ANTICORROSION PROTECTIVE FLUIDS MEETING THE ECOLOGICAL CRITERIA FOR ECO-LABELLING

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Abstract
Human industrial activities inflict harsh and often irreversible damage on the environment and upon critical resources. If we don't checked many of our current practices put at serious risk the future that we wish for human society and the planet and animal kingdoms, and may so alter the living world that it will be unable to sustain life in the manner that we know. Fundamental changes are urgent if we are to avoid the collision our present course will bring about.
For this reason, our research activities with directly leg work have as major goal, the development of environmentally friendly and ecologically clean film-forming anticorrosion protective fluids.
The basis of this paper is an interdisciplinary research for the study, manufacturing and characterization of a new range of corrosion preventing products in order to meet the EU requirements for the award of the Community ***eco-label****, referring to: technical performances; R phrases indicating environmental or health hazard; aquatic toxicity; biodegradability; exclusion of specific substances included in OSPAR list and renewable raw materials.*
The paper presents the data regarding the technical characteristics of some anticorrosion protective fluids, formulated based on renewable resources, referring to vegetable oils, ecological solvents, environmentally suitable additives and other safe components.
The technical performances of the products were assessed determining their anticorrosion capacity in different environment: marine, wet-tropical, etc. Eco-toxicity of these products was assessed on the basis of biodegradability and aquatic toxicity measurements, applying the common test methods used by the lubricant industry.

Keywords: *anticorrosion preventive fluids, biodegradability, toxicity*

1. INTRODUCTION

Many of the metallic parts, components and finished produced by the manufacturing industries may have bare metal surfaces which require to be protected until brought into use, or receive inter-stage protection prior to further assembly or processing. Other finished metallic parts need to receive some form of protection from corrosion during shipping or storage, or they may require some form of protection whilst in use. A temporary anticorrosion protective fluid is by definition a material that can be easily removed from the metal surface after treatment. These products ensure protection when metallic surfaces are exposed to a variety of different corrosive atmospheres, indoors, outdoors either under cover or fully exposed in a marine environment, under effects of direct sunlight, in the presence of specific chemical corrosives in an industrial environment, etc.

The classic temporary corrosion protective products have the disadvantage to be formulated on the basis of oiled derivatives (mineral oils, petroleum solvents), chlorinated solvents, aromatic solvents, harmful additive packages and corrosion inhibitors. Generally, they are manufactured with polluting technologies and represent a risk to human health and environment. Due to their application methods (immersion, pulverization), anticorrosion protective products are permanently in direct contact with the consumers, who are exposed to hazardous agents and emissions generated by the harmful chemicals from the products composition. Similar problems appear even during the fabrication process. As it is known, the mineral oils are generally low in biodegradability and are not suited to use in environmentally acceptable applications. Their poor biodegradability signify a potential for long-term pollution of the environment, besides being

known that refined petroleum products can cause severe harmful effects in contaminated ecosystem. At the same time, mineral oils and petroleum solvents are classified by International Agency for Research of Cancer as probably carcinogenic substances for humans.

EU's eco-label is part of a larger strategy, being meant not only to help the consumers to find the green products and services, but also to promote the rational consumption of materials during manufacturing process and low consumption of energy. At the same time, the eco-label is a „passport" which authorize goods free circulation within the free European market, a modern market instrument which promotes products on the unique European Market. According to Article 1 of Regulation (EC) 1980/2000, the objective of the Community Eco-label award scheme is to promote products which have the potential to reduce negative environmental impacts, as compared with the other products in the same products group, thus contributing to the efficient use of resources and a high level of environmental protection. The EU Eco-label criteria take into account the main environmental impacts of a product and the technically possible improvements. These criteria are established at the European level by the EU Eco-labelling Board. This Board involves the European Commission, the national EU Eco-label competent bodies, industry, consumers, environmentalists, trade unions and SMEs. The Decision 2005/360/EC establishes ecological criteria and the related assessment requirements for the award of the Community eco-label to lubricants. These criteria are:

1. **R phrases indicating environmental or human health hazards;**
2. **Additional aquatic toxicity requirements;**
3. **Biodegradability** and **bio-accumulation potential;**
4. **Exclusion of specific substances**
5. **Renewable raw materials**;
6. **Technical requirements;**
7. **Information appearing on the eco-label**

The products group "lubricants" comprises: hydraulic oils, greases, chainsaw oils, two stroke oils, concrete release agents and other total loss lubricants for use by consumers and professional users. The temporary anticorrosive products could be included in total loss lubricants subgroup.

In European countries consumers have became more and more aware of the risk that dangerous substances present in consumer goods can have on their health. This is the reason why large groups of ecologically labelled products guarantying the absence of toxic chemical substances enjoy great success, thus, by March 10, 2005, in UE the ecological label has been awarded to 16 groups of products, with more than 235 products.

