Protection and Conservation Measures
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The world is full of cultural heritage of all kinds. A large number of monuments and historical buildings spread all over the world constitute one of the finest examples of mankind's rich cultural heritage. These specimens of cultural property not only instill a sense of awe amongst ourselves but are also symbols of man's cultural identity and continuity. Therefore, one of the major tasks before the present day generation is to rise to the challenge of preserving this vast and varied cultural heritage for posterity.

The stability of a monument is largely dependent upon the nature of its various constituents and a variety of factors classified as physical, chemical and biological are responsible for its decay (Winkler, 1975). These factors interact amongst themselves as well as with the constituents of the structure. However, in any case the deterioration of a building is normally a combination of any of these factors, although under specific circumstances, any one of the factors may be more dominant. For example, in tropic or regions where the climatic conditions are quite conductive to the growth of biological agencies, a variety of biological growths over monuments have been reported by several workers (Srinivasan, 1949; Kamchandran, 1953; Lal, 1962; Riederer, 1981).

In order to control biodeterioration processes the most suitable methods and products must be used. With regard to the principles and the nature of the means employed, control methods can be classified as mechanicals, physicals, biologicals, or biochemicals, even if those based on active principles in solution (chemicals) are the more frequently applied (either as wide-spectrum active principles, or more specific fungicides, algaecides, herbicides, insecticides and repellents for birds).
Direct Methods:

Mechanical Methods:

All the techniques described as "mechanical" have in common a method of displacing the biodeteriogens. Traditional mechanical methods involve the physical removal of biodeteriogens either by hand or with tools such as scalpels, spatulas, scrapers, air abrasive or vacuum cleaners. Although frequently used in the past, these methods do not produce lasting results and the eradication of vegetation could do not completely arrest its vegetative activity. Moreover, mechanical methods can damage the substrate, even if they have the advantage to not add on it any substance that might cause further deterioration. In some cases the mechanical methods alone can be sufficient to eradicate some of these biodeteriogens such as, mosses, foliose lichens and annual herbaceous plants. Nevertheless a preliminary biocide treatment is surely advantageous to facilitate the removal of the biological growth and to hinder the diffusion of the colonization of lichens, reproducing by means of soredia, through their dispersal due to mechanical cleaning methods (Ionita, 1971). The mechanical removal of lichens on stone can be facilitated by applying beforehand some alkaline solutions (e.g. 5% of ammonia) in order to swell and soften the thalli.

Physical Methods:

The methods used experimentally are: ultraviolet rays (UV), gamma rays, low frequency electrical current systems, heat, deep-freeze temperatures and ultrasonic.

Ultraviolet rays have been used especially against bacteria, algae and fungi in the treatment of renders and plasters (De Cleene, 1994). The part of the UV
spectrum with germicidal activity is between 300-200 μm, with a maximum of activity between 275-230 μm. Microorganisms vary in sensitivity depending on their growth phase (greater during the logarithmic phase) and the nature of the substrate on which they are found. UV radiation is more effective at low RH values (less than 50-60%). It has a poor penetration power and can modify some materials (e.g., cellulose, proteins) and the colours (natural or dyes) of surfaces.

Gamma rays are a form of electromagnetic radiation. They are extensively used for sterilizing micro flora and killing insects, especially on organic materials such as paper, parchment and wood (Hickin, 1971; Van Der Molen et al., 1980). A dose of 500 Gy is required to kill larvae and to prevent the emergence of adult insects. Moulds are less sensitive to ionising radiation than insects, and different strains show different levels of sensitivity; generally most fungi are killed by a total dose of 10 kilo Grays (kGy). Despite its power, gamma irradiation does not induce any secondary radioactivity, does not damage oil and tempera polychromy, leaves no hazardous residues and penetrates completely into the objects. Moreover, a large quantity of materials can be treated at one time. Paper is much more sensitive than wood to the effects of gamma radiation. A possible negative effect of gamma rays on musical instruments has been verified in the modification of the "sound" of a violin after treatment. Repeated treatments are not recommended because the effects are cumulative. Gamma rays have recently been employed to cause the polymerization of resins used in the impregnation of decayed wooden objects. In this case, wood-boring insects are exterminated at the same time.

