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## TOXICOLOGICAL AND ECOTOXICOLOGICAL PROPERTIES OF AN IRON BASED COMBUSTION MODIFIER FOR LIQUID FUELS

## WŁASNOŚCI TOKSYKOLOGICZNE I EKOTOKSYKOLOGICZNE MODYFIKATORA ŻELAZOWEGO SPALANIA PALIW CIEKŁYCH

**Abstract:** It is necessary to use specific modifiers in order to reduce harmful emissions arising in the combustion of liquid fuels into the atmosphere. Such modifiers include organic metal salts which are soluble in fuels and tend to form metal oxides under combustion process conditions, improving the oxidizing properties of fuels. The modifier, described in this paper was used in liquid fuel combustion tests, showing a desirable effect of reducing CO, NO<sub>x</sub> and hydrocarbon emissions.

For such modifiers to be approved for use, examination of their physico-chemical, toxicological and ecotoxicological properties is required according to REACH Regulation. REACH is intended, first of all, to provide appropriate protection to the environment and human health, while striving to maintain competitive-ness of European enterprises in the global market.

Discussed in this paper are the results of selected tests of the effect of an iron-based modifier for liquid fuels on human health and on the land and air and the aquatic environment. The modifier was subjected to physico-chemical analyses, and toxicological and ecotoxicological tests in accordance with good laboratory practice and OECD guidelines.

The test results indicate that the modifier is a safe substance, posing no hazard to human health or the environment.

Keywords: fuel modifiers, toxicology, ecotoxicology, combustion, liquid fuels

## Introduction

Fuel combustion processes generate harmful emissions into the atmosphere. Specific additives are used commercially in the power industry to reduce the emissions. Such additives include modifiers based on organic metal salts, dispersed in organic solvents. Soluble without limitation in the combusted liquid fuels, they are added directly to the fuel. The combustion reaction environment generates metal oxides which catalyze the

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oxidation of fuel components. The advantages of the use of modifiers include: maintaining stable boiler performance, longer boiler operation and reduced costs of maintenance and repairs, more effective combustion due to reduced levels of hydrocarbons in flue gas, lower emission of harmful gases into the atmosphere (CO, NO<sub>x</sub>,  $SO_2$ , dust, polycyclic aromatic hydrocarbons), and absence of carbon deposit in the combustion chamber, resulting in improved boiler efficiency [1].

The manufacturing and marketing of more than 100 Mg per year of the above mentioned modifiers is planned, therefore, it is necessary to evaluate the toxicological and ecotoxicological properties of the product according to REACH [2]. Manufacturers and importers of chemicals are required under REACH to provide registration documents comprising information about the chemical substance, specifically its toxicological and ecotoxicological properties [3].

The toxicological tests are intended to assess any undesirable or harmful effect of chemical substances or other factors on living organisms, and to perform a probability analysis for their occurrence in various exposure conditions [4, 5].

Ecotoxicological properties are established in examinations of organisms, populations, communities, biocenoses, and ecosystems in the aspect of their exposure to chemical factors, their penetration from the environment into the organisms, as well as any toxic effect that may occur [6].

Discussed in this paper are the results of selected toxicological and ecotoxicological tests of an iron-based modifier for liquid fuels. The findings will subsequently be indispensable in preparing a chemical safety assessment report. The necessary tests were selected on the basis of the planned production volume and data incorporated in REACH Annexes VII–IX [2]. Tests, enabling the assessment of risks to human health and the environment, were carried out in accordance with Good Laboratory Practices at the Institute of Industrial Organic Chemistry, Pszczyna, Poland. Toxicological and ecotoxicological tests were made in the second quarter of 2014.

### Methodology

### Assessment of environmental risks

Ecotoxicological tests were discussed on the example of respiration inhibition in activated sludge micro-organisms according to OECD Guideline No. 209 (Method C.11) [7, 8] and acute immobilization of *Daphnia magna* according to OECD Guideline No. 202 (EU Method C.2) [9, 10].

