

## POLYMERS AND RESINS AS FOOD FOR MICROBES

Robert J. Koestler

*Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art, 1000 Fifth Avenue, New York, NY 10028-0198, USA*

**Key words:** biodeterioration, polymers, resins

**Abstract:** Preserving art objects, especially outdoor stone ones, from the ravages of man and time often entails application of a polymeric material. Unfortunately, some of these products may support or actually encourage microbial growth and cause unintentional problems. This paper summarizes studies that developed a screening test to quantify the effects of fungal activity on a variety of consolidants and resins, and FTIR-fungal studies on silicone-based resins. One of the studies was a five-week assessment of the ability of a mixture of six fungal species to use sixteen different polymer formulations. A quantitative ranking scale was developed for the products using a combination of organism growth, sporulation, weight change, and chemical change data. These data were applied in Duncan's Multiple Range test and Student-Newman-Keuls' test to statistically rank a series of conservation materials for their susceptibility to fungal attack. The products tested included three acrylics, five polyvinyls, five silicone-based polymers, one polyimide, and two natural resins. Damage to the products ranged from complete degradation to very little change. Some of the products that are degraded the most are quite prevalent in field use today (i.e., Conservare H40, Conservare OH, and Acryloid F-10). Fungal degradation may be related to the abundance of silanol molecules (Si-OH) for silicone-based products, C-H bonds for carbon-containing products, or the presence of 'inert' material used as bulking agents.

## 1. INTRODUCTION

Physical breakdown of materials is a subject that has long been studied with the aim of developing more durable materials and preserving art objects. Stone, one of the more durable materials, does nonetheless deteriorate. Deterioration of stone, whether in a man-made monument or in its natural form, is a constant and natural phenomenon, and can occur as a result of many causes, including those that are physical, chemical, mechanical, and biological. Recently researchers have begun to investigate how biological phenomena--at times in synergy with physical, chemical, and mechanical effects--can exacerbate deterioration of historically or culturally important stone materials (Koestler et al., 1994, 1997). Not only has the biodeterioration of stone become a topic of interest to the art conservation community, but also the susceptibility to biodeterioration of preservative materials applied to art objects has begun to be investigated (Koestler and Santoro, 1986, 1988; Leznicka et al., 1991; May et al., 1993; Nugari and Priori, 1985; Salvadori and Nugari, 1988). Preserving art objects, especially outdoor stone ones, from the ravages of time may entail application of one or more polymers or resins to the object. The material applied may be used as a waterproofing agent, as a (reinforcing) binding matrix to help hold the object together, or as a protective surface coating. Unfortunately, some of the products used may do more than expected and/or desired. They may act as a food source for and encourage the growth of microbes that inhabit the surface or interior of an object and lead to deterioration of that object.

There are many types of preservative treatments. The main types used today fall into four categories: silicone-based chemicals, which include silicone resins, alkoxy silanes, and silicate esters; synthetic organic polymers, which include acrylics, epoxies, vinyl polymers, and polyurethanes; inorganic materials, which include the alkali earth hydroxides such as barium hydroxide and various siliceous compounds such as silico-fluorides (many include the silicate esters within this group rather than with the silane-based treatments); and waxes and natural resins.

Assessing the resistance of a protective polymer or resin to microbiological attack is typically a lengthy process necessitating long-term field trials. Laboratory studies attempt to predict field trial results in a reduced time frame and have some advantages over field trials since micro-scale changes in the materials are more easily noted and studied in the laboratory. Often large-scale testing of materials can be avoided by application of a short-term screening test to narrow the field to those materials that are potentially the least susceptible to microbial attack. The screening study described in Part 1 assayed 16 polymers and resins for their resistance to fungal attack during a five-week screening period.

long been studied  
serving art objects.  
heless deteriorate.  
t or in its natural  
occur as a result of  
, mechanical, and  
te how biological  
, and mechanical  
lturally important  
he biodeterioration  
mmunity, but also  
ials applied to art  
oro, 1986, 1988;  
, 1985; Salvadori  
r stone ones, from  
polymers or resins  
roofing agent, as a  
or as a protective  
may do more than  
or and encourage  
of an object and

main types used  
, which include  
organic polymers,  
thanes; inorganic  
parium hydroxide  
many include the  
ased treatments);

r or resin to  
itating long-term  
rial results in a  
als since micro-  
l studied in the  
be avoided by  
o those materials

The screening  
their resistance

In addition to the screening study, seven polymers and resins were subjected to one or two months of fungal growth and then analyzed by Fourier transform infrared spectroscopy in an effort to quantify chemical bond changes that occurred as a result of biological action. This is summarized in Part 2.

