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Biocides – Stabilizers Against Biodegradation: New Frontiers

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The contributors are discussing the problems of properties and applications of biocides. Biocide classification, investigation technique, kinetic of biomass growth in a medium containing biocides, kinetic constants are presenting in the article.

Keywords Bacteria; biocides; biodegradation; biomass; kinetics; microscopic fungi; properties; stabilizers; suppression

Introduction

Biofactors are organisms (bacteria, microscopic fungi) and their associates which cause the breakdown of useful materials. The actions of biofactors can be mechanical, chemical or biological. The degradation of an object caused by biological factors is called biodegradation. The chemical compositions which provide protection against biofactor effects are referred to as biocides and (or) fungicides in the case of protection from microscopic fungi effect.

Systematic research concerning the protection from biodegradation was begun in the 1920s and 1930s. At that time the focus was on biocides development for such materials as textiles, leather, paper glues, etc. Development of new materials, increased consumption, short supply of raw materials, and the increased requirements for trouble-free long term performance, coupled with the ecological problems of disposal of polymeric materials prompted, in the late 1980s, the start of a very active research to discover new and more effective biodegradation protectors.

The leading biodegradation protectors are substances-biocides, whose application is characterized by high efficiency in a variety of forms. Biocides can be: introduced directly into the volume of a material, applied to the material surfaces, added to impregnating or lubricating media, etc. Several thousands of such compounds are known and substances containing alcohol and oxidizing groups, heavy metal ions and surfactants belong to biocides.

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Table 1 shows properties of some well-known volatile biocides (fumigants). Tables 2 and 3 show examples of suppressing microorganism growth (development) by biocides in technical products, obtained by usual estimation technique.

The effectiveness of biocide action is explained by their capability to penetrate into a microorganism cell or on its surface, and interfere with at least one of the vitally important processes or accumulate microorganism. For example, halogen- and sulfur-containing biocides cause oppression of microorganism respiration. Iodides and fluorides decrease the activity of some enzymes. Toxicity of metal-organic compounds possessing heavy metal atoms in their composition is stipulated by their influence (effect) on sulfohydryl groups of enzymes.

Modern biocides are required to possess a high activity against destructive functions of biofactors, but their application must be free of all harmful influences on the environment. In addition, the biocides must be stable at elevated temperatures and on exposure to water and air, etc. It is obvious that the application of biocides must not cause any undesirable effects on physico-chemical, mechanical and other properties of materials. They must not accelerate or cause material aging, corrosion, processibility etc.

Beside these general demands there are some special requirements for biocides, connected with certain features of protected material, its production technology and exploitation conditions. For example, biocides designed for protecting polymer and paint should be easily soluble in organic solvents, combine with other components of materials or evenly (uniformly) distribute in them forming stable emulsions or suspensions.

Biocides designed for wood protection should easily penetrate and chemically interact with cellulose and not affect its painting and adhesive characteristics. The toxicological requirements for biocides are:

1. Nontoxicity to warm-blooded animals and human beings, and
2. No effects associated with carcinogenesis, mutagenity, embryo-toxicity and allergenity.

Biocide Classification

Chemical biodegradation protectors are classified according to their biological action, chemical composition and purposes. The following subdivision is based on their biological action:

1. Fungicides, used for protecting materials and articles (appliances) from degradation by fungi;
2. Bactericides, used for protecting from putrid (patrefective), acid-forming and other bacteria;
3. Algicides, used for protecting ships and technical buildings from algae and mollusks;
4. Insecticides-from insects;
5. Zoocides-from rodents.

Biocides are also classified into following groups of materials based on their technical purposes and application:

1. Wood, paper, cardboard;
2. Synthetic polymer materials, compounds, rubbers (caoutchoucs);
3. Textile materials;
4. Natural (real) leather and articles from it;

Table 1. Properties of some well-known volatile biocides (fumigants)

Name	Molecular mass	Temperature of boiling, °C	Solubility in water	Inhibiting concentration, mg/l	Penetrability to material	Biocidal activity
1. Methylbromide	95	4.6	Weak	3500	Excellent	Weak
2. Propylene oxide	58	34	Good	800 ÷ 2000	Excellent	Excellent
3. Formaldehyde	30	-21	Good	3 ÷ 10	Excellent	Excellent
4. Ethylene oxide	44	10.4	Complete	400 ÷ 1000	Moderate	Moderate
5. β-propyolactone	72	162	Moderate	2 ÷ 5	Does not penetrate, sterilizes from surface	Moderate

Table 2. Suppression of microorganism growth by influence of different additives, %

Petrol additive	Concentration, %	Mixture of fungi	<i>Glago sporium resinae</i>	<i>Pseudomonas pyncyaneum</i>	<i>Mycobacterium lacticolum</i>
Mixture of aliphatic amines	0.1	100	100	100	100
Dimethyl aminomethyl-para-chlorophenol	0.5	60	80	100	100
Trialkylphenyl ester of cyclohexyl phosphine	0.5	40	40	80	80
T-1* petrol with no additives	—		Plentiful growth		

*Russian trade mark.

