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Chemical and Physical Methods for Protecting Biopolymers against Pests

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CHEMICAL AND PHYSICAL METHODS FOR PROTECTING BIOPOLYMERS AGAINST PESTS

Preface

Protection of natural biopolymers: proteins (collagen, keratin), carbohydrates (starch, cellulose) and others, is a very acute problem. Numerous fungi, insects and rodents damage raw materials, and finished products both during manufacturing and at storage. To study methods and protection facilities we systematized information on main types of biodestructors and gave numerous examples of synthesis of the most known and active preparations to control insects and other organisms damaging natural polymers in light and food industries.

The monograph is written by a group of authors famous for their papers on chemistry of low-molecular bioregulators and means for plant protection. It is designed for specialists engaged in problems of biopolymer protection.

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Introduction

Pesticides (from Latin *pestis* – pest + *caedere* – kill) are chemical compounds applied for protection of plants, agricultural products, wood, articles made of wool, cotton, leather, for killing animal ectoparasites and for combating carriers of serious diseases.

Agricultural activities of a human being have resulted in concentration of large amounts of proteins and carbohydrates in comparatively small area. Due to this fact there appeared favorable conditions for development of different kinds of pests then forced to spend a lot of time and efforts to find means of subsistence. Since ancient times, manufacturers and consumers of various biopolymer products and materials have been searching for ways and means of protection thereof against pests.

With the development of chemistry it became possible to make efficient preparations widely applied in combating pests and rodents. New categories of insecticide-active organic compounds were found, e.g. organophosphorous pesticides and analogs of natural substances: juvenile hormones, insect pheromones, pyrethroids, etc. Table 1 shows that in 1990 among 150 applied insecticides 6 were inorganic, but in 2000 there were 3 such insecticides left only. Over 50% of all applied categories of compounds account for organophosphorous chemical pest-killers and pyrethroids. It should be mentioned therewith the decrease of total amount of preparations from 150 to 104, which can testify to creation of more active and effective preparations, as well as to development of more efficient ways of applications thereof making it possible to achieve better results through less number of preparations.

Fumigants (methyl bromide, methallyl chloride, dichloroethane, phostoxin, phosphine) and contact chemical pest-killers (carbophos, trichlormetaphos-3, metathion, volaton, actellic, malathion) are often used for combating grain insects and grain and cereal disinfection. Practically all these preparations possess acute toxicity for both man and warm-blooded animals, besides there is a risk of chronic poisoning of animals and people using treated grain as food: up to 1.0 mg/kg of carbophos is permitted in groats and bread [1]. Methyl bromide contained in the composition of widely advertised mixture of methyl bromide and phosphine is referred to as ozone-depleting compounds [2, 3]. Regular application of known preparations facilitates insecticide resistance with insects. Such circumstances in the course of time will undoubtedly result in full ban for applying highly toxic and environment-damaging pesticides in countries with developed agriculture and will promote for scientific research in finding new forms and kinds of highly active and environmentally safe preparations.

Table 1. Dynamics of spectrum of insecticides and acaricides (1990-2000)

Chemical group of preparations	1990		2000	
	Number of preparations	reactant	Number of preparations	reactant
Inorganic	6	5	3	1
Chloroorganic	8	6	-	-
Bromic	2	2	1	1
Nitro-containing	3	3	2	2
Carbamates	13	8	8	5
Organophosphorous compounds	59	24	27	10
Pyrethroids	41	16	31	12
Nereistoxin	1	1	1	1
Neonicotinoids	1	1	5	4
Phenylpyrazoles	-	-	4	1
Mixtures	3	2	5	5
Other groups	13	12	17	12

*Acaricide – a chemical preparation for plant protection against harmful mites.

This monograph contains information on up-to-date methods for protecting agricultural products (biopolymers of vegetable and animal origin) at storing and processing, methods for preparation synthesis and ways for successful application in practice.

Chapter 1

1. Living Organisms Damaging Biopolymer Materials

Among general reasons for damadging stored tissues, leather, furs and other biopolymers the first is high humidity, sharp temperature fluctuations. However these factors could not be so harmful if they did not provoke to putrefaction, mold appearance i.e. consequences of microorganisms activity (microscopic mold fungi). Besides, great harm can be caused by more highly organized things, mainly Arthropoda of insects and chiggers class. One must know basics of biology of harmful organisms to efficiently find methods for protecting fur and leather-processing production.