The main source of biological contamination of stone is the surrounding soil, which usually contains large numbers and many different types of bacteria, fungi, and algae (Strzelczyk, 1981). These can contaminate the stone shortly after quarrying, or they may be within the stone before quarry extraction. Stone can also be contaminated by windblown detritus or by rising groundwater infiltration. The effect of microbial attack is not necessarily confined to the surface of the stone: Many studies have shown that microorganisms and organic matter may penetrate stone from depths of a few centimeters to almost a meter, especially, in cases of porous limestones or sandstones (Koestler et al., 1985; Krumbein, 1972). The organisms found within and colonizing the surfaces of rock and stone are essentially the same as normal soil microflora, both heterotrophic and chemotrophic organisms (Webley et al., 1963). The various microorganisms constitute a complex ecological intercommunity capable of carrying on the normal processes of stone weathering and soil formation.

Many bacterial heterotrophic species have been isolated from stone. Stone in the open air is likely to be covered and infiltrated with dirt and organic matter from rain, groundwater and airborne sources, and animal sources such as pigeon excrement, which has been seen to be a rich source of nutrients and encourages deterioration of marble statues (Bassi and Chiatante, 1976). These have been shown to contribute to the dissolution of siliceous and calcareous stones by the production of various organic acids, mainly 2-ketogluconic acid (Henderson and Duff, 1963). Bacteria isolated from calcareous sandstone monuments have been shown to have the ability to cause severe, rapid weight loss in sandstone by attack of the calcareous matrix of the stone with organic acids (Lewis et al., 1987). A variety of fungi have also been isolated from and associated with decaying stone (Bassi and Chiatante, 1975; Koestler et al., 1985); the fungi are generally assumed to attack stone by the excretion of organic acids, such as oxalic, citric, and fumaric acid.

The majority of previous studies on consolidants have focused on aspects of chemical or mechanical deterioration--not on biological deterioration. On a macro scale, it is of use to establish the relative durability of selected polymers and resins, in addition to understanding the mechanisms of deterioration. The screening study was designed as a way of measuring on a macro scale the relative biodurability of polymers and resins and thus providing the conservator with a fuller understanding of their strengths and



weaknesses, in this case knowing the relative susceptibility of these polymers or resins to fungal deterioration.

Clearly the physical and chemical state of the active agent (e.g., consolidant, catalyst or additive) is important in assessment of microbiological attack (Hueck et al., 1968). After the active inhibitory agents fade, the protection value of the film as a barrier covering the material to which it was applied continues to be important. Some assessment of effects of washing and leaching of potential inhibitory components as related to weight loss were noted and are presented in the full study (Koestler and Santoro, 1988). Therefore, the stability of the coating over time is an important factor in evaluating its efficacy in preventing biological attack. Another important consideration is the permeability to moisture and gases; this will have a marked effect on microbial growth.

## 2. PART 1, THE SCREENING STUDY

For the 5-week screening study, materials selected were polymers and resins currently used in conservation or of research interest. The methodology of the biodeterioration testing has been reported in full in Santoro and Koestler (1991) and is summarized below. Using short-term laboratory exposures under conditions of high relative humidity, 16 samples of polymers and resins were evaluated for their ability to support fungal growth. Growth of the organisms was ascertained by assessing macroscopic, microscopic, and physico-chemical changes of these materials over the 5-week testing period. Based upon their sensitivity to fungal deterioration, the polymers and resins tested were ranked in order of least to most susceptible to biological attack.

Briefly, multiple samples of each consolidant, prepared as a thin film on large glass slides, were inoculated concurrently with two different concentrations (104 and 108 spores/ml) of fungal spore mixtures. Fungi utilized were: 2 *Penicillium* spp; *Fusarium* sp.; *Cladosporium* sp.; and 2 *Aspergillus* spp. Inoculated samples were grown in a temperature- and humidity-controlled chamber for 5 weeks and assayed weekly using grid matrix and random field procedures for signs of visible growths of fungi, for weight loss after fungal action, and for chemical changes to the consolidant after fungal exposure. Details of sample preparation and exposure conditions can be found in Santoro and Koestler (1991).

The polymers and resins tested are listed in the following table.