Table 3. Fungicidity of heterocyclic arsenic derivatives*

Substance	Concentration, ml/l				
	1	10	50	75	150
10-Phenylphenoxarsin	—	—	—	—	—
10-Chlorphenoxarsin	+	+	+	+	—
10-Ethylphenoxarsin	+	+	—	—	—

5. Petroleum products (petrols, oils, lubricants);
6. Lubricating fluids,
7. Paint and vanish materials and coverings.

Biocides are subdivided as follows according to their chemical structure:

1. Inorganic compounds;
2. Hydrocarbons, halogen hydrocarbons and nitrocompositions;
3. Alcohols, phenols and their derivatives;
4. Aldehydes, ketones, organic acids and their derivatives;
5. Amines, amine salts and quaternary ammonium compositions;
6. Elementorganic compositions;
7. Heterocyclic compositions.

Characteristics of most useful biocides are shown in Table 4.

Biocide Investigation Technique

Traditional methods of biocide activity investigations are based on test analysis of the determination of their inhibiting capability of microorganism development at incubation on solid agarized surface. Fungicide activity is determined by the following equation:

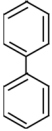
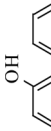

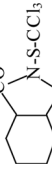
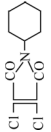
$$R = \frac{(d_0 - d_1) \times 100}{d_0} \quad (2)$$

Here d_0 is the control diameter of colonies (mm); d_1 is the diameter of colonies in presence of a fungicide. A similar approach is used to determine the fungicide activity on microorganism biomass in fluid culture medium.

A new approach to estimate the biocide efficiency is based on determination of kinetic parameters characterizing the growth of microorganisms and materials. The set of these kinetic parameters allows us to select the biocides for specific applications with consideration of time dependence of their effectiveness. In this case the estimation of biocide effectiveness is based on the estimation of biomass deceleration with the help of rate constants of biomass growth.

Under normal conditions of biomass growth and parallel degradation of materials we must not rule out the effects of biomass metabolites. That is why we must consider the time dependence of biomass growth rate including its degradation supporting and inhibiting effects. To achieve this goal the initial rates of microorganism development must be determined which involves some experimental difficulties.

Table 4. Fungicides protecting nonmetal materials from mold fungi

Class	Purpose	Substance	Solubility in water, %	Toxicity, D ₅₀
1. Inorganic compounds	Wood, paper, cotton and flax fibers	Sodium silicofluoride Na ₂ SiF ₆	0.66% at 20°C	High, 50 mg/kg
	Wood anticeptic	Sodium fluoride NaF	4% at 20°C	High, 100 ÷ 200 mg/kg
	Wood anticeptic	Sodium dichromate Na ₂ Cr ₂ O ₇	200% at 0°C	Very high, 7 ÷ 8 mg/kg
2. Hydrocarbons, halogen hydrocarbons alcohols and phenols	Paper	Diphenyl 	Insolible	Low, 3000 mg/kg (rats)
	Natural (real) leather	2-oxydiphenyl 	~0.07% at 25°C	Low, 2700 mg/kg
	Cotton thread	Phthalan 	Insoluble	Very low, ~10 ⁴ mg/kg
3. Aldehydes, ketones, carbonic and carboammonium acids	Paint and vanish coverings, PVC, polymer materials etc.	N-(trichlormethyl thio)phthalimine 		
	Film materials (leather, PVC)	Cyclohexylimide of dichlormaleic acid (cimide) 	Insoluble	Moderate, 5200 ÷ 7500 mg/kg


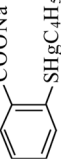
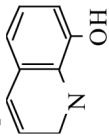
4. Amines, amine salts, quaternary ammonium compositions	Rubber composites	Tetramethyl-thiuramdisulfide $(\text{CH}_3)_2\text{NCSSCN}(\text{CH}_3)_2$ 	Insoluble	High, 780 mg/kg
5. Elementorganic-compounds	Volatile fungicide for optical appliances protection	High, 16 ÷ 20 mg/kg	Cyclohexylamine chromate	4%
	Paper, foamy plastics, optical surfaces	Ethylmercurthio-salicylic acid, Na-salt 	100%	High, 44 mg/kg
6. Heterocyclic-compositions	Petroleum lubricating materials	8-oxyquinoline 	Low soluble	Moderate, 1000 mg/kg

