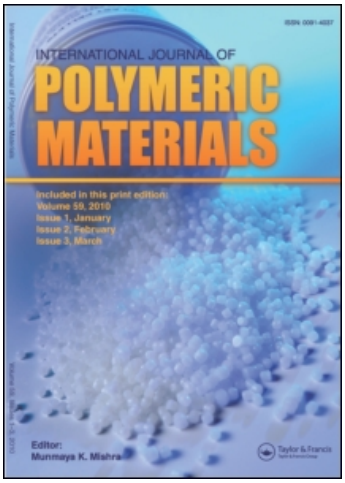

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Stabilization of Polymers from the Influence of Biological Media: Kinetic Estimation of Biocide Efficiency

G. E. Zaikov[a]; K. Z. Gumargalieva[a]; I. G. Kalinina[a]; S. A. Semenov[a]; A. N. Ryzhkov[a]; N. V. Moiseev[b]; S. N. Mironova[c]
[a] Institute of Chemical Physics, RAS, Moscow, Russia [b] Scientific-Research Institute of Storage, [c] Institute of Microbiology, Belarus Academy of Sciences,

To cite this Article Zaikov, G. E. , Gumargalieva, K. Z. , Kalinina, I. G. , Semenov, S. A. , Ryzhkov, A. N. , Moiseev, N. V. and Mironova, S. N.(1995) 'Stabilization of Polymers from the Influence of Biological Media: Kinetic Estimation of Biocide Efficiency', International Journal of Polymeric Materials, 30: 3, 181 — 198
To link to this Article: DOI: 10.1080/00914039508028596
URL: http://dx.doi.org/10.1080/00914039508028596

Intern. J. Polymeric Mater., 1995, Vol. 30, pp. 181–198
Reprints available directly from the publisher
Photocopying permitted by license only

Stabilization of Polymers from the Influence of Biological Media: Kinetic Estimation of Biocide Efficiency

G. E. ZAIKOV, K. Z. GUMARGALIEVA, I. G. KALININA, S. A. SEMENOV and A. N. RYZHKOV

Institute of Chemical Physics, RAS, 4 Kosygin Ste., 117334 Moscow, Russia

and

N. V. MOISEEV

Scientific-Research Institute of Storage

and

S. N. MIRONOVA

Institute of Microbiology, Belarus Academy of Sciences

(Received November 6, 1994)

The usefulness of kinetic methods to estimate the biocidic activity of substances is presented. The procedure for a quantitative estimation of biocide efficiency, independent on their solubility in water, is discussed. It is shown, that inhibited kinetics of microscopic fungi growth on nutriments with biocides can be described by the equation of logistic function. The investigation of the relationship between aging and biodeterioration processes showed that: i) Metabolites of *Aspergillus niger* microscopic fungus may influence physically the material, leading to a decrease of strength. This process may proceed at short times of influence of microorganism, when concentration of organic acids is low, and their diffusion in the material is practically absent. ii) On microorganism influence on polymer, chemical reactions take place acting according to the chance law. This leads to the decrease of important use properties; formation of degradation products during the aging process, and facilitation of the microorganisms growth.

KEY WORDS Biocides, polymers, efficiency, microscopic fungi, growth kinetics.

The substances which protect polymeric materials and their products from the influence of microorganisms are called biocides. The list of substances having biocidic properties is growing rapidly. With regard to the use of chemical stabilizers for various types of polymers, there are numerous studies characterizing their efficiency.[1–5] The investigation of biocidic action of substances are still semiquantitative, and their selection empirical.[6–7] The existing methods of estimation the

microorganism growth on polymeric surface do not allow us to estimate the influence of biocides in different stages of their growth. Since the biogrowth on the materials is developed with the time, kinetic methods of the investigation are best suitable for determining the inhibiting action of biocides.

The goal of kinetic method is to select and determine the value of the microorganism growth parameter, which allows us to predict the growth changes as a function of time.

MATERIALS AND METHODS

Development of microorganisms was estimated by growth of colony biomass. The amount of biomass was determined by weighing the dry mass, separated by filtration using the Millipore system and drying in at 105°C temperature until the constant weight was observed.

The following widely used biocides were selected for our investigations: mertiolate (sodium salt of ethylmercury-tiosalicilic acid), nyctedin (1,6-diguanidinohexandihydro-chloride), and oxidiphenil (ODP), copper sulfate. These commercially available products were used, without additional purification. The following fungi were selected as bioagents: *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus terreus*, *Trichoderma viride*, *Penicillium chrysogenum*, *Penicillium funicolosum*, *Paecilomyces varioti*.

The preliminary screening of selected strains showed, that *Aspergillus niger* represented well the effect of other species on the polymeric substrates. Therefore, this microscopic fungus was used in our experiments.

It is known, that the equation, describing the development of biological systems of this type, has the following form[8]:

$$\varphi(t) = \frac{1}{m} \cdot \frac{dm}{dt}, \tag{1}$$

where $\varphi(t)$ = specific rate of microorganism growth; m = biomass amount at time t.

The solution of this equation is:

$$m = m_0 \exp\left[\int \varphi(t)\, dt\right], \tag{2}$$

where m_0 = the value of germinating spore biomass (initial amount of biomass).

This equation may be applied if the nature of $\varphi(t)$ dependence is known.

One of possible solutions of the Equation (1) is so-called logistic function given by[9]:

$$\varphi(t) = \frac{b}{1 + \exp \frac{a}{b} t} \tag{3}$$

and

$$m = \frac{m_\infty}{1 + a \exp(-bt)}, \tag{4}$$

where a and b = parameters; m_∞ = maximum amount of biomass, reached during microorganism growth.

This function describes satisfactorily the growth of biomass of microscopic fungus *Aspergillus niger* applied on Chapeck-Dox nutriment (Figure 1) before the biomass starts to decrease.

The analysis of Equations (3) and (4) allows us to make assumptions about the probable physical meaning of parameters "a" and "b." Thus, at t approaching zero $\varphi_0 = b/2$ and $a = m_\infty - m_0/m_0$, i.e. parameter "b" characterizes the specific rate of fungus growth on the present nutriment and equals quantitatively $\frac{1}{2}$ of the maximal possible growth rate. Parameter "a" characterizes the possibility for a spore to form biomass under the present conditions of incubation. For a given time t, the amount of biomass increases with increasing value of "b," therefore, "b" has the meaning of the rate constant of the microorganism growth process.

