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ASSESSMENT OF ECOLOGICAL RISK IN THE PAINT AND COATINGS INDUSTRY FROM THE PERSPECTIVE OF THE AQUATIC ECOSYSTEM

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Abstract. *In assessing ecological risk in the paint and coatings industry, stressors are examined from the perspective of exposed hazardous substances, whether as input substances or substances leaving the technological process and entering the environment. The extent of their negative impact on humans, living organisms, non-living nature, and material goods depends on their characteristics and the frequency and degree of their effects. When assessing risks, the frequency and degree of their effects are considered in terms of regular operational regimes and accident scenarios. The spatial distribution of hazardous substances reaching watercourses is also presented based on calculations of maximum emission quantities and volumes of substances, as well as the determination of the area of contaminated watercourses. Risk is assessed concerning the probability of the most likely unwanted events in the paint and coatings industry and their consequences for human life, health, and the environment.*

Key words: *ecological risk, paint and coatings industry, aquatic ecosystem*

1. INTRODUCTION

Ecological hazard is the probability of compromising human health and environmental conditions due to uncontrolled emissions of pollutants. Environmental risk includes risks that endanger the health and lives of people, as well as risks that threaten the condition of the environment. It can result from various technological processes applied in the chemical industry, among other factors. The assessment of ecological risk arising in the chemical

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industry is linked to the consequences resulting from the actions of hazardous substances on ecosystems, which are inherently complex.

The technological processes used in the paint and coatings industry, as part of the chemical industry, are heterogeneous. The raw materials and intermediates used vary in terms of the hazards and damages they can cause during different accident scenarios. The production of paints and coatings represents the culmination of a highly complex chemical industry chain. Within this chain, pigments of organic or inorganic origin are synthesized, followed by polymers used in paint production, and finally, solvents that serve as the base for paints and coatings.

During the operation of this industry, as well as in accident scenarios, various pollutants are released into water, air, and soil. A particular risk in the paint and coatings industry is the release, spillage, or leakage of hazardous substances that often reach surface watercourses uncontrollably. The extent of degradation of watercourses depends on the transformation of hazardous substances into harmful ones. The conversion of hazardous substances into harmful ones depends on the physicochemical and toxicological characteristics of the substances, as well as their quantities and the specific characteristics of the watercourses themselves.

Understanding the chemical composition and physicochemical properties of input substances and substances leaving the technological process and entering the environment is fundamental for assessing ecological risk during regular operations and in accident scenarios.

2. The Presence of Hazardous Substances in Watercourses

Hazardous substances used in the paint and coatings industry can enter watercourses as part of wastewater or in the event of accidental (incidental) incidents. Wastewater is generated in the processes of washing and cleaning production areas and equipment, and its quality depends on the properties of the substances used in the production process. It can also originate from the process of caustic cleaning of tanks and secondary pipelines. Wastewater in the paint and coatings industry is typically alkaline in nature, with a small percentage of oils and fats, and characterized by low BOD (Biological Oxygen Demand) values. Wastewater can have high COD (Chemical Oxygen Demand) values due to the presence of organic substances used, such as solvents, preservatives, styrene, acetone, benzene, phenol, etc. Additionally, liquid waste may contain residues of heavy metals that come from the pigments used. All paints contain pigments in their composition, which are natural or synthetic compounds. Pigments are powdery substances that can be most simply classified as organic and inorganic; they are soluble in water, alcohol, or oil used in the technological process. Table 1 presents the classification of inorganic pigments. Synthetic organic pigments are hydrocarbon compounds and can have varying degrees of toxicity [1].