Table 5. Initial rates or biomass accumulation V_0 and threshold m_∞ values on the surface of different polymer materials

Support	$m_\infty, \mu\text{g}/\text{cm}^2$	$V_0, \mu\text{g}/\text{cm}^2 \times \text{day}$	$k_{\text{eff}} \times 10^6, \text{s}^{-1}$
Cellulose	10.5 ± 1	0.60 ± 0.05	1.0
Polyethylene terephthalate	2.4 ± 0.15	0.16 ± 0.02	1.2
Polyethylene	1.5 ± 0.20	0.27 ± 0.02	0.9
Polytetrafluorethylene	1.1 ± 0.1	0.04 ± 0.01	0.7

The radioisotopic technique is used for determining the initial mass: polymer materials, charged as suspension in water or in Chapek-Doj culture medium of microscopic fungi possessing 10^6 cell/ml concentration are incubated tritium water vapours. Tritium accumulation in biomass is proportional to microorganism biomass growth, which possess $\sim 85\%$ of water in the composition. Biomass amount is determined by difference in irradiation intensities of charged and control polymer samples and other supports with the help of liquid oscillation counter.

Experimental kinetic curves are exponential, and equilibrium biomass value m_∞ , initial biomass growth rate V_0 and effective rate constant are determined from them. Effective rate constant is determined from logarithmic anamorphose of experimental kinetic curve. These values represent initial characteristics of the material in relation to the existing class of microorganisms. Table 5 shows these parameters for *Aspergillus niger* microscopic fungus of 10^6 cell/ml concentration, which is specific in relation to polymer materials and some polymer surfaces.

Kinetics of Biomass Growth in a Medium Containing Biocides

Figure 1 shows a typical S-dependence of *Aspergillus niger* biomass growth at cultivation in liquid Chapek-Doj culture medium.

The curve is described by exponential function:

$$m = \frac{m_\infty}{1 + a \exp[b(t - L)]} \tag{2}$$

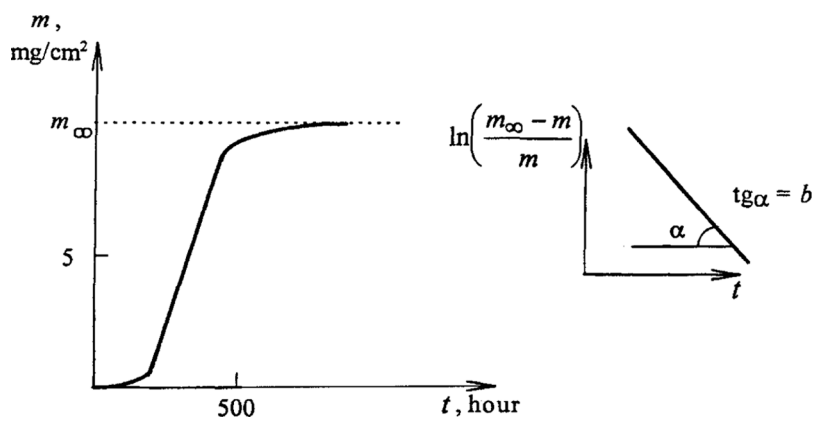


Figure 1. *Asperillus niger* biomass dependence on cultivation time in Chapek-Doj medium.

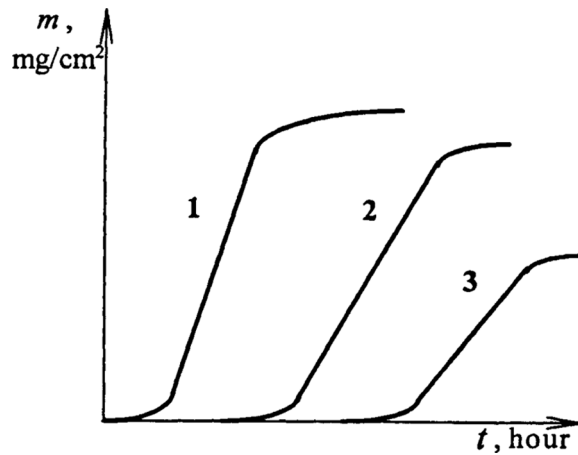


Figure 2. Dependences of the biomass growth at cultivation in liquid culture medium containing different concentrations of biocides: 1 – 0.1 mg/l; 2 – 0.3 mg/l; 3 – 0.5 mg/l of merthiolate (sodium salt of ethylmercursalicilic acid).

here **a** and **b** are kinetic parameters; m_{∞} is the threshold biomass value; **L** is time of microorganism adaptation to culture medium, the lag-phase.

