Assessment of the Susceptibility to Biodeterioration of Selected Polymers and Resins

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ASSESSMENT OF THE SUSCEPTIBILITY TO BIODETERIORATION OF SELECTED POLYMERS AND RESINS

Final Report

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by

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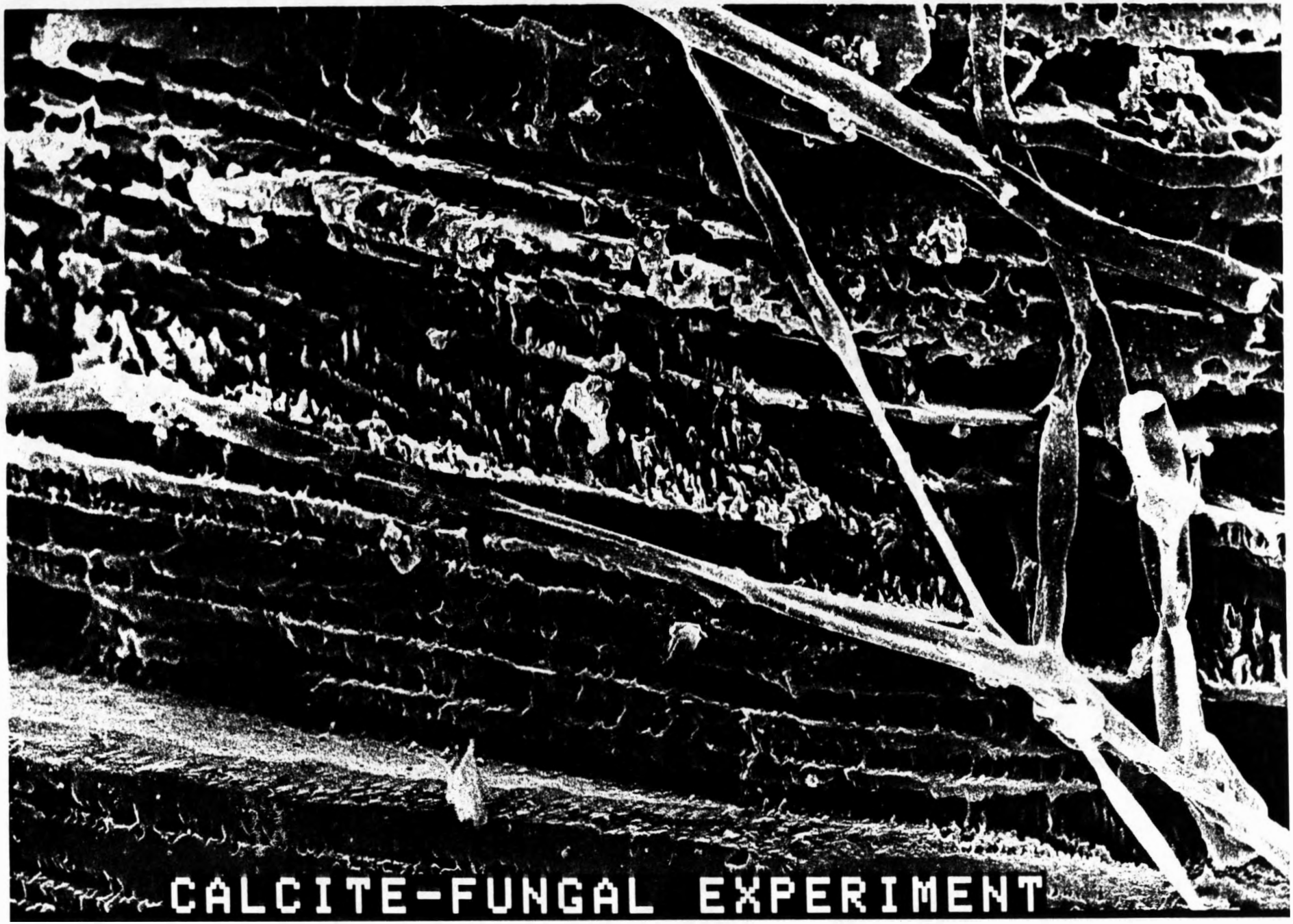
Summary

EXECUTIVE SUMMARY

The prevention of deterioration of stone materials used in works of art and in construction is of widespread interest. While many studies have considered the physical and chemical mechanisms that contribute to this deterioration, fewer have focused on the particular problem of biological attack on these materials. The present study represents what may be the first large-scale attempt undertaken in the conservation field to screen preservative coatings for microbial susceptibility prior to their application on objects. It is clear that microorganisms exacerbate deterioration of stone and that any coating placed on the stone should not provide a medium upon which microbes may grow.

In this study 16 polymers and resins important in preserving art materials, particularly stone, were evaluated for their ability to support fungal growth. Growth of the organisms was ascertained by macroscopic, microscopic, and physico-chemical changes of these materials over a 5-week testing period. Based upon their sensitivity to fungal deterioration, the polymers and resins tested were quantitatively ranked in order of least-to-most susceptible to bio-attack. The materials that were least affected were **Rhoplex AC-234**, **Tegovakon V**, and **AYAA**; those most affected were **AYAC**, **Conservare H40**, **Acryloid F-10**, **Imron 192S**, and **Dammar**.



Photofigure 1. Scanning electron micrograph of fungal attack on calcite. The fungi used in the calcite study, pictured here (Koestler et al. 1985) were similar to those used in the present study.

Section 1

1 INTRODUCTION

1.1 BACKGROUND

Physical breakdown of materials is a subject that has long been studied, with the aim of providing more durable materials. Deterioration of stone, whether in a man-made monument or in its natural form, is a constant and natural phenomenon, and can occur through many causes (Clifton, 1980; Plenderlieth, 1956; Winkler, 1982; Amoroso and Fassina, 1983; Koestler et al., 1985). Recently researchers have begun to investigate how biological phenomena --at times in synergy with physical effects--can exacerbate deterioration of stone materials. Studies by Koestler et al. (1985; 1987a,b) have begun to bring out the importance of microbes in the breakdown and recrystallization of stone materials and their protective coatings. Heretofore microbes were considered to play a minor role, if any, in stone and coating deterioration. In our view, though, microbiological attack on these materials can actively promote material decay and may act in synergy with physical means of deterioration. Studies by Webley (1963), Henderson and Duff (1963), and Hueck van der Plas (1968), among others, have shown fungi to be among the more deleterious microorganisms. This is indeed clearly the case in tropical climates, where high relative humidity and temperatures, among other factors, exacerbate material decay. Coating materials with resins or polymers that act to promote the growth of microorganisms will be of dubious value as a preservative measure. With this in mind, the present study was undertaken as the first phase in a screening of 16 resins and polymers for their susceptibility to microbiological deterioration.