The study of *Aspergillus niger* growth under various conditions of cultivation showed, that the values of parameters "a" and "b" do not depend on initial

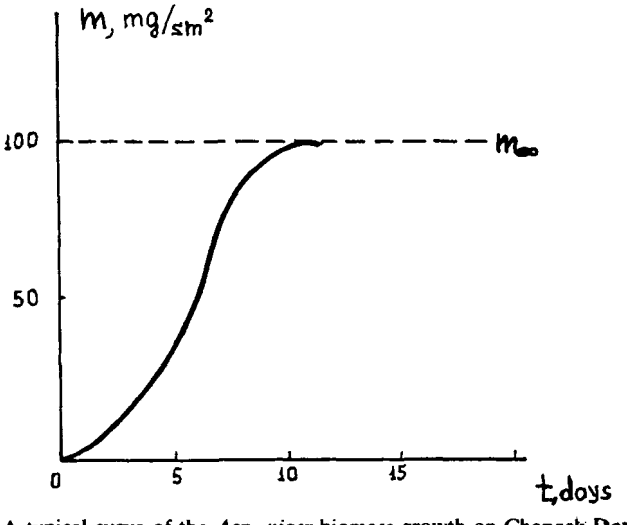

FIGURE 1 A typical curve of the *Asp. niger* biomass growth on Chapeck-Dox nutriment.

TABLE I

Values of "*a*" and "*b*" parameters for the growth of *Aspergillus niger* in various conditions of cultivation (liquid Chapeck-Dox medium, nutriment volume—50 ml)

Concentration of spores, ml^{-1}	m_∞, mg/cm^2	$m_0 \cdot 10^2$, mg/cm^2	a	b, 10^2, h^{-1}
10^6	10.2 ± 0.3	3.2 ± 0.2	316 ± 26	3.7 ± 0.3
10^4	9.5 ± 0.2	3.0 ± 0.2	316 ± 28	3.7 ± 0.3
10^2	5.2 ± 0.2	1.6 ± 0.2	316 ± 26	3.7 ± 0.3
Nutriment volume, ml				
50	10.2 ± 0.4	3.2 ± 0.2	316 ± 26	3.7 ± 0.3
20	3.8 ± 0.3	3.4 ± 0.2	115 ± 15	3.8 ± 0.2
10	2.5 ± 0.2	3.3 ± 0.3	75 ± 10	3.7 ± 0.3
5	1.8 ± 0.2	3.5 ± 0.3	51 ± 5	3.8 ± 0.2

concentration of spores introduced into the nutriment. In addition, the value of parameter "*b*" does not depend on the nutriment volume (Table I).

The data show, that the specific rate of microscopic fungus growth is defined only by the nature of nutriment. This allows us to use the logistic function equation in the study of kinetics of microorganism growth rate in presence of biocides. The same equation can also be used for the estimation of the efficiency of biocide action.

1. Water-Soluble Biocides

Figure 2 shows kinetic curves of biomass growth of *Aspergillus niger*, applied to liquid Chapeck-Dox nutriment, containing various concentrations of widely used biocides mertiolate and nyctedin. It is seen, that the phase lag duration (the time, passed after enoculation until the moment of biomass observation) increases significantly with increasing biocide concentration. The change of curve slope on the increase of biocide concentration shows, that even at concentrations lower than those at which the microorganism growth is absent nyctedin and mertiolate decelerates the fungus growth.

All presented curves are described by the equation of logistic function of the following type:

$$m = \frac{m_\infty}{1 + a \exp(-b\tau)}, \tag{5}$$

where $\tau = t - L$; L = Lag-phase duration (induction period).

The value of parameter "*b*" changes with the increase of biocide concentration, however in every experiment at constant biocide concentration specific rate of the growth, calculated according to the Equation (3), changes insignificantly for an extended period of time.

That is why it can be concluded, that during the initial stage of microorganism growth, the specific rate, does not depend of the consumption of components of

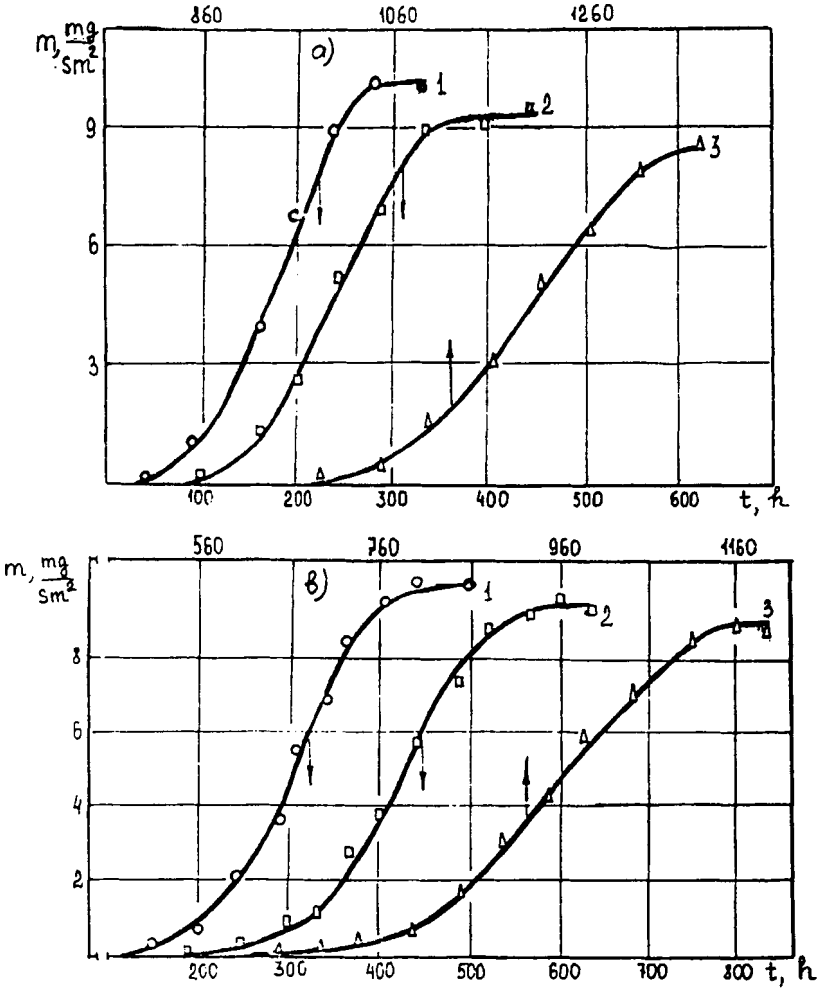

FIGURE 2 The kinetic curves of the *Asp. niger* biomass growth on liquid nutriment Chapeck-Dox in the presence of biocides: a) mertiolate: 1—0; 2—0.1 mg/l; 3—0.5 mg/l; b) nyctedine: 1—30 mg/l; 2—50 mg/l; 3—90 mg/l.