Table 1 Classification of inorganic pigments based on chemical composition

Compounds	Chemical formula
Oxide pigments	TiO_2, ZnO, α-Fe_2O_3, α-$FeOOH$, γ-Fe_2O_3, Fe_3O_4, Cr_2O_3, $CrOOH$, PbO, Pb_3O_4, Mn_3O_4, -$MnOOH$, Sb_2O_3
Complex oxide	$CoAl_2O_4$, $CuCr_2O_4$, Co_2TiO_4, $(Ti,Ni,Sb)O_2$, $(Ti,Cr,Sb)O_2$
Carbonate hydroxide	$2PbCO_3 \cdot Pb(OH)_2$, $2CuCO_3 \cdot Cu(OH)_2$, $CuCO_3 \cdot Cu(OH)_2$
Sulphide, selenium	ZnS, CdS, $Cd(S,Se)$, $CdSe$, γ-Ce_2S_3, HgS, As_2S_3
Chromate, molybdate	$PbCrO_4$, $Pb(Cr,S)O_4$, $Pb(Cr,S,Mo)O_4$, $ZnCrO_4$, $BaCrO_4$, $SrCrO_4$
Bismuth	$BiVO_4$, $4BiVO_4 \cdot 3Bi_2MoO_6$
Tin	Pb_2SnO_4, $PbSn_2SiO_7$, Co_2SnO_4, $CoSnO_3$
Phosphate	$Co_3(PO_4)_2$
Antimony	$Pb(SbO_3)_2$
Arsenic	$Cu(AsO_3)_2$
Ultramarine	$Na_6Al_6Si_6O_{24}(NaS_n)$
Hexacyanoferrate	$K[Fe^{III}Fe^{II}(CN)_6] \cdot xH_2O$ ($x = 14–16$)
Tantalum oxide	$CaTaO_2N$, $LaTaON_2$
Elements	C, Al, Cu, Cu/Zn, Au

Determining the maximum amount of pigments in the composition of wastewater, as well as solvents or other hazardous substances, can be considered one of the relevant factors in risk assessment. Hazardous substances such as chromium, copper, lead, zinc, titanium, and others cannot be found in their original form in the influent because, during the production process, they mix with various other substances and solvents.

The largest amount of wastewater from the paint and coatings industry is generated from equipment cleaning, accounting for about 80% of the influent. According to statistical data, approximately 70% of wastewater from the paint and coatings industry is discharged untreated into natural river basins and contains hazardous substances that vary in their solubility, volatility, and toxicity [2,11].

In the event of an accidental incident, a spill or leak of hazardous substances can occur, leading to their release into watercourses in their original form. The degradation of the watercourses will depend on the toxicity level, quantity, volume, and area of the contaminated watercourses, as well as the exposure time.

3. RISK ASSESSMENT

Assuming that an accidental event or incident in the chemical industry occurs as a result of a leak of hazardous substances, the risk can be modeled as the product of the number of participants in the scenario and the frequency of the incident.

risk = frequency of the incident x number of participants in the scenario

The frequency of accidents is analyzed using data from the following dataset:

1. Reliability data was prepared by determining accident and equipment failure data in the factory.
2. Equipment failure frequency data provided by equipment manufacturers.
3. Reliability data provided by the European reliability database for industry.
4. Reliability data for non-electronic components.

Representative data on the frequency of most likely accidents related to the paint and coatings industry are presented in Table 2 [3].

Table 2 Annual frequency of accidents

Initial event	Known probabilities of events (on an annual basis)
Court cancellation under pressure	10^{-6}
Pipeline failure due to malfunction (at 100 m)	10^{-5}
Pipeline leak (at 100 m)	10^{-3}
Atmospheric tank failure	10^{-3}
Flange/valve leak	10^{-3}
Pump/compressor leak	10^{-3}
Premature opening of the spring valve	10^{-2}
Malfunction during water cooling	10^{-1}
Discharge/filling hose failure	10^{-2}
External fire	10^{-2}

In the Republic of Serbia, there is no available systematic database regarding accidents and malfunctions of equipment and facilities in the paint and varnish industry, so the risk assessment of each plant can be performed using the REHRA method, according to the scheme given in Figure 1.