Parameters **a** and **b** possess certain physical meaning: **a** characterizes the capability of a spore to form biomass under present conditions, **b** characterizes specific rate of microorganism growth in present culture medium. Values of **a** and **b** are determined graphically (Fig. 1) linearization of Eq. (2) as follows:

$$\ln\left(\frac{m_{\infty}}{m} - 1\right) = \ln a - b(t - L) \quad (3)$$

Injection of water soluble biocide into the culture medium causes no change in kinetic dependence character of biomass growth (Fig. 2).

All kinetic curves are described by Eq. (2). For different biocide concentrations parameters **a**, **b** and **L** change. Consequently, these parameters may be used for estimation of the biocide efficiency.

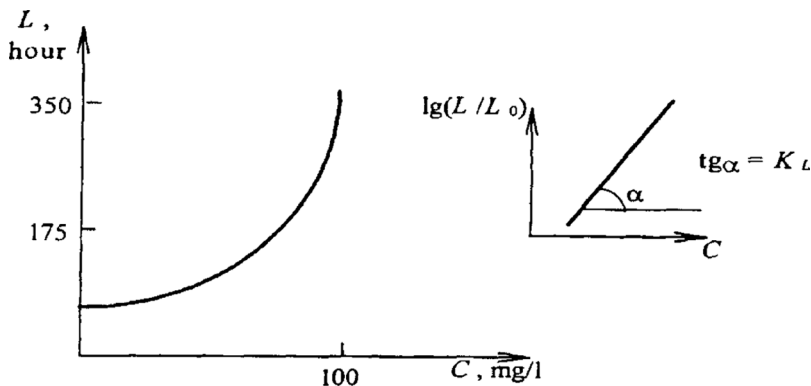


Figure 3. Concentration dependence of the lag-phase (*Aspergillus niger* fungus development in presence of the fungicide – Nictedin (1,6-diguanidino hexandihydrochloride)).

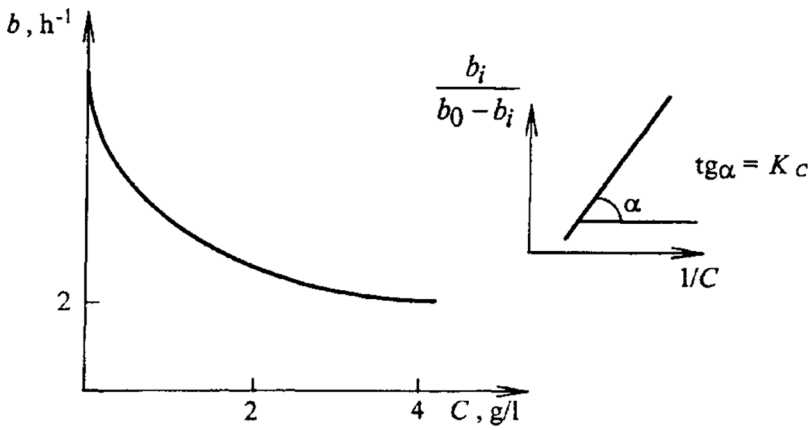


Figure 4. The dependence of **b** parameter on the biocide concentration (*Aspergillus niger* development in presence of CuSO_4).

Estimation of biocide properties of water insoluble substances is usually performed in agarized culture media, but this method is not suitable for qualitative estimation because of irregular distribution of water in which biocide is insoluble. That is why hydrogel supports, made from hydroxyethylmethacrylate-porous hydrophilic polymer material, should be used for water insoluble biocides, which form the greater part of fungicide family.