nutriment and it is defined only by the presence of biocide. This gives us the possibility to use a single-factor equation of noncompetitive fermentation reaction for the analysis of biocide influence[10]:

$$\phi_u = \frac{\varphi_0 K_c}{K_c + C_u}, \tag{6}$$

where $\varphi_u = b/2$ = maximally possible specific rate of micromycete growth in presence of biocide; φ_0 = maximally possible specific rate of micromycete growth on the present nutriment without biocide; C_u = biocide concentration in nutriment; K_c = the constant, quantitatively equal the concentration of biocide, at which $\varphi_u = \frac{1}{2}\varphi_0$.

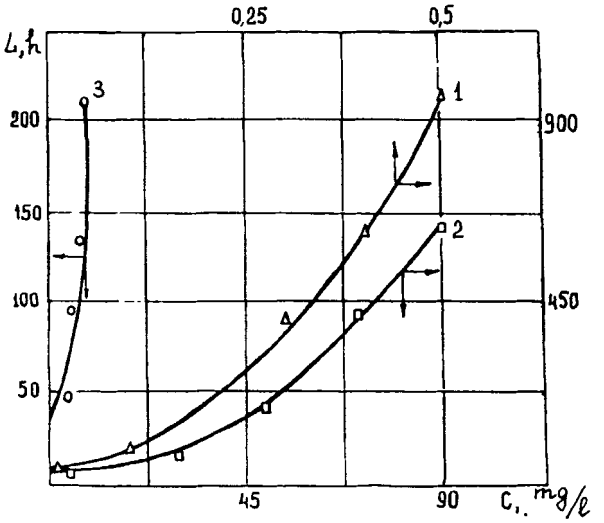

FIGURE 3 Phase-lag versus biocide concentration: 1—mertiolate; 2—nyctedine; 3—AMDB.

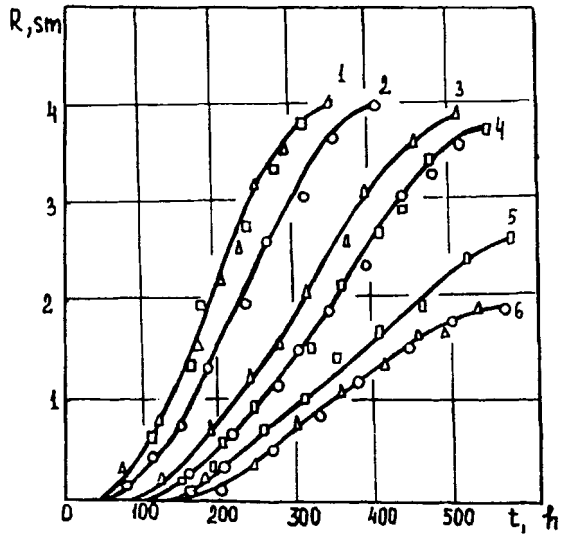

FIGURE 4 The inhibition of the colony growth of different microscopic fungi: *Asp. niger* (1, 2); *Trichoderme viride* (3, 4); *Pen. cyclopium* (5, 6) on the agar nutriment of Chapeck-Dox in the presence of biocyde ionole: □—2.5 mg/l; ○—5.0 × 10^4 mg/l; ▲—7.5 × 10^4 mg/l.

Equation (6) can be solved for K_c;

$$K_c = \frac{\varphi_u C_u}{\varphi_0 - \varphi_u}. \tag{6}$$

For each investigating biocide, K_c is practically independent on concentration with the range of experimental error. Therefore, it can be concluded, that K_c has

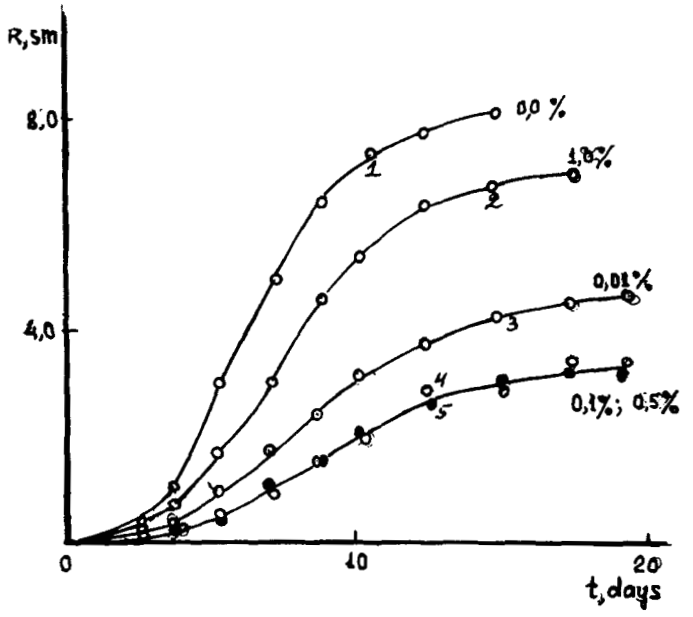

FIGURE 5 The kinetic curves of *Asp. niger* colony growth on the agar nutriment with different concentrations of ionole: 0% (1); 1% (2); 0.01% (3); 0.1% (4); and 0.5% (5).