2. MATERIALS AND METHODS

2.1. Methods

To establish the conformation degree of the anticorrosion protective fluids with eco-labelling criteria, a complex methodology to evaluate the biodegradability and eco-toxicity was assimilated, according to

OECD requirements.

Biodegradation is defined as the ability of chemicals to break down, by organisms (bacteria, fungi) or their enzymes. According to Decision 2005/360/EC, concerning establishing ecological criteria for the award of the Community eco-label to lubricants, a substance is considered *ultimately biodegradable* if in a 28-day biodegradation study according to OECD or equivalent test the following levels of biodegradability are achieved:

-a biodegradation $\geq 70\%$ in the OECD 302 C test or equivalent test methods;

-a biodegradation $\geq 60\%$ in the OECD 301 test based on oxygen depletion or CO_2 generation

The **acute aquatic toxicity** tests are used for assess of the substances toxicity upon one or a great species of aquatic organisms (plants, algae, amphibians, mollusk, crustaceans and fish).

The most common test methods used by lubricant industry for evaluating the aquatic toxicity of their products are OECD 201, 202, 203 and EPA 560/6-82-002. These tests determine the concentration of a substance that produces a toxic effect on a specified percentage (50%) of test organisms in 96 hours. An individual substance may exhibit one of the following degrees of aquatic toxicity:

Non-toxic	Acute aquatic toxicity $\geq 100 mg/l$
Harmful	10mg/l< Acute aquatic toxicity $\leq 100 mg/l$
Toxic	1mg/l< Acute aquatic toxicity $\leq 10 mg/l$
Very toxic	Acute aquatic toxicity < 1mg/l

The aquatic toxicity requirements for the end-products and main components for eco-labelling, are presented in table 1.

Table1. Limits with regard to the aquatic toxicity of the total loss lubricants

Criterion	**Total loss lubricants**
Aquatic toxicity for the fully formulated product	$\geq 1000 mg/l$
Aquatic toxicity for each individual component	$\geq 100 mg/l$

Technical requirements

According to Decision 2005/360/EC, the total loss lubricants shall fit for purpose. The technical performances of the products studied have been assessed applying the accelerated corrosion tests. The purpose of an accelerated corrosion test is to cause, corrosion, degradation or failure in a shorter time period than under normal conditions without change in failure mechanism(s). This can be accomplished using cabinet tests, simulated service tests, electrochemical corrosion testing, immersion tests, atmospheric corrosion tests and in service corrosion tests. In our research work we applied the following test methods:

-Humidity cabinet test, according to DIN 50017-KFW method,

-Salt spray test, according to ASTM B-117, method.

2.2 Materials

2.2.1 Base fluids

Temporary corrosion preventives are considered as colloidal dispersions of a thickener and a package of additives in a base fluid, the main components of these products being the base fluids, thickeners, corrosion inhibitors, dispersants and surfactants.

In terms of volume, base fluid is the most important component of one temporary protective fluid it determines its price and its biodegradability and aquatic toxicity. Manufacturing products that fulfil the EU Eco-label award criteria assumes good knowledge of the materials, because consumers can be reticent in buying a product if the ecological advantages do not merge with other criteria: cost, performance, quality. As a rule, product's costs depend on its performance and its environmental parameters, so it is shown in figure 1.