Introduction of higher biocide concentration causes the increase of the lag-phase duration **L** (Fig. 3) and is described by the following equation:

$$L = L_0 \exp K_L C. \quad (4)$$

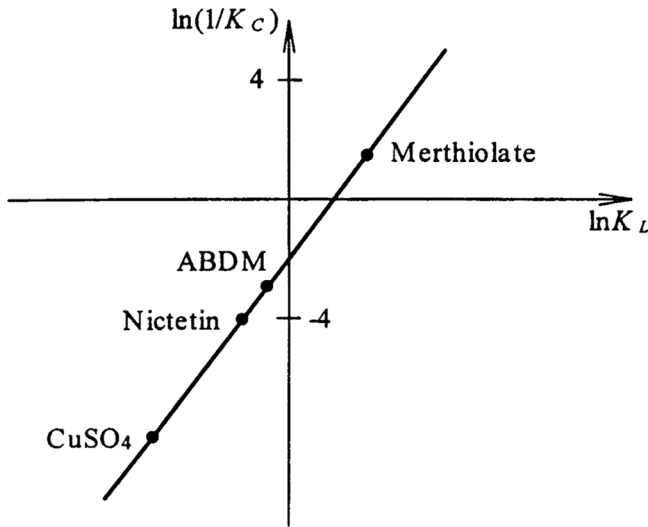


Figure 5. Kinetic constants of the biocide activity of some substances. ABDM is alkylbenzyl-methylammonium chloride.

Table 6. Constants of biocide action effectiveness of chemical substances

Biocides	Water soluble biocides		Water insoluble biocides			b_0 , day ⁻¹	L_0 , day
	K_L , l/mg	K_C , mg/l	K_L , cm ² /mg	K_C , mg/cm ²			
1. Sodium merthiolate (ethylmercurisalicilic acid salt)	6.7	0.76	—	—		0.0015	1.67
2. ABDM (alkylbenzene dimethylammonium chloride)	0.17	8.9	—	—		0.0015	1.67
3. 1,6-diguanidinohexadi- hydrochloride (nictedine)	0.028	80.5	—	—		0.0015	1.67
4. Copper(II) sulfate (CuSO ₄)	0.0005	1950	—	—		0.0015	1.67
5. Oxydiphenyl (ODP)	250	0.004	—	—		0.0015	1.67
6. N-paratolylmonimide (PTMI)	62.8	0.05	—	—		0.0015	1.67
7. Bis(0,0-1-chlor-tri-brom- isopropyl)-3-chlor-2- brompropylphosphanate (phlamal)	—	—	1.9	0.7		0.0015	1.67
8. 2,6-ditertbutyl-4-methyl-phenol (ionol)	—	—	0.2	17.5		0.0015	1.67
9. Pentachlorophenol	—	—	125.2	0.012		0.002	2.8
10. Salicilanilide	—	—	44.5	3.79		0.0016	2.2
11. Trilan	—	—	21.2	0.02		0.001	1.67
12. Biocine	—	—	20700	9.95		0.0025	

Here L_0 is the lag-phase duration in culture medium possessing no biocide; C is biocide concentration; K_L is the kinetic constant, obtained from the graphics (Fig. 3) by linearization of Eq. (4):

$$\ln \frac{L}{L_0} = K_L C. \tag{4}$$

Specific growth rate of a microorganism b decreases after biocide injection, if all other factors are equal. The inhibited specific growth rate is described by

$$b_i = \frac{b_0 K_C}{K_C + C}. \tag{5}$$

Here b_0 is specific growth rate in absence of biocide; C is biocide concentration in the medium; K_C is the constant quantitatively equal to biocide concentration at which $b_i = b_0/2$. K_C is determined from experimental data (Fig. 4) by linearization of Eq. (6)

$$\frac{K_C}{C} = \frac{b_i}{b_0 - b_i}. \tag{6}$$

K_C constant of this biocide is practically independent on concentration and may be used for quantitative estimations of the biocide activity. The higher K_C value is, the lower is the efficiency of the biocide.

Biocide activity constants K_C and K_L are clearly connected with each other and with the biocide effectiveness. For investigated substrates, the values characterizing their effectiveness presented in $\ln 1/K_C - \ln K_L$ coordinates, fit the straight line (Fig. 5).

Such regularity is used for comparative estimation of biocides and preliminary determination of their concentrations in a material required for reliable protection from biodegradation [3–8]. General characteristics of biocides of inhibition of microorganism development based on kinetic estimates are shown in Tables 6 and 7.

Table 7. Kinetic parameters of *Aspergillus niger* biomass growth. The fungicide is copper(II) sulfate (CuSO₄)

Conditions of fungus growth	Fungicide concentration, mg/l							
	C = 0				C = 2000			
	Kinetic parameters							
	b , h ⁻¹	L , h	a	m_∞ , μg/cm ²	b , h ⁻¹	L , h	a	m_∞ , μg/cm ²
Liquid Chapek-Doj culture medium	0.037	40	230	8.5	0.019	120	200	7.8
Hydrogel	0.035	40	113	4.0	0.020	120	90	3.5

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