## Polymers and resins tested in 5-week screening study

Product name	Manufacturer	Additives or contaminants
<u>Acrylics</u>		
Acryloid B-72	Rohm and Haas	Information not available (2)
Acryloid F-10	Rohm and Haas	Information not available (2)
Rhoplex AC-234	Rohm and Haas	Formaldehyde <0.08% (1) Ammonia <0.3%. (1) Probably soaps as emulsifiers
<u>Polyvinyls</u>		
Bakelite-AYAA	Union Carbide	No additives (2)
Bakelite-AYAC	Union Carbide	Acetic acid <0.05% (1)
Bakelite-AYAF	Union Carbide	No additives (2)
Bakelite-AYAT	Union Carbide	No additives (2)
Mowital B-20-H	Amer. Hoeschst	No additives; may be some byproducts from the polymerization process such as PVAC, PVOH, butyraldehyde (2)
<u>Silicones</u>		
Conservare H	ProSoCo	Dibutyltin dilaurate = catalyst (2)
Conservare H40	ProSoCo	Dibutyltin dilaurate = catalyst (2)
Conservare OH	ProSoCo	Dibutyltin dilaurate = catalyst (2)
Silicone 1048	General Electric	100% silicone resin (2)
Tegovakon V	Goldschmidt	Solvent + alcohol (2) Tin catalyst (2) Silicic acid ester = binder replacement
<u>Polyimide</u>		
Imron 192S	Dupont	HCl or triethylamine as an initiator (3) Activator 192S has no additives (2)
<u>Natural resins</u>		
Dammar	AF Suter	Natural resin
Shellac	AF Suter	Natural resin

(1) Manufacturer's literature and/or safety data sheet

(2) Phone call to manufacturer

(3) Jim Druzik, The Getty Conservation Institute, Los Angeles, CA

## 2.1 Organism growth assessment

Over the 35-day exposure interval, fungal growth was mixed, with Imron 192S, Dammar, Conservare H40, Mowital B-20-H, Bakelite-AYAF, and Bakelite-AYAT showing consistently high fungal growth over the testing interval.

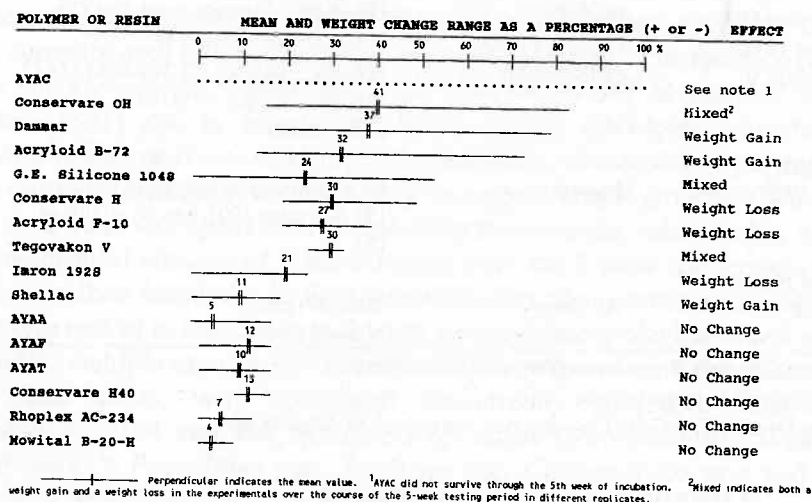
Conversely, G.E. Silicone 1048, and Rhoplex AC-234 showed no fungal growth or minimal growth over the interval. Bakelite-AYAC showed little growth over 2 weeks at which time the exposed strips broke up--this was not seen in the controls and was therefore assumed to be related to fungal attack.

Indeed AYAC is not noted to be resistant to at least bacterial attack (product literature, Union Carbide Corp., USA).

In order to combine these polymers and resins into statistically significant groupings ( $\alpha \geq 0.05$ ), a Wilcoxon's two-sample test was performed from the individual data points. Little consistency in the pattern of growth for polymers or resins within a similar group (e.g., polyvinyl acetates) was noted over the study (see Koestler and Santoro, 1988 for detailed discussion).

Comparisons of the random field procedure (RFP) to both visual and optical viewing techniques revealed that the RFP proved to be more precise than the visual scoring procedure and provided numerical assessment in a statistically valid manner, especially when compared to higher magnification viewing (Koestler et al., 1988). In many cases visual scoring proved too inaccurate due to discoloration of the sample from the sterile water droplet rather than from actual fungal growth. High magnification viewing provided a check on fungal reproduction (by the presence of fruiting bodies).

Table 1. Mean weight change of the polymers and resins over the 5-week exposure interval.



## 2.2 Weight Loss Measurements

For the majority of the polymers and resins tested, no massive weight losses or gains were noted for control or experimental samples (see Table 1). The weight loss methods allowed for observation of large weight changes. It should be noted that some polymer and resin material was lost when scraping the material from the slide. In addition, after washing, some organisms could have adhered to the sample, resulting in higher weights associated with the

Robert .

experim  
weight c  
had we  
samples  
31-60%  
differen  
Imron 1  
which  
Convers  
fungus-  
of organ

## 2.3

Port  
transfor  
below:

- Silic
- than
- Poly
- chan
- individ
- inter
- Poly
- Acry
- C-H
- Acry
- show
- Natu
- Whi
- hydr
- Poly
- The
- chemica
- change a
- and por
- obtaine
- the othe
- investiga



erial attack (product  
 atistically significant  
 performed from the  
 growth for polymers  
 ) was noted over the  
 sion).

to both visual and  
 d to be more precise  
 ical assessment in a  
 higher magnification  
 scoring proved too  
 sterile water droplet  
 on viewing provided  
 g bodies).

week exposure interval.