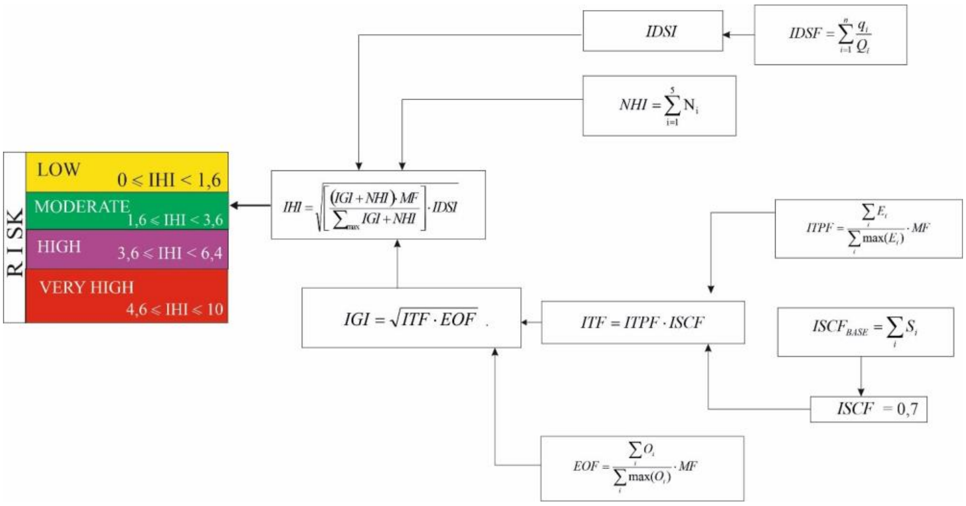

Fig.1 Summary of risk assessment within facilities applied in the industry [2,5]

Calculation of the number of participants in the scenario is based on establishing the boundaries of hazardous substance leakage so that the leakage zone defines the radius from the source of leakage to the furthest point of dispersion. The level of potential adverse consequences resulting from the entry of hazardous substances into watercourses can be determined by identifying the maximum quantities of substances entering the watercourses and determining the volume they occupy in the watercourses.

The maximum amount of hazardous substances that can be released into a surface watercourse is determined by Equation 1. [4,5]

$$Q_{ws} = Q \times f_1 \times f_2 \quad (1)$$

Q_{WS} is the maximum mass of a substance that can reach water or soil after its release.
Q is the maximum quantity of a given substance that can be discharged from the equipment (in tons).
f_1 is the reduction coefficient based on the physical properties of the released substance.
f_2 is the reduction coefficient associated with technical protective measures aimed at retaining discharged hazardous substances from the facility.

The reduction coefficients are determined according to Tables 3 and 4, and their values range from 0 to 1.

Table 3 Criteria for selecting the value of reduction coefficient f_1

f_1	Description
1	If the boiling point of the substance at atmospheric pressure is higher than 55°C
1 - 0.75	If the boiling point of the substance at atmospheric pressure is between 21°C and 55°C
0.75 - 0.5	If the boiling point of the substance at atmospheric pressure is between 0°C and 21°C
0.5 - 0.2	If the boiling point of the substance at atmospheric pressure is between -35°C and 0°C
0.2 - 0	f the boiling point of the substance at atmospheric pressure is below -35°C

Table 4 Criteria for selecting the value of coefficient f_2

f_2	Description
1	If the spillage goes directly into the final receptor (soil or watercourse) without any protective barrier
1 - 0.8	If the spillage does not go directly into the final receptor (soil or watercourse), but it's not possible to divert the contents to a separate treatment system or retention basin
0.8 - 0.4	If part of the spilled contents can be directed to a collection system or can be retained in a retention basin
0.4 - 0.1	If there is a spillage in the retention basin or if a larger portion of the spilled contents can be directed, treated, or somehow recovered

To conduct a relevant risk assessment for the discharge of hazardous substances into surface waters, in addition to determining the volume of contaminated water, the possibility of spreading (spillage) of hazardous substances is also considered. The extent of contamination of watercourses primarily depends on the physical properties of the substances and the presence of specific barriers to the spread of discharged hazardous substances.

To assess the quantity of endangered water, hazardous liquid pollutants are categorized into water-soluble and water-insoluble substances. Water-soluble hazardous pollutants tend to spread homogeneously in watercourses, whereas substances are considered water-insoluble when their solubility is below 10%.

Determining the surface area of watercourses contaminated by the release of water-insoluble liquids is carried out using equation 2 [5,8].

$$W_s = \frac{Q_{ws}}{\rho_s \times d_s} \tag{2}$$

Ws is the surface area of water contaminated by the discharge of water-insoluble liquids (m^3).
d_s is the average thickness of the substance layer on the surface of the watercourse (m).
ρ_s is the density of the discharged substance (kg/m^3).