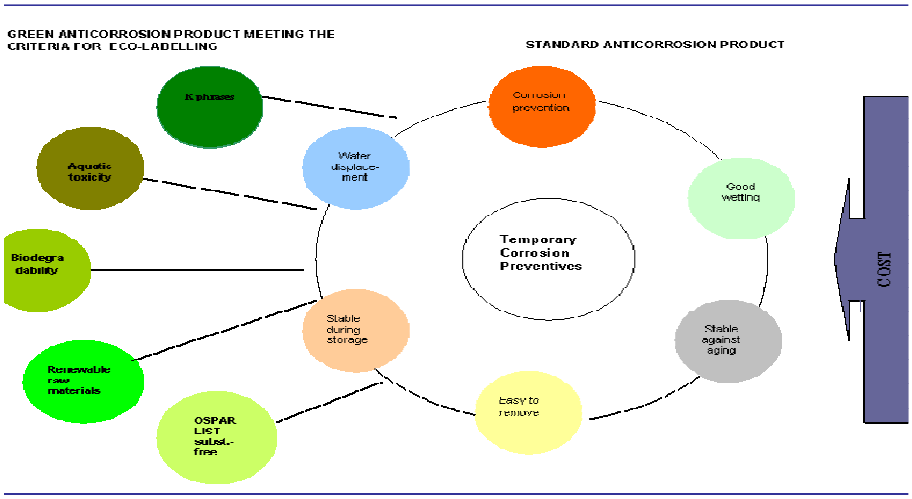

Fig.1. Requirements for anticorrosion products

At first view, we would be tempted to think the price of ecological products, should be greater than the price of the standard products. This statement isn't valid in case of environmentally friendly products that meet the criteria for eco-labelling, because the components are selected from the category of materials with low impact on the environment, of recyclable materials and less energy consumers. Thus, the vegetable oils (soybean oil, sunflower oil) and their derivatives such as methyl esters or ethyl esters of vegetable oils obtained from their trans-esterification, have been used in our research work as base fluids to the disadvantages of mineral oils and petroleum solvents, usually used in manufacturing of the standard temporary corrosion preventives. Because of their low toxicity, biodegradability of up to 80% and recycling potential, in Europe, the consumption of vegetable oils for industrial purposes has risen considerably during the last years. It is estimated that by the year 2010 the percentage of products based on vegetal derivatives will be 35% of the total amount of lubricants. Long term it is estimated that 90% of the total quantity of lubricants will be biodegradable. They have advantages of being almost completely biodegradable. The explanation can be found in their chemical structure. By their chemical nature, vegetable oils are triglycerides, where the building blocks are glycerol and typically three fatty acids, as it is shown in figure 2.

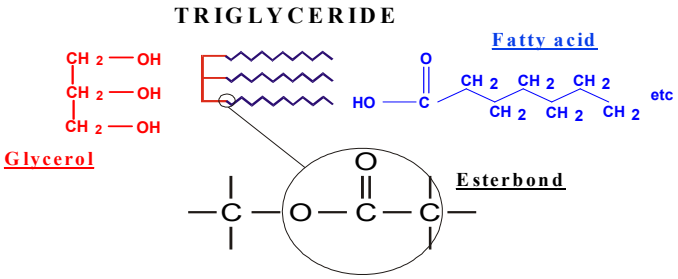

Fig.2. Typical composition of vegetable oils

Triglycerides contain elements with labile structure, generally with "double-link", 'group β-CH" and "ester-bond". Structural elements with "double-link" and "group β-CH" are unstable, especially at thermal field and oxidant environment. The "ester-bond" is easily dissociated in water (hydrolysis), hydrolysis being the first stage in biodegradation. On the other hand, chemical stability of vegetable oils is low, because of their polyunsaturated (linoleic and linolenic) acids content. The resistance to aging of vegetable oils id directly related to the level of the iodine value. In table 1, the iodine values of some vegetable oils are presented.

Table1. Iodine value of vegetable oils

Oil Types	Iodine Value, g/100 I_2
Rapeseed	94-106
Soybean	103-109
Castor	82-90
Sunflower	127-136
Olive	80-85

The sensitivity to oxidation of vegetable oils represents a disadvantage and it could be reduced by different methods like hydrogenation of the conjugated bonds, by derivative of vegetable oils or by antioxidants. Additionally, vegetable oils and their derivatives are renewable resources. When supplies are low, more crops such as soybeans and corn can be planted to make up the shortfall, which is an added bonus to agricultural economies. Petroleum, on the other hand is a finite resource.

In table 2 are presented the characteristics of the base fluids used in our formulation related to the criteria for eco-labelling, comparative with the mineral oil and white spirit, found in the standard temporary anticorrosion products.

Table2. Base fluids characteristics

Characteristic / **Base fluid**	**CAS No.**	**R phrase**	**Biodegradability, %**	**Bioaccumulative potential, log K_{ow}**	**Aquatic toxicity, CL_{50}, mg/l**
Methyl Esters of Soybean Oils	67784-80-9	No	95	1.7	1318.26

Soybean Oil	8001-22-7	R-phrases	98	4.7	Over 1000
Sunflower Oil	8001-21-6		97	4.6	Over 1000
Mineral oil	64741-88-4	R 45	35	3.2	500
White spirit	8052-41-3	R 45, R65	45	3.4	400

2.2.2 Thickeners selection

As thickeners, the aluminium soaps or inorganic thickener, such as quaternary ammonium compounds, beeswax and wool fats, were selected because they are known as non harmful to environment. Also we tested by point of view of the eco-toxicity petroleum waxes. The values obtained for lethal concentration $CL_{50\text{-}96h} > 1000mg/l$, show that this raw materials is non-toxic. On the other hand the biodegradability value of 40%, situated under admissibility limit for the awarding of the eco-label, makes it unusable for manufacturing

2.2.3 Additives

Anticorrosion products contain a range of performance-enhancing additives to decrease oxidation, and to improve corrosion ability. In conventional fluids many of these additives, are recognized to be toxic for human and environment. Some are sensitizers, skin irritants, carcinogens or toxic to organisms. Till now, only very few additives have been recommended for use in biodegradable products. With more and more research activities being directed toward biodegradable lubricants, new environmentally friendly additives have been developed and investigated. Table 3 shows the different types of selected additives which we used to formulate biodegradable lubricants.