Δ (+ or -)	EFFECT
100 x	
...	See note 1
	Mixed <sup>2</sup>
	Weight Gain
	Weight Gain
	Mixed
	Weight Loss
	Weight Loss
	Mixed
	Weight Loss
	Weight Gain
	No Change
	No Change
	No Change
	No Change
	No Change
	No Change

... indicates both a  
 .. indicates both a

no massive weight  
 mples (see Table 1).  
 weight changes. It  
 lost when scraping  
 ne organisms could  
 associated with the

experimental trials. To account for these sources of error, an arbitrary 15% weight change was considered not to be significant. Seven polymers or resins had weights that were essentially unchanged (<15%) from the control samples, 5 had a change in weight of 15-30%, 3 had a change in weight of 31-60%, and one fell apart completely. Of the materials showing a weight differential from the controls, AYAC, Conservare H, Acryloid F-10, and Imron 192S consistently had weight losses associated with the experimentals, which could signify loss caused by fungal grazing on the surface. Conversely, Dammar, Acryloid B-72, and Shellac had weight gains in the fungus-exposed test strips, which could signify water absorption, or adhesion of organism remnants on the polymer or resin during the weighing procedure.

### 2.3 Qualitative Fourier Transform Infrared Spectroscopy

Portions of each polymer and resin samples were analyzed by Fourier transform infrared spectroscopy (FTIR). The conclusions are summarize below:

- Silicone Resins--Most of the silicone resins showed stronger OH absorption than the controls, indicating a higher degree of hydration.
- Polyvinyl Acetates--Each of the PVACs showed different patterns of changes. However, these changes seem to be consistent within the individual polymer sets. There were apparent differences in carbonyl intensities, indicating a change in C=O bonds.
- Polyvinyl Butryl--Polymer seemed unaffected by fungal growth.
- Acrylics--Samples of Rhoplex showed variations in peak height ratios of C-H stretch bonds that correspond to chain breakage. Samples of Acryloid B-72 did not exhibit these changes. Samples of Acryloid F10 showed slight and inconsistent changes.
- Natural Resins--Dammar appeared to be unaffected by fungal exposure. While Shellac showed slight changes consistent with those expected from hydrolysis and chain scission.
- Polyimide--Imron showed some hydration of the samples.

The inconclusive nature of the results may have resulted because the chemical changes were below the sensitivity limit of FTIR, which is a 5% change and/or because the fungal growth on the samples was inhomogeneous, and portions of the sample without growth were analyzed. The results obtained, however, neither support or refute the biological effects observed in the other parts of the study. Part 2, reported below, attempted to further investigate chemical changes with FTIR.

## 2.4 Sporulation assessment

Assessment of the sporulation scale versus the other growth parameters used in the study showed good agreement with the RFP procedure and high magnification viewing.

As would be expected, the sporulation scale approximates the colony growth data. However, in certain consolidants such as G.E. Silicone 1048, sporulation was not evident until the fifth week of the experiment. Imron 192S, on the other hand, viewed at the fifth week of incubation showed no sporulation despite having had fruiting bodies during the first four weeks of incubation. Acryloid B-72 and Acryloid F-10 had consistently higher sporulation, which was not manifested in a greater colony growth formation.

## 2.5 Composite Scoring

This study developed physical and chemical methods with which to describe deterioration associated with fungal interaction on a coating surface. In the conservation field a combination of the factors of weight change, chemical change, and physical change are of importance to the conservator, over and above growth of the organism on a substrate. Thus the conservator may not care if an organism resides on the surface of a coating but would consider the effects of this residence--for example, discoloration of the object or a resultant loss of weight or a chemical change--to be of greater importance. With this in mind, a priority order was assigned to the results of the Wilcoxon's two-sample test for sporulation and colony growth, weight change, Duncan's Multiple Range Test and the FTIR results. By convention these groupings were set up for each of the above results (low, medium and high) and numbers were assigned (a 1, 2, or 3, respectively) to consolidants/resins within the groups as a weighting factor to give greater value to those effects believed to be of most importance to conservators. For example, an organism sporulating on the surface of an object would not necessarily be visible to the naked eye, or lead to colony growth; therefore it is of lower importance than a large colony growth resulting in a discoloration of the surface. The weighting scale employed gave greater emphasis to weight change, less emphasis on colony growth, and the least emphasis on the sporulation scale and the FTIR results. The results of this scoring are presented in the Table 2. In brief, the lower the composite score, the less affected the polymer or resin was by the fungi.

