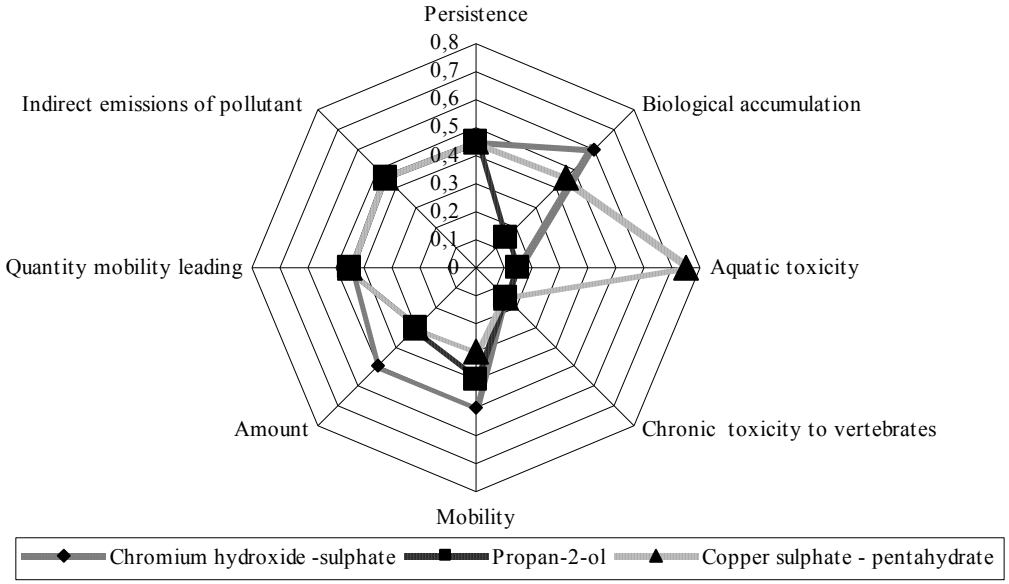

Fig.2. Risk factors of chromium hydroxide - sulphate, propan-2-ol and copper sulphate pentahydrate

As you can see from the picture, the highest risk of chromium hydroxide - sulphate to the environment is caused by its mobility and quantity. Propan-2-ol is risky for its durability, indirect emissions and conditions affecting its mobility. Copper sulphate pent hydrate is dangerous for its toxicity to the aquatic environment, bio-retention and durability. Having combined all the 8 points (Fig.2) of the risk factors assessment, the environmental risk index is obtained, where the chromium hydroxide-sulphate equals to 3.25, propan-2-ol – to 2.50 and of copper sulphate pentahydrate – to 3.30.

3.4. Comparison of analyzed chemicals and their alternatives

3.4.1. Comparison of the surveyed risk assessment results in the workplace

Having compared the preparations containing sodium dichromate, formaldehyde and naphthalene with the chemicals of new alternatives, it can be concluded that the usage of alternatives does not leave any hazardous substances belonging to groups "E" and "D". There is no risk for fertility, unborn child, cancer, and suffering from toxic poisoning by inhalation.

Table 9. Comparison of the quantity of materials in preparations

Material	Hazard Group	Quantity previous preparations kg per year	Quantity alternatives kg per year
Formaldehyde	C/S	185	-
Methyl alcohol	C/S	75	-
Copper sulphate pentahydrate	B/S	-	480
Sodium dichromate	E/S	9025	-
Chromium hydroxide sulfate	C/S	-	6706
Sodium dichromate	C/S	-	2874
Naphthalenes	D/S	500	-
Propan-2-ol	C/S	-	558,6
Quaternary ammonium compounds	C/S	-	1,4

Having compared the hazardous chemical substances and their quantities in the previously used products with their alternatives, it can be concluded that (Table 9):

- the number of substances that fall under "E" risk group diminishes; the quantity is about 9,025 kg per year for the same amount of the output produced;
- "D" in the risk group is also reduced to about 500 kg per year for the same amount of the output produced
- since the former changed and discarded options reduce the risk of any particular impairment, can not be described.

3.4.2. Comparison of the results of the environmental risk assessment

The synthesis of the environmental risk assessment results shows that the environmental risk index of chromium hydroxide - sulphate (in effect) is 0.75 units lower than that of sodium dichromate, and therefore it can be assumed that the selected alternative will have a slightly lower environmental impact than sodium dichromate. It also appeared that the environmental risk index of propane-2-ol (present in the option) is 1.25 units lower than that of naphthalene. The examination of the environmental risk assessment results has shown that the environmental risk index of copper sulphate pent hydrate (in effect) is 0.15 units lower than that of formaldehyde (Fig.3). The only conclusion after comparison of these substances is that after the replacement a negative environmental impact should not increase.

