Translated from *Uspekhi Khimii*, 49, 2241-2254 (1980) U.D.C. 666.1.056:620.197

The Attaching of Biologically Active Compounds to the Surfaces of Optical Materials

A.Baigozhin

The methods of forming chemisorbed molecular films with fungicidal, hydrophobic, and other useful properties on the surfaces of optical materials as well as the prospects for the employment of such films are surveyed.
The bibliography includes 105 references.

CONTENTS

I. Introduction 1112
II. Methods for the formation of biologically active films on the surfaces of optical components 1112
III. The grafting of biologically active compounds to the surfaces of optical materials 1113
IV. The mechanism of the fungicidal action of organoelementosiloxane films bound chemically to the surfaces of optical glasses 1116

I. INTRODUCTION

Under the conditions of a moist tropical climate, materials are infected with microorganisms, which leads to their premature ageing. Microscopic fungi cause considerable damage to materials such as leather, textiles, rubber, optical glass, and others[1-18]. It is known that under moist tropical conditions the surfaces of optical components (lenses, prisms, etc.) in instruments are coated by growing microscopic fungi and are damaged by them[2-12,17,18]. Even small amounts of fungi on the surface of optical components, invisible to naked eye on other materials, lower the quality of the optical systems of instruments. Many valuable optical instruments and optical equipment have been put out of order as a consequence of infection by microorganisms[3-6].

In order to protect from biological damage materials and articles designed for use under tropical conditions, it is suggested that substances with fungicidal or fungistatic properties be used; with the aid of fungicides, it is possible to increase the reliability and the useful lifetime of articles under the conditions of a moist tropical climate[16-18].

Volatile fungicides have been proposed[4,5,14,17,19-21] (impregnation of packing material, fungicide placed in cartridges and in porous materials, introduction of fungicide into greases, putty, and varnishes, used in the inner spaces within apparatus). However, these attempts did not yield the desirable results, because certain fungicidal substances, while protecting the instrument from biological growth, caused the corrosion of metallic components or, by condensing, formed deposits on the surfaces of optical components which impaired their light transmittance. In order to impart biological stability to different materials, they have been frequently impregnated with fungicidal solutions or emulsions[16-23]. In this case the fungicides protect the materials only for a short time, since they are washed away. Much attention has therefore been devoted to the creation of materials in which biologically active compounds would be attached to the surface by chemical bonds[18,22-24,49-54].

During recent years extensive experimental data have accumulated on the formation of chemisorbed molecular biologically active films on the surfaces of optical components, which do not change the optical properties of glasses but effectively protect them from biological growth and damage. This review is a brief survey of research devoted to the attaching of compounds with biological activity and other useful properties to the surfaces of optical materials. Its aim is to survey the accumulated data in this field, which is of significant theoretical importance and has a wide variety of practical applications.

II. METHODS FOR THE FORMATION OF BIOLOGICALLY ACTIVE FILMS ON THE SURFACES OF OPTICAL COMPONENTS

The classical study by Academician Grebenshchikov on the chemistry of glass has shown that the surface properties of glass are determined mainly not by its composition but by new formations arising in the course of its interaction with water[25]. Grebenshchikov used the term "prosvetlemie optiki" [deposition of non-reflective layers on optical glass] for the formation on glass of thin films leading to a decrease of the amount of light reflected from its surface. Studies on the coating of optical glass and the formation of thin transparent films on its surface have been surveyed in monographs[26,27]. Further investigation of the mechanism of the production of new formations and of their properties made it possible to modify specifically the properties of the surfaces of optical glasses over a wide range[28-30,51]. One of such methods involves the attaching of organoelemental compounds, with biological activity and other useful properties, to the surfaces of optical materials.

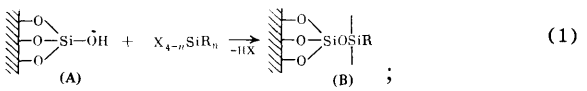
The attachment of biologically active compounds directly to the surfaces of optical materials presents considerable difficulties. The unmodified surface of the glass cannot retain appreciable amounts of the substance preventing the development of microscopic fungi. The modification of the surfaces of silicate materials by organosilicon compounds in order to impart to them hydrophobic properties[27,31,32], to form optical coatings[27,33,34], to reduce[35,36] or increase[36,37] the adhesion of polymeric resins, or as a finish to reinforced plastics has been the subject of a large number of studies surveyed in a series of reviews and monographs[27 31,37,43,47,48]. However, in these investigations the problems of attaching biologically active compounds to the surfaces of optical materials were not considered.

A series of investigations have been devoted to the development of fundamentally new methods, based on chemical reactions, for the specific modification of the surface properties of optical materials[18,49-54]. It was of interest to synthesise biologically active films by the chemical modification of glass. Such films must satisfy the following requirements:

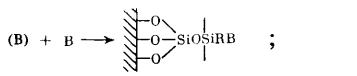
(a) they must adhere effectively to the glass and must be mechanically strong; (b) they must be stable during use under specified climatic conditions; (c) they must not impair the optical properties of glasses; (d) they must not act on the materials forming part of the construction of the instrument or apparatus.

For the chemical modification of the surface of glass, it proved promising to investigate organosilicon compounds of the type R_nSiX_{4-n}. The interest in this group of substances is due to the fact that they contain two types of reactive groups among which groups X (chlorine or lower alkoxy-groups) react with the OH groups on the surface of glass and groups R (organic substituent containing functional groups) interact with the binders. As a result of this, it is possible to carry out a wide variety of reactions on the basis of compounds of this type as a function of the type and nature of the functional groups and the reacting (binding) substances. Carbofunctional organosilicon compounds have found extensive applications for increasing the adhesion of polymeric resins to various materials[38–48] and particularly for increasing the resistance of transparent plastics to water[43,48].