#### The respiration inhibition test according to OECD Guideline No. 209

The test was intended to assess the toxic effect of the iron-based modifier on micro-organisms in activated sludge. The test system was a mixture comprising water, a synthetic sewage feed, activated sludge, and a reference material solution.

Two sets of test samples were prepared in the initial experiment, one set comprising a nitrification inhibitor. A N-allylthiourea (ATU) solution at a concentration of 2.32 g/dm<sup>3</sup> was used for inhibiting nitrification.

Every test system includes abiotic control (sample  $F_A$ ), experimental control (samples  $F_{B1}-F_{B2}$ ), test material control (samples  $F_{T1}-F_{T5}$ ) and reference material control (samples  $F_{R1}-F_{R5}$ ). Activated sludge from a biological waste-water treatment plant was used as a microbial inoculum. The respective amounts of the test material components are shown in Table 1.

Table 1

Commence of minteres	Amounts in test vessels					
Components of mixtures	$F_{T1}$	F <sub>T2</sub>	F <sub>T3-5</sub>	F <sub>B1-2</sub>	F <sub>A</sub>	
Test material [mg]	5	50	500	0	500	
Synthetic sewage feed [dm <sup>3</sup> ]	0.016	0.016	0.016	0.016	0.016	
Activated sludge [dm <sup>3</sup> ]	0.25	0.25	0.25	0.25	0	
Water [dm <sup>3</sup> ]	A volume of water was added to obtain a total of 0.5 dm <sup>3</sup>					
Total volume of mixture [dm <sup>3</sup> ]	0.5	0.5	0.5	0.5	0.5	
Concentrations in the mixtures:						
of test material [mg/dm <sup>3</sup> ]	10	100	1000	0	1000	
of activated sludge (suspended solids) [g/dm <sup>3</sup> ]	1.5	1.5	1.5	1.5	0	

Amounts of components in the respective mixtures (test material: iron-based modifier)

All mixtures were aerated intensely and incubated for three hours. The test material was used at the following concentrations: 10.0; 1000.0; 1000.0 mg/dm<sup>3</sup>. The reference material was used at the following concentrations: 0.5; 5.0; 10.0; 20.0; 50.0 mg/dm<sup>3</sup>. Each sample was transferred into a BOD bottle after 3 hours and the concentration of oxygen was measured within 10 minutes using an oxygen electrode.

Oxygen consumption rate (*R*), as expressed in milligrams per liter per hour  $[mg/dm^3 \cdot hr]$ , and specific respiration rate (*R<sub>s</sub>*), as expressed by the amount of oxygen consumed by 1 gram of dry weight of the microbial activated sludge per hour  $[mg/g \cdot hr]$ , were calculated using the following formula (Equations 1–2):

$$R = (Q_1 - Q_2) / \Delta t \cdot 60 \tag{1}$$

where:  $Q_1$  – is the oxygen concentration at the beginning of measurement [mg/dm<sup>3</sup>];

 $Q_2$  - is the oxygen concentration at the end of measurement [mg/dm<sup>3</sup>];

 $\Delta t$  – is the duration of measurement.

$$R_S = R / SS \tag{2}$$

where: SS – suspended solids concentration, as found at the beginning of the experiment [g/dm<sup>3</sup>].

Based on the data obtained from Equations 1 and 2, the inhibitory effect of the test material on micro-organisms in the activated sludge was measured. This enables the calculation of the value of  $EC_{50}$ , defined as the median effective concentration which induces in the environmental sewage feed a respiration inhibition of 50 % [1].

$$I = \left[1 - \frac{(R - R_A)}{R_B}\right] \cdot 100\%$$
(3)

where: I – is the percentage of respiration inhibition;

R – is the oxygen consumption by the test sample [mg/dm<sup>3</sup> · hr];

 $R_A$  – is the oxygen consumption by the abiotic control [mg/dm<sup>3</sup> · hr];

 $R_B$  – is the oxygen consumption by the experimental control [mg/dm<sup>3</sup> · hr].