High-frequency current can be used to kill wood-destroying insects (Anobiidae), but only in the absence of metals (Van Der Molen et al. 1980).
Low-frequency electrical current systems have recently been used to keep away birds from roosting on monuments (Horakova and Mertinek, 1984). This method is completely harmless for animals and humans.

Heat (dry or wet) is used in the disinfestations and disinfections of organic materials. The application of moist heat for disinfections of books is still one of the most widely used techniques (Zuffi, 1988). A temperature of 95°C and 40% RH for 4 hours is recommended.

Other methods used to eliminate infestations of books are exposure to blast-freeze temperatures or to substitute the atmosphere in close container with N₂ or with O₂ scavengers (concentration below 0.05%). Reduction in pressure, using vacuum dryers, causes cell's explosion. Use of light traps for controlling insects attracted by light, in museums, and the exclusion of light, using opaque plastic sheets, to prevent the photosynthesis by biodeteriogens present on statues in wooden environments are the other common methods suggested for physical control biodeteriorating agents.

**Biological Methods:**

This application is based on the presence of parasitic or antagonistic organisms of the biodeteriogens. Bacteria, insects and phage might be used, but up to now this kind of intervention has been applied chiefly in the agricultural sector. Antagonistic or predators species have been introduced for pull away the birds from cities.

**Biochemical Methods:**

In this group of biodeterioration control systems, the chemical compounds of biological origin are used, even if many of these are now synthetically produced.
Antibiotics are substances produced by microorganisms during their growth in order to avoid the competition of other species, which are inhibited or killed. These compounds are active at very low doses, but can lose effectiveness after storage. The enzymes are proteins that catalyse biochemical reactions. They have been used on rare occasions as biocides and are sometimes mentioned for cleaning of adhesives (Gargani, 1968).

The proteolytic enzyme trypsin has been used for the removal of lichenic crusts, but reports have indicated disadvantages in the practical difficulty of maintaining a good enzymatic activity, as a function of temperature and pH (Sorlini, 1984).

Pheromones are volatile substances produced by one individual, which have a specific action on the opposite sex of the same species. Some experiments have been made with one of this for controlling insects in museums with sexual attractants traps. These substances could by very useful as preventive, taking into account the difficult for liquid biocides to deeply penetrate inside the object attacked by boring insects.

**Chemical Methods:**

Many organic and inorganic compounds have been used, as biocide agents, to eliminate the biodeteriogens from cultural objects.

Pesticides are chemicals used for killing undesirable biological growth. They have a biocide action with a specific toxicity for the species to be eliminated. These are classified in different ways depending on their chemical nature (e.g., organic or inorganic) or on the target pest species. It is also possible to classify pesticides according to their chemical groups or their mode of action. In addition to the
pesticide, other ingredients, such as carriers or additives to improve the effectiveness of the product or to facilitate its application, are present in the chemical formulation. These are called coformulants and could have negative effects on the objects to be treated.

Disinfectants are chemicals that destroy vegetative forms but are not always effective against survival resistant or quiescent phase structures (bacterial spores, fungal conidia and insect eggs).

A side problem with the use of pesticides is the persistence of the product in the soil or water. This problem is especially prevalent with herbicides that are applied or dispersed in external environments, with high risk for soil and water contamination.

Inorganic Substrata:

The biodeterioration of monumental stones, rock and archaeological remains is a worldwide problem. In fact, the growth and development of many organisms, belonging to different systematic groups, acting alone, together or in ecological succession, surely enhance the stone decay and makes their conservation more difficult. For these reasons adequate interventions must be taken to stop or at least slow down the biodeterioration process.

Once assessed the active presence of organisms on stone monumental surfaces and before to adopt any remedial measures, is necessary to properly evaluate the entity of damages induced by this presence. In fact, when this is very slights and a regular maintenance is impossible, any biocide treatment is useless. The same when the biological patina (lichens) could act as protective layer against
major injuries due to physical-chemical factors. Otherwise is necessary to intervene in order to eliminate or control the biodeteriogens.

