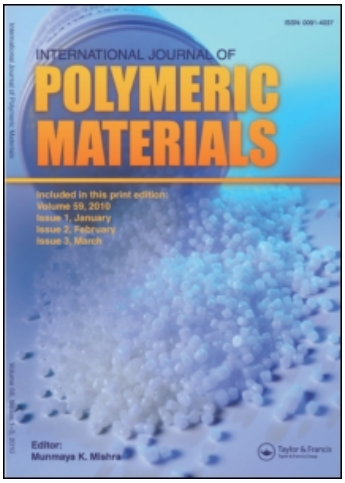


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Biocides- Stabilizers Against Biodegradation: New Frontiers

K. Z. Gumargalieva[a]; G. E. Zaikov[a]
[a] Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russian

To cite this Article Gumargalieva, K. Z. and Zaikov, G. E.(1997) 'Biocides- Stabilizers Against Biodegradation: New Frontiers', International Journal of Polymeric Materials, 35: 1, 179 — 191
To link to this Article: DOI: 10.1080/00914039708039763
URL: http://dx.doi.org/10.1080/00914039708039763

Intern. J. Polymeric Mater., 1997, Vol. 35, pp. 179–191
Reprints available directly from the publisher
Photocopying permitted by license only

Biocides- Stabilizers Against Biodegradation: New Frontiers

K. Z. GUMARGALIEVA and G. E. ZAIKOV

Institute of Biochemical Physics, Russian Academy of Sciences, 4 Kosygin Str., 117334 Moscow, Russian

(Received 12 April 1996)

Recent advances in biocide science and technology are reviewed and the methodology to establish their effect on biomass growth and product biodegradation is outlined. The importance of determining the kinetic parameters characterizing the biomass growth and biodegradation is presented. This kinetic approach allows us to properly select the biocides for specific applications.

Keywords: Biocides; biodegradation; kinetics of biomass growth; evaluation

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.

Table I shows properties of some well-known volatile biocides (fumigants). Tables II and III show examples of supressing 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.

TABLE I

Name	*Molecular mass*	*Temperature of boiling, °C*	*Solubility in Water*	*Inhibiting concentration, mg/l*	*Penetrability to material*	*Biocidic 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 II Suppression of microorganism growth by influence of different additives, %

Petrol additive	*Concentration, %*	*Mixture of fungi*	*Glagosporium resinae*	*Pseudomonas pyncyaneum*	*Mycobacterium lacticolum*
Mixture of aliphatic amines	0.1	100	100	100	100
Dimethyl aminomethyl-para chlorphenol	0.5	60	80	100	100
Trialkylphenyl ester of cyclohexyl phosphine	0.5	40	40	80	80
T − 1[1] petrol with no additives	–			Plentiful growth	

[1] Russian trade mark.

TABLE III Fungicidity of heterocyclic arsenic derivatives[2]

Substance	*Concentration, ml l*				
	1	*10*	*50*	*75*	*150*
10-Phenylphenoxarsin		—	—	—	—
10-Chlorphenoxarsin	+	+	+	+	—
10-Ethylphenoxarsin	+	+	—	—	—
10, 10-bis (Phenoxarsin) oxide	+	—	—	—	—
10-fluor-5, 10-dihydrophenoxarsin	+	+	—	—	

[2] + -fungus growth (development); - -no fungus growth.

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, embriotoxicity 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;
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 the Table VI.

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:

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

Here d_0 is control diameter of colonies (mm); d_1 is 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

TABLE IV Fungicides protecting nonmetal materials from mold fungi

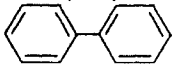
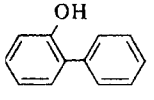
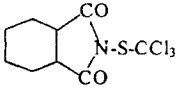
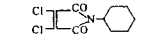
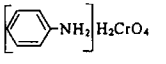
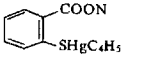
Class	*Purpose*	*Substance*	*Solubility in water, %*	*Toxicity, D_{50}*
1. Inorganic compounds	Wood, paper, cotton and flax fibers	Sodium silicofluoride Na_2SiF_6	0.66% at 20 C	High, 50 mg/kg
	Wood antiseptic	Sodium fluoride NaF	4% at 20 C	High, 100 ÷ 200 mg/kg
	Wood antiseptic	Sodium dichromate $Na_2Cr_2O_7$	200% at 0 C	Very high, 7 ÷ 8 mg/kg
2. Hydrocarbons,	paper	Diphenyl 	Insoluble	Low, 3000 mg/kg (rats)
halogen hydrocarbons alcohols and phenols	Natural (real) leather Cotton thread	2-oxydiphenyl 	~ 0.07% at 25 C	Low, 2700 mg/kg
3. Aldehydes, ketones, carbonic and carboammonium acids	Paint and vanish coverings, PVC, polymer materials etc.	Phtalan N-(trichlormethyl thio)phtalimine 	Insoluble	Very low, ~ 10^4 mg/kg.