There are many types of preservative coatings. The main types used today can be divided into four categories. These are,

first, the silane-based chemicals, which include the silicone resins, the alkoxy silanes, and the silicate esters. Next are the synthetic organic polymers, which include the acrylics, the epoxies, the vinyl polymers, and the polyurethanes. A third group, inorganic materials, includes the alkali earth hydroxides such as barium hydroxide, and various siliceous compounds such as the silico-fluorides (many include the silicate esters within this group rather than with the silane based treatments). Last are the waxes and the natural resins. The chemistry of each group is discussed in Appendix A, along with the advantages and disadvantages of each as a protective coating.

Assessing the resistance of a protective coating to microbiological attack is typically a lengthy process necessitating long-term field trials under ambient conditions. Laboratory studies attempt to predict field trials in a reduced time-frame and have some advantages over field trials in that microscale 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. In designing this screening technique we have built on the experience of Argawal and Nanda (1971), among others, who compared the effectiveness of laboratory testing versus field testing. Their results, on textiles in the tropics, showed that a six-month laboratory exposure was more deleterious than a one-year field trial. We therefore felt that a laboratory test would give a reasonably reliable and rapid assessment of biodeterioration susceptibility. Since the fungi--rather than algae, bacteria, and other microorganisms--are believed to be the main deteriorative agents they were used for this study.

1.1.1 DEGRADATION OF STONE

Stone decay phenomena include those factors that serve to alter the appearance, strength, coherence, dimensions, or chemical behavior of the material. These factors include:

- Chemical etching or erosion of stone by acidic substances
- Mechanical disruption caused by the expansion inside the stone of water
- Disfigurement due to the migration into the stone of colored materials such as rust, dirt, or paint
- Leaching from the stone of one or more of its component materials
- Abrasion or attrition due to wind-driven particles
- Stress-cracking due to vibrations from seismic activity or nearby traffic, or due to accidental contacts
- Damage due to poor construction or design
- Damage from poorly executed attempts at repair or conservation
- Deterioration from the actions of bacteria, fungi, algae, mosses, lichens, higher plants, insects, and animals.

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 to a depth of a few centimeters to almost a meter inside stone, especially porous limestones or sandstones (Krumbein, 1972; Myers and

McCready, 1966). 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.

Heterotrophic organisms are those that require organic nutrients (Stanier et al., 1976). 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). Many bacterial heterotrophic species have been isolated from stone. 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 sandstone monuments have been shown to have the ability to cause severe, rapid weight loss in sandstone by attack of the calcium matrix of the stone with organic acids (Lewis et al., 1987). Various fungi have also been isolated from and associated with decaying stone (Bassi and Chiatante, 1975; Koestler et al., 1985). These also attack stone by the production of organic acids, such as oxalic, citric and fumaric acids.

Biological deterioration of stone is a well studied phenomenon in the field of soil science, but is somewhat ignored in the field of art conservation. Stone may be damaged by one, many, or all of the physical and biological mechanisms discussed above. For treatment to be successful, though, the cause needs to be recognized and understood. This is often not the case with biological deterioration.

Section 2

2 MATERIALS AND METHODS

2.1 MATERIALS USED

The materials selected were polymers and resins currently used in conservation or materials that could be used in the future. For example, polyvinyl butyrl was included to represent Robert Feller's stability class B polymers, which both Dr. Feller and the GCI are beginning to examine with greater frequency. A few other natural resins were included to examine their vulnerability to fungi, even though they would never have utility as consolidants. The materials tested are presented in Table 2.1-1

TABLE 2.1-1 POLYMERS AND RESINS TESTED

PRODUCT NAME	MANUFACTURER	ADDITIVES OR CONTAMINANTS
ACRYLOIDS		
G--Acryloid B-72	Rohm and Haas	Information not available (2)
J--Acryloid F-10	Rohm and Haas	Information not available (2)
E--Rhoplex AC-234	Rohm and Haas	Formaldehyde <0.08% (1) Ammonia <0.3% (1) Probably soaps as emulsifiers
POLYVINYLS		
O--AYAA	Union Carbide	No additives (2)
N--AYAC	Union Carbide	Acetic acid <0.05% (1)
H--AYAF	Union Carbide	No additives (2)
M--AYAT	Union Carbide	No additives (2)
D--Mowital B-20-H	Amer. Hoeschst	No additives; may be some byproducts from the polymerization process such as PVAC, PVOH, butyraldehyde (2)
SILICONE-BASED		
F--Conservare H	ProSoCo	Dibutyltin dilaurate = catalyst (2)
K--Conservare H40	ProSoCo	Dibutyltin dilaurate = catalyst (2)
I--Conservare OH	ProSoCo	Dibutyltin dilaurate = catalyst (2)
A--Silicone 1048	General Electric	100% silicone resin (2)
B--Tegovakon V	Goldschmidt	Solvent + alcohol (2) Tin catalyst (2) Silicic acid ester = binder replacement
POLYIMIDE		
P--Imron 192S	Dupont	HCl or triethylamine as an initiator (3) Activator 192S has no additives (2)
NATURAL RESINS		
C--Dammar	AF Suter	Natural resin
L--Shellac	AF Suter	Natural resin

(1) Manufacturer's literature and/or safety data sheet
(2) Phone call to manufacturer
(3) Jim Druzik, GCI

2.2 OVERVIEW OF METHODOLOGY

A flow chart of the experimental design is presented in Fig. 2.2-1. In brief, the method required multiple samples of thin-films of each polymer or resin. After curing, the thin film test strips were exposed to a high concentration (10^4 or 10^8) of a fungal spore mixture. At 7-day intervals triplicate samples of each consolidant (plus controls) were removed and assayed for deterioration effects.

The fungi were applied in mixed cultures, instead of pure (i.e., individual) cultures, since this has been found to be more reproducible than pure cultures (Klausmeir, 1971). In addition, triplicates of each consolidant, with two different densities of fungi, were tested concurrently, with appropriate controls (approximately 140 samples), to further control statistical validity and reproducibility.

