
BIOCIDES USED IN PRESERVATION, RESTORATION AND CONSERVATION OF THE PAPER

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Abstract

The number of materials of cellulosic nature treated with biocides used as support for editing of the books has increased considerably in recent years in order to have control over the bacteria and fungi, the natural phenomenon of biodeterioration, the appearance of stains and odours caused by microorganisms action. The purpose of this article is to highlight the role played by biocides in the destruction of microorganisms that attack irreversibly the paper, but also in the processes of preservation, restoration and conservation. The information printed on cellulosic material - paper, has a special significance as it ensures the link between present and future by sending a set of values from one generation to another. The microorganisms that can grow on cellulosic materials produce different organic acids, which determine the decrease of pH attacking the paper, making it fragile and, ulterior, predisposed to deterioration; by the action of biocides these phenomena are stopped.

Keywords: biocides, preservation, restoration, conservation, paper

1. Introduction

It is well known the importance of books, as they represent the main trusted source for finding useful, current and accurate information, which have the role to broaden the horizon of humans, to arouse interest in knowledge, training, development and improvement. In addition, books represent a part of the cultural heritage of a country whereas facilitates the formation of a culture and make the connection between past, present and future, being surest way to transmit a set of values from one generation to another. This aspect leads us as nation to take measures for development of some appropriate programs for preservation, conservation and restoration, necessary to avoid the degradation of the books over time, which was found to be irreversible.

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The main way to avoid degradation of documentary heritage is preservation, which has at the base a set of activities that ensures extended life of a document. For a proper preservation of the books we must keep in mind the following steps:

- proper design of buildings and spaces where books are stored: walls of the building, floor must be covered with fireproof material and must have smoke hatches;
- insurance of some regular repair of buildings where books are stored;
- insurance of some optimal conditions of temperature (15°C - 25°C), pH, luminosity, ventilation, a relative humidity of the air between 40-65%, etc. in rooms where books are stored, because storage conditions influence the conservation of books;
- staff training regarding behaviour in emergencies;
- development of an action plan in case of calamity;
- achievement of microbiological and ethnological inspections of the books;
- implementing of some activities of disinfection, pest and vermin control of areas where books are stored;
- conducting of regular checks on the state of conservation of books.

All libraries must have preservation policies in order to ensure accessibility to information and minimize degradation of the books.

Digitization, at this moment, is an effective method for conservation and preservation of books, which facilitates the process of capitalization of information but does not solve the problems of preserving documents in original form. A first disadvantage of the digitization is that it can not be used for a longer period of time because the applications and systems that were used to create and provide the reading of the books cannot be used anymore because the appearance of others, more efficient and effective [1, 2].

Another snag of this solution is that the reader of a book feels the difference between a book made by electronic support and the one on paper. The book made on cellulose support, the paper, can be read, understood, perceived by human senses, while the electronic one can only be read using the computer by a special software.

The major handicap of the digitization would be that it may occur different problems related to the software that ensures reading documents and that could bring important cultural prejudices of a country.

Having considered these issues, as a person that formed and developed intellectually using books made on paper support, I plead for this cause and support all efforts developed in the preservation, restoration and conservation of paper.

Conservation of books on cellulosic support consists of actions by which it follows the 'preservation of documents in their original format' and which prevents the early appearance of degradation and aging phenomenon, which can lead to irreversible destruction of the cellulose fibres. Conservation has a preventive character based on application of the best and appropriate means to

protect books by the action of the factors from the environment or the damage caused by humans.

Restoration of degraded documents is done through several irreversible activities that together define the process of restoration. Therefore, it is preferable to make all necessary arrangements to ensure the best possible conservation of paper and in this way avoid the necessity of restoration of books and important documents over time.

In conclusion, in the moment in which it was decided that the paper should be subject to restoration is necessary to consider all the factors that contributed to the degradation in order to adopt best practices and treatments that to preserve the information contained in the book, to ensure permanence and stability of the cellulosic material [3].

2. The importance of the biocides used for the protection of cellulosic materials

Paper is a fibrous material, anisotropic, which has a laminar structure and has as main component a natural polymer - cellulose. The materials used to papermaking are woody species that have the highest content of cellulose, which is between 42-51%, plus lignin, hemicelluloses, small amounts of resins, fats, waxes, tannins, protein and mineral compounds [4, 5].

Cellulose has the composition: C 44.4%, H 6.26% and O 49.34%, being degraded by ultraviolet radiation, the presence of air, humidity and is easily decomposed by microorganisms.