Calculating the volume of contaminated water affected by toxic substances discharged from industry is done using equation 3 [4,5].

$$V = \frac{Q_{rws}}{LC_{50} \times P \times BCF} \tag{3}$$

V is the volume of contaminated water (m^3).
Q_{rws} is the maximum amount of substance reaching the water (g).
LC_{50} is the lethal concentration (mg/dm^3).
P is the persistence factor (dimensionless).
BCF is the bioconcentration factor (dimensionless).

To determine the ecological risk arising from the discharge of hazardous substances into watercourses, Equations 1 and 2 (REHRA) can be applied.

In case of an accidental event, organic solvents of varying toxicity levels can be discharged into watercourses. Table 5 provides the maximum quantity of organic solvents that can be released into watercourses during accidents, determined using Equation 1. To calculate the maximum quantity that can be found in the watercourse, data on the maximum permitted quantities of substances used in production according to SEVESO plant regulations are used. A substance that reaches watercourses and dissolves in water immediately can endanger the watercourse depending on its toxicity. The volume of surface water that is endangered in such cases can be determined using Equation 3 and is provided in Table 5.

Based on the calculations provided in Table 5, it can be concluded that the maximum mass of substance released into watercourses can be reduced by a factor of ten, depending on whether there are specific systems for collecting the discharged substance or if it is directly discharged into watercourses. If there is a spillage in the retention basin or if a larger portion of the spilled content can be directed, treated, or somehow recovered, the mass of discharged substance into watercourses during an accidental event can be reduced by a factor of ten.

To predict or assess the risk resulting from the discharge of hazardous substances into surface waters, it is crucial to determine the volume of endangered (contaminated) water for which damage is assessed according to Tables 6 and 7. After determining the consequences or damage of the unwanted event, as well as the probability of its occurrence according to Table 8, a risk matrix is formed as shown in Figure 2. [6]

Table 5 Quantity of discharged substance into the surface watercourse and volume of endangered water [2]

Substance	If the spillage goes directly into the final receptor (soil or watercourse) without any protective barrier		If the spillage does not go directly into the final receptor (soil or watercourse), but it's not possible to divert the contents to a separate treatment system or retention basin		If the spilled content can be directed to a collection system or retained in a retention basin		If there is a spillage in the retention basin or if a larger portion of the spilled content can be directed, treated, or somehow recovered	
	Q_{WS} (t)	V (m^3)	Q_{WS} (t)	V (m^3)	Q_{WS} (t)	V (m^3)	Q_{WS} (t)	V (m^3)
Aromatic hydrocarbons								
Benzene C_6H_6	50	3.88	40	310	20	1.55	5	0.39
Toluene C_6H_6	50	7.05	40	5.64	20	2.82	5	0.71
Xylene C_8H_{10}	50	6.58	40	5.27	20	2.63	5	0.66
Naphthalene $C_{10}H_8$	50	11.5	40	9	20	4.5	5	0.75
Alcohols								
Methanol CH_4O	50	0	40	0	20	0	5	0
Ethanol C_2H_6O	50	0.01	40	0.01	20	0	5	0
Propanol C_3H_8O	50	0.01	40	0.01	20	0.01	5	0
n-Butanol $C_4H_{10}O$	50	0.05	40	0.04	20	0.02	5	0
Amyl alcohol $C_5H_{12}O$	50	0.10	40	0.08	20	0.04	5	0.01
Cyclo-hexanol $C_6H_{12}O$	50	0.09	40	0.08	20	0.04	5	0.01
Ethylene glycol $C_2H_6O_2$	50	0	40	0	20	0	5	0
Benzyl alcohol C_7H_6O	50	0.14	40	0.12	20	0.06	5	0.01
Etars and acetals								
Ethyl ether $C_4H_{10}O$	42.5	0.02	34	0.01	17	0.01	4.25	0
n-Propyl ether $C_6H_{14}O$	50	263.16	40	210.53	20	105.26	5	26.32
Dioxane $C_4H_8O_2$	50	0.49	40	0.39	20	0.19	5	0.05
Aldehydes and ketone								
Aceta-ldehyde C_2H_4O	36.5	1.07	29.2	0.86	15	0.44	3.65	0.11
Acrolein C_3H_4O	45	2368.42	36	1894.74	18	947.37	4.5	236.84
Furfural $C_5H_4O_2$	36	1,5	28.8	1.18	14.4	0.60	3.6	0.5