Base unit of all vegetable and animal organisms is a cell (Figure 1). Elementary organisms contain one cell, when their structure is complicated cells start making various essential functions and thus forming tissues and bodies. Cell contains cytoplasm where basic cellular organelle and chromosomes are found, i.e. genetic mechanism providing procreation, or cells either scattered without any limitations or contained in a nucleus.

By their systematic position these organisms belong to eukaryotes (nuclear) unlike prokaryotes (prenuclear) represented by bacteria and cyanobacteriae. It is availability of a nucleus, strictly limited by a membrane from cell contents, containing heredity basis i.e. a set of chromosomes, defines difference between eukaryotes and prokaryotes. Chromosomes of *y* prokaryotes are within nucleoplasm. They do not separate from the remaining part of a living cell. Prokaryotes have become the first living organisms appeared on Earth, while eukaryotes are the result of saltation which revealed infinite prospects for development before the world.

Despite the fact that prokaryotes, due to simplicity of structure and reproduction, and ability to use different substrates as energy source which are even of inorganic origin, are widely distributed, they are considered as cladotype (relict) in their current position.

Nucleation has become the beginning for differentiation deepening and making conditions for appearance of multicellular organisms whose development and complication in the course of evolution has resulted in diversification of the current living world.

Basis for differences between eukaryotes kingdom is way of how they use energy resources, i.e. nutrition. Animals are heterotrophs, i.e. they get substances necessary for their development from the outside only together with nutrition. But plants, especially higher ones, belong to autotrophs as they synthesize all organic substances necessary for life activity by themselves through photoactive pigments (chlorophyll, carotene) using sunlight as the energy

source, and inorganic components (water, carbon dioxide, inorganic compounds of nitrogen, phosphorus, potassium and other elements) as building materials. However, there are many heterotrophs among plants leading either saprophytic (i.e. upon organic but not living substrates), or parasitic (upon living organisms) mode of existence.

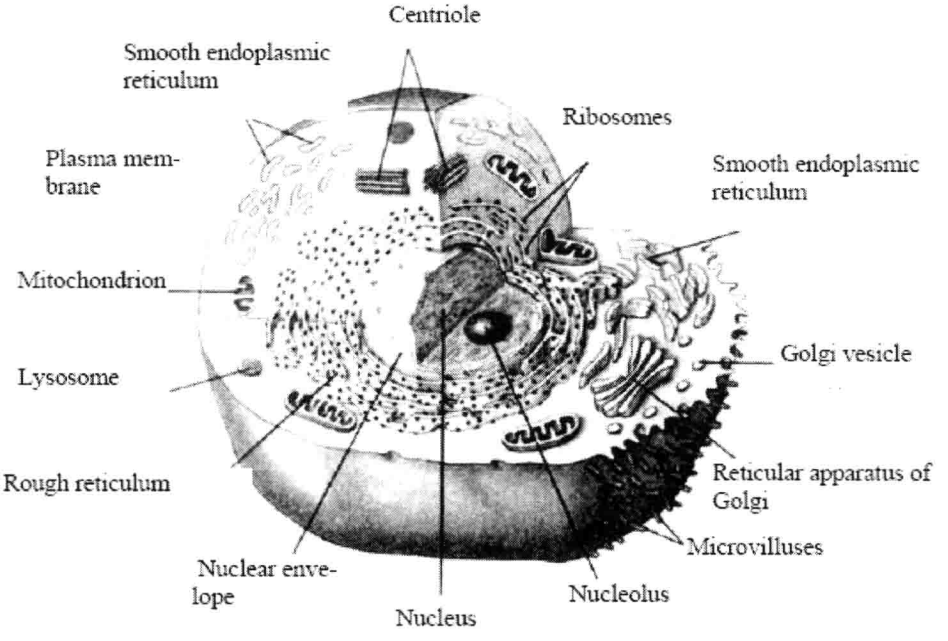

Figure 1. Structure of living organism cell.