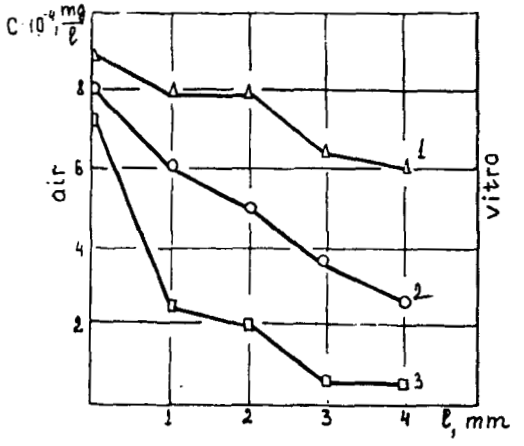

FIGURE 6 The volume distribution of ionole in agar nutriment containing 1—7.5 × 10^4 mg/l; 2—5.0 × 10^4 mg/l; 3—2.5 × 10^4 mg/l of ionole.

a constant value, characterizing the activity of a given biocide with respect to a given microorganism.

Thus, K_c constant may be applied for a quantitative estimation of biocidic activity of various substances. The calculations showed that for mertiolate K_c is 0.78 mg/l, and for nyctedin—79.5 mg/l. Actually, in practice the mertiolate is used in concentrations above 1 mg/l, and nyctedin above 1 g/l.

The dependence of phase lag duration on biocide concentration (Figure 3) is described by the following exponential equation:

$$L = L_0 \cdot e^{K_l C_u}, \tag{7}$$

where K_l is a constant.

Consequently, the K_l constant may be also used for comparative estimation of biocide efficiency. The presented data show, that the application of kinetic method for the study of water-soluble biocides allows us to use K_c and K_l constants for their characterization.

2. Water-Insoluble Biocides

From the physico-chemical point of view the water-insoluble biocides are more promising for technological uses. However, the use of agar type nutriments to estimate of the efficiency of these biocides may lead to erroneous results. For example, in the estimation of biocidic activity of water-insoluble stabilizer ionole, the change of its concentration does not lead to corresponding change of kinetic curves of microorganism growth estimated by the change of colony radius (Figure 4). This is caused be the inhomogeneous distribution of ionole in the nutriment volume (Figure 5).

The ionole extraction with alcohol from agar medium followed by spectrophotometric determination of its concentration showed that ionole is inhomogeneously distributed in nutriment volume and is concentrated close to agar-air interphase (Figure 6). In this case, the ionole concentration in the surface layer is practically in dependence on the amount of ionole introduced into the system. Similar complicated volume distributions in agar medium are observed also with other water-insoluble substances. Therefore, the application of agar nutriment for the study of water-insoluble substances leads to wrong conclusions.

The testing of water-insoluble substances requires the development of special techniques involving a support which provides continuous access of nutrition substances to microorganism growing on its surface. Since the growth of fungus takes place in the volume of the medium as well as on its surface, the support must also allow an easy and complete removal of biomass from the medium. These requirements are met by the hydrogel of three-dimensionally linked hydroxyethylmetacrylate (poly-NEMA), having a porous structure.[11] In this case, the pore size and degree of cross-linking are easily controlled during the synthesis. The hydrogel, developed for medical purposes, may easily be sterilized, and the biomass is easily removed from the surface because the adhesion of microscopic fungi to it is weak.

The testing is carried out according to the following procedure: the biocide is first solved in a solvent and then precipitated on a glass support and covered by a hydrogel plate. In this case, the biocide adheres to the hydrogel surface. The hydrogel plate is then turned upside down and placed into a Petri dish (or a similar container) filled with the liquid nutriment to a level providing contact between nutriment and the lower surface of the plate.

Because of the porous structure of the material, the medium is "drawn in" and nourishes the surface to which the biocide is applied. This provides continuous access of nutrition substances to growing microorganisms. The biomass removal from the support is carried out by washing with distilled water.

The hydrogel is also applicable for testing water-soluble biocides. In this case,

the biocide is introduced in required concentration into liquid nutriment contacting the support.

It should be noted that even in this case the growth of microscopic fungus is described by the logistic function. Figure 7 shows the kinetic curves of *Aspergillus niger* growth on hydrogel which is in contacts with the medium containing different concentrations of $CuSO_4$. It is seen, that phase lag time increases with increasing concentration, of $CuSO_4$ while the scope of the biomass growth decreases.

The analysis of results of growth kinetics of *Aspergillus niger* biomass on hydrogel support and liquid nutriment containing $CuSO_4$, (Table II) shows, that values of specific rate of growth and lag-phase duration are independent of the method used. The values of parameter "*a*" and final biomass m_∞, however, changes significantly. This is because in the case of hydrogel support the fungus growth takes place only

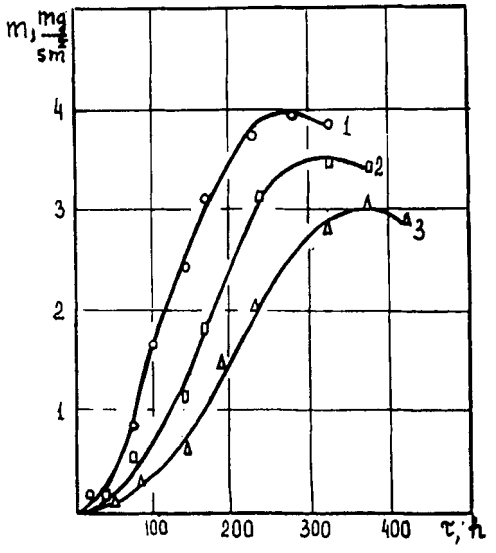

FIGURE 7 Kinetic curves of *Asp. niger* biomass accumulation on the surface of the poly-HEMA hydrogel support as a function of the $CuSO_4$ concentration: 1—1000 mg/l; 2—2000 mg/l; 3—2500 mg/l.

TABLE II

The parameters of the Equation (7) for biomass accumulation in the presence $CuSO_4$

	Condition of Cultivation									
	Liquid Medium of Chapek-Dox					Poly-HEMA* Platesupport on the Medium of Chapek-Dox				
[$CuSO_4$], mg/l	m_0, 10^2 mg/cm²	m_∞, mg/cm²	a	b, 10^2 h^{-1}	L, h	m_0, 10^2 mg/cm²	m_∞, mg/cm²	a	b, 10^2 h^{-1}	L, h
1000	3.6	4.08	111	2.4	48	3.5	100	2.4	2.4	48
1500	3.3	4.00	122	2.1	72	3.5	80	2.1	2.1	72
2000	3.7	3.75	104	1.9	120	3.7	90	1.9	1.9	126
2500	3.7	3.54	93	1.6	168	3.5	80	1.6	1.6	168

*Hydrogel polyhydroxymethylmethacrylate.