Acetone C_3H_6O	50	0.01	40	0.01	20	0	5	0
Acetic acid $C_2H_4O_2$	50	0.57	40	0.45	20	0.23	5	0.06
Formic acid HCOOH	50	0.38	40	0.31	20	0.15	5	0.04
Esthers								
Methyl formate $C_2H_4O_2$	41	0.46	32.8	0.36	16.4	0.18	4.1	0.05
Ethyl formate $C_3H_6O_2$	47.5	0.28	38	0.22	19	0.11	4.8	0.03
Butyl formate $C_5H_{10}O_2$	50	1.84	40	1.47	20	0.73	5	0.18
Methyl acetate $C_3H_6O_2$	50	0.19	40	0.15	20	0.08	5	0.02
Ethyl acetate $C_4H_8O_2$	50	0.29	40	0.23	20	0.12	5	0.03
Chlorinated hydrocarbons								
Chloroform$CHCl_3$	50	0.44	40	0.35	20	0.17	5	0.04
Carbon tetrachloride CCl_4	50	5.49	40	4.39	20	2.19	5	0.55
Dichloro-ethane $C_2H_4Cl_2$	50	0,.44	40	0.36	20	0.18	5	0.04
Trichloro-Ethylene C_2HCl_3	50	3.25	40	2.6	20	1.3	5	0.33
Tetrachloro-ethylene C_2Cl_4	50	7.25	40	5.8	20	2.98	5	2.72
Chloro-benzene C_6H_5Cl	50	0.69	40	0.55	20	0.28	5	0.07
Organic nitrogen compounds								
Aniline C_6H_7N	50	4.72	40	3.77	20	1.89	5	0.47
m-Toluidine C_7H_9N	50	1.38	40	1.10	20	0.55	5	0.14
Pyridine C_5H_5N	50	0.53	40	0.43	20	0.21	5	0.05
Acetonitrile C_2H_3N	50	0.03	40	0.02	20	0.01	5	0
Nitro-benzene $C_6H_5O_2N$	50	0.54	40	0.43	20	0.22	5	0.05
Organic sulfur compounds								
Carbon disulfide CS_2	47	15.67	37.6	12.53	18.8	6.27	4.7	1.37
Compounds with multiple functional groups								
Methylene glycol $C_3N_8O_2$	50	0.43	40	0.34	20	0.17	5	0.04
Ethylene glycol $C_4N_{10}O_2$	50	0	40	0	20	0	5	0
Diethylene glycol $C_4N_{10}O_3$	50	0	40	0	20	0	5	0
o-Chloro-aniline C_6N_6ClN	50	11.70	40	9.36	20	4.68	5	1.17

Table 6 Categorization of consequences on human life and health

Consequences on human life and health			
Category	Extent of consequences	Criterion *	Selected
1	Minimal	<50	
2	Minor	50-200	
3	Moderate	201-500	
4	Severe	501-1500	
5	Catastrophic	>1500	

*Total number of people affected by a hazard (deceased, injured, ill, evacuated, displaced - homeless, accommodated, and sheltered)

Table 7 Categorization of consequences for economy/ecology

Consequences for economy/ecology			
Category	Extent of consequences	Criterion **	Selected
1	Minimal	exceeding 1% of the budget	
2	Minor	exceeding 3% of the budget	
3	Moderate	exceeding 5% of the budget	
4	Severe	exceeding 10% of the budget	
5	Catastrophic	exceeding 15% of the budget	

**Total costs include healthcare or medical treatment costs, immediate or long-term emergency measures, building restoration costs, public transport and infrastructure costs, material goods, cultural heritage, ecological restoration costs, costs of business interruption, and insurance premiums paid.

At the national level, economic/ecological consequences are assessed relative to the budget of the Republic of Serbia.

At the level of autonomous provinces and local self-governments, economic/ecological consequences are assessed relative to the budgets of autonomous provinces and local municipalities.

Consequences for companies and other legal entities are expressed as the sum of fixed assets and working capital values, calculated as a percentage according to the categories mentioned above.