TABLE IV (Continued)

Class	*Purpose*	*Substance*	*Solubility in water, %*	*Toxicity, D_{50}*
	Film materials (leather, PVC)	Cyclohexilimide of dichlormaleic acid (cimide) 	Insoluble	Moderate, 5200 ÷ 7500 mg/kg
	Rubber composites	Tetramethyl-thiuramdisulfide $(CH_3)_2NCSSCN(CH_3)_2$ (S, S)	Insoluble	High, 780 mg/kg
4. Amines, amine salts, quaternary ammonium compositions	Volatile fungicide for optical appliances protection	Cyclohexylamine chromate 	4%	High, 16 ÷ 20 mg/kg
5. Elementorganic compounds	Paper, foamy plastics, optical surfaces	Ethylmercurthio-salicilic acid, Na-salt 	100%	High, 44 mg/kg
6. Heterocyclic compositions	Petroleum lubricating materials	8-oxyquinoline 	Low soluble	Moderate, 1000 mg/kg

including its degradation supporting and inhibiting effects. To achieve this goal the initial rates of microoganism development must be determined which involves some experimental difficulties.

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 ~ 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 V 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:

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

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

TABLE V Initial rates of biomass accumulation V_0 and threshold m_∞ values on the surface of different polymer materials

Support	m_∞, $\mu g/cm^2$	V_0, $\mu g/cm^2 \times day$	$k_{eff} \times 10^6\ s^{-1}$
Cellulose	10.5 ± 1	0.60 ± 0.05	1.0
Polyethylene terephtalate	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

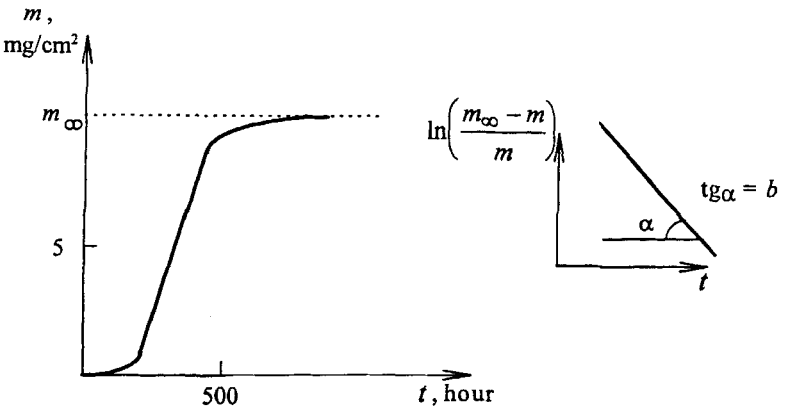


FIGURE 1 *Aspergillus Niger* biomass dependence on cultivation time in Chapek-Doj medium.

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 the Equation (1) as follows:

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 Equation (1). For different biocide concentrations parameters a, b and L change. Consequently, these parameters may be used for estimation of the biocide efficiency.

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 lag-phase duration L (Fig. 3) and is described by the following equation:

$$L = L_0 \exp K_L C. \tag{3}$$

Here L_0 is lag-phase duration in culture medium possessing no biocide; C is biocide concentration; K_L is kinetic constant, obtained from

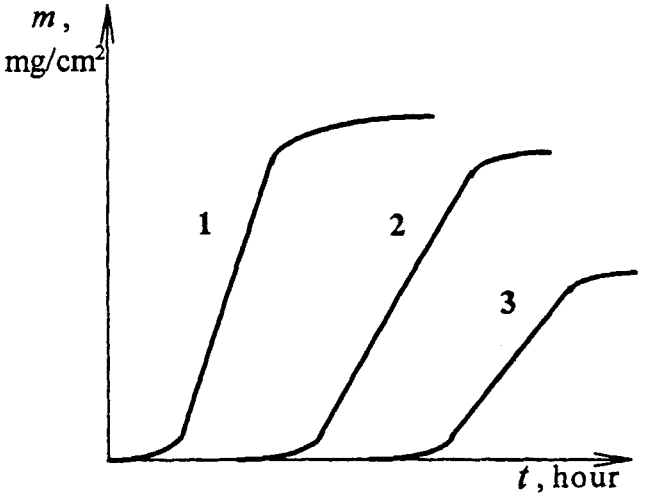


FIGURE 2 Dependences of biomass growth at cultivation in liquid culture medium containing different concentrations of biocides: 1–0.1 mg l; 2–0.3 mg l; 3–0.5 mg/l of merthiolate (sodium salt of ethylmercursalicilic acid).