Ro

Tab

Rho

AY

Teg

G.E

AY

Mo

Con

Acry

AY

She

Con

Dan

Imro

Acry

Con

AY

<sup>a</sup> Ba<sup>b</sup> Ba<sup>c</sup> Ba<sup>d</sup> Fir

sam

<sup>e</sup> Lo

3.

3.1

of s

dete

deca

then

mat

deer

state

Con

sulta

resu



Table 2. Polymer and resin composite scoring.

Polymer/Resin	Sporulation <sup>a</sup> scale	Weight <sup>b</sup> Change	Rankings		FTIR <sup>a</sup>	Totals <sup>e</sup>
			Colony <sup>c</sup> Growth	Multiple <sup>b</sup> Range Test		
Rhoplex AC-234	1	3	2	3	2	11
AYAA	1	3	4	3	2	13
Tegovakon V	1	6	2	3	1	13
G.E. Silicone 1048	1	6	2	6	1	16
AYAF	2	3	4	6	2	17
Mowital B-20-H	2	3	6	6	1	18
Conservare H	2	6	4	6	1	19
Acryloid B-72	2	9	4	3	1	19
AYAT	2	3	6	6	2	19
Shellac	2	3	6	6	2	19
Conservare OH	1	9	2	6	2	20
Dammar	2	9	6	3	1	21
Imron 192S	3	6	6	6	1	22
Acryloid F-10	3	6	4	9	1	23
Conservare H40	3	3	6	9	2	23
AYAC <sup>d</sup>						>23

<sup>a</sup> Based upon a factor weight of 1.

<sup>b</sup> Based upon a factor weight of 3.

<sup>c</sup> Based upon a factor weight of 2.

<sup>d</sup> Final composite rank not computed since fungal treatment resulted in complete breakup of samples

<sup>e</sup> Lower scores indicate more resistance to fungal attack

### 3. DISCUSSION

#### 3.1 Criteria for Protective Coatings

The conservation of stone monuments usually follows a standard sequence of steps (Torraca, 1975). The object being treated should be studied to determine the extent of the damage and the cause or causes of the damage or decay, with the idea of eliminating these factors if possible. The surface is then usually cleaned, with the physical or chemical removal of dirt, foreign materials or weathering crusts. Preconsolidation of the surface may be deemed advisable before cleaning if the surface is friable or in an advanced state of decay. Stone that has lost cohesion is then treated with a consolidant. Consolidation is the impregnation of the damaged areas of stone with a suitable product that reaches down into the underlying undamaged layers, and results in a strong cohesive structure. Surface protection consists of a

superficial film applied to unweathered stone as a preventive measure, or applied to weathered stone after consolidation treatment. This is meant to act as a barrier to the actions of atmospheric pollutants, rainwater, or biological growths, while at the same time the surface coating should be permeable to water vapor within the stone. Surface treatments may also be effective in reducing the defacing of the surface by graffiti, by allowing spray-paints and the like to be removed more easily. A surface coating may sometimes replace consolidation when the stone surface has been eroded but the remaining stone is sound. Reconstruction, or the assembly of pieces of cleaned and consolidated stone with an adhesive, may sometimes also be needed.

### **3.2 Biocidal Agents**

The proprietary nature of the materials tested, and manufacturer reticence, precluded a precise understanding of any potential biocidal additions in the 16 products tested, but the available information indicated that six of the polymers contained additives that may act as a biocide. One such additive is dibutyltin dilaurate, which is contained in Conservare H, Conservare OH, Conservare H40, and, perhaps, Tegovakon V. Other presumed additives that may have a biocidal effect are formaldehyde, contained in Rhoplex AC-234, and acetic acid, contained in AYAC. Proceeding from the assumption that six of the polymers and resins contained biocides, these six were examined for changes in colony growth and/or sporulation which might be associated with a perceived leaching effect of potential active biocidal agents presumed present in the polymers. Based upon this analysis, no apparent biocidal effect was noted.

Of the 10 polymers and resins that did not apparently contain any biocidal additives or contaminants, only one, G.E. Silicone 1048, showed a lag phase of sporulation over the study period. No sporulation or growth was noted over the first 4 weeks of incubation, but after week 5, an average number of fruiting bodies was noted, although with no apparent colony growth. This could indicate a short-term resistance by G.E. Silicone 1048, followed by organism growth.