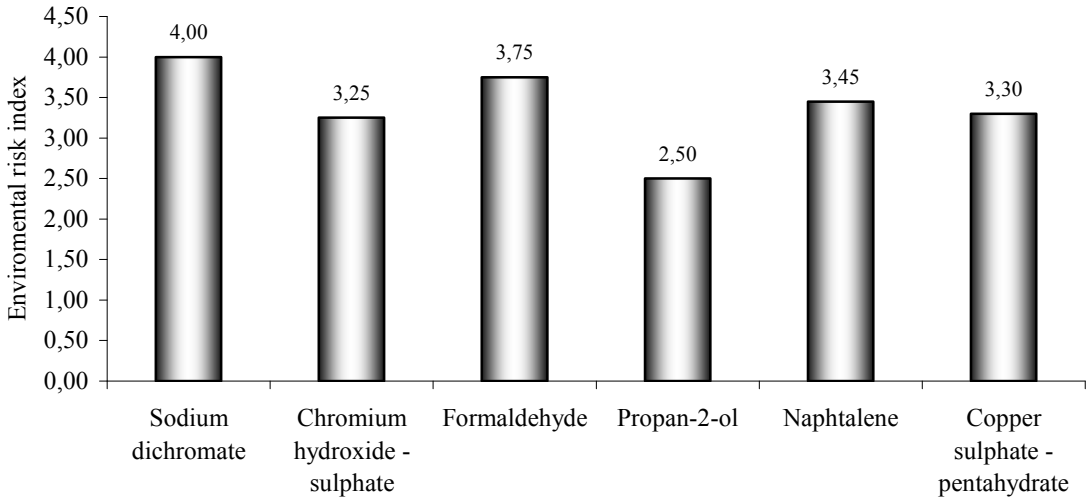

Fig.3. Comparison of the environmental risk factors

4. Conclusions

Evaluation of the alternatives to hazard chemicals has revealed that the chemicals are attributed either to a very moderate or low risk groups. The assessment (points) of the alternatives environmental risk is as follows: chromium hydroxide-sulphate equals to 3.25, propan-2-ol to 2.50 and copper sulphate pentahydrate to 3.30.

Comparison of the workplace risk assessment of the chemicals used in the analyzed preparations with their alternatives shows that no dangerous chemicals are left in case the alternatives are used. Consequently, there is no risk to fertility, unborn child, cancer, and suffering from toxic poisoning by inhalation.

Indices of the level of environmental risk show that in case chromium hydroxide - sulphate is used, the impact on the environment is reduced by 0.75 points and the impact of naphthalene on the environment is reduced by 1.25 points, and in case of formaldehyde - only by 0.15 points.

The following is suggested to enterprises using the analyzed substances:

- to approach the suppliers with a request to update the safety data sheets about the use of chemical substances and preparations;
- to compile a list (registry) of used chemicals which can be included in a comprehensive evaluation of the substances;
- to discard dangerous preparations containing sodium dichromate, formaldehyde, naphthalene;
- to search for alternatives and replace hazardous chemicals with less dangerous;
- to change the production technology.

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MSc. Birutė Vaitelytė, researcher at the Institute of Environmental Engineering, Kaunas University of Technology.
Main research areas: chemicals control, water management
Address: K. Donelaičio str. 20
LT-44239, Kaunas, Lithuania
Tel. +370 37 300767
Fax: +370 37 209372
E-mail: birutevaitelyte@gmail.lt

Dr. Jolanta Dvarionienė, researcher at the Institute of Environmental Engineering, Kaunas University of Technology
Main research areas: chemicals control, cleaner production, environmental impact assessment, water and waste management
Address: K. Donelaičio str. 20
LT-44239, Kaunas, Lithuania
Tel. +370 37 300767
Fax: +370 37 209372
E-mail: jolanta.dvarioniene@ktu.lt

Pavojingų cheminių medžiagų rizikos vertinimas Lietuvos kailių pramonėje

Birutė Vaitelytė, Jolanta Dvarionienė
Aplinkos inžinerijos institutas, Kauno technologijos universitetas

Straipsnyje nagrinėjamos pavojingų cheminių medžiagų pakeitimo galimybės mažiau pavojingomis medžiagomis. Įmonėms tai ypač aktualu tapo priėmus REACH reglamentą. Straipsnyje nagrinėjama kailių pramonė ir tradicinės joje naudojamos cheminės medžiagos – natrio dichromatas, naftalinas ir formaldehidas. Pagal savo savybes tiriamosios medžiagos pretenduoja būti įtrauktos į REACH reglamento autorizuotinų medžiagų sąrašus. Straipsnyje nagrinėjama tariamųjų medžiagų keliama rizika darbo vietai ir aplinkai. Taip pat ieškoma alternatyvų, vertinama jų rizika. Lyginamos tiriamosios medžiagos ir alternatyvos tam, kad būtų atskleistas konkretus rizikos mažėjimas. Straipsniu siekiama aptarti cheminių medžiagų keliamą riziką aplinkai ir jos mažinimo galimybes. Sudarius tiriamosios įmonės cheminių medžiagų registrą, tolesniam tyrimui buvo pasirinktos šios medžiagos: natrio dichromatas, formaldehidas ir naftalinas. Siekiant išsiaiškini nagrinėjamų medžiagų pakeitimo mažiau pavojingomis galimybes, buvo išanalizuotas preparatų, naudojamų kailių pramonės įmonėse paplitimas ir priežastys. Pagal aprašytą metodiką įvertintos tiriamosios medžiagos ir alternatyvų rizika aplinkai.