# The acute immobilization of *Daphnia magna* according to OECD Guideline 202

It was the objective of the acute immobilization of *Daphnia magna* to determine, after 24 and 48 hrs of exposure: the concentration that causes immobilization of 50 % *Daphnia magna* (EC<sub>50</sub>) and the values of LOEC and NOEC. The LOEC is understood as the minimum concentration of the toxicant (iron-based additive) that causes an observable effect on the test organisms within the prescribed time of testing. The NOEC is the highest concentration of the toxicant that causes no observable effect on the test organisms during the test [1].

This semi-static acute toxicity test was done on young daphnids (*Daphnia magna*) aged less than 24 hours at the start of the test. The organisms were exposed, for 48 hrs, to the effect of the test material (iron-based modifier) at the following concentrations: 0.09, 0.20, 0.43, 0.94, 2.06, 4.54 and 10.0 mg/dm<sup>3</sup> and the control (0.0 mg/dm<sup>3</sup>). The concentrations were used in groups comprising five daphnids each, in four repetitions. The reference material, used for comparing the results, was potassium dichromate.

It was the objective of the test to observe immobilization of the test daphnids after 24 and 48 hours of exposure. The organisms which are not able to swim within 15 seconds after gentle agitation of the test vessel are considered to be immobilized.

### Assessment of risks to human health

Toxicological tests are discussed according to OECD Guideline No. 405 (Method B.5) for the acute irritation/corrosion of the eye in rabbit [11, 12] and OECD Guideline No. 406 (Method B.6) for skin sensitization [13–16].

# Test for the acute irritation/corrosion of the eye in rabbit according to OECD Guideline No. 405

It was the objective of the test to provide information about the potential health risks, caused by the impact of the iron-based modifier on the eye.

In the experiment,  $0.1 \text{ cm}^3$  of the test material (iron-based modifier) was applied into the conjunctival sac of one eye of a test animal; the other eye, which remained untreated, served as the control. The test was carried out in three animals to confirm the actual irritant effect or absence of irritation.

For the duration of the experiment, the animals were subjected daily to general clinical observation in respect of disease incidence and lethality. Detailed clinical observations for any lesions in the cornea, iris and conjunctiva were assessed after the lapse of 1, 24, 48 and 72 hours from the application of the test material.

The scoring of acute irritation/corrosion of the eye was defined using the grading of ocular lesions, as shown below (Table 2). The grading concerns lesions in the cornea, iris and conjunctiva.

Table 2

Cornea (opacity: degree of density)				
No ulceration or opacity	0			
Scattered or diffuse areas of opacity, details of iris clearly visible	1			
Easily discernible translucent area, details of iris slightly obscured	2			
Nacreous area; no details of iris visible, size of pupil barely discernible	3			
Opaque cornea, iris is not discernible through the opacity	4			
Iris				
Normal	0			
Markedly deepened rugae, congestion, swelling, moderate hyperaemia or injection; iris is reactive to light	1			
Hemorrhage, gross destruction, or no reaction to light	2			
Conjunctiva – redness (refers to palpebral or bulbar conjunctiva; excluding cornea and iris)				
Normal	0			
Some blood vessels hyperaemic	1			
Diffuse, crimson color; individual vessels not easily discernible	2			
Diffuse, beefy red	3			
Conjunctiva – swelling (refers to eye lids and/or nictitating membranes)				
Normal	0			
Some swelling above normal	1			
Obvious swelling, with partial eversion of lids	2			
Swelling, with lids about half closed	3			
Swelling, with lids more than half closed	4			

Grading of ocular lesions [6, 7]

### Skin sensitization test according to OECD Guideline No. 406

The skin sensitization test according to OECD Guideline No. 406 was started with a pilot test to establish the test substance concentrations for use in the principal test. In

step I of the principal test (induction exposure by intradermal injections) the selected test material concentration was 6 % and caused a moderate effect on the skin. In step II of the principal test (induction exposure by topical application) the selected test material concentration was 30 % and caused a moderate effect on the skin. In step III of the principal test (challenge exposure – topical application) the selected test material concentration was 0.2 % and caused no effect on the skin. In the principal experiment, 20 test animals (guinea pigs) and 8 control animals were used.

