Gas Evolutions from Paints and Varnishes When Fungus Molds and their Metabolites Act on Them

V Smirnov¹, D Svetlov², A Bulgakov³, M Vildiaeva⁴, D D Svetlov⁵

¹Department of Biochemistry and Biotechnology, Nizhny Novgorod State University named after Lobachevsky, 23 Gagarina Av., Nizhny Novgorod 603950, Russia
²Department of Management, Closed Joint Stock Company "Soft Protector", 5 Driving St., St. Petersburg 191002, Russia
³Department of Building Materials and Technologies, Mordovia State University, 68 Bolshevikskaya Str., Saransk 430005, Russia
⁴Department of Surgery, LLC Treatment and rehabilitation center "Vita-Med", 18a Democratic St., Saransk 430000, Russia
⁵Department of Management, Graduate School of Biotechnology and Food Production 48-50 Novorossiyskaya St., St. Petersburg 194021, Russia

E-mail: agi.bulgakov@mail.ru

Abstract. In this article are presented the results of a study of the biodegradation of paints and varnishes. For testing were used enamels based on phenol-formaldehyde and epoxy resins. Samples from the studied materials were tested under the influence of micellar fungi of the species aspergillus niger, penicillium chrusogenum, trichoderma viride, as well as in the products of their metabolism: a mixture of oxalic, succinic, citric, malic, fumaric, α-ketoglutaric and oxalacetic acid and enzyme of peroxidase. The experimental and control samples were kept in a thermostat at a temperature of 29 ± 2.0 ° C and relative humidity of 98%. The qualitative composition of gas evolution was determined by chromatographic identification methods using chemical methods. The dynamics of gas evolution from paints based on enamels during their biodegradation by micromycetes and their metabolites has been experimentally determined. After only one month of exposure to aggressive media, the composition of gas evolution was changed significantly compared to gas evolution from control samples. By the third month of exposure, the total concentration of gas evolution was increased by 3.8 and 6 times compared with gas evolution from control samples. When the samples were kept in the products of fungal metabolism, a difference in the composition of gas evolution was revealed when microscopic fungi were being acting on these materials.

1. Introduction

In the construction industry, various composite construction materials are widely used, which primarily include concrete of various types and paints and varnishes [1-17]. Many building materials based on inorganic and organic binders, including polymeric paints and varnishes, under conditions of high humidity, are subjected to biological corrosion, mainly mold. Biodeterioration of composite building materials was studied in the works of various authors [18-25]. The scientific concept of designing composite building materials is to provide a binder, and a composition based on it, that is strong, durable, gas-tight, waterproof, and antifouling by
microorganisms [1-4,23-25]. The following works [26–34] are devoted to the issues of increasing the biostability of building materials based on inorganic and organic binders.

Paint and varnish materials (PVM) used for the manufacture of protective paint and varnish coatings (PVC) of building structures are formed from synthetic resins, plasticizers, hardeners, dyes. With the defeat of paint and varnish materials by mold fungi, various products of their vital activity (enzymes, organic acids, amino acids, etc.), as well as products of their destruction, are released into the environment.

Paints and varnishes based on phenol-formaldehyde and epoxy resins are widely used in construction, in particular, enamel FL-62 and enamel EP-255, which are not resistant to mold fungi, determined according to relevant technical norms and rules. To obtain polymer materials with a given biostability, knowledge of the degradation mechanisms of such polymers is necessary, but there is practically no information on this issue in the literature.

2. Research objectives
The purpose of this study was to determine the composition of the products of the destruction of enamels based on phenol-formaldehyde and epoxy resins of the FL-62 and EP-255 grades under the action of molds and their possible metabolites on them. The following tasks were being solved:

- to carry out the investigation of paints and varnishes based on epoxy and phenol-formaldehyde resins on biological effects
- to determine gas evolution from enamels of the grades FL-62 and EP-255 under the influence of them of mycelial fungi
- to identify the features of gas evolution from polymeric materials in case of exposure to metabolic products of mycelial fungi
- to analyze the evolution of gas from biodegradable materials in comparison with samples aged in normal temperature and humidity conditions.