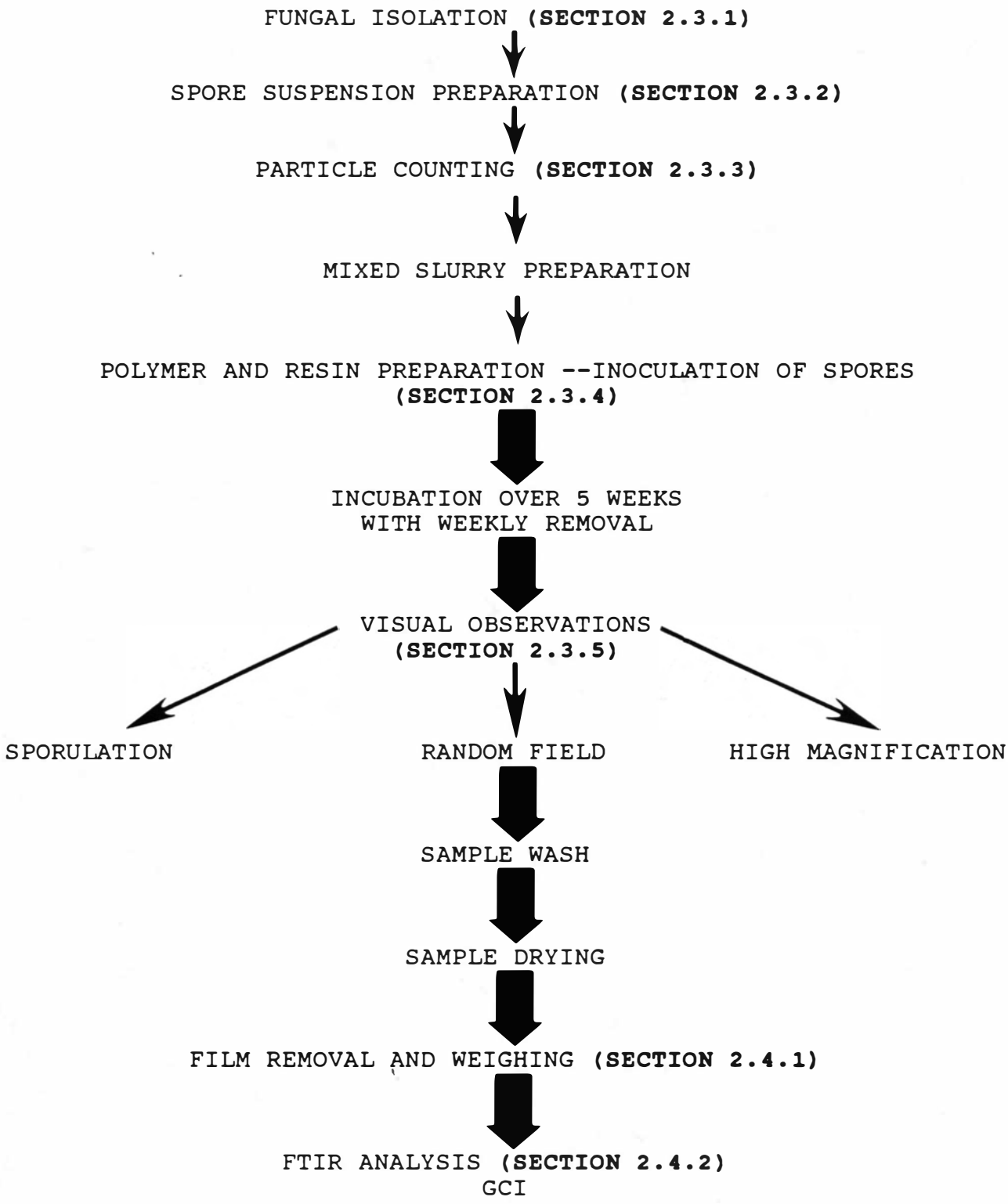
2.3 GROWTH ASSESSMENT PROCEDURES

2.3.1 ISOLATION OF FUNGI

Six species of fungi were isolated from cultures obtained from a Carrara marble statue (St. Gaudens' Hiawatha), which had been exposed to the semi-tropical conditions of Florida for some 80 years. A list of the fungi used is presented in Table 2.3-1.

Upon evaluation of the preliminary results and isolation techniques used in our earlier research (Koestler et al., 1987a,in press; and Koestler et al., 1987b, in press), it became apparent that for a more accurate and complete isolation of fungi present in the original samples, an antibiotic had to be

FIGURE 2.2-1
EXPERIMENTAL FLOW CHART



incorporated into the isolation medium to reduce or eliminate bacterial growth, which interfered with fungal growth. The antibiotic Achromycin (Tetracyline-HCl, Lederle Lot #117-488 Exp. 5/90) was added in 35 μg/ml concentration to the primary isolation medium of Sabaroud's agar (SAB). The tetracycline was prepared separately and added just before the agar was poured into Petri dishes. One gram of tetracycline was added to 150 ml sterile distilled water. Before plates were poured, 0.05 ml of this solution was added to 10 ml of agar medium.

Cultures from all original samples were inoculated onto the SAB-tetracylcine medium. Colonial morphology was recorded in young cultures of no more than 7-10 days old, since morphology changes greatly as cultures get older. Plates were examined daily for fungal growth. Plates had mold as well as yeast growth, while bacterial growth was inhibited by the antibiotic. The different mold colonies were then isolated and transferred to the center of a SAB plate. This was done by touching the surface of the colony with a flame-sterilized needle that had been cooled in sterile medium and transferring the adherent spores to the center position on the solidified medium in the Petri dish. Yeast colonies were isolated on SAB using the simple streak plate technique used for bacterial isolation.