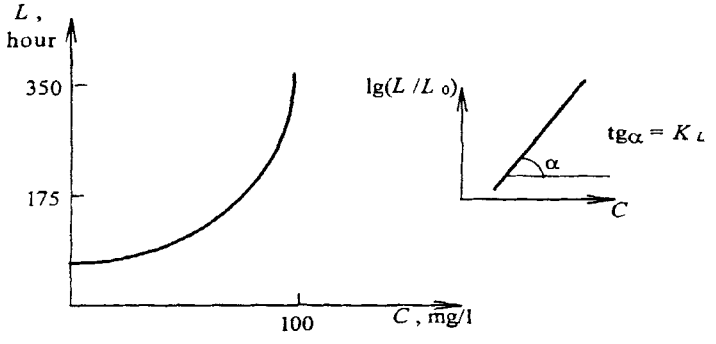


FIGURE 3 Concentration dependence of the lag-phase (*Aspergillus Niger* fungus development in presence of the fungicide-Nictedin (1,6-diguanidinohexandihydrochloride)).

graphics (Fig. 3) by linearization of the Equation (3):

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

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 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 lineari-zation of the Equation (5)

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

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 presanted in ln $1/K_C$-lnK_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. General characteristics of

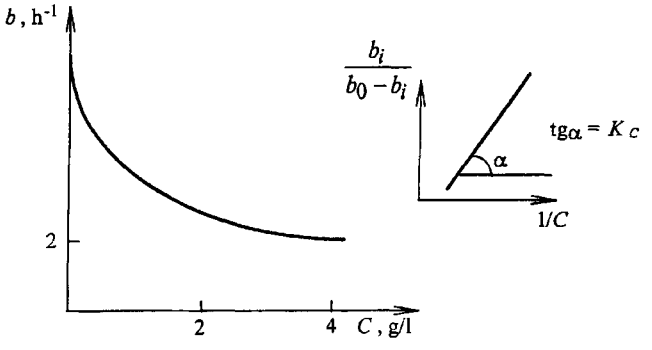


FIGURE 4 The dependence of b parameter on biocide concentration (*Aspergillus Niger* deve-lopment in presence of $CuSO_4$).

TABLE VI 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 (ethylmercursalicilic 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-diguanidinohexadihydrochloride (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-paratolylmonoimide (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. Pentachlorphenol			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	

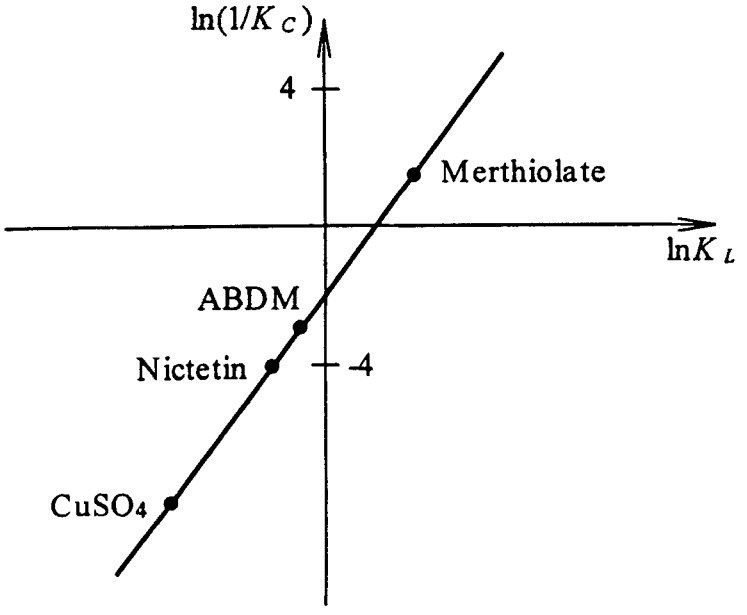


FIGURE 5 Kinetic constants of the biocide activity of some substances. ABDM is alkylbenzylmethylammonium chloride.

TABLE VII Kinetic parameters of *Aspergillus Niger* biomass growth. The fungicide is copper (II) sulfate ($CuSO_4$)

Conditions of fungus growth	*Fungicide concentration, mg/l*							
	$C = 0$				$C = 2000$			
	Kinetic parameters							
	b, h^{-1}	L, h	a	$m_\infty, \mu g/cm^2$	b, h^{-1}	L, h	a	$m_\infty, \mu g/cm^2$
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

biocides of inhibition of microorganism development based on kinetic estimates are shown in Tables VI and VII.

References

[1] Collection. 'Actual questions of biodegradation', *Nauka*, Moscow, (1983).
[2] Gumargalieva, K. Z. and Zaikov, G. E. (1995). Biodegradation of polymer materials. Generalized kinetic data, *Chemical Physics*, **14**(10), 29–38.