3. Materials research methods
Enamels based on phenol-formaldehyde resin brand FL-62 (technical regulations (TR) 6-10-1814-81) and epoxy resin brand EP-255 (GOST 23599-79) were considered as test materials. The following mycelial fungi were used as a test of organisms during biological investigations: Aspergillus niger, Penicillium chrysogenum, Trichoderma viride. Of the metabolic products of mycelial fungi was used a mixture of acid solutions: oxalic, succinic, citric, malic, fumaric, α-ketoglutaric, oxalacetic, and peroxidase enzyme.

For the investigations, it was used the previously developed gas chromatographic method for analyzing gas evolution from paintwork samples, which involved air sampling using special concentrates.

Samples of paints and varnishes in the form of coatings were prepared as follows. PVM was applied to the silicate glass and dried in accordance with the TR. Some of the samples were placed on a lawn from molds, most often affecting paints and varnishes: Aspergillus niger, Penicillium chrysogenum, Trichoderma viride. Several samples were sunk in a mixture of acid solutions: oxalic, succinic, citric, malic, fumaric, α-ketoglutaric, oxalacetic and peroxidase enzymes, which are the most characteristic metabolites of molds that they emit during biodeteriorating industrial materials. The concentration of organic acids in solution is 10⁻² M, the peroxidase enzyme is 10⁻⁶ M. The number and activity of metabolites acting in each case on the material depend on the species composition of microorganisms, as well as on the structure and properties of the material itself. Control samples were not exposed to fungi and their metabolic products. The experimental and control samples of paintwork materials were kept in a thermostat at a temperature of 29±2.0 °C, relative humidity of 98 %. After holding for 1.2 and 3 months, the samples were transferred to hermetically sealed liter round-bottom glass flasks and placed in a thermostat at 28-29 °C for 4 days until the thermodynamic equilibrium was established. Then samples were taken for analysis (60-100 ml) by the aspirated method or by passing a stream of nitrogen through the flask. The qualitative composition of gas evolution was
determined by chromatographic identification methods using chemical methods. Quantitative processing of the results was carried out by the absolute calibration method.

4. Experimental investigations and analysis of the results

The test results of the resistance of coatings to molds and their metabolites for enamels FL-62 and EP-255 are shown in the tables 1,2.

Table 1. Dynamics of gas evolution from coatings based on FL-62 during their biodegradation by micromycetes and their metabolites.

| Components          | First month | Second month | Third month |
|---------------------|-------------|--------------|-------------|
|                     | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Acetone             | 0.59 | 1.03 | - | - | - | - | - | - | - |
| Methanol            | 0.33 | 1.19 | - | - | - | - | - | - | - |
| Butyaldehyde        | 0.78 | 0.99 | 4.91 | 7.78 | - | 39.6 | 0.64 | 2.75 | 1.08 |
| Ethyl acetate       | - | - | 24.06 | 0.90 | 0.90 | 0.28 | 0.20 | 4.46 | 4.03 |
| Nonan               | - | - | 0.23 | 0.17 | 0.17 | 0.05 | 0.006 | 0.07 | 0.02 |
| N-butanol           | - | - | 0.37 | 0.41 | 0.41 | 0.28 | 0.91 | 0.38 | 0.24 |
| The sum of gas      | 3.21 | 29.73 | 29.73 | 9.47 | 9.47 | 40.33 | 1,906 | 7.66 | 5.37 |

1 - control; 2 - metabolites; 3 - fungus

Table 2. Dynamics of gas evolution from PVM based on EP-255 in the course of biodegradation by micromycetes and their metabolites.

| Components          | First month | Second month | Third month |
|---------------------|-------------|--------------|-------------|
|                     | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Acetone             | 1.04 | - | - | - | - | - | - | - | - |
| Methanol            | 0.73 | - | 0.08 | 0.08 | 0.06 | - | - | - | - |
| Ethanol             | - | 0.33 | 0.52 | 0.77 | 0.58 | 0.99 | - | 0.25 | 0.30 |
| Ethyl acetate       | - | 0.93 | 61.3 | - | - | 1.91 | 1.16 | 9.45 | 7.10 |
| Toluene             | - | - | 0.02 | 0.02 | 0.03 | 0.02 | 0.03 | 0.02 | 0.04 |
| Dibutyl ether       | 1.23 | - | 0.05 | 0.09 | 0.20 | 0.06 | 0.03 | 0.06 | 0.07 |
| Butyl acetate       | 2.65 | - | 0.24 | 0.08 | 0.31 | 0.07 | - | 0.09 | 0.16 |
| Xylene              | 11.91 | - | - | - | - | 4.14 | - | - | 2.99 |
| The sum of gas      | 17.56 | 1.26 | 62.26 | 1.04 | 1.16 | 7.19 | 1.49 | 9.87 | 10.73 |

