New methods of protection during the conservation of books I. Tzvetanska^{1*}, V.Lasheva²

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The libraries storing paper funds are often forced to withdraw from circulation a series of books that have become unusable due to bio-corrosion. Usually destroyed materials are weakened, pigmented paper and crumbling, covered with barnacles, with colorful spots and often with tight glued pages. The species composition of microorganisms that break down the cellulose component of the paper in terms of libraries are not adequately studied and is of interest both in theoretical and in practical terms. In conservation libraries new worldwide environmental technologies are being implemented. For the disinfection of bibliographical and museum cultural heritages are designed especially new specific methods of treatment without toxic substances and chemicals. The method "anoxia" is a non-toxic disinfection by controlled oxygen-free environment and embedded control pest insects, without any risk to the literary heritage of people and the environment. In the method "anoxia" the atmosphere artificially changing, by the removal of oxygen to levels below 0.5%, and is introducing inert gas (nitrogen in most cases). At the same time control the levels of temperature and relative humidity to be maintained within certain parameters for the efficiency of the method. Anoxia eliminate parasites by dehydration and suffocation. The mortality of the pests was 100%, irrespective of their stage of development.

The studies presented in this experiment are the applications of the method "anoxia", which are being carried out in the regional library in Rousse in Bulgaria.

Key words: Conservation, books, paper, anoxia

INTRODUCTION

Preservation of documentary book heritage is a constant challenge for institutions and professionals, responsible for its storage. Efforts are oriented towards identifying agents that cause damage of documents and the application of measures to prevent or combat the attack of these agents. Measures are developed to protect and provide acceptable conditions for storage of documents and ensure their durability.

Creation of microenvironment with oxygen deficiency is a perspective for long-term storage of documents from paper and not only for them. This method is safe, non-toxic and completely inert with respect to the objects to be treated and may delay the degradation and destruction of sensitive and vulnerable documents mainly caused by oxygen, pollutants and inadequate levels of humidity and temperature.

As the most promising non-toxic methods are considered freezing and modified atmosphere with inert gases, carbon dioxide and oxygen absorbers.

The method of anoxia atmosphere / environment without oxygen / is a technique for eradication and control of pests. It consists in removing the oxygen

*) To whom all correspondence should be sent: E-mail: book_restore@vip.bg from enclosed space in which the materials or objects have been isolated for treatment or preventing.

Modified atmosphere anoxia can be made in three versions: with application of CO_2 or inert gas, oxygen absorbers or both processes simultaneously.

The results are dehydration and suffocation of microorganisms and insects no matter in which evolutionary stage of development they are egg, pupa, larva, adult. Nitrogen is often used as an inert gas. It does not kill directly, but prevents the unwanted influence. The anoxia method is applicable to all types of organic / paper, leather, fabric, wood / and inorganic materials. Anoxia method is non-toxic to humans and the environment, and is widespread as a suitable alternative within the concept of protection of collections and cultural heritage. This process requires equipment with high sensitivity and precision control temperature, humidity, concentration of oxygen and inert gas content.

The purpose of this work is to study feasibility and efficiency of this non-toxic method - anoxia pest control and disinfection, restriction of degradation of documents from biological agents and its implementation in Bulgaria.

EXPERIMENTAL

In this work the method of dynamic system anoxia is applied. In this system CO_2 gas and / or inert gases are used for blowing down oxygen from the hermetically sealed space to the oxygen concentration from 0.5 to 0.1%.

In the dynamic system anoxia gas CO₂ is used and the gas flow is controlled by a flow regulator. The most suitable are large reusable cameras. To control the lethal effect the relative humidity, temperature and oxygen levels are constantly monitored by equipment. In cameras can be installed moisturizers and dryers, in order to maintain the natural moisture of the material. Schafer [1] recommends the use of fans inside the large package to avoid formation of gas layers. By air movement the gases are mixed and reach to all levels of materials in the package. According Selwitz and Maekawa [2] CO₂ is effective for insect mortality at a concentration of 60% and 80%. A high accuracy at sealing of packages is not required and fluctuations in the concentration of CO₂ do not affect the effectiveness of treatment. CO₂ is cheaper than N2. However, according to Schafer CO₂ at concentration of 100% reduces metabolism of some insects, which leads to a state of latency and does not cause mortality. In addition, if there is moisture in the packing material, removed during the treatment of the exhibits, there is a high risk CO2 to transform into carbonic acid. This acid will increase the acid content in exhibits causing additional damage of documents on paper, pigments, metal. Therefore, experts should be aware of these consequences and evaluate them before choose a method of processing.