The principal test comprised three steps: induction exposure in two steps and challenge exposure. In step I of the principal test, the test animals were exposed by intradermal injection to a 6 % solution of the iron-based modifier dissolved in peanut oil with Freunds Complete Adjuvant (paraffin or mineral oil emulsion with tubercle bacilli suspended in it) [17, 18]. In step II of the principal test, 30 % of the iron-based modifier solution was applied on the skin in the intradermal injections region after being dissolved in peanut oil. In the control animals, peanut oil (medium) was applied instead of the test material.

The challenge exposure was performed by applying a 0.2 % iron-based modifier solution in peanut oil to the right flank of the test and control animals. Pure peanut oil (medium) was applied to the left flank. The skin reaction in the test and control animals was evaluated after 24, 48 and 72 hours from the end of the challenge exposure.

During the principal test, all the animals were subjected to general clinical observations. Detailed observations of the skin reactions were made after 24, 48 and 72 hours from the end of exposure. The animals were examined for any symptoms of erythema and swelling of the skin in the exposed region.

The challenge patch test reactions were evaluated according to OECD Guideline No. 406/Method B.6.: 0

- no visible change
- 1 - discrete or patchy erythema
- moderate and confluent erythema 2
- intense erythema and swelling 3

Sensitization reaction was understood as a reaction of the skin observed in the animals 48 and/or 72 hours after the exposure, because the maximum intensity of the sensitization reaction is observed at that time. The changes observed after 24 hours only were considered as changes caused by irritation of the skin.

The intensity of sensitization was classified based on the percentage of animals which showed sensitization changes. That percentage was found from the following formula:

$$X = A / B \cdot 100 \% \tag{4}$$

where: X – percentage of sensitized animals;

- A number of animals in which sensitization changes were observed;
- B number of animals in the exposed group.

### The following classification was adopted (Table 3):

Table 3

Classification of the intensity of sensitization according [19, 20]

% sensitized animals	Intensity of sensitization
> 0-8	very weak sensitization
9–28	weak sensitization
29–64	moderate sensitization
65–80	strong sensitization
81–100	very strong sensitization

## Results

## Assessment of environmental risks

### The respiration inhibition test according to OECD Guideline No. 209

After the experiment, the following calculations were made for every sample: oxygen consumption (R), specific respiration rate ( $R_S$ ) and percentage of respiration inhibition (I) in the activated sludge micro-organisms by the test material (iron-based modifier). The test results are shown in Table 4.

Table 4

Concentration of test material	Oxygen consumption [mg/dm <sup>3</sup> · hr]	Specific respiration rate [mg/g · hr]	Percentage of respiration inhibition in micro-organisms from activated sludge [%]
Control	32.46	21.64	
Test material concentration: 10 mg/dm <sup>3</sup>	32.70	21.80	0.74
Test material concentration: 100 mg/dm <sup>3</sup>	32.28	21.52	2.03
Test material concentration: 1000 mg/dm <sup>3</sup>	31.94	21.29	3.08

Results of tests for various concentrations of the iron-based modifier

It was established that the concentration of the iron-based modifier, causing 50 % percentage of respiration inhibition in micro-organisms from the activated sludge ( $EC_{50}$ ) was higher than 1000 mg/dm<sup>3</sup>.