1 - control; 2 - metabolites; 3 - fungus

From the research results, the following can be distinguished. Under the action of a mixture of aggressive metabolites, the composition of gas evolution from LKM samples after 1 month of exposure is changed significantly compared to gas evolution from control samples. In gas evolution from samples after 2 months of exposure, there is a decrease in the concentrations of all components of the FL-62 enamel and an increase in the concentration of dibutyl ether and butyl acetate for the EP-255 enamel. As a result, the total concentration of gas evolution from the FL-62 after 1 month of testing was remained at the same level, after 2 months it was decreased by 8 times compared with the control sample. For EP-255, it was being remained at the same level after 2 months of testing, and after 1 month it has been decreased by 15 times. After 3 months of exposure, the concentration of ethyl acetate in gas emissions from PC samples was sharply increased, which led to an increase in the total concentration from FL-582 PCs by 3.8 times, and EP-255 by 6 times compared with gas releases.
from the control sample. The obtained data indicate that the effect of metabolites on PC is ambiguous and is dependent on the composition of the paintwork. When molds act on EP-255 enamel based on a non-resistant towards the fungal epoxy that susceptible to biocorrosion, as a result of which the concentration of emitted gaseous products is increased. In gas evolution from FL-62 enamel samples treated with molds, after one month there is a sharp increase in the concentrations of butyric aldehyde and ethyl acetate, after 2 months of exposure - butyraldehyde. Attention should be paid to the fact that the qualitative and quantitative composition of the gas emission under the influence on PVM of model aggressive metabolites differs from the composition of the gas emission when microscopic fungi act on these materials. This may be due to the fact that the initial mechanisms of PVM destruction in each of these variants are different, due to the fact that the model composition of aggressive metabolites does not fully coincide with the composition of those metabolites that secrete fungi during growth on the corresponding PVM.

5. Conclusion

Composite building materials based on inorganic and organic binders are subjected to biodegradation. Gas evolution from paints and varnishes based on phenol-formaldehyde and epoxy binders was investigated when exposed to samples of mycelial fungi (Aspergillus niger, Penicillium chrysogenum, Trichoderma viride) and their metabolic products (a mixture of solutions of oxalic, succinic, citric, malic, fumaric, and fumaric acids oxalacetic and peroxidase enzyme). It has been established that the qualitative and quantitative composition of the gas released under the influence of model aggressive metabolites on paintwork materials differs from the gas released under the action of mycelial fungi on this material.