Many authors have used several products having biocide characteristics, in order to eliminate the biodeteriogens developing on stone monuments or rock sites. These products are commercially available both as active principle or formulate and cover a wide range of chemical classes, from very simple inorganic compounds such as Na and Ca hypochlorite to very complex organic ones such as the Quaternary Ammonium Compounds (Preventol R50, Neo-Desogen). Furthermore, they can possess a strictly specific mode of action such as the urea derivatives (Diuron, Karmex) that block the photosynthetic process, or a broad toxic spectrum like the Organotin compounds (TBTO). A list of the most frequently applied products and the different methodologies used for their application are described in various articles (May et al., 1993; Caneva et al., 1991; Richardson, 1976, 1988; Capponi and Meucci, 1987; Allsopp and Allsopp, 1983; Martin and Johnson, 1992; Tiano and Caneva, 1987; Misra et al., 1995). Any biocide intended for use on historic monuments and rock sites must be not only effective against biological growths but at the same time cause no damage to the stone material either by direct action or by leaving deposits on it which may result in successive damage (May et al., 1993; Ciarallo et al., 1985). Furthermore, these products must be tested under similar "real case" conditions as the interactions among type of substrates, biocides and organisms can give a more realistic indication of how a biocide will perform in situ (Allsopp and Allsopp, 1983).

The treatment of weeds and higher plants can be made either using pre or post-emergence products. In the first case the treatment must be done in winter in
order to block the seed's germination; in the second case the treatment is made in summer by spraying the product (piloram, sebumenton) on leaves.

The problem represented by the birds roosting on monuments can be easily solved by placing on these either low current wires or simple plastic needles (unaesthetical). The more general problem of the invasion of the urban areas by this fauna has been fronted either with the use of feeding materials mixed with anti pregnant products together with their periodic capture and release in other sites.

**Effectiveness of Action of Biocides:**

The product should be chosen on the basis both of the organisms to be eliminated and of its highest efficacy at lowest dosage (Caneva et al., 1996). Normally the results of positive biocide treatments are clearly visible on the "in situ" biological growth with the exception of lichens which can remains macroscopically unchanged for a long time even if the treatment was effective (Mishra et al., 1995). The lasting of a treatment in outdoor conditions is ranging from 1 to 3 years depending both on type of the chemical used and environmental conditions to which the treated stone is exposed. Moreover, if the biocide must be wash off, after its action, or leave as preventive on the surface is a matter of discussion (Tiano, 1979; Frey et al., 1993), included the extreme suggestion made for the conservation of the Acropolis of Athens, where the preventive biocide treatments of the critical spots, perhaps even the whole buildings, seem to be as unavoidable as daily tooth brushing for the biological status of human teeth (Tiano et al., 1994).
Interaction Biocide/Stone/Organisms:

Possible negative effects on stone surface treated with biocides have been detected either with SEM observations or determined by colorimetric measurements (Nugari et al., 1993; Anangnosidis et al., 1995). It was ascertained the influence (positive or negative) addition, the same biocide can be more or less active on different strains present in the consortium to be eliminated (Young et al., 1995). Hence the selected biocide should always be tested on test specimen made with the same material of the monument, possibly colonized with the same biocenosis developing on it. More recently some applications have been made using protective or consolidating polymers alone or mixed with biocides in order to enhance their efficiency (Grant and Bravery, 1985; Tiano et al., 1995a,b), while simple cleaning procedures with water-jet have been tentatively used for eradicate biological growth (Leznicka, 1992). The ultimate approach is to increase the susceptibility of organisms to biocides prior to treatment, using product as EDTA (Pentazidou and Theoulakis, 1997) or ionizing radiation (Tayler and may, 1994) which could lead to the use of even lower concentrations of biocides with low environmental impact. Some attempt have been made using enzymes such as protease instead of biocides for the elimination of lichens (Petushkova et al., 1988; Caneva et al., 1991).