Nitrogen and argon are the most commonly used inert gases. Researchepcs [3,4,5] and publication of Selwitz and Maekawa "Inert gases in pest control in a museum" [2], show 100% mortality under controlled conditions of temperature and relative humidity.

At combinations of temperature, relative humidity and duration of exposure, the results show a complete mortality of the insects after 80 hours at 25 ° C, 75% RH (humidity) and 0.5% of O₂ (99,5% N2). Rust and Kennedy [5] report about their indepth entomological studies of modified system anoxia with nitrogen. They found that using nitrogen in test cameras in which the content of oxygen is strictly controlled below 0.1% only 72 hours at 25° and 55% RH are required for complete destruction of pests of all stages of their development for most types. However, 192 hours / 8 days / have been necessary to achieve the total mortality of the eggs and all forms of *Lasioderma* *serricorne*. Therefore, minimal exposure of 10 days in 0.1% O_2 containing nitrogen and 25 ° C, 55% humidity is recommended to achieve efficiency of anoxia in museum exhibits.



Researchers and specialists in other institutions [6, 7] reported about success of nitrogen atmosphere in destroying of insects and microorganisms in museum exhibits. Later they made assessments and fulfilled new analyzes using not only nitrogen but also argon. Infected objects were subjected to detailed entomological review. It was found that shorter exposure time is needed for full mortality by argon than by nitrogen.

Figure 1 and Figure 2 show the effect of temperature during exposure / days / needed to achieve complete mortality of insects at 40% RH and a low concentration of $O_2 / 0.1\%$ / in a nitrogen and argon atmosphere for the following types: (1) Hylotrupes bajulus, (2) Lasioderma serricorne, (3) Anobium punctatum, (4) Xestobium rufovillosum, (5) Lyctus brunneus, (6) Stegobium paniceum, (7) Nicobium castaneum, (8) Attagenus piceus.

RESULTS AND DISCUSSION

The method of dynamic atmosphere anoxia is used in Ruse Regional Library by combination of carbon dioxide and nitrogen and in the National Library of Bulgaria only by nitrogen.

It has been shown that the application of anoxia atmosphere for the treatment and prevention of materials on a protein carrier, when the humidity is in the range 33-40% and the oxygen content is 0.1%. There were no changes in the physicochemical properties of the objects [8].

Argon and nitrogen have proven their effectiveness in the eradication of all forms of life in depriving them of oxygen, leading to anoxia. If the oxygen content of the inert atmosphere is 0.1% argon shows more rapid effectiveness as compared to nitrogen, because it is heavier than nitrogen and more quickly deposits on the objects subjected to anoxia [9].



Kinds of insects

Figure 1. Mortality of insects using nitrogen. The required duration of exposure to this inert environment depends on the types of microorganisms and insects, from their stage of life, oxygen content, and type of inert gas, relative humidity and temperature. According to Selwitz and Maekawa [2] noble inert gas helium can also be effective, but it has a very high rate of diffusion through plastic film and a higher price. According Elert and Maekawa [10], the oxygen concentration must be below 0.3% over a period of 14 days to ensure complete mortality of the insects in all stages /eggs, larvae, pupae and adults/. The temperature inside the system should be about 25-30 C and relative humidity not more than 50%. However, according to Beck [11], the high humidity requires exposure time of 15 to 22 days. According to studies of Elert and Maekawa [10], the species, stage of development and the environmental conditions during the treatments are important factors that must be taken into account in order to achieve a complete liquidation of the microorganisms and insects. According to studies of Selwitz [2], by increasing of temperature the rate of metabolism and oxygen consumption in insects increases, i.e. they consume more oxygen and lose more body fluid, leading to dehydration and death with lower humidity. Another factor is the time of exposure to low concentrations of oxygen. Rust and Kennedy [5] observed mortality at all stages after 192 hours / 8 days / of exposure in an oxygen-free atmosphere at concentration of 0.1% of oxygen, temperature 25,5°C and 55 RH. Elert and Maekawa [10] showed that most microorganisms and insects can be removed after 8 days at oxygen concentration below 0.3%, temperature of 25 $^{\circ}$ C and RH 50%. However, these authors recommend a treatment within 14 days under the above mentioned conditions in order to ensure complete destruction. To establish anoxic condition it is desirable to add about 2-3 days safety margin above experimentally proven time of life. However, at temperatures below 25 ° C the processing time 204