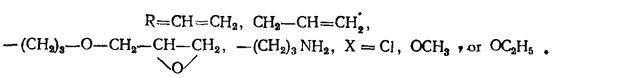
The possibility of attaching biologically active substances to the surfaces of optical materials with the aid of organosilicon compounds containing functional groups has been demonstrated in a number of studies[18,49–54]. Biologically active films are synthesised via mechanisms (1) and (2):



(1)



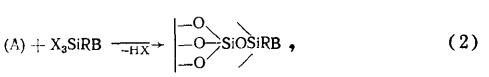
;



Here (A) is the surface of the glass, (B) the modified surface of the glass, and B the biologically active compound inhibiting the development of microorganisms.

Films are synthesised in two stages via mechanism (1)—initially a carbofunctional organosilicon compound and then the biologically active substance are deposited on the surface of the glass. This yields organoelementosiloxane films which protect the surfaces of optical components from microbiological growth and damage[49–52,54].

The synthesis of surface-active compounds via mechanism (2), where biologically active groups are already contained in the initial organosilicon compound, i.e. in the organic group R, is more promising and technologically more useful[53]. Thus it is possible to graft biologically active compounds to the surfaces of glass or other materials in a single stage:



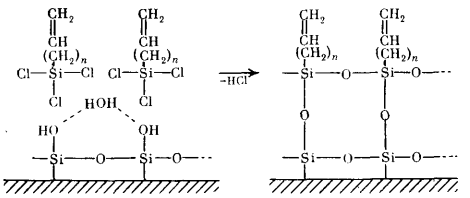
(2)

where R is an organic substitutent or a substituent containing a functional group, B is a biologically active group (for example, HgR′, AsR'_2, and SnR'_3, where R′ is an organic substituent or an acid residue), and X = OCH_3 or OC_2H_5.

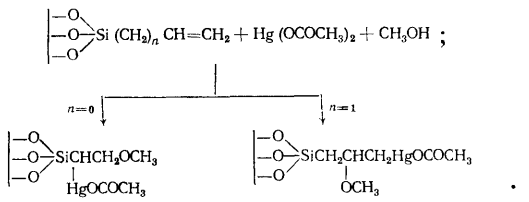
Mechanism (2) has been studied very little, since the methods of synthesis of organosilicon compounds containing biologically active fragments have been developed only recently [55–58]. The modification of the surfaces of materials by organoelemental siloxanes via mechanism (2) in order to alter specifically their surface properties is undoubtedly of great interest. Examples of the attaching of biologically active compounds to the surfaces of optical materials via the mechanisms described above will be considered below.

III. THE GRAFTING OF BIOLOGICALLY ACTIVE COMPOUNDS TO THE SURFACES OF OPTICAL MATERIALS

It is known that organomercury compounds are the most universal fungicides, effective against a wide range of microorganisms and active at very low concentrations[59–62]. For example, alkyl(aryl)mercury acetates prevent the growth of a wide variety of microorganisms at a dilution of $1 : 8 \times 10^6$ and some of them at a dilution of $1 : 2 \times 10^7$. A two-stage method for the synthesis of organomercurisiloxane films on the surfaces of optical glasses has been developed[49,50,54]. Optical components made of different brands of silicate glasses are treated initially with a solution of trichlorovinyl(or allyl)-silane in a non-polar solvent or with solution of triethoxy-vinyl(allyl)silane in water or alcohol. In the hydrolysis of alkenyltrichloro(ethoxy)silanes the aqueous film and the hydroxy-groups present on the surface of the glass are involved in the reaction. The reaction of alkenylsilanes with the surface of the glass is represented schematically as follows[38,44,50]:



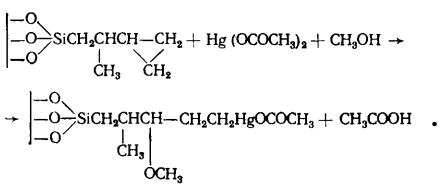
Hydrophobic alkenylsiloxane films are then formed on the surface of the component. These components are then treated further with a methanol solution of mercury acetate. Mercury acetate in methanol or aqueous solutions is known to add quantitatively to the ethylene linkage[62–66]. The reaction of the alkenylsiloxane film with mercury acetate can be represented by the following scheme:



As a result of the exposure to a methanol solution of mercury acetate of glass treated with trichloro(ethoxy)vinyl(or allyl)silane, molecular films of α-acetoxy-β-methoxymercuriethylsiloxane and 3-acetoxy-2-methoxymercuripropylsiloxane are formed respectively. The addition of mercury acetate in methanol to vinylsiloxane takes place contrary to the Markovnikov rule, the mercury atom with the acid residue forming a bond with the carbon atom containing fewer hydrogen atoms, which is caused by the electropositive properties of the silicon atom; the addition to allylsiloxane proceeds in conformity with the Markovnikov rule. The validity of these reaction mechanisms has been confirmed by the model synthesis with trimethylvinylsilane[67].

A method has been proposed for attaching an organomercury compound on the surface of glass using trichloro-2-(cyclopropyl)propylsilane instead of alkenylchlorosilanes[18]. Cyclopropane derivatives are capable of undergoing a reaction, involving the opening of the ring, with mercury acetate in methanol[68], and the products exhibit an extremely high

biological activity[69]. The formation of an organomercury compound on the surface of the glass can be represented by the following scheme:



The addition of mercury acetate to alkenylsiloxane groups proceeds in the course of 1–2 h (complete saturation with mercury), while the addition to 2-(cyclopropyl)propylsiloxane groups is somewhat slower: complete saturation takes place only after six days, but the resulting molecular film of 5-acetoxy-3-methoxy-2-methylmercuripentylsiloxane is stable over a period of time[18].