Table 3.The most common environmentally friendly additives

Additive Type	**Class of Substances**
Antioxidants	Phenolic AO (dimer)
	Alpha tocopherol
Corrosion inhibitors	Synthetic Ca-sulfonate
	Ester Sulfonate (ashless)
	Succinic Acid Partial Ester

3. RESULTS AND DISCUTIONS

Based on the raw materials presented above, we formulated two types of temporary anticorrosive products. The products were named, in accordance with the classification of the British Standard 1133/91, thus:

- TP 1 b, product that deposits a hard film, slow drying (manufactured based on methyl ester of soybean oil);
- TP 2 b, product that deposits a soft film, also displaces moisture from wet surfaces (manufactured based on soybean oil).

The manufacturing process of temporary anticorrosion products meeting the ecological criteria for eco-labelling must take into account the particularities of components, such as the low thermal and oxidant stability of soybean oil. For getting good performances, the antioxidants have to use just first stage of the

process. The usual equipment is satisfactory for the manufacturing of green anticorrosive products, but this must be properly cleaned to prevent contamination with conventional products and their components.

In order to verify compatibility of the formulated end-products with the proposed Eco-label criteria 1, 2, 3 and 6, have been determined the physical-chemical characteristics, technical performances and their eco-toxicological properties, assessed in terms of biodegradability degree and aquatic toxicity.

The results of laboratory tests are shown in the next table.

Table 4. Physical-chemical, technical performance and eco-toxicological characteristics

Characteristic	**TP 1 a**	**TP 2 b**	**Test Method**
Physical-chemical characteristics			
Film appearance	Uniform, continuous, clear		visual
Kinematics viscosity,@40^{0}C cSt,	23.15	50.12	STAS 117-87
Flash point, ^{0}C	130	> 200	ASTM D 92
Density@20^{0}C, g/cm^3	0,8975	0.9358	STAS 33-81
Film thickness, µm	32	17	ICERP Method
Technical performances			
Copper corrosion, 3h/100^{0}C	1 a	1 b	ASTM D 130
Humidity cabinet test, (cyclic corrosion test), 21 cycles*	pass	pass	DIN 50017-KFW
Salt spray test, 240 h	pass	pass	ASTM B 117
Eco-toxicological performances			
Biodegradability, %	88	91	CEC-L-33-A-94
Aquatic toxicity,$CL_{50\text{-}96h}$, mg/l	1584,89	1812,62	OECD C01& INCD-ECOIND-PO-01-BPL
R-phrases	No R- phrases		According to DPD

Looking at the results presented in the table 4 we could say:

The anticorrosive protective fluids formulated based on Safety-Healthy-Environmentally components, meet the main criteria for the award of the Community eco-label because:

- the biodegradability values over 80%, determined by CEC method show that the products are ready biodegradable and are in compliance with requirements of Decision 2005/360/EC (Criterion 3);
- they meet the technical performances, laid down in ASTM B-117 and DIN 50017 KFW (Criterion 6);
- the data on aquatic toxicity, expressed as acute lethal concentration $LC_{50\text{-}96}$, over 1000 mg/l, shown the products are practically non-toxic for aquatic organisms (Criterion 2);

We mention that the formulated end-products don't contain the substances appearing in the Community list of priority substances in the field of water policy and the OSPAR List of Priority Action. Also they don't contain organic halogen compounds, nitric compounds or metals or metallic compounds, excepting the aluminium salts that are accepted as thickeners in the lubricants that meet the requirements for the award of the Community eco-label, so that the temporary anticorrosion products are in compliance with the Criterion 4 of Decision 3005/360/EC.

3. CONCLUSIONS

1. The new range of temporary anticorrosion products, offer the advantages of meeting the ecological criteria for eco-labelling to total loss lubricants, according to Decision 2005/360/EC.

2. Using industrial products with the least harmful effects to the human health and environment, will increase the life quality, ensuring better work conditions.
3. To establish the conformation degree of the new realized products with the EU eco-labelling criteria, a complex methodology was applied.
4. The generated knowledge which contains information about eco-labelling will be useful for further ecological products development from the lubricants' group (metalworking lubricants, compressor oils, engine oils, etc.)

REFERENCES

[1] Decision 2005/360/EC establishing ecological criteria and the related assessment and verification requirements for the award of the Community eco-label to lubricants.

[2] Eng. Florentina Flueraru, Dr. Eng.George Razvan Rapeanu, Dr. eng. Marcel Luca, Biologist Daniela Popescu "FUTURE TRENDS IN CORROSION PROTECTING COATINGS USED IN MANUFACTURING PROCESSES"- Journal of the Balkan Trybological Association, Book 4, 2006, ISSN 1310-4772.

[3] Draft User Manual –EUROPEAN ECO-LABEL LUBRICANTS-14 September 2004