These improved techniques resulted in a higher variation of mold isolates as well as in the isolation of yeast, which was absent in our preliminary findings. The various molds and yeast isolated were kept refrigerated on SAB slants until used. Many of these isolates have been identified to the genus level using colony characteristics as well as microscopic examination. Figure 2.3-1 shows the macroscopic colony growth characteristics of the fungi used in the experiment. A presentation of the colonial morphology of all cultures isolated is in Appendix B. Table

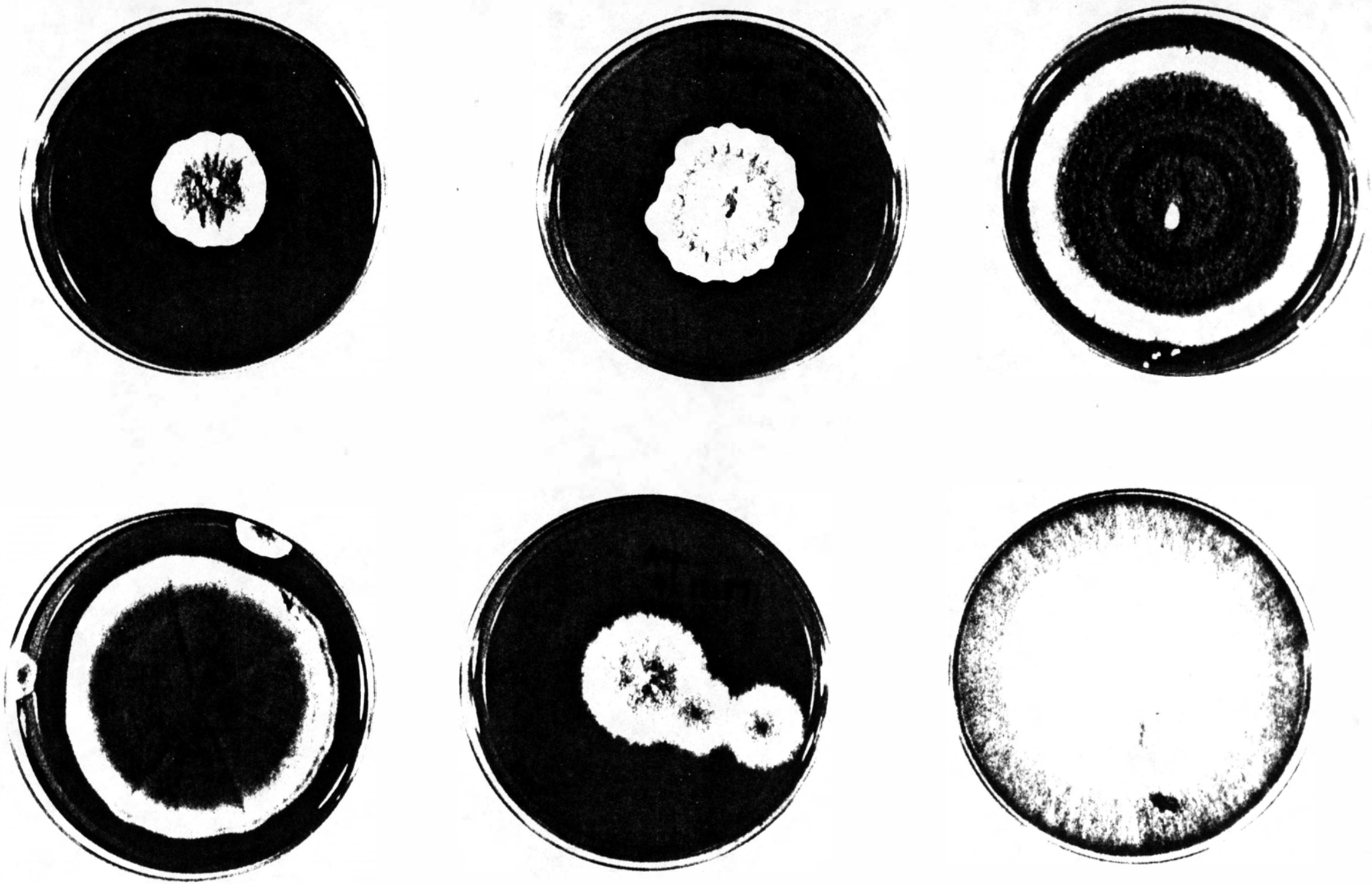
2.3-1 presents the fungal isolates used in this study along with their descriptive colonial morphology. Colony morphology was described based upon visual observation. Microscopic morphology was determined by preparing a wet mount in lactophenol cotton blue solution and examining the preparation under oil immersion optics.

2.3.2 Fungal Spore Isolation

From these cultures fungal spore suspensions were obtained utilizing the method of Klausmeier (1972), to provide spores for inoculation. Immediately prior to inoculation spore suspensions were counted with a Spectrex Corp. Particle Counter. The major steps in the preparation of fungal spore suspensions are identified in Table 2.3-2.

For inoculation in spore suspensions, 0.6 ml of a mixed spore suspension was shaken vigorously for 15 seconds; then it was inoculated onto each of the test samples. On each slide, one sample served as an experimental control. The inoculated drop of spore suspension was spread across the entire sample surface with a sterile slide. Each inoculated test strip was incubated under the following incubation conditions:

Temperature	25.3 ± 2° C
Relative humidity	75 ± 16%
Lighting	four 4-ft fluorescent lamps
Light/dark cycle	14/10 h
Consolidant film size	42 x 38 mm
Type of test vessel	Petri dish with glass slides
No. of organisms/test	10^8 spores/ml
No. of replicates	3
Test duration	35 days
Exposure interval	0,7,14,21,28,35 days
Random field viewing area	2.1 mm^2/grid; minimum of 5 grids per subsample



Photofigure 2. Photograph of six fungal islolates used in the current study. Top row: Aspergillus sp., Penicillium sp., Penicillium sp.; Bottom row: Cladosporium sp., Aspergillus sp., Fusarium sp.

2.3.3 PARTICLE COUNT METHODS

Prior to inoculating, to ensure that the desired spore concentrations were obtained, particle counting of the spore suspensions was performed with an in-situ liquid particle counter, Model ILI 1000 (Spectrex Corp.). In this method a focused laser beam is directed through a sample solution and particles are detected when they pass through the laser in the focus area. Light is scattered from the particle and a photo-electric cell detects that portion of the light reflected. The light pulse is analyzed by a detection unit. Particle densities (<1000/ml) are kept low so there is little chance of coincidence (shielding of a particle) as particles are crossing the laser path. Variation between replicates is reported to be less than 5% (Chung, 1982; Clayton, Blanchard, et al., 1976). Using this technique, spore concentrations of 10^4 and 10^8 were obtained and inoculated onto the polymers and resins.

Specific vendor-related information on the Spectrex unit is presented in Appendix C, along with a summary table of the particle counts obtained for the respective spore suspensions.