In time, paper made from cellulose fibres is subjected to degradation due to the natural phenomenon of aging, the attack of organisms and microorganisms and of some physical, chemical factors. Among the factors leading to deterioration of the paper one can mention [6]:

- abiotic factors (humidity, temperature, light sources, pH, pollutants in the atmosphere, radiation) that determine the most important degradation processes and the effects are irreversible;
- biotic factors (bacteria, fungi, insects) - lead to irreversible degradation of the documents on paper support;
- endogenous (internal) factors - appear as the result of technological treatments or can pre-exist in the structure of cellulosic material;
- exogenous (external) factors - leads to oxidation reactions with the oxygen from the environment and hydrolysis reactions under the action of the humidity in the air at a pH less than 5.6 [7].

In the process of paper manufacturing, besides fibrous materials are added a number of additives that are natural or synthetic materials, in order to obtain some benefits regarding the properties of paper and the way in which takes place the process of obtaining it. Some of these additives include: fillers, products that improve the resistance paper, dyes, anti-foaming agents, biocides.

In the process of conservation of the paper, an important role is played by biocides because they present the following advantages:

- they keep the paper in good hygienic conditions over time, reducing harmful microorganisms (bacteria, fungi);
- they avoid formation of odours due to biodegradation;
- they prevent the spread and transfer of the pathogens on cellulosic materials;
- they remove formation of mould and protects against degradation and decomposition of paper;
- they offer paper a longer life that does not affect the cellulose support;
- they offer paper durability making it more resistant to action of internal and external factors over a longer period of time;
- they protect cellulosic material against biodeterioration, because the organic and aqueous environment is a favourable environment to develop microorganisms.

Biocides are substances or groups of active substances that prevent, neutralize and exercise a control effect on any harmful organism by chemical or biological means [M. Ciocanu, *Bioetic si biocid in zootehnie*, online at: <http://ciocanu.ro/bioetic-si-biocid-in-zootehnie>, 2010]. In paper conservation, the most used biocides are:

- Biocides with oxidizing properties that have a broad spectrum of activity and act quickly resulting in destruction of microorganisms (destroy all types of bacteria including filamentous bacteria, spore formers and anaerobes). Some biocides such as isothiazolinone, Bronopol and DBNPA (Dibromo nitrilopropionamide) are more effective in oxidizing environments. Oxidants are used for bleaching paper and eliminate odours (chlorine, chlorine dioxide, peroxides) and biological control (peracetic acid, ammonium bromide, sodium hypobromite, chloramines, hypochlorous and hypobromites acids).
- Biocides with non-oxidizing properties are used to control microbiological growth in paper manufacturing process, to avoid the contamination of paper with microorganisms that would lead to its deterioration.



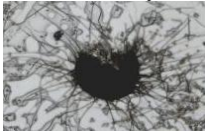
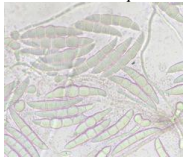
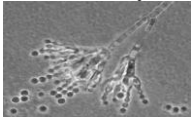

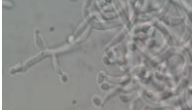
The biocides most widely used to solve all microbiological problems are mixtures which contain the following active substances: MBT (Methylene bis-thiocyanate), TCMTB ((Thiocyanomethyl thiobenzothiazole)), CMIT/MIT (Chloromethylisothiazolinone/Methylisothiazolinone), BIT (1,2-benzisothiazolin-3-one), DBNPA (Dibromo nitrilopropionamide), bronopol, glutaraldehyde.


3. Fungi and bacteria determining the deterioration of the paper

The main microorganisms that attack and destroy the paper, degrade it and make it unusable are bacteria and fungi. In conditions in which temperature and humidity exceed the limits of rules, the bacteria and fungi multiply very easily and quickly, feeding on organic materials. These microorganisms release enzymes that lead to the dissolution of macromolecules in components, after that

they feed on cellulose, eliminate wastes which are of acidic nature and leads to the destruction of material of which book is made.

Table 1. Information on the main fungi and bacteria that attack the paper.