### **3.3 Polymer and resin composite scoring**

It is apparent that no polymer class behaves in a uniform manner when subjected to fungal spores; therefore, no class can be chosen based upon any one positive feature (i.e., low growth, no weight change, etc.).

For example, Table 2 shows that silicone-based polymers can be both resistant to fungal attack (e.g., Tegovakon V) and poorly resistant (e.g., Conservare H40). Due to a lack of company-supplied product data and failure

of the FTIR to detect any significant bond changes, it is not possible to determine why one silicate ester is better than another; this is also generally true for the other polymer and resin classes studied. There is, however, some suggestion that during reformulations of some products, e.g., Conservare H40, up to 5% of 'inert' material may be added to 'bulk up' the product. Additives at this level would not be detected by FTIR. Further, the additives, from the manufacturers' point of view, need only prove inert to the consolidating activity of the product, not inert to microbes. It may be that a product like Tegovakon V has little or no 'inert' material added to it and, therefore, is less biodegradable than a product with 'inert' additives.

The acrylic polymer class also showed divergent behavior. Acryloid F-10 showed poor resistance to microbial growth while Acryloid B-72 showed moderate resistance. Rhoplex AC-234 ranks as the best overall in resistance to fungi.

The polyvinyls, composed of polyvinyl acetates (PVAs) and polyvinyl butryl (PVB), were interesting. As a group, the PVAs all showed moderate to good resistance to biodeterioration, AYAA, AYAF, and AYAT having composite scores of 13 to 19, with the exception of AYAC that had what we consider to be the most significant break-up of all experimental samples in that the fungus-exposed resin did not survive past week two of the experiment, while the control remained intact to the end of the 5-week test. The single sample of a PVB, Mowital B-20-H, showed better resistance to microbiological deterioration than the polyvinyl materials AYAT or AYAC. The product literature for the PVAs claims all but AYAC do not support bacterial growth. AYAC is used in the food industry as an additive, and may be expected to be biodegradable. As to the natural resins, the one used extensively in paintings conservation, Dammar, was highly degradable. Shellac, widely used in wood conservation, showed a moderate resistance to degradation.

The single polyimide, Imron 192S, fell in the poorly resistant grouping, having a composite score of 22.

Based upon the total weighted scores, those polymers or resins that showed the most overall resistance to fungal deterioration (i.e., the lowest score) were Rhoplex AC 234, Bakelite-AYAA, and Tegovakon V, with composite scores of 11, 13, and 13, respectively. G.E. Silicone 1048, Bakelite-AYAF, and Mowital B-20-H also had low weighted scores (16, 17, and 18). The polymers or resins having the poorest (or highest scores) were Bakelite-AYAC, Conservare H40, Acryloid F-10, and Imron 192S (>23, 23, 23 and 22, respectively). Other polymers or resins having a higher score were Conservare OH, and Dammar (with scores of 20 and 21, respectively). The rest of the polymers and resins (Conservare H, Acryloid B-72, Bakelite-AYAT, and Shellac) fell between the extremes, with composite scores of 19.



#### 4. PART I, CONCLUSIONS

After considering the combined effects of organism growth, sporulation, weight change, and chemical change, it was concluded that, in regard to fungal deterioration:

- Rhoplex AC 234, Bakelite-AYAA, and Tegovakon V had high resistance.
- Conservare H40, Acryloid F-10, Imron 192S, and Dammar all showed poor resistance.
- Bakelite-AYAC was completely degraded by fungal action after 2 weeks of incubation.
- The remaining polymers and resins showed levels of resistance between those of the first two groups.

The polymers or resins that showed poor resistance to fungal deterioration, Dammar, Acryloid F-10, and Conservare H40, are extensively used in conservation today. It is therefore recommended that: (1) Conservators be made aware of the potential biodeterioration problems of these products and of any environmental controls that may reduce their susceptibility to attack; (2) usage should be restricted to 'safe' environments; and (3) these products should be replaced with more resistant products or perhaps have a biocide included within them. If a biocide is added to these products, further testing should be carried out.

#### 5. INTRODUCTION, PART 2 FTIR OF SILICONE-BASED POLYMERS

To further elucidate the nature of the changes occurring in polymers as a result of fungal attack seven silane-based polymers currently in use in stone conservation were studied with FTIR after one and two months of fungal growth. (Analyses performed by Dr. Gretchen Shearer, The Metropolitan Museum of Art; and Dr. Peter Zanzucchi, David Sarnoff Research Labs., Princeton, NJ.).