The addition of mercury acetate has been monitored on the basis of the variation of the wetting angle for the wetting of organosiloxane films with water, by determining the amount of mercury on the surface of the glass, and on the basis of the results of microbiological tests[18,50,51].

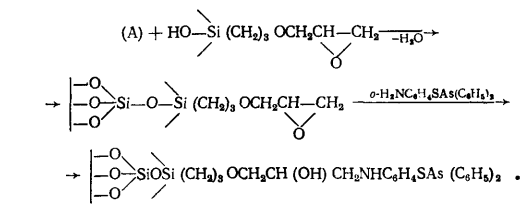
It has been shown[18] that the calculated area per hydroxy-group of the SiO_2 surface hydrated to the maximum extent varies from 10.4 to 16.8 Å^2. It has been established[70] that the actual surface of polished quartz is 2.4 times greater than the geometrical surface. On the basis of these data, it is easy to show in relation to a monomolecular layer that there should be approximately 0.9×10^{-6} g of mercury per cm^2 of the treated surface of the glas [it has been found[18,50] that the amount of mercury per cm^2 is $(1.0–1.2) \times 10^{-6}$ g].

Microbiological tests have demonstrated[50,51,71,72] that optical glasses coated by organomercurisiloxane films are not damaged by moulds when they are deliberately infected by aggressive fungal cultures under conditions imitating a moist tropical climate in the course of one and a half years, while control glasses are damaged by such fungi after 10–15 days. These results were confirmed by a special investigation under natural subtropical and moist tropical conditions[18,50,51]. One should note that the surface of the glass treated solely with organosilanes or solely with a methanol solution of mercury acetate without a preliminary deposition of an alkenyl- or cyclopropyl-siloxane film does not prevent the development of the spores of moulds or exhibits only a very weak activity which disappears after the first month of tests.

One should note that fungicidal organomercurisiloxane films with a thickness of 10–15 Å do not influence the optical properties of glasses[50–51]. These films can be formed on all optical silicate materials. They are also applicable to non-silicate materials when non-reflective layers are deposited on their surfaces. Optical materials are as a rule coated using refractory metal oxides (Ti, Zr, Hf, Se, etc. oxides). Non-reflective layers made of these oxides are obtained by a chemical method or by vacuum sputtering[27] and in multilayer coating the last layer is usually silica.

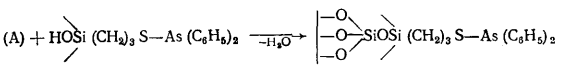
2. Organosiloxane Films Containing Arsenic

In order to obtain fungicidal films, certain organoarsino-siloxanes have been investigated. They are of interest, because they combine the known properties of polysiloxane with the ability to prevent the development of various micro-organisms. These properties permit their use both as agents imparting hydrophobic properties and as fungicides. According to mechanism (1), the glasses are initially treated for this purpose with an ethanol solution of 2,3-epoxypropoxypropyl-triethoxysilane and then with a toluene solution of *o*-amino-phenylthiodiphenylarsine[18]:



Optical glasses treated in accordance with this scheme are not affected by moulds under conditions imitating those in a moist tropical climate.

In recent years methods have been developed for the formation of trialkoxysilylalkyl esters of arsenic(III) thioacids[73,74]. The most active compound—triethoxy-γ-(diphenylarsinothio)-propylsilane—forming thin transparent fungicidal films on the surface of glass, was selected from these esters[53]:



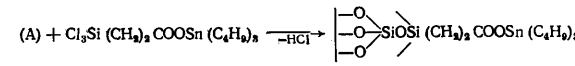
The γ-(diphenylarsinothio)propylsiloxane film is mechanically strong and is not washed away by organic solvents. Optical glasses protected in this way are resistant to microbiological growth[85].

3. Films Based on Organotin(Silicon) Compounds

It has been established[75,76] that organotin compounds of the type R_3SnX, where R = alkyl and X is an organic or inorganic acid residue, exhibit an extremely high fungicidal activity, comparable to that of mercury compounds. In contrast to R, the nature of the acid residue does not have a significant influence on the activity of the compound. It has been shown[76] that, among asymmetric acyltrialkylstannanes, maximum toxicity to fungi is shown when the total number of carbon atoms is 9–12, regardless of the nature of the individual groups.

Organotin compounds of the type indicated above have found extensive applications for the protection of a wide variety of materials against microbiological growth[77–83]. Among compounds of this class, triethylmethacryloxystannane (TEMS) proved to be of greatest interest. Its alcoholic solutions form on the surface of glass transparent but mechanically weak films. This disadvantage was eliminated by combining TEMS with tetraethoxysilane and polydimethylphosphorosiloxane (GSF-3).[84,85] Films obtained from a mixture of solutions of the above compounds are mechanically strong and effectively protect optical components made of chemically unstable glasses (of the type STK, TBF, TFK, and others) against biological damage[85]. Furthermore, TEMS mixed with a PTFE varnish forms a film on the surfaces of optical components made of LiF crystals, which does not alter the optical properties of the crystals and protects them against moisture and biological growth[86].

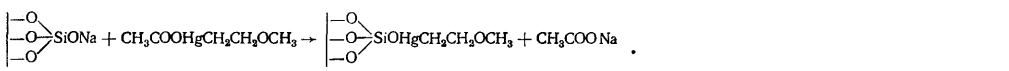
These films can be used to protect silicate and non-silicate materials. At the same time methods have been proposed for the grafting of organotin(silicon) compounds by treating the glass with solutions of trialkyltin trichlorosilylalkanoates, for example, tributyltin β-trichlorosilylpropionate[87]:



The β-(tributylstannylcarboxy)ethylsiloxane film is hydrolytically unstable and therefore protects the glass against biological growth only for a short time. A film with an increased hydrolytic stability has been obtained on the basis of β-(triethylstannylthio)ethyltriethoxysilane[105].