Table 8 Categorization of the probability of occurrence of a hazardous event

Probability or frequency				
Category	a) Qualitative	b) Qualitative	c) Qualitative	Selected
1	Negligible	< 1 %	1 event in 100 years or less	
2	Low	1 - 5 %	1 event in 20 to 100 years	
3	Moderate	6 - 50 %	1 event in 2 to 20 years	
4	High	51- 98 %	1 event in 1 to 2 years	
5	Very high	> 98 %	1 event annually	

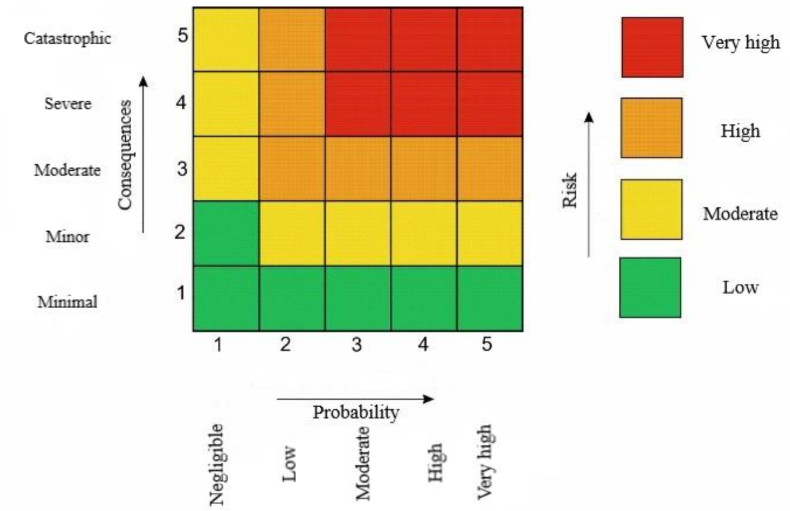

Fig. 2 Risk Assessment Matrix according to the methodology of the Republic of Serbia

Therefore, the risk to the aquatic ecosystem can be determined as the product of the probability of occurrence of the unwanted event (P) and the resulting damage or consequences (W), according to Equation 4 [6, 7].

$$R = P \times W \tag{4}$$

Assessing risk is essential for making decisions regarding the need to implement risk management procedures.

4. CONCLUSION

In the production of paints and coatings, a wide range of substances with varying properties and characteristics are used, many of which fall into the category of hazardous substances. Comparing substances within this group, it is concluded that the most significant ecological risks are associated with the emission of organic solvents and pigments, which can enter watercourses during accidental events. The quantity, volume, and area of contaminated water can be determined using the REHRA methodology. Ecological risk assessment relative to contaminated water involves evaluating the probability of an undesirable event leading to the release of hazardous substances into watercourses and the resulting environmental and health impacts on exposed populations. The probability and consequences, treated as damage, are determined according to the methodology. Calculations show that the maximum mass of substances released into watercourses can be reduced by up to tenfold depending on whether specific collection systems are in place for the discharged substances or if they are directly released into watercourses. If containment basins are used or if a significant portion of the spilled content can be removed, treated, or otherwise recovered, the mass of released organic solvents into watercourses during an accident can also be reduced by up to tenfold.

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PROCENA EKOLOŠKOG RIZIKA U INDUSTRIJI BOJA I LAKOVA SA ASPEKTA VODENOG EKOSISTEMA

Pri proceni ekološkog rizika, u industriji boje i lakova, stresori se posmatraju sa apekta opasnih supstanci koje su u ekspoziciji, a koja se mogu koristiti kao ulazne supstance i supstance koje napuštaju tehnološki proces i dospevaju u životnu sredinu. Koliki će njihov negativni uticaji biti na čoveka, živi svet, neživu prirodu i materijalna dobra zavisi, pored njihovih karakteristika i od učestalosti i stepena njihovog delovanja. Učestalost i stepen njihovog delovanja, pri proceni rizika, u radu se posmatra sa aspekta redovnog režima rada i udesnog događaja. Takođe u radu je prikazana prostorna raspodela opasnih supstanci koje dospevaju do vodotokova na osnovu proračuna maksimalnih količina i zapremina supstanci koje su u emisiji, kao i određivanje površine kontaminiranih vodotokova. Rizik se posmatra u funkciji verovatnoće najverovatnijih neželjenih događaja u industriji boja i lakova i posledica po život i zdravlje ljudi i ekologiju.

Ključne reči: *ekološki rizik, industrija boja i lakova, vodeni ekosistem*