TABLE 2.3-1
FUNGAL ISOLATES AND MORPHOLOGY

	MORPHOLOGY	
FUNGUS	**VISUAL**	**MICROSCOPIC**
Penicillium sp	Sulfur light to green colony with yellow underside.	Septate conidiophores terminating in broom-like whorl of branches
Penicillium sp	White colony with exudate.	"
Fusarium sp	Off-white to light gray colonies.	Microconidia are oval; macroconidia appear septate and sickle shaped.
Cladosporium sp	Thick velvety colonies deep green in color. Black on underside.	Spores in large tree-like clusters, conidia are distinctly verruculose.
Aspergillis sp	Small colonies with white periphery and light orange-grayish center.	Nonseptate conidio-phores have enlarging toward apex. Phislides bearing conidia.
Aspergillis sp	White periphery with yellow cotton-like center.	"

TABLE 2.3-2 OUTLINE OF PREPARATION OF FUNGAL SPORE SUSPENSIONS

(AFTER KLAUSMEIER, 1972)

- Inoculate culture on potato dextrose agar.
- Incubate at room temperature for 14 to 21 days. (Make sure that plates are covered with parafilm to preserve the moisture.)
- Harvest the spores using 10-ml sterile flasks.
- Remove mycelial fragments by macerating in sterile flasks containing sterile glass beads.
- Filter through a thin layer of sterile glass wool.
- Dilute to approximate count needed.

2.3.4 POLYMER AND RESIN PREPARATION

Resins were applied on glass substrates (5 x 20 cm by air-brushing Paasche) through an aluminum template that permitted four 3.5 x 4.0 cm samples. Approximately 10 plates for each material were produced to make about 30 replicates.

Solution concentrations ranged from 2% for the PVACs and 5% for the acrylics, to 40% solids for the acrylic emulsions, on up to 75-96% for the silanes. Concentrations and spraying techniques were balanced to achieve as consistent a film thickness between different materials as possible.

Film-forming consolidants produced rather even layers immediately; however, nonfilm-formers, such as MTS + ethyl silicate, needed a different strategy. With these materials as even a layer as possible was applied to the substrate and allowed to polymerize. Under magnification this appeared as small hard droplets on the glass. In stepwise fashion subsequent coats served to "fill in" between previously applied coats. Thus an approximation to a film was built up.

After the final application and air-drying, a 2-3-mm rag board mat was cut and glued to the edges of the substrate and a second glass plate was taped over the mat. Thus the coatings were protected from most dust, fingerprints, or other adventitious contaminants. Groups of 10 plates were finally wrapped in aluminum foil to protect them from light.

2.3.5. VISUAL ASSESSMENT PROCEDURES

To ensure that an effect could be measured in a statistically valid manner, 15 samples of each polymer or resin were prepared. These 15 samples represent triplicate runs over five sampling intervals of 7, 14, 21, 28, and 35 days exposure. Triplicate samples provide the minimum number for statistical assessment of any observable effect. Once a sample was removed from the incubation chamber, it was subjected to a series of observations by two persons, as described below:

1. The percentage of organism coverage was ascertained visually as a function of test strip discoloration.

2. In microscopic random field viewing, the sample was separated into 100 evenly spaced and numbered boxes approximately 2.1 mm^2 in size. Five grids were chosen for viewing via a random number table. Using a light microscope at low power (32x), the presence or absence of organisms on the grids was recorded.

3. Higher magnification (400x) viewing was done to describe hyphal length, presence of fruiting bodies, colony formation, etc. For further assessment, the sporulation scale presented in Smith and Nadim (1983) was also used.

2.4 PHYSICAL AND CHEMICAL ASSESSMENT PROCEDURES

2.4.1 WEIGHT LOSS MEASUREMENTS

Weekly samples removed from the incubation chamber and analyzed for growth parameters were washed with a 5% hydrogen peroxide solution to remove the majority of fungal growth prior to FTIR analysis. After air drying in a negative pressure chamber, they were scraped from the glass slides with clean razor blades (one blade per sample). Every effort was taken to ensure complete film removal prior to weighing. Controls were incubated and washed in a similar manner to the experimentals. All weights were taken using a Sartorius Model R160P analytical balance scale, accurate to 0.00001 g.

2.4.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

This section, on procedures, is excerpted from Valentin and Derrick (1988).

For this experiment, some fungi were isolated from marble and inoculated onto selected consolidants. The consolidants were in the form of a film on glass supports. After the set incubation period, several visual measurements were made on the samples; then they were cleaned using a 5% H_2O_2 solution. Previous FTIR analysis (GCI, Derrick, May 1987), showed that the peroxide solution did not produce any IR detectable chemical damage to the polymers with the exception of the polyimide, **Imron 192S**. After cleaning, a portion of each sample and its corresponding control were placed in vials, sealed with aluminum foil caps and sent to GCI for FTIR analysis.

One hundred and twenty seven samples of polymers (inoculated samples and controls) were received in three different sets by GCI for infrared analysis.

Infrared spectra were obtained at 4 cm^{-1} resolution on a Digilab 15-E FTIR spectrophotometer equipped with a Motorola 3200 computer and a dry nitrogen purge. A wide range, cryogenically cooled MCT detector was used to examine the mid-IR region from 4000-500 cm^{-1}. Each spectrum is the accumulation of 200 scans.

For comparative purposes, computer subtraction routines were used to amplify existing spectral differences. The subtraction techniques can provide an accurate evaluation of changes in a material due directly to a procedure, thus providing a reference point on which to base the degree of subtraction. In these studies, attempts were made to correlate changes using samples that were different initially. Thus the degree of subtraction applied in each case was arbitrary and designed to provide maximum amplification of differences between the spectra examined. This method for subtraction provided indications of relative differences, rather than absolute changes, between the materials and an assumption was made that the samples were spectrally identical prior to inoculation in order to gain information on structural changes due to the fungal deterioration of the polymer. The subtraction method does not provide an accurate indication of the relative proportions of the strongest peaks in the spectrum.

The samples were analyzed by three different infrared analysis techniques depending on the amount of sample available and its solubility. The three methods used were:

1. Attenuated Total Reflectance (ATR)--A portion of the sample in the form of a film was placed against a reflective crystal (XRS-5) for surface analysis. This is primarily used for free films, and was not often used in these analyses.