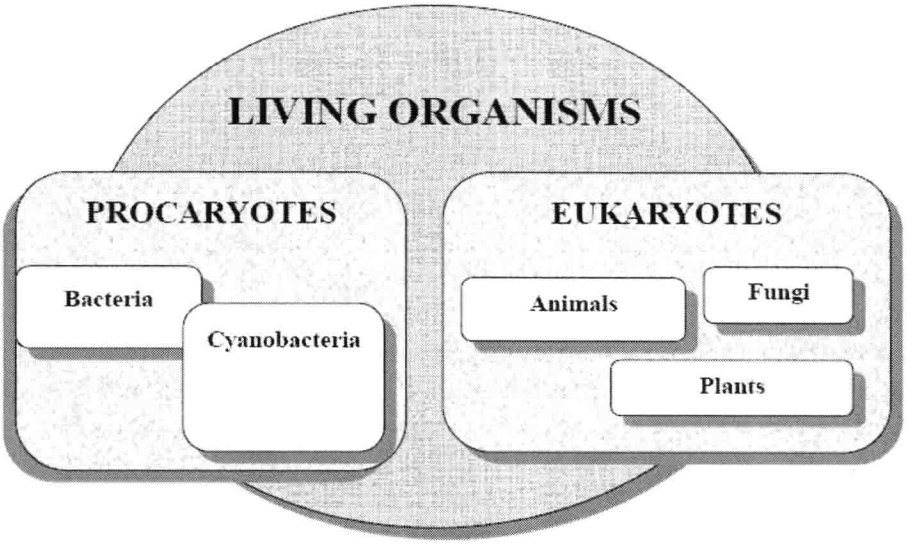

Figure 2. Systematics of living world.

Principal distinctions between animals and plants are availability of rigid cytoderm in plants and ability to active movements and change of places in animals. There are also some metabolic processes. Scientific systematic considers fungi as a separate kingdom of living organisms (Figure 2), although still recently they were included to plant kingdom within sub-kingdom of inferior plants.

1.1. Unicellular Organisms

Among protozoa one can also find pests of biopolymers of grain and cereals. Bacteria of *B.Subtilis ssp. mesentericus* (potato bacillus) subspecies being developed in bread-crumb cause potato disease. Potato bacillus occurs widely in nature. It is found in soil, air, plants, and others. These bacteria cause main problems in flour mills and bakeries.

If grain is not washed before grinding but moistened during grinding, potato bacillus gets into flour. Under favorable conditions potato bacillus bacteria are promptly reproduced. Temperature of about 40°C, moisture, nutrient medium, and sub-acidity are optimum conditions for development of potato bacillus spores. Its cells die when heated up to 80°C, but its spores are still viable at 120°C. Thus, bacteria die at baking, but their spores remain viable.

Acid medium inhibits development of potato bacillus bacteria. Therefore, potato disease rarely occurs in rye-bread with acidity.

Failure to comply with sanitary and technological rules for storage and treatment of grain, flour, as well as baking of bread and its storage significantly affects potato bacillus reproduction. Due to this much attention is paid to observance of current sanitary and technological rules applicable in grain-elevators, flour-milling and baking industries, as well as in trade.

With development of potato disease, reproduction of potato bacillus bacteria is strongly intensified. Due to affect of active amylases of potato bacillus, amount of dextrins* making a bread-crumb stick, is increased. Protein breakdown products formed therewith under influence of proteolytic enzymes of potato bacillus possess sharp specific smell. Potato disease-affected bread has sticky crumb which is stretched by threads if strongly affected and then in the middle of the loaf there is a black cavity with strong putrefactive odor.

To prevent spread of potato disease certain measures in all steps (soil, grain, bread) are to be conducted. For prevention thereof wheat flour ground down at mills is to be checked for potato bacillus through sample laboratory baking. The resulting molded bread in 1.5-2 hours after baking is wrapped in moistened porous paper in two layers and is placed in thermostat for 24 hours at 36-38°C and relative moisture of 83-87%. In 24 hours afterwards bread is unwrapped, cut up and checked for disease indications (specific smell, sticky crumb), then it is inspected in 36 hours.

Flour affected by potato disease is to be immediately realized, and all transportation links, equipment and premises of the mill and bakery are to be sanitized and disinfected. Surfaces are to be cleaned by 3% solution of acetic acid. Besides, all doors, windows, panels,

* Dextrines are oligomerhomologs formed under partial hydrolysis of linear regular homopolysaccharides.

floors and windows are cleaned by soap-wetted rags, then 3% solution of chlorinated lime and hot water ablution is applied.

1.2. Microscopic Fungi

Availability of cytoderm within fungi cells, as well as sap vacuoles contained within cells; protoplasm current well visible under microscope; absence of ability to active movements make it all possible to consider them close to plants, although fungi are heterotrophs (i.e. hemoorganoheterotrophs using chemically processed organic substances) by nutrition way. Fungi have no chlorophyll and its cell organelles – plastids).