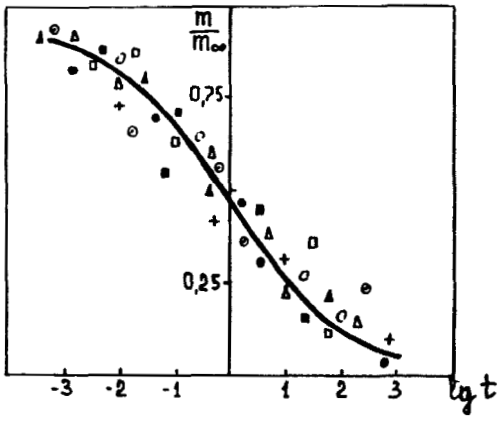

FIGURE 8 Generalized kinetic curve of *Asp. niger* biomass inhibited growth in the presence of different biocides: mertiolate (⊙); nictedine (▲); ABDM (△); $CuSO_4$ (■); ODPh (□). PPMI (●), ionole (+), phlamale (○). ABDM—alkylbenzyldimethylammoniumchlozide, PPMI—N-paratopylmaleimide, ODPh—oxydiphenylphenol, Phlamale-bis (chlorotribromoisopropyl) trichloro-2-bromopropyl-phosphonate.

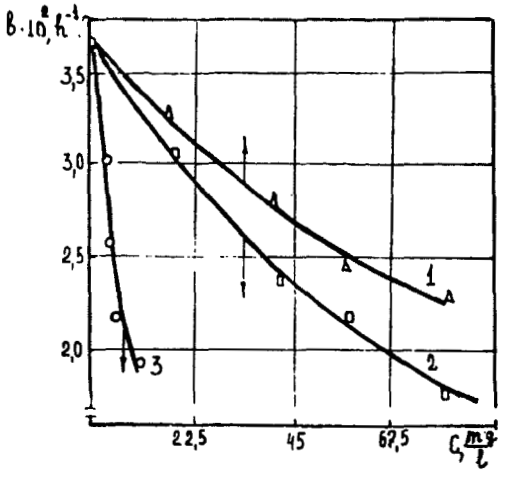

FIGURE 9 Parameter "*b*" versus concentration for different biocides: 1—mertiolate; 2—nictedine, 3—AMDM.

on the surface. Consequently, parameters "*a*" and m_∞ cannot be applied for characterization of biocide.

According to the proposed research plan, we investigated a series of water-soluble and insoluble substances. Among these substances were known fungicides and substances, performing as stabilizers of polymeric materials, antoxidants, anticorrosion agents, etc. We found that in every case the kinetic curves conform the logistic function. In this case the growth kinetics of *Aspergillus niger* in presence of biocides can be presented by the generalized curve (Figure 8) for all investigated substances. Consequently, the general macrokinetic regularities are independent of the mechanisms of biocidic action.

The dependences of phase lag time and parameter "*b*" of the Equation (5) on

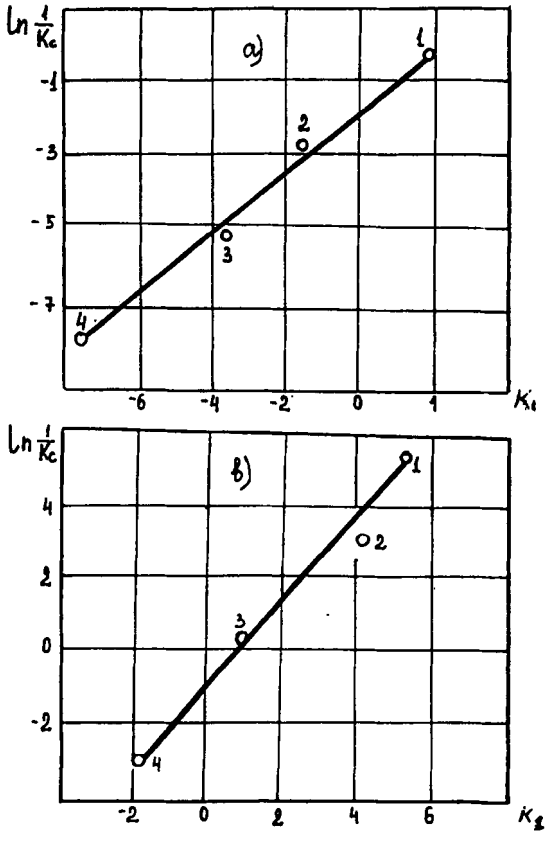

FIGURE 10 Constants K_i versus K_j for water soluble biocides (a): 1—mertiolate, 2—ADBM, 3—nictedine; water unsoluble biocides (b): 1—ODPh, 2—PPMI; 3—phlamal; 4—ionole.

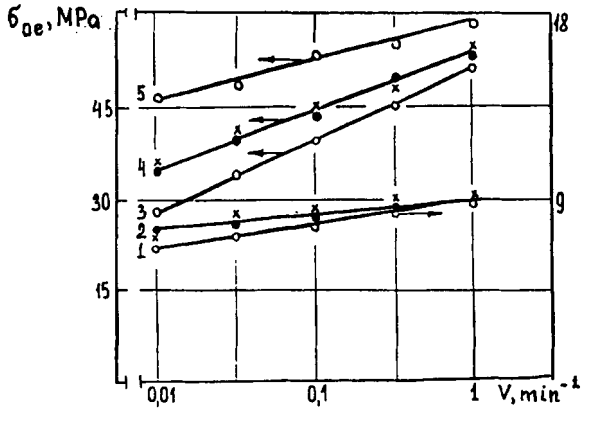

FIGURE 11 Modulus of elasticity of PMMA (σ_{ae}) versus the rate of deformation (V) in the media: 1—PE cultivation nutrient after *Asp. niger* colony growth; 2—PE, water (●), nutrient Chapeck-Dox (×); water (●) and nutrient Chapeck-Dox (×); 5—air.