# The acute immobilization of *Daphnia magna* according to OECD Guideline 202

Initially, immobilization of Daphnia magna was assessed after 24 and 48 hours of exposure. No immobilization was observed after 24 hours of exposure in the control and at the test material concentrations of 0.09; 0.20; 0.43 and 0.94 mg/dm<sup>3</sup>. At the test

substance concentrations of 2.06; 4.54; 10 mg/dm<sup>3</sup>, immobilization was 10, 5 and 45 %, respectively. No immobilization was observed after 48 hours of exposure in the control and at the test substance concentrations of 0.09 and 0.20 mg/dm<sup>3</sup>. At the test substance concentrations of 0.43; 0.94; 2.06; 4.54 and 10 mg/dm<sup>3</sup>, immobilization was 10, 85, 80, 95 and 100 %, respectively. The results of immobilization after 24 and 48 hours are shown in Fig. 1.



Fig. 1. Percentage of immobilization of *Daphnia magna* after 24 and 48 hrs of exposure to various concentrations of the iron-based modifier

In the second phase of the experiment, the ToxRat Professional 2.10 was used to calculate the mean effective concentrations, causing 100 % ( $EC_{100}$ ), 50 % ( $EC_{50}$ ), 20 % ( $EC_{20}$ ), 10 % ( $EC_{10}$ ) of immobilization, the highest concentration causing no immobilization, as well as the lowest concentration causing a statistically significant effect, as compared with the control (LOEC) and the highest test concentration at which no significant effect was observed in comparison with the control (NOEC) after 24 and 48 hrs of exposure. Final values based on nominal concentrations of the iron-based modifier and potassium dichromate (reference material) are shown in Table 5.

Table 5

Final values	Time of exposure				
	Reference	e material	Iron-based modifier		
[ing/diff]	24 hrs	48 hrs	24 hrs	48 hrs	
EC50	0.84	0.60	13.2	0.84	
EC20	0.69	0.55	5.38	0.44	
$EC_{10}$	0.62	0.53	3.36	0.31	
$EC_0$	0.32	0.32	0.94	0.20	
EC100	1.8	1.0	> 10.00	10.00	
LOEC	1.00	1.00	10.00	0.94	
NOEC	0.56	0.56	4.54	0.43	

Final values based on nominal concentrations of the iron-based modifier

### Assessment of risks to human health

# Test for the acute irritation/corrosion of the eye in rabbit according to OECD Guideline No. 405

Ocular lesions were observed in the conjunctiva in rabbits after application of the test material (iron-based modifier), although such changes were not detected in the iris or cornea. Clinical observation 1 hr after the test substance application detected diffuse crimson redness in the conjunctiva in three rabbits, accompanied by congestion of the nictitating membrane and circumcorneal injection. Moreover, minor conjunctival swelling and swelling of the nictitating membrane alone was found in rabbits 2 and 3, while swelling of the nictitating membrane alone was observed in rabbit 1.

24 hours after the test substance application, rabbits 1 and 3 showed hyperaemia of some blood vessels and of the nictitating membrane, while rabbit 2 showed diffuse crimson redness, hyperaemia of the nictitating membrane and circumcorneal injection. In addition, swelling of the nictitating membrane was observed in rabbits 1 and 2.

Clinical observation 48 hours after the test substance application showed hyperaemia of some blood vessels and of the nictitating membrane in the conjunctiva in the three rabbits. 72 hours after the test substance application, no ocular lesions were found in the conjunctiva in rabbits 1 and 3 while only rabbit 2 continued to have hyperaemia of some of its blood vessels and of the nictitating membrane.

Table 6 shows grading of acute eye irritation/corrosion based on the grading scale referred to in Table 2, pursuant to OECD Guideline 405 (Method B.5). The effect of acute eye irritation/corrosion in rabbit was assessed based on average results observed after 24, 48 and 72 hours. Pursuant to the OECD Guideline, results observed 1 hour after the application of the iron-based modifier are omitted from such grading.