Occurrence. Just few kinds of fungi can be found in aqueous medium, while they are widely spread overland. Saprophytes are actually found everywhere, where there can be organic substrates available as food. Generic diversification of saprophytic fungi is enormous. It includes mold fungi known elsewhere and edible fungi also known to everyone.

Parasitic species are widely numerous. They are capable to live using either plants or animals, including a man, as their hosts. Many of them are serious disease-producing organisms. Parasitic fungi give rise to outbreak of cultivated plants disease (epiphytotics) resulting in significant crop losses as well as to mycosis with animals and man difficult to cure. Pathogens of powdery mildew, black grain and ringworm are examples of this species.

General texture. Fungi are weakly differentiated multicellular living organisms with a simple texture. Fungus body consists of fibers (hyphae) and is called thallus. All range of thallus fibers is called mycelium (Figure 3).

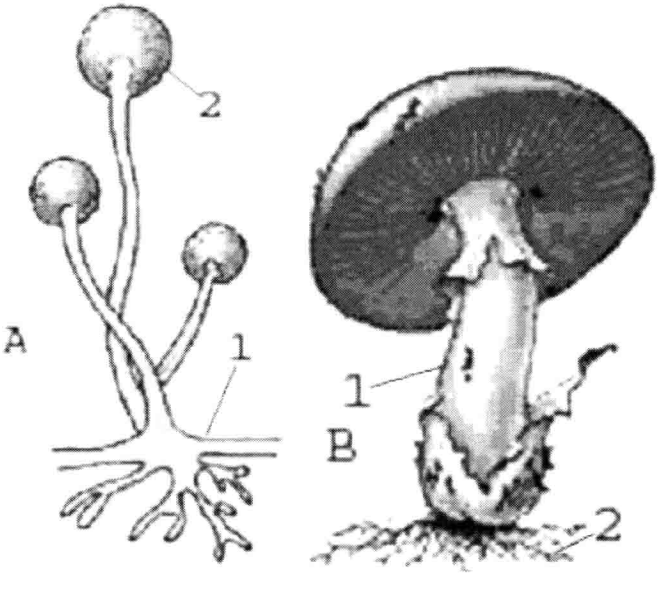

Figure 3. Fungi structure. A. Lower fungi: 1. Mycelium-formed hyphae. 2. Mycothallus. B. Higher fungi: 1. Mycothallus. 2.Rhizomorphs.

At some steps of fungi mycelium development there appear dense interlacements resembling tissue called plectenchyma (false parenchyma which is regarded as real tissue made of living cells). For example, edible mycothallus of blewits consists of plectenchyma. Differentiation of functions of parts of an organism in higher fungi resulted in appearance of rhizoid formations i.e. rhizomorphs also mycelium-formed.

Fungi hyphae possess cytoderms, and one can see vacuoles with cellular fluids and nucleus within through a microscope. Higher fungi and some kinds of lower ones contain transverse partitions dividing cytoplasm i.e. septa. Cytoplasm of neighboring cells is connected through pores contained within septa centers. Septa are not available with the majority of lower fungi.

Fungi cytoderm is dense and clearly expressed and usually contains chitin (N-acetyl-D-glucosamine polymer), and rarely cellulose.

Vegetative phase (period when there is growth only without cloning) with lower fungi is characterized by absence of cytoderm and formation of plasmodium i.e. multinuclear mobile protoplasmatic mass surrounded by thin membrane only, or pseudoplasmodium i.e. aggregation of mononuclear cells also possessing membrane only. There is no plasmodium or pseudoplasmodium in higher fungi, and vegetative phase is represented by hyphae only.

Systematic. Before being allocated to a separate kingdom fungi were included into sub-kingdom of lower plants as a division. Fungi classification is based upon both their phylogenetic (evolutionary-kindred) relations and practical aims. Fungi nomenclature is binary, it includes name of genus and species; e.g. mold fungus mucor known to everyone has generic name *Mucor* and specific name *mucedo*. Similar species are grouped into genera, genera into families *(–aceae)*, families into orders (*–ales*), orders into classes (*-mycetes*). Mold fungi of practical importance for fabrics, leather and furs manufacture are grouped to zygomycetes class (lower fungi) and ascomycetes (higher fungi) (Table 2).