Class of microorg.	The name of organism	Effects of microorganisms on paper	Other useful information about microorganisms
Fungi	<p><i>Alternaria sp.</i></p> 	<i>Alternaria</i> degrades the paper forming some spots with irregularly shaped coloured in red, purple, yellow, brown, black, etc.	<i>Alternaria</i> species are found in living organisms, in the terrestrial, air, water environment. It develops on textiles and synthetic materials, parchment, paper, food, plants, rubber, natural and synthetic paints, paintings, etc. <i>Alternaria</i> has a pathogenic action in people with a weakened immune systems.
	<p><i>Aspergillus sp.</i></p> 	Dangerous species because increase and develop in substrates with low water content and is found frequently in the archives of books.	The species is found in the terrestrial, air environment, and especially in organic materials which are in the process of decomposition. <i>Aspergillus</i> grows on paper, textiles, synthetic materials, food. <i>Aspergillus</i> species cause disease in humans resulting in weakening the immune system.
	<p><i>Chaetomium sp.</i></p> 	Species that degrade serious the material of cellulosic nature.	It lives, naturally, in the terrestrial, air environment and plant materials. It grows on textiles, wood, paper, food.
	<p><i>Fusarium sp.</i></p> 	Species causes different stains of red, purple, brown, black, etc leading to degradation of paper.	The species is found in aquatic and terrestrial environment and on all types of organic matter. It is a pathogen agent for humans. It develops on textiles, paper, wood, etc. <i>Fusarium solani</i> is the most common species of <i>Fusarium</i> which is a pathogen for humans.
	<p><i>Penicillium sp.</i></p> 	Species that grows on the paper substrates in low humidity conditions and destroy the paper.	Species is found in the aquatic, terrestrial, air environment, and plant materials. These grow on paper, textiles and leather, food.
	<p><i>Stachybotrys atra</i></p> 	Species that destroy the cellulosic material and leads mainly to loss of mechanical properties.	The species is found in air environment, in wetlands. This grows on plant debris and substrates rich in cellulose.
	<p><i>Trichoderma sp.</i></p> 	The species destroy cellulosic material.	Species widespread in the terrestrial environment and that grows on wood, paper, textile and synthetic materials, food, etc.

Bacteria	Aerobic bacteria (<i>Pseudomonas sp.</i> , <i>Bacillus sp. etc</i>)	Cellulosolytic that attack materials containing cellulose.	Bacteria that grow aerobically using the oxygen. These develops in deposits of paper.
	Facultative bacteria (<i>Escherichia coli</i> , <i>Klebsiella sp. etc.</i>)	Cellulosolytic that attack materials containing cellulose.	Bacteria that grow aerobically using the oxygen but in its absence they adapt to anaerobic conditions. They can be found in paper making systems.
	Anaerobic bacteria (<i>Desulfovibrio sp.</i> , <i>Clostridia sp.)</i>	Cellulosolytic that attack materials containing cellulose.	These species develop anaerobically.
Insects	<i>Caries</i>	They attack the materials that contain cellulose (wood) and adhesives.	In the larva stage, the caries destroy the book because they dig galleries in cellulosic material. Larva is colourless.
	<i>Psocoptera</i> 	It feeds on adhesives and mould that develops on the books.	Has a size of 1 mm and it is colourless or beige.

The main fungi and bacteria that attack the paper are described and presented in Table 1 [8].

4. The importance of creating a database (DB) of the biocides used in processes of preservation, restoration and conservation

Lately, the large number and diversity of synthesized biocides impose their systematization for the application in various fields, reason for which were introduced databases that facilitate access to information and allow the analysis of substances with biocidal properties.

DB is a collection of operational data recorded on the addressable support, under the logical interdependence, together with the description of data and relations between them, which are processed in computer applications in all areas of activity [9]. DB ensures independence program-data as well as access control and data handling, allowing the processing, the quick sorting of the information and their extraction on different search criteria, so that database systems, as software application have come to represent the most important achievement in engineering computer programming [10].

We designed and realized a database data on biocides used in various industries (pulp and paper, textile and leather industry etc) in which we introduced useful and practical information.

A database has a public character and is accessible to anyone who wants to obtain specialized, complete information about the substances with biocidal properties. The access to the database is simple by creating a user account with username and password [11].

After we have created an account we can select to view all substances that were introduced or seek whatever we want in the database. We can also visualize the latest new issues on biocides used in different research areas which present a real interest (Figure 2).

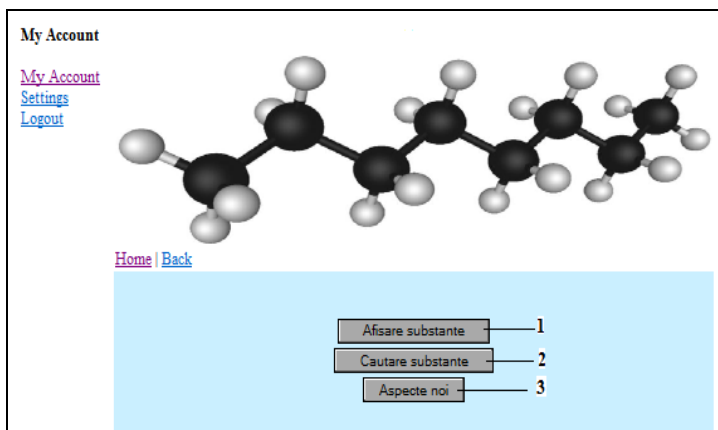


Figure 2. Ways to display data in the database where: (1) - display substance, (2) - search substance, (3) - new issues.