Organic Substrata:

The organic materials require more care during treatment. Most of these objects are maintained in closed environment and the development of biodeteriogens, especially microfungi, is always due to unexpected increasing of the water content of the air or of the material itself. Thus the first steps is to individuate the source of the humidity and to block it, then the material could be dried in a
ventilated environment, and successively the biological infestation can be gently brushed without any chemical treatments. The application of biocides is foreseen in very special cases, when a material is heavily attacked and for different reason the drying is very difficult or too slow.

For the elimination of bacteria, microfungi and actinomycetes have been used either specific products such as antibiotics or broad-spectrum biocides, in the first group, streptomycin pimaricin, kanamycin, echinazol and nystatin, together with pimaricin, for the treatment of textiles with good results (Hill, 1990). In the second group have been used the same products used for inorganic substrata (TBTO and Benzalkonium chloride) together with some chlorine derivatives (sodium pentachlorophenate, O-phenyl-phenol, P-choro-m-cresol) very active against fungi but with possible drawbacks due to the liberation of chlorine in the substrate.

For the elimination of insects developing inside wooden structures the best solution is the use of poisonous gases, highly penetrating and effective also against eggs, but this is practically very difficult to do. This treatment needs special precaution and mobile objects can be treated. Normally these biodeteriogens are eliminated with application of insecticides, either of synthesis (dichlorovos and dieldrin) or natural derivatives (resmethrine and permetrine), in organic solvents. The efficiency of the treatment is linked to a complete absorption of the product by the wooden structure because its action (neural block) is effective only after the ingestion of treated wood by the larvae.

In deposit and unsafe confined environment there exist the possibility that small rodents can deteriorate the objects made with organic materials. In this case specific products mixed with food (rice or flour) can be leave inside.
Application Procedure:

Spraying and brushing of diluted biocide solutions are the most common systems of treatment. The spraying method is preferred for paintings with a very deteriorated surface layer and, generally, when the component material is in poor condition. In the case of organic materials, such as paintings of paper, prints, parchment or old books, spraying or brushing biocides is not always possible because some liquid solutions can dissolve pigments and inks.

Application of poultices is carried out especially in the case of hard encrustations in order to increase the contact time and use the dissolving action of water itself. These compresses are made of carboxymethyl cellulose, paper pulp or inert materials that are soaked in the biocide solution. They are covered with sheets of polyethylene or something similar in order to reduce dehydration of the compress itself. The length of application ranges from one day to several days. Sometimes the chosen biocide can be added to a gelatinous solvent paste used for cleaning stone and mural paintings. In some cases, the removal of biological or chemical incrustations on stone is obtained through non-selective absorbent clays (e.g., sepiolite or attapulgite).

Injection of pesticides, using the larvae’s tunnels, can be used to increase their diffusion for infested wooden structures. When trees or bushes have high root system and their eradication can be dangerous the injection of concentrated antigerminative substances inside stumps, is needed to completely block new emergencies. In the case of subterranean termites, injection is performed under pressure into the soil.

Fumigation methods are widely employed for organic materials. The treatment consists of distributing the fumigant (gas) in the air and through materials.
This method has rapid effectiveness and reach deep penetration inside the object. Due to the high toxicity of fumigants, they must be applied in airtight chambers or in perfectly sealed spaces (sometimes created with polyethylene sheets), where the pressure can be modified to improve the penetration of the gas. Fumigants require highly trained applicators and have no residual effects after aeration. As an alternative to conventional fumigation techniques, researchers have recently investigated the possibility of employing inert gases, such as nitrogen, together with low RH for controlling museum pests (Nugari et al., 1987; Gilbert, 1989). The advantage of this system is that it is safe, inexpensive and not invasive, but more tests are necessary to assess its effect against the various species of microorganisms and insects. Treatments with substances active as vapour have similar advantages and, moreover, do not require complicated equipment because the products generally used in vapour form are not very toxic. The object can be treated in a polyethylene bag or airtight cabinet to permit the concentration of vapours.

When either spraying and brushing treatments or poultices are used, it is sometimes advisable to wash off the biocide residues in order to avoid possible secondary reactions (due to the degradation of products) or toxicological difficulties (high-persistence products on premises open to the public or for operators).