Table 2. Main fungi groups

Lower fungi (Phycomycetes)	Higher fungi (Eukomycetes)
Chytridiomycetes	Ascomycetes (cup fungi)
Oomycetes	Basidiomycetes
Zygomycetes	Deuteromycetes (imperfect fungi)

Reproduction. Fungi are reproduced both agamogenetically and syngenetically, with both of these methods and peculiarities thereof being the most important basis for fungi classification.

Fungi hyphae grow apically, with any part of mycelium being able to grow independently thus forming new thallome.

Fungi agamogenesis is possible by simple cell division into two parts, like bacteria, but there are such methods as pullulation (pinching with further full separation of mother cell, or outgrowth generated through preformed convexity into which one of nuclei passes after

regular mitosis*) typical for yeast; hypha decay into separate cells; and finally spore formation.

When reproduced through hyphae decay into pieces these separate cells are called oidia or arthrospores. If these spores are surrounded by thick-walled shell they are called chlamydospores. If these spores are placed in special capsules i.e. sporangia, they are called sporangiospores.

When spores are formed through pitching of the upper part of hypha they are called conidiospores. Hyphae bearing sporangia or conidia are called sporangiophores and conidiospores accordingly. Spores of lower fungi keeping to water mode of life are active, have filaments and are called zoospores.

Fungi gamogenesis includes mandatory nuclear fusion of parental germ cells i.e. gametes containing half (haploid) number of chromosomes. When gametes are invisible they are called isogametes. Gametes of some fungi are formed in special differentiated cells i.e. gametangia. If gametangia are differentiated by form, then male gametangia are called antheridia and female ones are oogonia. If both male and female gametes are formed on one thallus from one original cell, then fungi with this way of syngenesis are considered homothallic, while if there are sex differences between thalluses they are called heterothallic.

Fungi are differentiated by way of gamete joining: lower fungi have both active gametes (planogametes), and their joining (conjugation) takes place outside gametangia.

Oomycetes have active male gamete entering oogonia and fertilizing ovules, and conjugation of polykaric gametangia is seen in zygomycetes.

Higher fungi have two forms of syngenesis. The first one is through fertilizing of female reproductive structure by antheridium, with no nuclei fusion taking place initially thus forming divisible dikaryons from which after the fusion of nuclei during fertilization (karyogamy) asci with spores (ascomycetes) are formed. The second one is through joining two cells of vegetative mycelium i.e. somatogamy with formation of basidiospores (basidiomycetes). Syngenesis of imperfect fungi is replaced by parasexual process where nuclear fusion takes place after their transition to another cell.

Genera *Aspergillus* and *Penicillum* are grouped into cup fungi. Cup fungi (ascomycetes) are divided into three groups depending on carposome forms (ascocarpus):

- Plectomycetes having absolutely closed carposomes (cleistothecia);
- Pyrenomycetes having flask carposomes (perithecia);
- Discomycetes – open, cotyloid carposomes (apothecia).

Aspergillus and *Penicillum* are grouped into plectomycetes. These genera are differentiated in conidia formation; if *Penicillum* conidia are formed directly on vertically growing conidiophore, then *Aspergillus* conidia are found on sterigmas to be formed on follicles, which vertically standing hyphae are ended with (Figure 4).

Microscopic fungi as biodecomposers. When textiles, leather and furs are stored in conditions of high humidity, mold being colonies of microscopic fungi can appear thereon.

* Mitosis (from Greek mitosis – thread) is indirect cell and cell body division. Due to mitosis a number of cells is increased.

More often they grow and develop on fabrics made of natural fibers and genuine leather, however, there are some species capable to live in synthetic fabrics and leatherette.

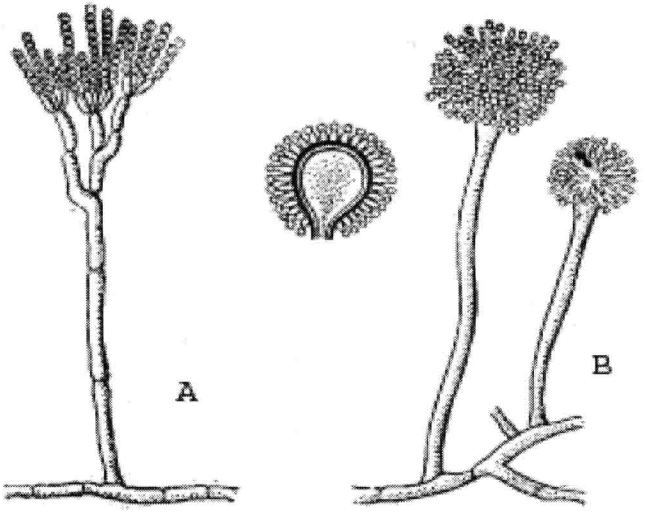

Figure 4. Forms of fruiting hypha with *Penicillum* (A) and *Aspergillus* (B).