4. Films Containing the Si–O–M Group

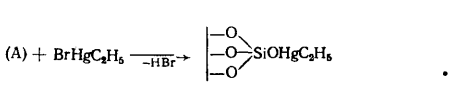
It has been suggested that glasses be treated with an ethanol solution of methoxyethylmercury acetate in order to protect optical components from damage by moulds[88,89]. It is suggested that such treatment results in the formation of a fungicidal coating—methoxyethylmercury silicate—via the mechanism[89]



When sodium ethyl- or methyl-siliconate is deposited on textile fabrics, the surfaces of the latter become hydrophobic. There is evidence[90,91] that, when fabrics treated in this way are immersed in an aqueous solution of a copper salt, sodium ions are replaced by copper ions and the fabric then requires resistance to moulds. On this basis and bearing in mind the use of the oligodynamic properties of noble metals, it was of interest to obtain such compounds on the surface of glass. For this purpose, glasses were initially coated with sodium ethyl- or methyl-siliconate and then with solutions of copper, silver, and platinum salts; as a result of such treatment, the glasses were not affected by fungi for two months[18,50].

It has been suggested that optical components be protected by depositing coatings from a mixture of an alcoholic solution of tetraethoxysilane, lead acetate, and boric acid[92]. Heat treatment (at ~400 °C) of this coating results in the formation of silicon, boron, and lead oxides on the surface of the glass; the oxides retard the development of moulds, but rapidly become turbid on the surface of the glass under the influence of atmospheric moisture. The composition of this coating resembles that of lead borate glasses (BSZ, TS8, etc.), which are chemically unstable and require protection from atmospheric moisture.

The authors of a patent[93] deposited a fungicidal coating from hydrolysable solutions of silicate and titanate esters in the presence of soluble copper or mercury compounds. However, the deposition of fungicidal coatings on the surface of glass from hydrolysable solutions of tetraethoxysilane with introduction of copper, silver, mercury, and lead salts as well as certain organic fungicides—chlorophenols, nitro-(fluoro)benzenes, and other compounds—proved to be insufficiently effective against damage by moulds[18,50,94]. A method has been proposed[95] for protecting optical components in accordance with the scheme

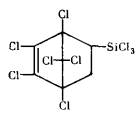
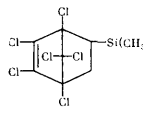
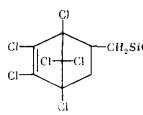
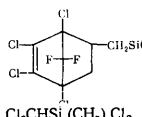


The fungicidal coating thus obtained inhibit the development of microorganisms only for a short time (for 2–3 months). This is because compounds containing the group $\geq$Si–O–M (where M = Hg, Ag, Cu, Pb, or B) are readily hydrolysed under the influence of atmospheric moisture, losing their fungicidal properties.

5. Halogeno-organosiloxane Films

The comparative study of the properties of chloro- and fluoro-derivatives of organosiloxanes on the surfaces of optical glasses appeared of interest because in many instances the introduction of a fluorine atom instead of chlorine or their joint presence in the composition of organic molecules greatly increases the fungicidal action of the compound. On this basis, films of compounds of the type R_nSiX_{4-n} [R = organochloro(fluoro)-group], the formulae of which are given in the Table, have been obtained on the surface of glass[18,50]. These compounds contain active chlorosilyl groups, which interact chemically with the surface of the glass on which there are covalently bound hydroxy-groups and adsorbed water molecules, and give rise to thin halogeno-organosiloxane films,

The fungicidal activities of organofluoro(chloro)siloxane films on the surface of glass[18,50].

No.	Formula of film-forming compound (Ref.96)	Resistance of glass* with a film to fungi
1		—
2		—
3		—
4		—
5	$Cl_2CHSi(CH_3)Cl_2$	—
6	$Cl_2CHSi(CH_3)(OC_2H_5)_2$	—
7	Cl_3CSiCl_3	—
8	$Cl_3CSi(CH_3)Cl_2$	—
9	$F_2CHCH_2Si(CH_3)Cl_2$	—
10	$F_2CHCF_2Si(CH_3)Cl_2$	—
11	$CF_2{=}CFSi(C_2H_5)Cl_2$	—
12	$F_2CHCF_2O(CH_2)_3SiCl_3$	—
13	$[F_2CHCF_2O(CH_2)_3]SiCl_2$	—
14	$4\text{-}FC_6H_4Si(CH_2CH_2CF_3)Cl_2$	—
15	$CF_3CH_2CH_2SiCl_3$	+
16	$(CF_3CH_2CH_2)_2SiCl_2$	+
17	$F_2CH(CF_2)_3Si(CH_3)Cl_2$	+

Note: "–"—not resistant to fungi; "+"—resistant to fungi.

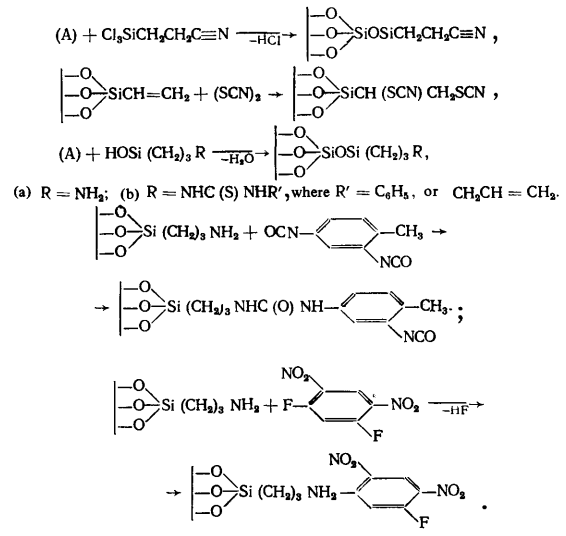
Chloro-organosiloxane films on the surface of glass do not prevent the development of moulds. Fluoro-organosiloxane films, obtained from compounds Nos.15–17 (see Table), suppressed the development of the spores of moulds in the course of 3–4 months, but subsequently the growth of fungi intensifies. The remaining fluoro-derivatives of silanes listed in the Table do not protect glass from the growth of moulds[18,50].