The seven products tested were:

- Tegovakon T (Tetraethoxysilane and methyltriethoxysilane, solvents)
- Tegovakon V (Tetraethoxysilane only and solvents)
- Tetraethoxysilane
- Brethane (Methyltrimethoxysilane, solvents and catalyst)
- H40+ (more polymerized Conservare OH, plus organo-iodide biocide)
- H40 (more polymerized Conservare OH)
- DF104/B-72 (polymer silane and acrylic resin)

Samples of the above products were spread on silicon wafers and incubated for one or two months with the fungal mixture used in Part 1 ( $10^8$

Robert

spores  
FTIR.

#### 5.1

The  
hydro  
two si  
pentan  
occurs  
presen  
in the  
unreac

Bio  
Tegova  
showed  
i.e., Te

It w  
additio  
and th  
water v

#### ACK

This  
assista  
screeni  
discuss  
contrib  
thanked  
analyzi  
many t  
when a  
who ha  
Institut  
study, a  
And las  
not esc

spores/ml). The samples were assayed quantitatively and qualitatively by FTIR. Two types of controls were prepared, dry and wet.

## 5.1 RESULTS AND DISCUSSION

The polymerization process of methyltriethoxysilane occurs in steps: an hydrolysis step with formation of a silanol, and then a condensation step when two silanols form a dimer. This reaction proceeds to form trimers, tetramers, pentamers, and so on to form larger oligomers. The more polymerization that occurs, the fewer the Si-OH molecules available for microbial attack. The presence of water is necessary for condensation to occur. This is clearly seen in the FTIR data from the wet and dry controls--the dry controls had more unreacted Si-OH than the wet controls.

Biological growth was clearly evident and extensive on all samples except Tegovakon V and Brethane. This fits in nicely with the FTIR results that showed a reduction of Si-OH groups in those products with fungal growth, i.e., Tegovakon T, H40+, H40, and DF104/B-72.

It was also felt that the weatherability of the silicones is improved with the addition of organics and the formation of copolymers (e.g., the DF104/B-72); and that since the silicone films are likely to be permeable to oxygen and water vapor they are therefore likely to be supportive of microbial activity.

## ACKNOWLEDGEMENTS

This work could not have been performed without the willing and able assistance of Mr. Edward Santoro. Ed was instrumental in devising the screening test and in statistical analysis, in addition to many hours of discussion of the topics. Mr. Mark Wypyski has made significant contributions to numerous parts of these studies for which he is sincerely thanked. Dr. Gretchen Shearer and Dr. Peter Zanzucchi spent many hours analyzing the consolidants in the second part of the study and have provided many tantalizing bits of information as to the behavior of the consolidants when attacked by fungi. Dr. A.E. Charola has been a friend and colleague who has lent a willing ear and eye to these studies. The Getty Conservation Institute kindly provided funding and intellectual input for the screening study, and The Kress Foundation kindly supported the FTIR study in part 2. And lastly, I express by warmest thanks to my editor, Vicki Koestler, who can not escape the many requests for her help in polishing my papers.