Table 6

D 11.4	Eye part	After				Average results after 24,
Rabbit		1 hr	24 hrs	48 hrs	72 hrs	48 and 72 hours
1	Cornea	0	0	0	0	0.0
	Iris	0	0	0	0	0.0
	Conjunctiva – redness	2	1	1	0	0.7
	Conjunctiva – swelling	1	1	0	0	0.3
2	Cornea	0	0	0	0	0.0
	Iris	0	0	0	0	0.0
	Conjunctiva – redness	2	2	1	1	1,3
	Conjunctiva – swelling	1	1	0	0	0.3
3	Cornea	0	0	0	0	0.0
	Iris	0	0	0	0	0.0
	Conjunctiva – redness	2	1	1	0	0.7
	Conjunctiva – swelling	1	0	0	0	0.0

Grading of acute eye irritation/corrosion

#### Skin sensitization test according to OECD Guideline No. 406

No sensitization skin reactions were observed in the exposed animals in the skin sensitization test (Table 7). No pathological changes were observed on the skin of the control animals.

Table 7

Designated parameter	Control group	Exposed group
Number of animals in the group	8	20
Number of animals subjected to final value assessment	8	20
Number of dead animals	0/8	0/20
Skin changes after challenge exposure in the region where the medium (peanut oil) was applied	no changes	no changes
Skin changes after challenge exposure in the region where the test material (iron-based modifier) was applied	no changes	no changes
Number of animals in which sensitization reaction was observed	0/8	0/20
% of sensitized animals		0 %

Skin sensitization test of the iron-based modifier

Using Equation 4, the intensity of skin sensitization of the iron-based modifier was then calculated; the result was 0 %.

The animals were examined for the occurrence of general clinical symptoms throughout the experiment and none were observed. After completion of the experiment, weight loss was observed in two animals in the exposed group whereas the other test or control animals were found to have gained on weight.

## Analysis of the test results

### Assessment of environmental risks

### The respiration inhibition test according to OECD Guideline No. 209

The results of tests of the iron-based modifier indicate that, in experimental conditions in a test concentration range from 100 to 1000 mg/dm<sup>3</sup>, the test material shows an inhibitory effect on respiration of micro-organisms in activated sludge. The test material concentration for which 50 % respiration inhibition of micro-organisms in the activated sludge was observed (EC<sub>50</sub>) is higher than 1000 mg/dm<sup>3</sup>.

# The acute immobilization of *Daphnia magna* according to OECD Guideline 202

Based on the test results and nominal concentrations of the iron-based modifier, it was demonstrated that the mean concentration causing immobilization (inability to swim) in 50 % animals after 48 hours of exposure was  $0.84 \text{ mg/dm}^3$ . The value for the reference material was  $0.6 \text{ mg/dm}^3$ .

The highest test concentration at which no significant effect, as compared with the control, was observed after 48 hours of exposure was  $0.43 \text{ mg/dm}^3$  (0.56 mg/dm<sup>3</sup> for the reference material). The lowest concentration at which a significant effect, as compared with the control, was observed was 0.94 mg/dm<sup>3</sup> (1.00 mg/dm<sup>3</sup> for the reference material).

The test results for the reference material and for the test material (iron-based material) indicate sensitivity of *Daphnia magna* to the materials.

### Assessment of risk to human health

## Test for the acute irritation/corrosion of the eye in rabbit according to OECD Guideline No. 405

After application of the test material (iron-based modifier), no ocular lesions were detected in the cornea and iris while the conjunctiva of the test animals showed only temporary lesions. Average results after 24, 48 and 72 for the conjunctiva in three rabbits were 0.9 for the redness and 0.2 for the swelling.

Based on the above results, it was found, pursuant to Annex to the Regulation of the Minister of Health of 10 August 2012 on the criteria and methods for the classification of chemical substances and mixtures, that the iron-based modifier for liquid fuels had no irritant effect on the eye in rabbit [21].

Moreover, pursuant to Regulation of the European Parliament and of the Council (CE) No. 1272/2008 of 16 December 2008 on the Classification, Labelling and Packaging of Substances and Mixtures (CLP), the iron-based modifier for liquid fuels is not categorized at all which means that it is not a hazardous substance and poses no risk to human health [22].