Iodine and its compounds are classical antiseptics. It is known that iodine adds quantitatively to unsaturated organic compounds and it has been shown that glasses with an

attached vinylsiloxane film, treated in iodine vapour or a solution of iodine in chloroform[18,52] are not overgrown by moulds in the course of 5 months under conditions imitating those in the tropics. However, iodo-organosiloxane films on the surface of glass have absorption bands in the visible region of the spectrum and in addition are unstable under the influence of light.

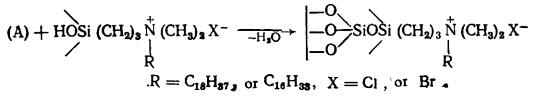
6. Nitrogen-Containing Organosiloxane Films

Since nitrogen-containing organosilicon compounds exhibit a high biological activity[55,56,97,99], it appeared of interest to attempt to use them for the formation of protective films on the surface of glass. For this purpose, the following reactions were carried out in succession on the surface of glass (A):[18,50,98,99]



Organosiloxane films containing cyano-, thiocyanato-, amino-, and phenyl(allyl)-thiourea groups and formed on the surface of the glass do not prevent the development of moulds. Fluoro(nitro)phenylaminopropylsiloxane films arrest the growth of fungi for a short time[18,50].

It has been shown[100] that the surfaces of materials, including glasses, are reistant to the action of a wide range of micro-organisms when they are treated with a solution of *N,N*-dimethyl-*N*-octadecyl-*N*-(3-trimethoxysilylpropyl)-ammonium chloride. As a consequence of a further development of these studies, the glasses were then treated with the products of the hydrolysis of organosilicon quaternary ammonium salts via the mechanism



Films obtained from the above compounds and tested by the method developed by Rodionova and coworkers[71,72] protected glasses from the growth of moulds for a short time.

It is noteworthy that the organosilicon quaternary ammonium compounds indicated above, deposited on the surface of glass, orient nematic liquid crytals homogeneously or homeotropically, depending on the functional groups in the organic substituent attached to the silicon atom and are used in the manufacture of liquid crystal devices[101].

IV. THE MECHANISM OF THE FUNGICIDAL ACTION OF ORGANOELEMENT SILOXANE FILMS BOUND CHEMICALLY TO THE SURFACES OF OPTICAL GLASSES

One of the current problems is the elucidation of the chemical mechanism of the action of fungicides, which is linked directly to their structure and reactivity. Numerous studies, surveyed in a number of reviews and monographs[61,102–104], have been devoted to the mechanism of the action of fungicides.

The majority of the known fungicides have been discovered empirically. Although complex biochemical and physicochemical mechanisms of the action of fungicides at a molecular level have been investigated inadequately, a definite idea about them has already been formulated. Three main types of action of fungicides have been distinguished[102–104]:

(1) inhibition of bioenergetic processes (cell respiration, oxidative phosphorylation, etc.);

(2) inhibition of the biosynthesis of low-molecular-weight (aminoacids, vitamins, etc.) and high-molecular-weight (proteins, DNA, RNA) compounds;

(3) the breakdown of the permeability of cell membranes (physicochemical breakdown of cell structures).

In general, the mechanisms of the action of fungicides bound chemically to the surface of glass agree with the mechanisms of the action of the usual fungicides indicated above, but they can have their characteristic features requiring amplification and refinement. It is known that enzymes (as biocatalysts) are involved in all biochemical processes in the cell and thus promote its growth and development. In this connection, we believe that the main function of organosiloxane films, containing biocidal groups in the organic substituent and bound chemically to the surface of glass, is to act against enzymes, i.e. the films should inhibit or disrupt the activity of vitally important "transport" enzymes with sulphydryl groups SH. This task can be fulfilled by organosiloxane films containing in the organic substituent heavy metal atoms, particularly Hg and Sn atoms. The methods for the synthesis of such organomercuri- and organostannyl-siloxane films on the surface of glass and their properties were examined above. These molecular films, with a thickness of ~10–15 Å, protect the glass from the growth of mould without altering its optical properties.

Next one must consider another possible mechanism of the action of organoelementosiloxane films on microorganisms. The majority of the cells in a living organism approach to some extent the crystalline state. A wide variety of types of molecules, occupying a more or less fixed position and oriented in a specific manner, exist in a "crystal-like state" in the cell. It is therefore possible that certain organoelementosiloxane films disrupt a specific orientation of the molecules within the cell and hence alter the normal cell metabolism, which suppresses its vital activity, i.e. the films act as fungistatic agents. For example, γ-trifluoropropyl- and bis-(γ-trifluoropropyl)-siloxane films prevent the development of fungi for 3–4 months under conditions where they are deliberately infected with the spores of moulds[18,50]. At the same time, it is known that organosiloxane films containing functional groups in the organic substituent give rise to a time-invariant orientation of the molecules of nematic liquid crystals towards the surface of the glass either homogeneously or homeotropically, depending on the type of substituents and their functional groups[101].

On the basis of experimental data, it is possible to arrive at quite definite conclusions concerning the principles governing the search for and selection of highly effective biologically active compounds and their use for the formation of molecular films on the surfaces of optical components,

which do not alter the optical properties of the glasses but protect them from microbiological growth and damage.