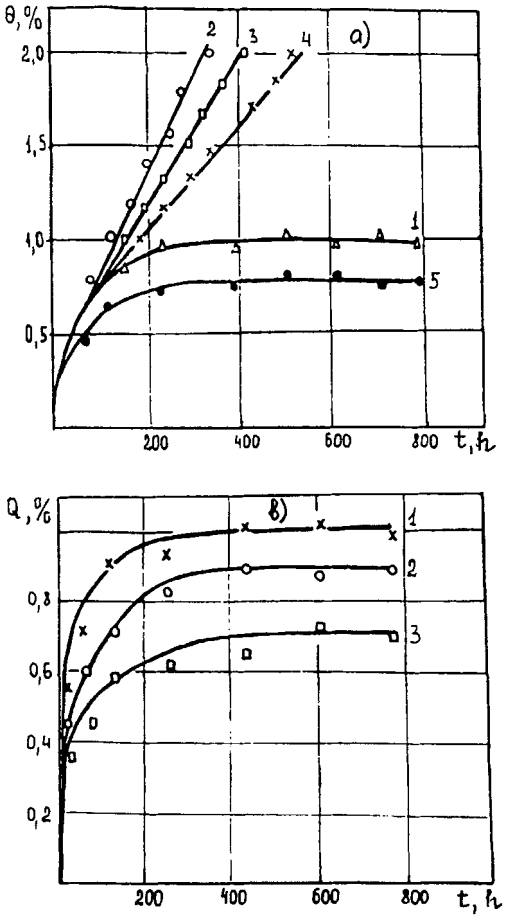

FIGURE 12 PMMA sorption of water (1) and acid solutions of different concentrations: a) 2—2 M oleic; 3—2 M propionic, 4—5 M acetic, 5—2 M acetic; b) 2—1 M tartaric, 3—2 M citric acids.

concentration of biocide are the same for water-insoluble and as for water-soluble substances. They can be described by Equations (6) and (7). Thus, the parameters K_0 and K_l reflect even in this case the characteristics of the biocide efficiency.

The concentration dependencies of parameter "b" and phase lag time can be presented for all investigated substances by generalized curves (Figure 9). This proves the supposition about the independence of microkinetic regularities of inhibited growth of microscopic fungi on cellular mechanism of biocide action. Consequently, there exists a "limiting" stage (or minimal time) of the interaction process between the biocide and microorganisms, which is about equal for all investigated substances. Apparently, this limiting stage reflects the penetration time of the biocide through the cellular membrane. In this case the ability of substance to penetrate into cell will be one of the most important properties, defining its efficiency as biocide.

We found with all investigated substances that parameters K_c and K_l are clearly connected with each other and with biocide efficiency (Figure 10). Note that the

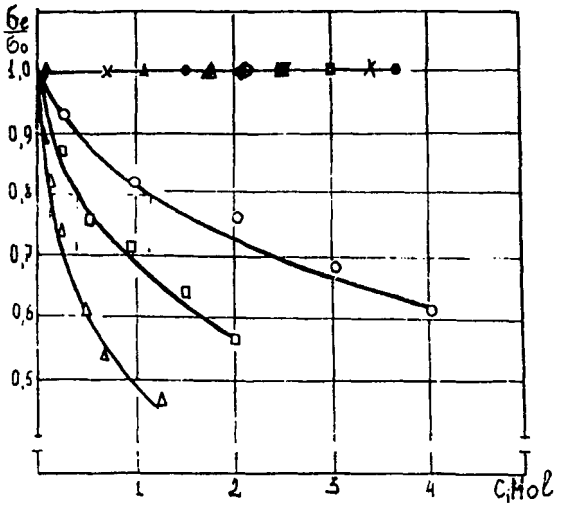

FIGURE 13 Reduced elastic elongation of PMMA samples in the acid solutions and water as a function of acid concentration: acetic (○), propionic (□), butyric (△), tartaric (●), citric (■), oxalic (▲), succinic (×) and fumaric (◆). Rate of elongation $-0.01\ min^{-1}$.

values of K_c and K_l plotted in corresponding coordinates, fall on a single straight line. This relationship can be used for practical purposes, namely the prediction of biocidic activity of substances and preliminary estimation of their required concentration for safe protection from biogrowth and biodeterioration.

3. The Influence of Aging on Bioresistance of Polymeric Materials

It is known that composition and structure of polymeric materials changes with time under the influence of various external factors. These changes which are often referred to as aging may facilitate the growth of microorganisms on polymers and their biodeterioration. In this case, even bioresistant polymers become accessible for the growth of microorganism colony through chemical degradation and other changes. This process may be caused by the assimilation of components of polymeric material and aging products by microorganisms or by the influence of metabolites, developed in bioagent material.

The influence of metabolites on polymers is in many cases similar to the influence of other aggressive media and may cause degradation, cross-linking, polymer-analog transformations, plasticifation, etc.[11]

On studying the influence of metabolites on mechanical properties of polymethylmetacrylate (PMMA), we noted that the change of mechanical properties is observed even at short (less than 1 minute) time of contact of PMMA with the metabolite solution. It is seen from Figure 11, that with PMMA the stretching in solution of metabolites—(of the liquid nutriment on which the microscopic fungus *Aspergillus niger* was grown)—the efficiency of medium action increases with the decrease of stretching rate. In this case, the effect of metabolites is similar to that of alcohol.[12]

The investigation of pH change of culture liquid and its spectrophotometry showed, that the development of colonies of *Aspergillus niger* is accompanied by accumu-

lation of organic acids. The diffusion of acids into PMMA follows the general regularities of electrolytic diffusion of water in polymers (Figure 12). For organic acids, possessing high volatility (acetic, propyonic, butanoic), the dependence of the amount absorbed on its concentration is presented by a curve having a minimum. For nonvolatile acids—citric, succinic, malic—the amount of absorbed medium decreases with the increase of solution concentration. At low concentrations these acids, the absorption levels in PMMA are small (lower than 1%).

The study of the mechanism of acid influence, participating in metabolite composition,[13] showed, that the change in the mechanical properties of PMMA correlates in general with the influence of volatile single-base acids (Figure 13). The influence of single-base acids on mechanical properties of PMMA follows the Duclo-Traube rule.[14] According to this rule, the increase of the size of organic compound radical by one unit $—CH_2—$, increases its surface activity in solution by a factor of three. Therefore, the concentration at which predicted changes in properties take place also decreases by approximately a factor of three. It was reported that the compliance with this rule reflects the absorptional mechanism of polymer strength decrease.[15] Thus, it can be inferred, that the changes of mechanical properties of the polymer result from physical (i.e. unrelated to chemical structure of macromolecules) as well as chemical influence of microorganism metabolites.