## REFERENCES

- Bassi, M. and D. Chiatante. 1976. The role of pigeon excrement in stone biodeterioration. *Int. Biodeterioration Bulletin* **12**: 73-79.
- Henderson, M.E.K. and R.B. Duff. 1963. The release of metallic and silicate ions from minerals, rocks and soil by fungal activity. *J. Soil Science* **14**: 236-246.
- Hueck van der Plas, E.H. 1968. The micro-biological deterioration of porous building materials. *Int. Biodeterioration* **4**: 11-28.
- Koestler, R.J., Charola, A.E., Wypyski, M.T. and J.J. Lee. 1985. Microbiologically induced deterioration of dolomitic and calcitic stone as viewed by scanning electron microscopy. *In* 5<sup>th</sup> Int. Congress on Deterioration and Conservation of Stone, G. Felix, (ed.), Presses Polytechnique Romandes, Lausanne p. 617-626.
- Koestler, R.J., Santoro, E.D., Preusser, F. and A. Rodarte. 1986. A note on the reaction of methyl tri-methoxy silane to mixed cultures of microorganisms. *In* Biodeterioration Research 1. C.E. O'Rear and G.C. Llewellyn (eds.) Plenum Press, New York p. 317-321.
- Koestler, R.J. and E.D. Santoro. 1988. Assessment of the susceptibility to biodeterioration of selected polymers and resins. Project report to The Getty Conservation Institute, Los Angeles, CA. **xi**, p. 98
- Koestler, R.J., Santoro, E.D., Druzik, J., Preusser, J., Koepp, L. and M. Derrick. 1988. Status report: Ongoing studies of the susceptibility of stone consolidants to microbiologically induced deterioration. *In* Biodeterioration 7. D.R. Houghton, R.N. Smith and H.O.W. Egging (eds.), Elsevier Applied Science, New York p. 441-448.
- Koestler, R.J., P. Brimblecombe, D. Camuffo, W. Ginell, T. Graedel, P. Leavengood, J. Petushkova, M. Steiger, C. Urzi, V. Verges-Belmin and T. Warscheid. 1994. How do environmental factors accelerate change? *In* The Science, Responsibility, and Cost of Sustaining Cultural Heritage, W.E. Krumbein, P. Brimblecombe, D.E. Cosgrove and S. Staniforth (eds.), Dahlem Workshop Report, John Wiley & Sons, New York p. 149-163.
- Koestler, R.J., T. Warscheid and F.E. Nieto. 1997. Biodeterioration: Risk factors and their management. *In* Saving Our Architectural Heritage: The Conservation of Historic Stone Structures, N.S. Baer and R. Snethlage (eds.) Dahlem Workshop Report ES20, Chichester, John Wiley & Sons Ltd. New York p. 25-36.
- Krumbein, W.E. 1972. Role des microorganismes dans la diagenese de la degradation des roches en place. *Revue Ecologie Biologique Solai*, **IX**(3). p.283.
- Leznicka, S., Kuroczkin, J., Krumbein, W.E., Strzelczyk, A.B. and K. Petersen. 1991. Studies on the growth of selected fungal strains on limestones impregnated with silicone resins (Steingestiger H and Elastosil E-41). *Int. Biodeterioration* **28**: 91-111.
- Lewis, F.J., May, E. and A.F. Bravery. 1988. Metabolic activities of bacteria isolated from building stone and their relationship to stone decay. *In* Biodeterioration 7, D.R. Houghton, R.N. Smith and H.O.W. Egging (eds.), Elsevier Applied Science, New York p. 107-112.
- May, E., Lewis, F.J., Pereira, S., Taylor, S., Seward, M.R.D. and D. Allsopp. 1993. Microbial deterioration of building stone--a review. *Biodeterioration Abstracts* **7**: 109-123.
- Nugari, M. and G.F. Priori. 1985. Resistance of acrylic polymers (Paraloid B-72, Primal AC 33) to microorganisms, First Part. *In* 5<sup>th</sup> International Congress on Deterioration and Conservation of Stone, Vol. 2, G. Felix (ed.), Presses Polytechnique Romandes, Lausanne p. 685-693.

Salvadori,  
used on  
Egging  
Santoro, E.  
polyme:  
Smith, R.N.  
T.A. O:  
Strzelczyk,  
Press, M  
Torraca, G  
Proc. In  
Webley, D  
weathe:



- biodeterioration.
- ate ions from
- ous building
- ologically induced
- electron microscopy.
- lix, (ed.), Presses
- on the reaction of
- deterioration
- York p. 317-321.
- biodeterioration of
- Institute, Los
- errick. 1988.
- s to
- ughton, R.N.
- p. 441-448.
- avengood, J.
1994. How do
- ty, and Cost of
- Cosgrove and S.
- York p. 149-163.
- factors and their
- f Historic Stone
- ES20,
- egradation des
- sen. 1991.
- ed with silicone
- 111.
- a isolated from
- 7, D.R.
- nce, New York p.
- o. 1993.
- tracts 7: 109-
- 3-72, Primal AC
- oration and
- andes,
- Salvadori, O. and M.P. Nugari. 1988. The effect of microbial growth on synthetic polymers used on works of art. *In Biodeterioration 7*, D.R. Houghton, R.N. Smith and H.O.W. Eggins (eds.), Elsevier Applied Science, New York p. 424-427.
- Santoro, E.D. and R.J. Koestler. 1991. A methodology for biodeterioration testing of polymers and resins. *Inter. Biodeterioration*. **28**: 81-92.
- Smith, R.N. and L.M. Nadim. 1983. Fungal growth on inert surfaces. *In Biodeterioration 5*, T.A. Oxley and S. Barry (eds.), John Wiley & Sons, New York p. 538-547.
- Strzelczyk, A.B. 1981. Stone. *In Microbial Biodeterioration*, A.H. Rose (ed.) Academic Press, New York p. 61-80.
- Torraca, G. 1975. Treatment of stone in monuments: a review of principles and processes. *Proc. Int. Symp. The Conservation of Stone I*, Bologna p. 297-315.
- Webley, D.M., Henderson, M.E.K. and J.F. Taylor. 1963. The microbiology of rocks and weathered stone. *J. Soil Science*. **14**: 102-112.

# OF MICROBES AND ART

The Role of  
Microbial Communities  
in the Degradation and  
Protection of Cultural Heritage



Edited by  
Orio Ciferri, Piero Tiano,  
and Giorgio Mastromei