6. References

[1] Edward G 2001 Fundamentals of High Performance Concrete eg. G Edward, P Navy p 302
[2] Mechtcherine V 2012 Application of superabsorbent polymers in concrete construction ed. V Mechtcherine H W Reinhardt (RILEM State of the Art Reports 2. Springer)
[3] Ghosh S 2009 Self-healing materials: fundamentals, design strategies, and applications (Weinheim) ed. Wiley WCH pp 183–218
[4] Figrovskaya V, Ivanov V, Barbalat A and Ershova N 2005 Journal of analytical chemistry vol 60 7 pp 707–710
[5] Fedosov S, Rumyantseva V, Krasilnikov I, Konovalova V and Evsyakov A 2018 Magazine of Civil Engineering 83(7) pp 198-207 doi: 10.18720/MCE.83.18
[6] Tsirkin O, Odintsova O and Rumyantseva V 2017 J. News of higher educational institutions. Technology of the textile industry 1(367) pp 134-139
[7] Ayatollahi M, Shadlou S, Shokrieh M and Chitsazzadeh M 2011 J. Polymer Testing 30(5) pp 548-556 doi: 10.1016/j.polymertesting.2011.04.008
[8] Allaoui A and, El Bounia N 2009 J. A review. Express Polymer Letters 3(9) pp 588-594 doi: 10.3144/expresspolymlett.2009.73
[9] Kathi J, Rhee K and Lee J 2009 J. Composites Part A: Applied Science and Manufacturing 40(6-7) pp 800-809 doi: 10.1016/j.compositesa.2009.04.001
[10] Gkikas G, Barkoula N-M, Paipetis A J. Composites Part B: Engineering 43(6) pp 2697-2705 doi: 10.1016/j.compositesb.2012.01.070
[11] Yatsenko E, Goltzman V, Bulgakov A and Holschemacher K 2019 Journal of Ore-dressing 2 pp 49-54 DOI: 10.17580/or.2019.02.09
[12] Tang L.-C, Zhang H, Han J.-H, Wu X and Zhang Z 2011 J. Composites Science and Technology 72(1) pp 7-13 doi: 10.1016/j.compscitech.2011.07.016
[13] Guadagno L, Vertuccio L, Sorrentino A, Raimondo M, Naddeo C, Vittoria V, Iannuzzo G, Calvi E and Russo S 2009 J. Carbon 47(10) pp 2419-2430 doi: 10.1016/j.carbon.2009.04.035
[14] Wernik J and Meguid S 2015 J. Materials and Design vol 59 pp 19-32 doi: 10.1016/j.matdes.2014.02.034
[15] Rahmanian S, Suraya A, Shazed A, Zahari R and Zainudin E 2014 *J. Materials and Design* vol 60 pp 34-40 doi: 10.1016/j.matdes.2014.03.039

[16] Msekh M, Cuong , Zi G, Areias , Zhuang, Rabczuk T 2018 *J. Engineering Fracture Mechanics* vol 188 pp 287-299 doi: 10.1016/j.engfracmech.2017.08.002

[17] Saeb M, Najafi F, Bakhshandeh E, Khonakdar H, Mostafaiyan M, Simon F, Scheffler C and Maeder E 2015 *Chemical Engineering Journal*. 201 vol 259 pp 117-125 doi: 10.1016/j.cej.2014.07.116

[18] Erofeev V, Smirnov V, Dergunova A, Bogatov A and Letkina N 2020 *J. Materials Science Forum* 974 MSF pp. 305-311 doi: 10.4028/www.scientific.net/MSF.974.305

[19] Erofeev, V, Smirnov F and Myshkin A 2019 *J. Proceedings* vol 19 pp 2255-2257 doi: 10.1016/j.matpr.2019.07.547

[20] Erofeev, V, Smirnov F and Myshkin A 2019 *J. Power Technology and Engineering* 51(4) pp 377-384 doi: 10.1007/s10749-017-0842-8

[21] Erofeev V, Rodin I, Kravchuk S, Kaznacheev S and Zaharova E 2018 *Magazine of Civil Engineering* 84(8) pp 48-56 doi: 10.18720/MCE.84.5

[22] Travush V, Karpenko N, Erofeev V, Rodin A, Smirnov V and Rodina N 2017 *J. Biotechnology and the Ecology of Big Cities* pp 21-28

[23] Smirnov V, Semicheva A, Erofeev V and Morozov E 2003 *J. Paint and varnish materials and their applies* vol 9 pp 21-26

[24] Erofeev, V, Kalashnikov V, Karpushin S, Rodin A, Smirnov V, Smirnova O, Moroz M, Rimshin V, Tretiakov I and Matviei4vskiy A 2016 *J. Solid State Phenomena* vol 871 pp 33-32 doi: 10.4028/www.scientific.net/MSF.871.33

[25] Erofeev V, Kalashnikov V, Karpushin S, Rodin A, Smirnov V, Smirnova O, Moroz M, Rimshin V, Tretiakov I and Matviei4vskiy A 2016 *J. Solid State Phenomena* vol 871 pp 33-39. doi: 10.4028/www.scientific.net/MSF.871.33

Acknowledgments

Published with the support of the RFBR grant RM No. 18-48-130013 "Comprehensive study of physicochemical processes in composite materials based on epoxy resins and other synthetic polymers that are promising for use in construction."