The time necessary for a substratum to be reinfested by biodeteriogens is depending on the preventive measures taken for its conservation. This can be very long (several years) if the restored objects are maintain in conditioned and safe confined spaces. Otherwise, it is surely very short (1-2 years) when these objects can not be moved inside and are left exposed in outdoor conditions, even if a biocide treatment is left as preventive.
Indirect Methods:

In this method certain measures are used to control the environment surrounding the objects. The control of weather variables is practically inapplicable for monumental stones, while for rock sites the construction of protective structures, preventing the water run-off of surfaces, can effectively reduce the biological growth (Valentin et al., 1990). An effective and simple good practice for limit the biodeterioration of exposed stones is their maintenance. In fact, the periodical simple cleaning of exposed surfaces eliminate the "soiling" effect due to the deposit of environmental particles, which can favour the development of reproductive bodies. Furthermore, after stone cleaning interventions some chemical substances (protective coatings or consolidants) can be applied to the object in order to increase its water repellence and cohesion. These products may prevent or retard the recolonization of the substrate decreasing its porosity, roughness and water content, but in critical environmental conditions, they could favour the development of specialized micro flora.

In order to reduce the biological risk, for the organic objects maintained in confined environments, taking into account that in our climates the temperature and humidity are for long periods of time favourable to the development of the widespread biological reproductive bodies (conidia, spores and eggs), these should be conditioned at values of temperature ranging between $16^\circ$ to $18^\circ$C and at relative humidity level below the 60%. This humidity value can be a limiting factor for the development of fungi.

Preventive measures against insects attack are the conservation of the objects inside cardboards, boxes or glass cases treated with insecticides, further the circulation of flying insects can be reduced with air filter and thin wires screens.
Bioremediation:

Chemical and physical techniques have been widely used for the cleaning of cultural objects but in order to decrease any possible risk for the materials treated, innovative systems related with biological methods have been introduced in this sector starting from the biological pact (Young and Wainwright, 1995).

Enzymes, such as lipase, have been successfully used to remove aged acrylic resin coatings in paintings (Moncrieff and Hempel, 1970), while for the removal of sulphates, nitrates and organic matter from artistic stone works, carefully selected microbial cultures have been used (Bellucci et al., 1999; Heselmeyer et al., 1991). A similar methodology has been applied for the elimination of insoluble calcium oxalate patinas from monuments. In fact, some bacteria and actinomycetes living in soils use the oxalate salts as sole source of carbon and energy (Ranalli et al., 2000).

The biomineralization process has been investigated in order to develop a new conservative method for monuments restoration. The precipitation of new calcite crystals inside stone samples was primarily tested utilizing the mineralization process mediated by the organic matrix extracted from mineralized hard parts of marine organisms. Preadsorption of soluble acidic matrix glycoproteins extracted from the shell of the mollusk Mytilus californianus was found to increase the amount and depth of penetration of calcite crystals formed inside the stone structure with a significant decrease of its porosity (Tiano et al., 1996). Furthermore, such a treatment seems to improve the stone superficial mechanical strength (Tiano et al., 1992).

Also, the precipitation of calcium carbonate crystals produced in nature by bacteria has been applied using specific bacterial Bacillus cereus strains (Tiano,
1995), even if the use of heterotrophic viable organisms does not seem appropriate for this purpose. In fact, chemical reactions with stone minerals due to metabolic by-products and the growth of fungi, due to the application of organic nutrients for bacterial development, can have negative effects on monumental stone materials. The results obtained using *Bacillus subtilis* and *Micrococcus sp.*, seem chiefly influenced by the presence of a big microbial mass, due to bacterial growth, rather than to the presence of new crystals due to calcite precipitation (Orial *et al.*, 1993). For these reasons the study of the genetic mechanism that controls bacterial calcite precipitation has been started. The *Bacillus subtilis* strain has been mutagenized and not-precipitating mutants isolated. This mutation has been successfully transferred, by transformation, to another *B. subtilis* strain, showing that it affected one gene only. The isolation of this mutant suggests the presence of a genetic control for crystal formation. Characterization of this mutation, and of possible other mutations, should allow the identification of the protein (s) involved in the process (Tiano *et al.*, 1999).