Evidently, according to the proposed working mechanisms (1) and (2), it is possible to set up organoelementosiloxane films with fungicidal and other useful properties. It has been shown that organomercuri(stannyl)siloxane films exhibit for a long time a fungistatic activity at very low concentrations, which is important for the protection of specific properties of materials. New highly effective fungicides have been found—film-forming tin compounds of the type R_3SnX, where R = ethyl or butyl and X is a residue of an unsaturated carboxylic acid (as, for example, in triethylmethacryloxystannane).

Tests on various organoelementosiloxane films on the surfaces of optical materials led to the following findings:

1. If the biologically active atom or group of atoms is bound to the organosiloxane fragment by a strong covalent bond, then the films do not prevent the development of moulds.

2. If the biologically active atom or group of atoms is bound to the organosiloxane fragment by an ionic, coordinate, or polar covalent bond, the films protect the optical components from the grown of moulds. The duration of action of the film depends on the nature of the chemical bond formed by the atom or group of atoms; it increases in the sequence ionic < coordinate < polar covalent bond.

In conclusion we may note that the data described above indicate fairly convincingly the extensive possibilities for the occurrence of a wide variety of reactions leading to the formation on the surfaces of optical materials of molecular films with useful properties. Similar reactions can be used to form films on other solid materials with covalently bound hydroxy- or other reactive groups on the surface. The present author believes that organoelementosiloxane films on the surfaces of materials can be used to set up models of enzymes or antienzyme systems, protein substances, highly effective medicinal preparations with a wide spectrum of therapeutic action, selective catalysts, corrosion inhibitors, orienting coatings for liquid crystals, and other systems.

REFERENCES

1. M.I.Khozyainov and M.M.Ioganson, Optiko-Mekhan. Prom., No.3, 3 (1935).
2. J.S.Turner, E.McLennan, J.Rogers, and E.Mathaei, Nature, **158**, 469 (1946).
3. G.Greathouse and C.Wessel, "Deterioration of Materials", New York, 1954.
4. L.Teitel and S.Berk, Ind.Eng.Chem., **44**, 1088 (1952).
5. S.Berk and L.Teitel, Ind.Eng.Chem., **46**, 778 (1954).
6. M.Rauschert, Z.Verein.Deutsch.Jng., **96**, 778 (1954).
7. A.G.Samartsev, Optiko-Mekhan.Prom., No.1, 3 (1957).
8. V.I.Mordasov, Optiko-Mekhan.Prom., No.1, 50 (1957).
9. A.Kaller, Feingeratetechnik, **8**, 359 (1959).
10. A.Kaller, Feingeratetechnik, **9**, 20, (1960).
11. A.Kaller, Feingeratetechnik, **11**, 45 (1962).
12. S.Minăr, Jemna mech.a optika, No.7, 235 (1959).
13. G.Polman and F.Oberlis, Glasstechn.Berichte, **35**, 60 (1962).
14. B.B.Saxena, S.S.Nigam, and S.R.Sengupta, Indian J. Technology, **1**, 283 (1963).
15. M.Richter and B.Bartakova, "Modification of Electrical Equipment for Tropical Conditions" (Translated into Russian from Czech), Gosenergoizdat, Moscow, 1962.
16. R.Blahnik and V.Zanova, "Mikrobialni Koroze" (Microbiological Corrosion) (Translated into Russian from Czech), Izd.Khimiya, Leningrad, 1965.
17. S.Nagamuttu, Intern.Biodeterior.Bull., **3**, 25 (1967).
18. A.Baigozhin, Candidate's Thesis, GOI, Leningrad, 1969.
19. P.W.Baker, Intern.Biodeterior.Bull., **3**, 59 (1967).
20. P.W.Baker, Intern.Biodeterior.Bull., **4**, 59 (1968).
21. A.Baigozhin, M.S.Rodionova, E.I.Panfilenok, L.V.Bereznikovskaya, L.V.Sergev, T.N.Naryshkina, and V.B.Geflikh, USSR P.210 561 (1966); Byul. Izobret., No.6 (1968).
22. Z.A.Rogovin, "Khimicheskie Prevrashcheniya i Modifikatsiya Tsellyulozy" (Chemical Transformations and Modification of Cellulose), Izd.Khimiya, Moscow, 1967, p.135.
23. A.D.Virnik, E.M.Akovbyan, L.S.Gal'braikh, and Z.A.Rogovin, Izv.Vys.Ucheb.Zaved., Tekhnol.Tekst. Prom., No.4, 103 (1968).
24. A.D.Virnik, Uspekhi Khim., **42**, 547 (1973) [Russ. Chem.Rev., No.3 (1973)].
25. I.V.Grebenshchikov and T.A.Favorskaya, Trudy GOI, 7, No.72 (1931).
26. I.V.Grebenshchikov, A.G.Vlasov, B.F.Neporent, and N.V.Suikovskaya, "Prosvetlenie Optiki" (Non-Reflective Coatings on Optical Materials), Gostekhizdat, 1946.
27. N.V.Suikovskaya, "Khimicheskie Metody Polucheniya Tonkikh Prozrachnykh Plenok" (Chemical Methods for the Preparation of Thin Transparent Films), Izd. Khimiya, Leningrad, 1971, pp.154, 172.
28. K.S.Evstrop'ev and V.S.Molchanov, Trudy GOI, **31**, 7 (1963).
29. A.Ya.Kuznetsov, Trudy GOI, **31**, 87 (1963).
30. N.V.Suikovskaya, Trudy GOI, **31**, 40 (1963).
31. V.Bažant, V.Chvalovsky, and J.Rathousky, "Organosilicon Compounds" (Translated into Russian from Czech), Moscow, 1960, p.285.
32. A.A.Pashchenko and M.G.Voronkov, "Kremniiorganicheskie Pokrytiya" (Organosilicon Coatings), Izd. Tekhnika, Kiev, 1969.
33. Z.V.Shirokshina, Optiko-Mekhan.Prom., No.9, 39 (1974).
34. A.P.Kuleshov, N.V.Suikovskaya, Z.V.Shirokshina, and K.V.Sarakhova, USSR P.550 356 (1977); Ref. Zhur.Khim., 24M169 (1977).
35. A.Ya.Korolev, Symposium, "Klei i Tekhnologiya Skleivaniya" (Adhesives and Technology of the Formation of Adhesive Bonds), Oborongiz, 1960, p.35.
36. P.V.Kozlov (Editor), Symposium, "Adgeziya Polimerov" (Adhesion of Polymers), Izd.Akad.Nauk SSSR, 1963, pp.3, 75, 99, 137.
37. W.A.Korel, K.Hoefelmann, and E.Plueddemann, Kunststoffe, **65**, 760 (1975).
38. J.Bjorksten, L.L.Yaeger, and J.E.Henning, Ind.Eng. Chem., **46**, 1632 (1954).
39. L.F.Biefeld and T.E.Phillips, Ind.Eng.Chem., **45**, 1281 (1953).
40. M.Jellinek, Mod.Plastics, **30**, 150 (1952).
41. N.M.Trivisonno, L.Lee, and S.Skinner, Ind.Eng. Chem., **50**, 912 (1958).
42. H.Clark and E.Plueddemann, Ind.Eng.Chem., **40**, 133 (1963).
43. B.A.Kiselev, Uspekhi Khim., **27**, 1101 (1958).
44. A.Baigozhin and L.V.Sergeev, Vysokomol.Soed., **4**, 972 (1962).
45. L.V.Sergeev, A.Baigozhin, and S.G.Fattakhov, Vysokomol.Soed., **4**, 977 (1962).
46. A.Baigozhin, L.V.Sergeev, A.K.Dabagova, and S.G.Fattakhov, Symposium, "Adgeziya Polimerov" (Adhesion of Polymers), Izd.Akad.Nauk SSSR, 1963, p.75.
47. S.Reichel, Plaste und Kautschuk, **15**, 501 (1968).
48. A.I.Mikhal'skii, Uspekhi Khim., **39**, 2050 (1970) [Russ. Chem.Rev., No.11 (1970)].