The above mentioned kinetic approach was used for the study of the main regularities, correlating the processes of aging and biodeterioration of polymeric materials. The growth kinetics of *Aspergillus niger* microscopic fungus on materials aged in artificial conditions was used as the model. For the study we selected the materials which are exposed to the influence of microorganisms during storage and technological use. These included resin treated fabrics for isolation of wires and tarpaulins, based on natural polymers of flax and cotton. Because of their high rate of aging, the selected materials may represent a good learning model.

The aging conditions simulate the most severe conditions encountered in use for PVC wire isolation from the thermal and humidity influence, for tarpaulins—the thermal and humidity effects with UV radiation. Samples with different aging times were inoculated by the suspension of *Aspergillus niger* spores. Kinetics of the development of microscopic fungus was estimated by biomass growth, which was removed from the test samples with distilled, filtered and then dried until constant weight was reached at 105°C.

The kinetic curves of *Aspergillus niger* biomass growth on PVC wire isolation material and tarpaulin are shown in Figure 14. It is seen, that overgrowth kinetics changes significantly with the increase of aging time. The overgrowth of aged samples proceeds more intensely.

Figure 15 shows the change of "b" parameter and phase lag time (L). It is seen, that the phase lag decreases on aging, while the specific growth rate characterizing parameter "b" increases. This can be attributed to the accumulation of products aging in the material, product that can be used by microorganisms as nutrition substances. For natural fibers, possessing aging times of 60 and 150 hours, the phase lag time is practically equal. This indicates that the processes, facilitating the

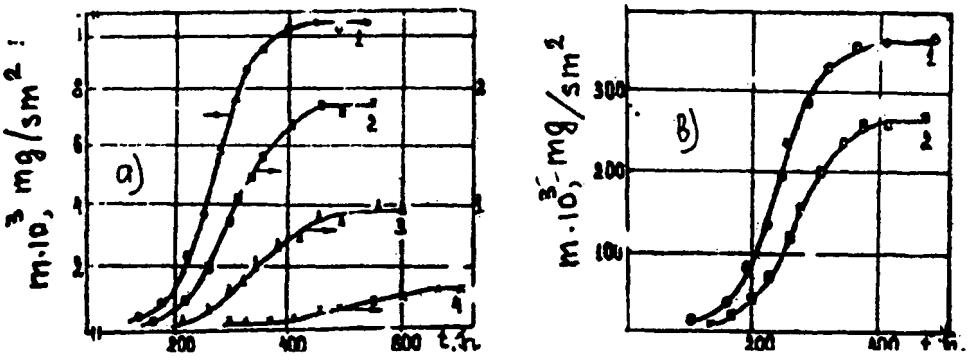

FIGURE 14 Kinetic curves of *Asp. niger* biomass accumulation on a) four types of wire insulating materials; 1—cellulose tri acetate, 2—PMMA, 3—PVC, 4—PE, and (b) two types of tarpauline textile; 1—linen, 2—cotton.

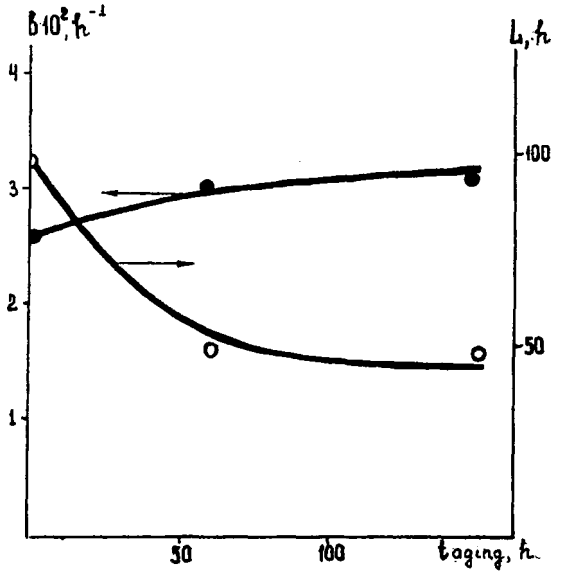

FIGURE 15 The relationship of constants *b* and *L* for PVC samples from wire insulation after aging for different time.

adaptation of microorganisms to the present material, are in fibers completed in relatively small aging times.

The growth of *Aspergillus niger* on investigated materials leads to the change of their use properties, also. Figure 16 compares the values of biomass and electrical resistance of wires. In the case of testing without the removal of the microorganisms from sample surface, the decrease of resistance correlates with the value of biomass on wires. If the biomass is removed from the wire isolation, the resistance values are restored to the level of the control. Such behavior is observed only at small times of the microorganisms influence. If this time is increased up to several months, then as it is seen from Figure 17, the value of the resistance decreases after biomass

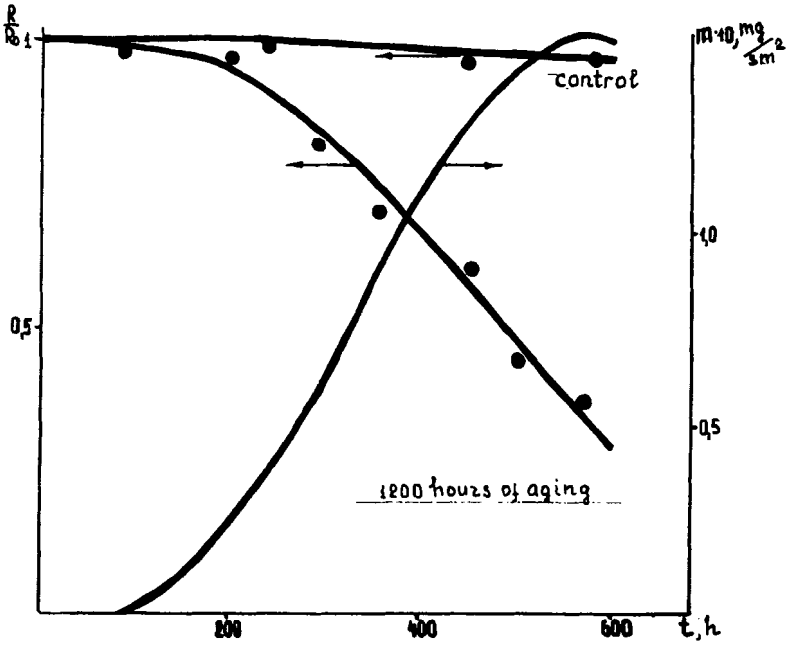

FIGURE 16 The relative electric resistance and biomass accumulation versus time for PVC wire insulation samples after aging for 1200 hours.