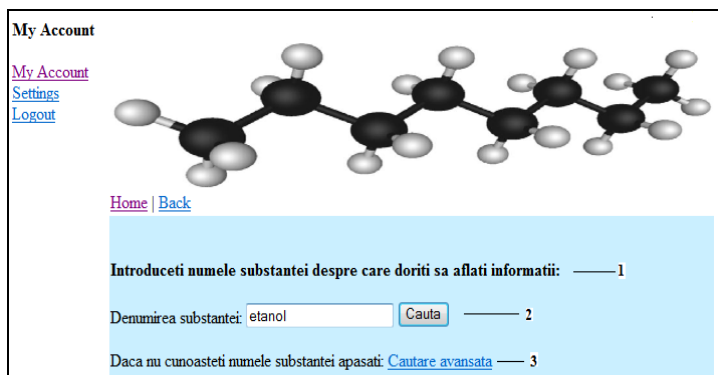


Figure 3. Representation of the search menu where: (1) enter the name of the substance for which you want to find information, (2) substance name/ethanol/search, (3) if you do not know the full name of the substance: advanced search.

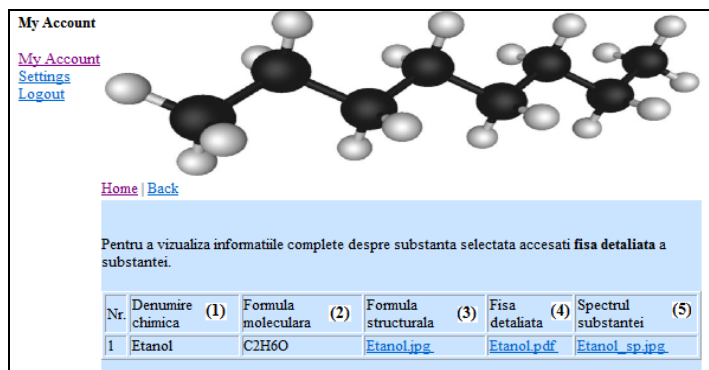


Figure 4. Search results for a substance (ethanol): To view complete information about the chemical substance selected, access detailed file of the substance, (1) chemical name, (2) molecular formula, (3) structural formula, (4) detailed file, (5) the IR spectrum of substance.

The user of the database can introduce the name of the substance about which he/she wants to know different information accessing the *search menu* (Figure 3) or can select the button *quick search* through which he/she can select the type of query, for example antimicrobial efficacy of the substance (we find out how effective is the biocide against bacteria, fungi), sustainable and efficient in use, environmental toxicity etc.

After what you have written the name of the substance which you want to know, various information appear on the interface represented in Figure 4 and by a simple click you can download in pdf format the file of the substance, its structural formula and the IR spectrum in jpg format.

Information fields as pdf file from DB were structured as follows [12]:

- chemical and commercial name,
- chemical and structural formula,
- code numbers: CAS-No, EINECS-No and other code numbers,
- short presentation of the history of substance,
- methods of manufacturing/production of the biocid,
- information about the framing in the chemical hazard category,
- physical, chemical, toxicological and ecotoxicological properties,
- antimicrobial effectiveness and applications of the biocidal product,
- Information on the antimicrobial action of the biocide on the bacteria, yeasts.

The database is a relational, based on conceptual model of an application that analyze biocides and which has a large size (over 400 compounds). The database provides access to various useful information on biocidal products and are presented in a concise and friendly format.

5. Conclusions

This paper presents the major importance of biocides in processes of preservation, restoration and preservation of books, and the need to create a database to facilitate access to information regarding these substances.

Biocides are essential to maintain the materials in good hygienic conditions, destroying the molds, microbes and pests and a well structured database offers a wide range of information on the biocides used to protect cellulose materials in the processes of preservation, restoration and conservation.

Through this paper we also want to emphasize that all libraries should adopt preservation and conservation policies because these provide a number of advantages:

- they offer the continuity and accessibility to information for the next generations;
- they prevent the necessity of restoration activities of the books;
- they stop the transfer on other supports, thus reducing the costs;
- they allow to the future readers, researchers to discover the books on the support which were made first time;

- they remove the necessity of some anti-aging treatments, which can subsequently lead to degradation of the cellulosic material;
- they determine the delay or even stop the biodeterioration process of the books.

In conclusion, due to the importance of the biocides for different areas, their diversity and number, in order to know and use them more effectively, the researches must continued in terms of their organization in specialized databases.

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