49. A.Baigozhin and A.T.Troshchenko, USSR P.116 493 (1958); Byul.Izobret., No.12 (1958).
50. A.Baigozhin, M.S.Rodionova, L.V.Bereznikovskaya, and L.V.Sergeev, Optiko Mekhan.Prom., No.7, 40 (1963).
51. A.Baigozhin, M.S.Rodionova, and L.V.Sergeev, Trudy GOI, 31, 103 (1963).
52. A.Baigozhin, E.I.Panfilenok, M.S.Rodionova, L.V.Bereznikovskaya, and N.V.Suikovskaya, USSR P. 233 190 (1967); Byul.Izobret., No.2 (1969).
53. A.Baigozhin, E.I.Panfilenok, M.S.Rodionova, L.V.Bereznikovskaya, and N.A.Chadaeva, USSR P. 341 771 (1970); Byul.Izobret., No.19 (1972).
54. A.Baigozhin, A.I.Sviridova, M.S.Rodionova, E.I.Panfilenok, and L.V.Bereznikovskaya, USSR P. 544 626 (1977); Byul.Izobret., No.4 (1977).
55. M.G.Voronkov and E.Lukevics, Uspekhi Khim., **38**, 2173 (1969) [Russ.Chem. Rev., No.12 (1969)].
56. M.G.Voronkov, G.Zelcans, and E.Lukevics, "Kremnii i Zhizn'" (Silicon and Life), Izd.Zinatne, Riga, 1978.
57. N.F.Chernov and M.G.Voronkov, Zhur.Obshch.Khim., **47**, 794 (1977).
58. N.F.Chernov, Candidate's Thesis, Irkutsk Institute of General Chemistry, Siberian Division of the USSR Academy of Sciences, Irkutsk, 1977.
59. W.A.Sexton, "Chemische Konstitution und biologische Wirkung", Stuttgart, 1958.
60. N.N.Mel'nikov, I.L.Vladimirova, and S.N.Ivanova, "Khimicheskie Sredstva Predokhraneniya Nemetallicheskikh Materiallov ot Razrusheniya Mikroorganizmami. Trudy NIUIF" (Chemical Means of Protecting Non-Metallic Materials Against Decomposition by Microorganisms. Transactions of the NIUIF), Moscow, 1959, No.165.
61. J.G.Horsfall, "Principles of Fungicidal Action" (Translated into Russian), Inostr.Lit., Moscow, 1948.
62. F.C.Whitmore, "Organic Compounds of Mercury" (Translated into Russian), ONTI, Leningrad, 1938.
63. L.G.Makarova and A.N.Nesmayanov, "Sinteticheskie Metody v Oblasti Metallorganicheskikh Soedinenii Rtuti" (Synthetic Methods in the Field of Organometallic Compounds of Mercury), Izd.Akad.Nauk SSSR, Moscow, 1945, p.59.
64. J.Chatt, Chem.Rev., 7 (1951).
65. M.Das, Anal.Chem., **26**, 1086 (1954).
66. O.A.Reutov, "Teoreticheskie Osnovy Organicheskoi Khimii" (Theoretical Foundations of Organic Chemistry), Izd.Moskov.Gos.Univ., 1964, p.266.
67. D.Seyferth and N.Kohlen, Z.Naturforsch., **14**, 137 (1959).
68. R.Ya.Levina and V.N.Kostin, Zhur.Obshch.Khim., **23**, 1054 (1953).
69. N.N.Lebedev, S.A.Efremova, V.N.Kostin, and R.Ya.Levina, Vestnik Moskov.Gos.Univ., No.3, 149 (1957).
70. A.K.Pogodaev and D.P.Dobychin, Zhur.Fiz.Khim., **32**, 2637 (1958).
71. M.S.Rodionova, Optiko-Mekhan.Prom., No.7, 40 (1962).
72. A.Baigozhin, M.S.Rodionova, L.V.Bereznikovskaya, and L.V.Sergeev,Optiko-Mekhan.Prom.,No.6,46 (1963).
73. N.A.Chadaeva, K.A.Mamakov, and G.Kh.Kamai, USSR P.364 620 (1971); Ref.Zhur.Khim., 2N531 (1974).
74. N.A.Chadaeva, K.A.Mamakov, and G.Kh.Kamai, USSR P.368 276 (1971); Ref.Zhur.Khim., 20N514 (1973).
75. G.J.M.Van der Kerk and J.G.Luijten, J.Appl.Chem., **6**, 56 (1956).
76. G.J.M.Van der Kerk and J.G.Luijten, J.Appl.Chem., **4**, 314 (1954).