Molds alone are not able to spoil textiles, leather and furs: destruction thereof is caused by fungi metabolic products i.e. metabolites liberated to environment, more exactly at substrate. It is essential that fungi metabolites are actively liberated when there is deficiency in any substance important for their activity. Organic acids and enzymes, liberated thereby, formed by fungi make the most destructive (deleterious) influence. Fungi make gluconic, lactic, oxalic, fumaric, succinic, malic, formic, acetic, and citric acids more often. The latter ones destroy natural organic materials and may cause destruction of synthetic fibers, changing structure and color thereof. Acids are formed involving other group of substances i.e. enzymes, which are very important for destruction. Main enzymes (exoenzymes) liberated by fungi belong to several groups:

- Oxidoreductases (oxygenases, dehydrogenases and oxydases): glucose oxydase, catalyze, peroxidase. Oxidoreductases catalyze redox reactions in the process of energy metabolism. Catalyze and peroxidase catalyze oxidation of different organic compounds by peroxide, mainly by hydrogen peroxide.
- Hydrolases – many of them are exoenzymes, they make substrata ready to be affected by other enzyme groups. They catalyze breakdown of ester bonds (esterases), bonds between glucose residues (glycosidases), peptide (amide) bonds (proteinases) by hydrolysis type.
- Lyases catalyze non-hydrolytic splitting of organic substances.
- Transferring enzymes catalyze transfer of atomic groups or parts of molecules from one sort of compounds to other ones.
- Isomerizing enzymes catalyze intramolecular transfer of radicals, groups, atoms thus forming isomers.

- Ligases (synthetases) catalyze synthesis of complex compounds from more simple ones.

Quiescent stages of microscopic mold fungi – spores – are easily scattered by air current and can survive for a long time in water, soil and other substrata not suitable for development. Thick-walled shell of spores makes them tolerant to both low and high temperatures, and ultraviolet radiation. Current chemical means for destroying fungi are fungicides which can be of either biological origin but mainly they are synthetic substances.

Usual methods of thermal heating – pasteurization (heating up to 60°C) and sterilization applying wet steam – boiling, autoclaving, or dry heat – warming up to 160-200°C cannot be applied for protecting textile, tanning, and fur industries goods. Thus, it is chemical means for protecting stored goods that are very important.

To choose the most efficient preparation one must define what kind of mold fungus does affect the stored materials. The attached table (table 3) presents development trends, the most typical substrates and description of fungi colonies. Combination of these features will help to define species of microscopic fungus-decomposer.

Table 3. Fungi affecting materials and tissues at storage

Species, genus	Substrate	Colony type	Development trends
Red-brown bissochlamys	Cotton yarn, paper, chamois leather, feather	From straw to brown-snuff color	High temperature (30-37°C)
Verrucate amauroascus	Putrefied leather	White color with further darkening	High temperature and humidity
Eurotium repens	Textiles, cellophane, plastics, rubber	Friable, red-orange with dark ring close to the edge	Lower humidity (13-15%), can grow at high salt content
Talaromyces flavus	Different fabrics and materials	Friable, with broken edge, of straw color with concentric orange rings	Can grow at high temperature
Chaetomium (different species)	Paper, cotton, ready-made clothes	Virescent, dark-primrose	High temperature and humidity
Penicillium purpurogenum	Paper, cotton fabrics, calico, leatherette	Velvet, dark-green with yellow border, the opposite side being purple-red	High humidity; can be found in soil, and grow at low temperature.
Penicillium expansum	Different materials	Velvet, with concentric yellow and green rings	
Aspergillus niger	Paper, leather, cotton fabrics	Brown or black color	High humidity
Aspergillus fumigatus	Wool, cotton	Velvetweed, cambridge blue or velvet, bluish-green	Affected materials are strongly heated when damaged by fungus
Aspergillus versicolor	Leatherette, calico, leather, canvas	Dense, raised, dark-green or bluish, often with pink border, the opposite side being rich red or cherry	Antiseptic-resistant
Fusarium	Calico, leatherette, leather	White, white-pink, pink-lilac or brown	High humidity and heat