### Skin sensitization test according to OECD Guideline No. 406

No sensitization changes were observed after application of the test material to the skin of the exposed animals. Based on the test results and classification of the intensity of sensitization according to Magnusson and Kligman, the iron-based modifier is classified as a material with no sensitizing effect.

## Conclusions

This paper presents the results of toxicological and ecotoxicological tests based on four selected examples. The toxicological results are discussed using the example of the acute eye irritation/corrosion test in rabbit and the skin sensitization test. No ocular lesions were observed in the cornea or in the iris while only temporary lesions were detected in the conjunctiva. The skin sensitization test has shown that the iron-based modifier is safe to the human health and causes not sensitization effect. Ecotoxicological tests have been discussed on the examples of the percentage of respiration inhibition in activated sludge and acute immobilization of *Daphnia magna*. The test results indicate that the modifier's concentration causing 50 % respiration inhibition in the activated sludge micro-organisms is higher than 1000 mg/dm<sup>3</sup>. As regards the test for acute immobilization of *Daphnia magna*, the mean concentration causing immobilization (inability to swim) in 50 % animals after 48 hours of exposure was found to be 0.84 mg/dm<sup>3</sup>. As a reference, for potassium dichromate, which is a known sensitizer in the case of *Daphnia magna*, the value was 0.6 mg/dm<sup>3</sup>. The animals are sensitive also to the test material (iron-based modifier), although the values are in the range reported in literature [23], therefore, the result is regarded as satisfactory.

Other results of toxicological and ecotoxicological tests indicate that the test iron-based modifier for liquid fuels is a safe substance, posing no risk to human health or the environment. Although not discussed in this paper, such tests are going to be used for preparing the product registration documents under REACH.

Based on the test results and pursuant to the Annex to the Regulation of the Minister of Health of 10 August 2012 on the criteria and methods for the classification of chemical substances and mixtures [21], the iron-based modifier for liquid fuels is found to be a safe substance, posing no risk to human health or to the land and air and the aquatic environment.

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#### References

- Tic WJ. Metal salts as the homogeneous catalysts for an effective combustion of liquid fuels. Pol J Environ Stud. 2008;17(3):439-441.
- [2] Regulation (EC) of the European Parliament and of the Council, on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH); No 1907/2006 of 18 December 2006.
- [3] Guziałowska-Tic J. Selected toxicological and ecotoxicological properties of additive for combustion of liquid fuels. Chemik. 2014;68(10):831-836.
- [4] Lilienblum W, Dekant W, Foth H, Gebel T, Hengstler JG, Kahl R, Kramer P-J, Schweinfurth H, Wollin K-M. Arch Toxicol. 2008;82:211-236. DOI: 10.1007/s00204-008-0279-9.
- [5] Gori GB. Regul Toxicol Pharmacol. 2014;70(3):575-576. DOI: 10.1016/j.yrtph.2014.10.001.
- [6] Cho S-J. Toxicol Environ Health Sci. 2014;6(4):233-237. DOI 10.1007/s13530-014-0210-0.
- [7] OECD Guideline No. 209: "Activated Sludge, Respiration Inhibition Test (Carbon and Ammonium Oxidation)"; 2010.
- [8] Commission Regulation (EC) laying down test methods pursuant to Regulation (EC) No. 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). Part V. Biodegradation – Activated Sludge Respiration. Inhibition. Degradation (C 11); No 440/2008 of 30 May 2008.
- [9] OECD Guideline 202 for the Testing of Chemicals: "Daphnia sp, Acute Immobilisation Test"; 2004.
- [10] Regulation of the Commission (EC) laying down test methods pursuant to Regulation (EC) No 1907/ 2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), Annex: Part C: Test Methods for Determination of Ecotoxicity, C 2; No 440/2008 of 30 May 2008.