2. Diffuse Reflectance (DRIFT)--A section of the sample (5 mg) was dissolved in solution, a drop was placed in powered KBr, the solvent evaporated, then the sample analyzed by diffuse reflectance. This method worked well and provided a representative, particle-free portion of the sample for analysis. This method was only used on a limited basis because of the sample solubility and the small amounts of material received in some of the vials.

3. Micropellet (MCP)--A small portion of the sample, <100 μg, was ground with KBr, then pressed into a 1.5 mm diameter micropellet and analyzed by transmission IR. This method was used for the majority of samples due to the limited amounts available for analysis. It is also the method that is most prone to the adverse effects of sample inhomogeneity and contamination because the amount of sample is so small.

While the spectra for each technique are very reproducible, the spectra from the different techniques may not be intercompared because reflectance and absorption phenomena are different. Thus one method was used consistently through each letter group, i.e., polymer, for the three batches.

Section 3

3 RESULTS

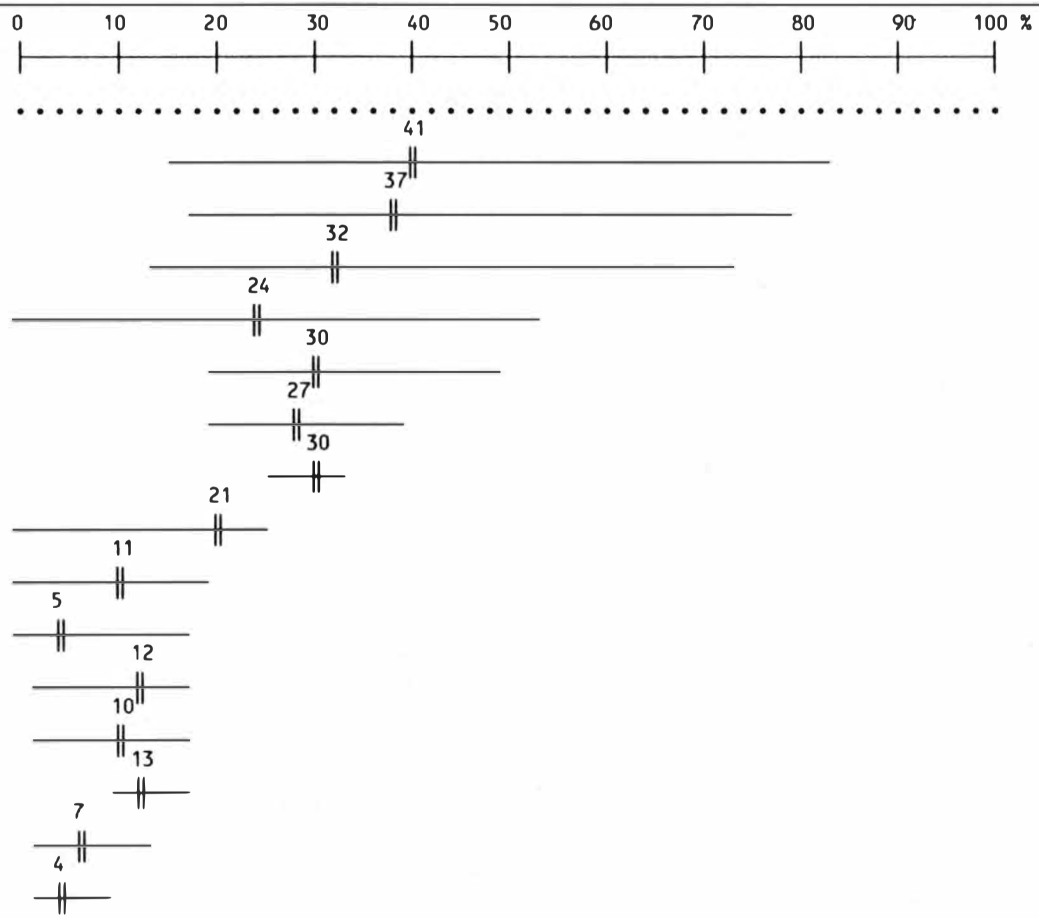
3.1 PHYSICAL OBSERVATIONS

3.1.1 WEIGHT LOSS

For the majority of the polymers and resins tested, no massive weight losses or gains were noted for control or experimental samples. The weight loss methods, as noted in section 2.4.1, allowed for observation of large weight changes. It should be noted that some consolidant 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 experimental trials. To account for these sources of error, an arbitrary 15% weight change was considered not to be significant. Based upon this level, Table 3.1-1 was prepared. As presented in that table, 7 polymers or resins had weights that were essentially unchanged (<15%) from the control samples, 5 had a change in weight of 15-30%, and 3 had a change in weight of 31-60%.

Of the consolidants showing a weight differential from the controls, **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.

TABLE 3.1-1
MEAN WEIGHT CHANGE OF THE POLYMERS AND RESINS OVER THE 5-WEEK EXPOSURE INTERVAL



Perpendicular indicates the mean value. [1]AYAC did not survive through the 5th week of incubation. [2]Mixed indicates both a weight gain and a weight loss in the experimentals over the course of the 5-week testing period in different replicates.

3.2 POLYMER AND RESIN RANKING

3.2.1 ORGANISM GROWTH ASSESSMENT

The results of the first week of laboratory observations were presented in Koestler et al. (1987c). Growth was observed in most of the polymers and resins exposed to 10^8 spores/ml; none was observed in any of the consolidants or resins exposed to a level of 10^4.

Over the 35-day exposure interval, fungal growth was mixed, with **Imron 192S** (Fig. 3.2-1), **Dammar** (Fig. 3.2-2), **Conservare H40** (Fig. 3.2-3), **Mowital B-20-H**, **AYAF**,and **AYAT** (Fig. 3.2-4) showing consistently high fungal growth over the testing interval. (See Table 2.1-1 for letter code definitions.)

Conversely, **G.E. Silicone 1048** (Fig. 3.2-3), and **Rhoplex AC-234** (Fig. 3.2-5) showed no fungal growth or minimal growth over the interval. **AYAC** showed little growth over 2 weeks (Fig. 3.2-4) 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.

In order to combine these polymers and resins into statistically significant groupings ($\alpha \leq 0.05$), a Wilcoxon's two-sample test was performed from the individual data points. The results of this analysis are presented in Table 3.2-1.