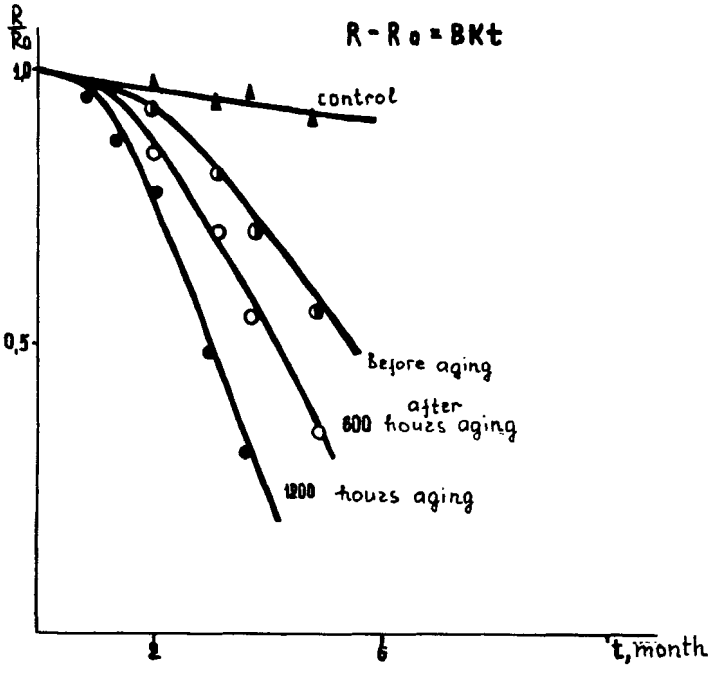

FIGURE 17 Decrease of relative resistance of PVC wire insulation versus aging time (R_0 = the resistance after biomass removal).

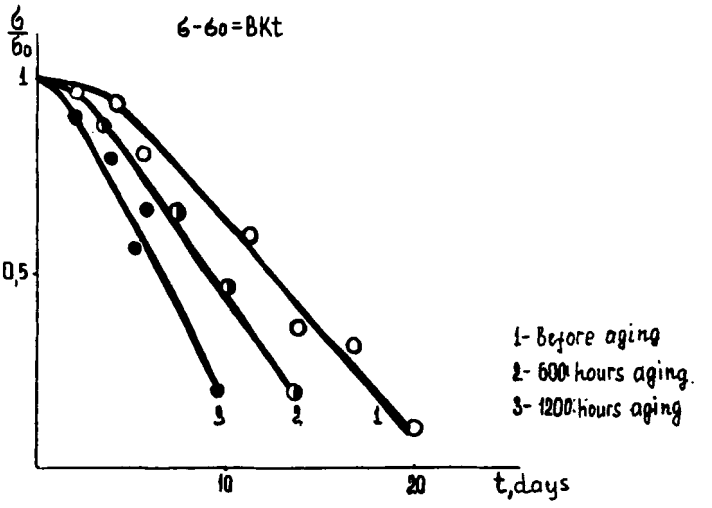

FIGURE 18 Breaking strength for filaments of tarpaulin versus time of action of *Asp. niger* biomass after aging at ambient use conditions for 600 hours (2) and 1200 hours (3), without preliminary aging (1); σ_o = strength after aging.

removal. All dependences presented in Figure 17, possess linear part, described by the following equation:

$$R = R_0 - BKt \tag{8}$$

where R, R_0 = present and initial value of electrical resistance; B, K = constants.

This form of property change dependence is associated with the degradation process proceeding according to the law of probability. Namely a statistical diffusion controlled chemical attack causing decomposition of macromolecules with the formation of active radicals.[11] In this case the rate of chemical reaction and the diffusion of aggressive medium into the material are comparable.

Similar characteristics of aging influence on bioresistance were noted with tarpaulins, also (Figure 18). Thus, the change of breaking strength of fibers proceeds faster with aged samples. The presence of linear parts on curves, described by the Equation (8) allows us to conclude that the change of strength stipulated by degradation reaction is a stochastic process. Thus, with the investigated materials the processes of aging and biodeterioration act in synergy, strengthening each other.

ACKNOWLEDGEMENTS

Authors would like to say many thanks for Professor Dusan Prevorsek who helped us very much in improving our English.

References

1. G. E. Zaikov, *Intern. J. Polymeric Mater.*, **24**, 1 (1994).
2. G. E. Zaikov, *ibid*, **16**, 1 (1992).

3. G. E. Zaikov, *ibid*, **13**, 81 (1992).
4. V. V. Kharitonov, B. L. Psikha and G. E. Zaikov, *ibid*, **26**, 121 (1994).
5. A. A. Popov, N. Ya. Rapoport and G. E. Zaikov, "Oxidation of Stressed Polymers," Philadelphia, Gordon and Breach, 1991, 336 pp.
6. "Actual Questions of Biodegradation," Moscow, Nauka, 1983.
7. E. I. Andrejuk, W. I. Bilai, E. Z. Koval and I. A. Kozlova, "Microbial Corrosion and Their Stimuli," Kiev, Naukova Dumka, 1980.
8. "Dynamic Theory of Biological Populations," ed. R. D. Poluektov, Moscow, Nauka, 1974.
9. J. A. Jacquez, *Mathematical Biosciences*, **3**, 205 (1970).
10. G. Shlegel, "General Microbiology," Moscow, Mir, 1987.
11. Yu. V. Moiseev and G. E. Zaikov, "Chemical Resistance of Polymers in Aggressive Media," New York, Plenum Publ., 1987.
12. E. A. Sinevich, R. P. Ogorodov and N. F. Bakeev, Doklady Akademii nauk SSSR, **121**, 1383 (1973).
13. A. A. Ryzhkov, E. A. Sinevich, N. N. Valiotti and N. F. Bakeev, Vysokomolekulyarnue soedineniya, **18**, 212 (1976).
14. S. S. Voyutskii, "Colloid Chemistry," Moscow, Khimiya, 1976, 511 pp.
15. S. S. Ivanov, S. A. Semenov, A. A. Ryzhkov and F. F. Agzogin, Fiziko-khimicheskaya mekhanika polimerov, **22**, 90 (1986).