- [11] OECD Guideline 405 for the Testing of Chemicals: "Acute Eye Irritation/Corrosion"; 2012.
- [12] EU Method B.5.: "Acute Toxicity: Eye Irritation/Corrosion". Regulation of the Commission (EC); No 440/2008 of 30 May 2008.
- [13] OECD Guideline 406 for the Testing of Chemicals: "Skin sensitization"; 1992.
- [14] EU Method B 6: "Skin sensitization". Regulation of the Commission (EC); No 440/2008 of 30 May 2008.
- [15] OECD Guideline 404 for the Testing of Chemicals "Acute skin sensitization/corrosion"; 2002.
- [16] EU Method B 4: "Acute toxicity: skin irritation/corrosion". Regulation of the Commission (EC); No 440/2008 of 30 May 2008.
- [17] Collin N, Dubois P-M. Vaccine. 2011;29S:A37-A39. DOI: 10.1016/j.vaccine.2011.04.125.
- [18] Snekhalatha U, Anburajan M, Venkatraman B, Menaka M. Z Rheumatologie. 2014;72:375-32, 2014. DOI: 10.1007/s00393-012-1083-8.
- [19] Kręcisz B, Kieć-Świerczyńska M, Piasecka-Zelga J, Chomiczewska-Skóra D, Stetkiewicz J. Int J Occup Med Environ Health 2012;25(3):251-257. DOI: 10.2478/S13382-012-0028-4.
- [20] Magnusson B, Kligman AM. Allergic Contact Dermatitis in the Guinea Pig. Springfield, Illinois: Charles G. Thomas; 1970.
- [21] Regulation of the Minister of Health of 10 August 2012 on the criteria and methods for the classification of chemical substances and mixtures. DzU of 2012, Item 1018.
- [22] Regulation of the European Parliament and of the Council (EC) on the Classification, Labelling and Packaging of Substances and Mixtures (CLP); No 1272/2008 of 16 December 2008.
- [23] ISO 6341:1996: Water quality Determination of the inhibition of the mobility of Daphnia magna Straus (Cladocera, Crustacea) Acute toxicity test.

#### WŁASNOŚCI TOKSYKOLOGICZNE I EKOTOKSYKOLOGICZNE MODYFIKATORA ŻELAZOWEGO SPALANIA PALIW CIEKŁYCH

#### Wydział Mechaniczny, Politechnika Opolska

**Abstrakt:** W celu ograniczenia emisji szkodliwych produktów spalania paliw ciekłych do atmosfery występuje konieczność stosowania specyficznych modyfikatorów. Jednym z rodzajów są rozpuszczalne w paliwie organiczne sole metali, które w warunkach procesu spalania tworzą tlenki metali poprawiające własności utleniające paliw. Opisany modyfikator zastosowany został w testach spalania paliwa ciekłego, gdzie wykazał korzystny wpływ w ograniczeniu emisji węglowodorów, CO i NO<sub>x</sub>.

Dopuszczenie do stosowania wyżej wymienionych modyfikatorów wymaga określenia ich własności fizykochemicznych, toksykologicznych i ekotoksykologicznych w ramach rozporządzenia REACH. Najważniejszym celem tego rozporządzenia jest zapewnienie właściwej ochrony zdrowia ludzkiego i środowiska, przy jednoczesnym dążeniu do zachowania konkurencyjności europejskich przedsiębiorstw na światowym rynku.

W pracy przedstawiono wyniki wybranych badań wpływu na zdrowie człowieka oraz na środowisko wodne, lądowe i powietrzne modyfikatora żelazowego do paliw ciekłych. Badania fizykochemiczne, toksykologiczne i ekotoksykologiczne tego dodatku wykonane zostały zgodnie z dobrą praktyką laboratoryjną oraz wytycznymi OECD.

Na podstawie uzyskanych wyników badań stwierdzono, iż badany modyfikator jest substancją bezpieczną i niestanowiącą zagrożenia dla zdrowia człowieka oraz środowiska.

Słowa kluczowe: modyfikatory paliw, toksykologia, ekotoksykologia, spalanie, paliwa ciekłe