Little consistency in the pattern of growth for polymers or resins within a similar group (e.g., polyvinyl acetates) was noted over the study.

Initial 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., 1987c). 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 (via the presence of fruiting bodies).

3.2.2 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.

Bar graphs of weekly sporulation scale data for the polymers and resins tested are presented in Figs. 3.2-6 through 3.2-10. As would be expected, the sporulation scale approximates the colony growth data. However, in certain consolidants such as **G.E. Silicone 1048**, sporulation was evidently beginning at the fifth week of the experiment (Fig. 3.2-8). **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 (Fig. 3.2-6). **Acryloid B-72** and **Acryloid F-10** had consistently higher sporulation, which was not manifested in a greater colony growth formation (Fig. 3.2-10). (See Table 2.1-1 for letter code definitions.)

For the most part, the lack of consistently similar fungal colony growth and sporulation scale may result from the arbitrary manner in which both were ranked.

In a manner similar to that used for the colony growth data, a Wilcoxon's two-sample test was performed on the individual sporulation data. This is expressed in Table 3.2-1. Although the significant middle groupings ($\alpha \leq 0.05$) are somewhat different from those obtained for colony growth, the extreme end groupings contain the same polymers or resins in both, albeit in different ranked order.

POLYIMIDE

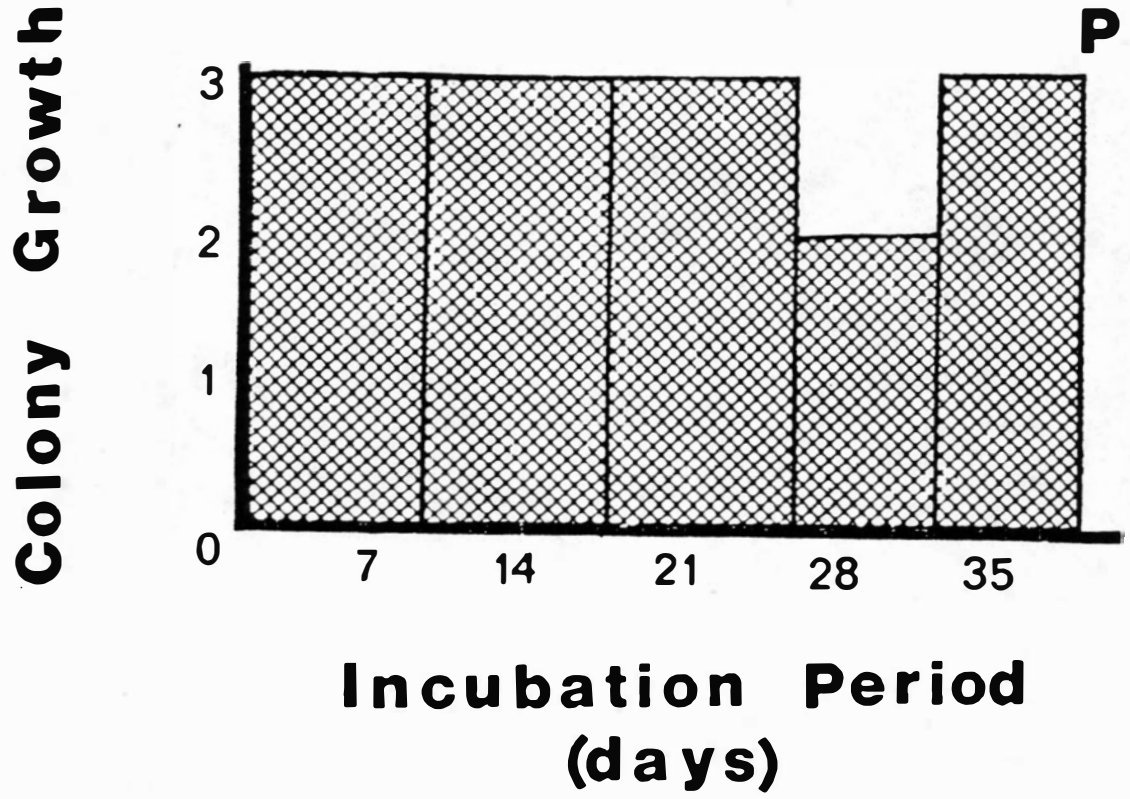
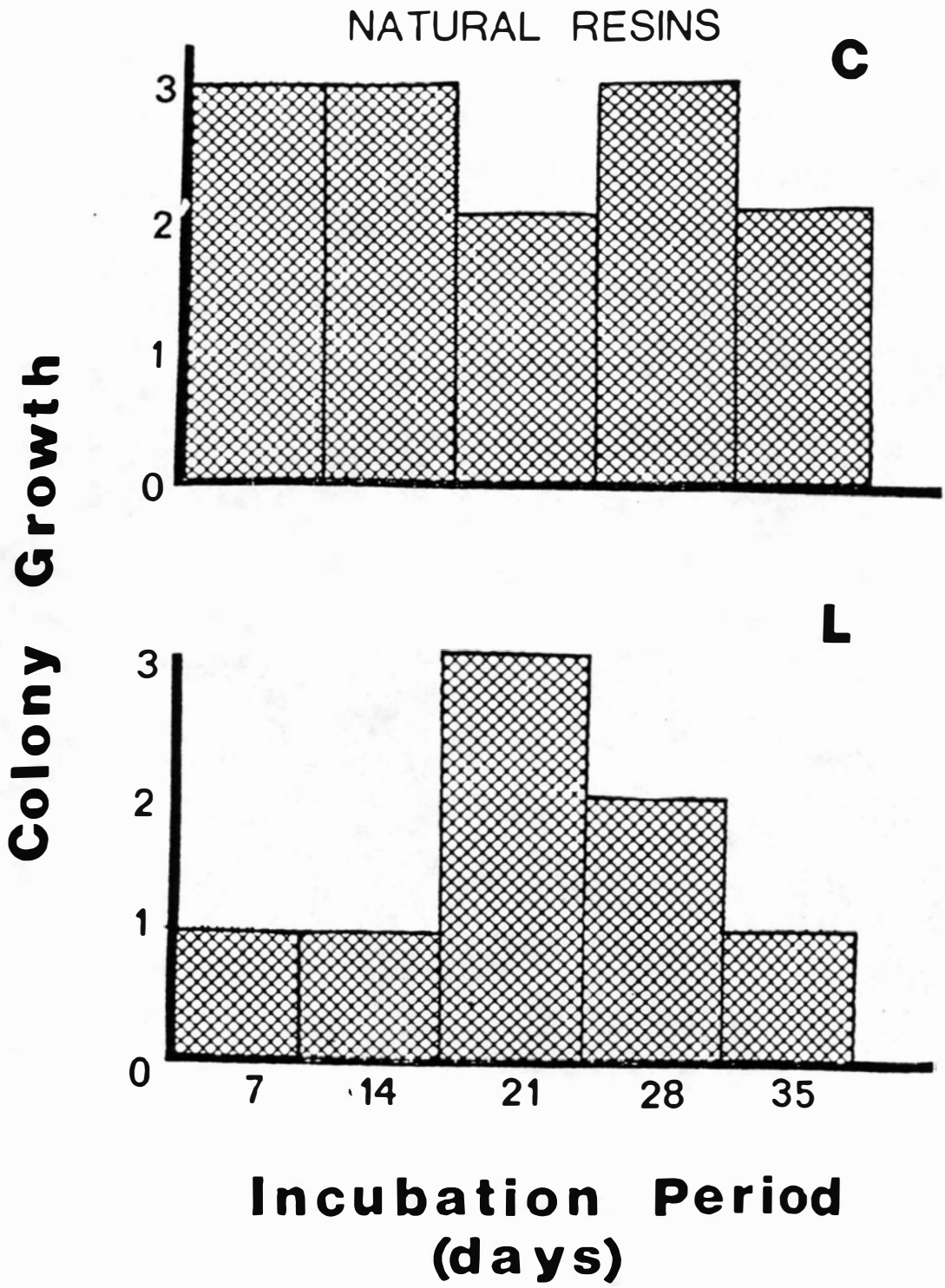