77. M.N.Arnold and H.J.Clarke, J.Oil and Colour Chem. Assoc., **39**, 900 (1956).
78. A.A.Goldberg and H.S.Jefferies, Paint Manuf., **27**, 436 (1957).
79. H.J.Hueck and J.G.Luijten, J.Soc.Dyers Colourists, **74**, 476 (1958).
80. D.A.Kochkin, P.I.Zubov, B.K.Flerov, S.M.Rzaev, I.V.Kazamanova, I.S.Novoderezhkina, N.A.Voronkov, K.P.Zabotin, V.V.Chebotarskii, M.M.Notkin, S.L.Semenov, L.A.Sukhareva, and P.A.Davidenko, USSR P.210 296 (1966); Byul.Izobret., No.30 (1973).
81. D.A.Kochkin and I.N.Azerbaev, "Olovo- i Svinetsorganicheskie Monomery" (Organotin and Organolead Monomers), Izd.Nauka, Alma-Ata, 1968, p.175.
82. W.N.Neumann, "Der organische Chemie des Zinns" Stuttgart, 1967.
83. R.G.Koroleva, E.I.Frost, and Yu.B.Rozhkov, Lakokrasochn.Materialy i Ikh Primenenie, No.4, 17 (1975).
84. A.Baigozhin, E.I.Panfilenok, I.V.Belova, M.S.Rodionova, L.V.Bereznikovskaya, and N.V.Suikovskaya, USSR P.562 525 (1975); Byul.Izobret., No.23 (1977).
85. A.Baigozhin, M.S.Rodionova, E.I.Panfilenok, L.V.Bereznikovskaya, and I.V.Belova, Optiko-Mekhan.Prom., No.7, 37 (1977).
86. M.S.Rodionova, A.Baigozhin, L.V.Bereznikovskaya, and I.V.Belova, Optiko-Mekhan.Prom., No.4, 34 (1977).
87. A.T.Troshchenko and G.I.Pustoshkin, USSR P.134 408 (1960); Ref.Zhur.Khim., 20K268 (1961).
88. A.T.Troshchenko and A.I.Sviridova, USSR P.106 455 (1956); Byul.Izobret., No.5 (1957).
89. A.T.Troshchenko, "Khimicheskie Sredstva Predokhraneniya Nemetallicheskikh Materiallov ot Razrusheniya Mikroorganizmami. Trudy NIUIF" (Chemical Means of Protecting Non-Metallic Materials Against Decomposition by Microorganisms. Transaction of the NIUIF), Moscow, 1959, No.165, p.75.
90. H.F.Payne, "Organic Coating Technology" (Translated into Russian), Goskhimizdat, Moscow, 1959, p.667.
91. G.D.Nassonova, E.K.Pogosyants, G.B.Markova, and K.P.Grinevich, Plast.Massy, No.1, 20 (1962).
92. G.A.Aleksandrov, USSR P.253 320 (1969); Byul. Izobret., No.13 (1970).
93. BRD P.1 032 899 (1958); Chem.Abs., **54**, 15 882 (1960).
94. A.I.Sviridova and N.V.Suikovskaya, Optiko-Mekhan. Prom., No.4, 61 (1957).
95. A.Kaller, DDR P.45 885 (1966); Chem.Abs., **65**, 9661 (1966).
96. V.A.Ponomarenko, Doctoral Thesis, Institute of General Chemistry, USSR Academy of Sciences, Moscow, 1962.
97. E.Lukevics and M.G.Voronkov, Dokl.Akad.Nauk SSSR, **216**, 103 (1974).
98. A.Baigozhin, Zhur.Obshch.Khim., **43**, 1408 (1973).
99. A.Baigozhin, I.V.Belova, and L.N.Arkad'eva, Zhur. Obshch.Khim., **45**, 2350 (1975).
100. A.J.Isquith, E.A.Abbott, and P.A.Walters, J.Appl. Microbiology, **24**, 859 (1972).
101. F.Kahn, Appl.Physics Letters, **22**, 386 (1973).
102. R.J.Lunkens, "Chemistry of Fungicidal Action", New York, 1971.
103. G.J.M.Van der Kerk, Bull.OEPP, No.10, 5 (1973).
104. Sistemfungizide, Internat.Symp.Reinhardsbrunn, Berlin, 1974; Ref.Zhur.Khim., 12O332 (1976).
105. A.Baigozhin, I.V.Belova, M.S.Rodionova, L.V.Bereznikovskaya, L.N.Kuznetsova, M.G.Voronkov, R.G.Mirskov, and O.S.Stankevich, USSR P.638 558 (1978); Byul.Izobret., No.47, 62 (1978).