Days



Figure 2. Mortality of insects using argon

should be increased, i.e. the treatment will last 22 days at a temperature of 20° C. But the most resistant insects may not be liquidated at 20° C for 22 days [10-14] Therefore, the parameters of temperature, relative humidity and oxygen concentration must strongly comply because the more resistant insects will survive for a longer time under conditions of anoxia.

An extremely important factor for efficient performed anoxia is the camera, etc. balloon or bag, where the materials will be placed for disinfection and treatment. Cameras are made of high barrier plastic or plastic with low oxygen permeability. Originally they were developed for the food industry and pharmacy, so that their products can be transported and stored long-term safe. High barrier materials are made of layers of different plastics such as polyethylene terephthalate RET18; polyvinyl vinylidene, PVDC19; polyamide (nylon) and polyester, joined by co-extrusion.

A new ultra-modern technology for extrusion of material from latest generation of polymers is PET. Its excellent mechanical, thermal and chemical parameters, safety for environment, combined with structural strength, crystalline transparency and gloss make it very valuable for barrier products. Because of its undoubted qualities in comparison with other polymer materials it is recommended by legislation in many European countries. It is necessary these high barrier polymers for anoxia atmosphere to be flexible, transparent and resistant to punctures, not to bend under seal with heat to not compromise the treatment.

CONCLUSIONS

The microenvironment created by the conditions of anoxia is alternatively proven method for prevention, treatment and long-term storage. Anoxia atmosphere prevents oxidation, biological and microbiological degradation of documents.

Collections of libraries, archives and museums are built from organic materials that are part of diet

Days

of microorganisms and insects so we must take regular preventive measures and treatment of infections if they are identified. It is necessary to know well the agents threatening collections in order to select the most appropriate methods for disinfection and treatment and establish a system for integrated control, adapted to the needs of each institution.

Modified methods atmosphere anoxia show good results in treatment of various kinds of collections, as we found in this study. Its methodology requires knowledge of various procedures, requirements and specific equipment. Through studies and adequate training of staff they can be applied systematically in damaged library collections.

In analysing the methodology of atmosphere anoxia, the key factors that ensure the effectiveness are:

- To maintain the oxygen concentration below 0.3%.
- The exposure time of the microenvironment created by reduced oxygen content.
- To maintain the relative humidity of about 50% inside the hermetic space.

The responsibility to these requirements during the course of treatment will lead to complete liquidation of microorganisms and insects, as above mentioned factors must interact in complete unity.

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НОВИ МЕТОДИ ЗА ЗАЩИТА ОТ БИОФАКТОРИ ПРИ КОНСЕРВАЦИЯ НА КНИГИ

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(Резюме)

При консервация на библиотечни фондове се прилагат нови световни екологични технологии. За дезинфекция на библиографични и музейни културни наследства специално са разработени нови методи на третиране без токсични субстанции и химикали. Методът "Аноксия" представлява нетоксична дезинфекция, посредством контролирана безкислородна среда и внедрен контрол на нашествия от насекоми, без никакъв риск за книжовното културно наследство, за хората и околната среда. При метода Аноксия изкуствено се променя на атмосферата, чрез премахването на кислорода до нива под 0,5 % и въвеждане на инертен газ / в повечето случаи азот/. В същото време се контролират нивата на температурата и относителната влажност, които се поддържат в определени параметри за ефективност на метода. Аноксията елиминира паразитите, чрез дехидратация и задушаване. Смъртността на вредителите е 100%, независимо от техния стадий на развитие. В настаящата разработка е представено приложението на метода "Аноксия" в България в регионалната библиотека в Русе.