FIGURE 3.2-1

VISUAL OBSERVATIONS OF FUNGAL COLONY GROWTH ON SELECTED POLYMERS AND RESINS: (0)- 5% or less colony growth,(1)- 5 to 35% growth,(2)- 35 to 70% growth, (3) 70 to 100% growth.

FIGURE 3.2-2

VISUAL OBSERVATIONS OF FUNGAL COLONY GROWTH ON SELECTED POLYMERS AND RESINS: (0)- 5% or less colony growth,(1)- 5 to 35% growth,(2)- 35 to 70% growth, (3) 70 to 100% growth.



SILICONE-BASED RESINS

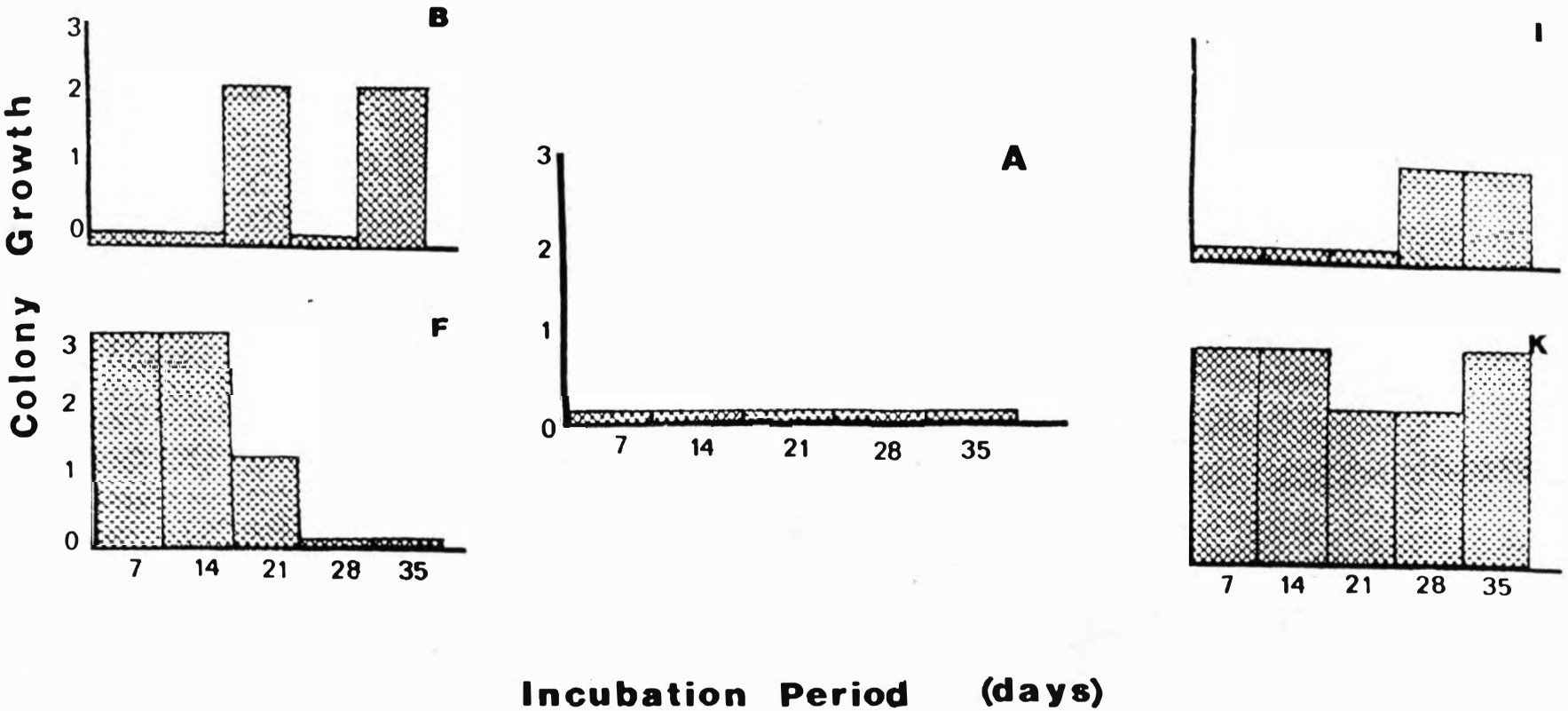


FIGURE 3.2-3

VISUAL OBSERVATIONS OF FUNGAL COLONY GROWTH ON SELECTED POLYMERS AND RESINS: (0)- 5% or less colony growth,(1)- 5 to 35% growth,(2)- 35 to 70% growth, (3) 70 to 100% growth.

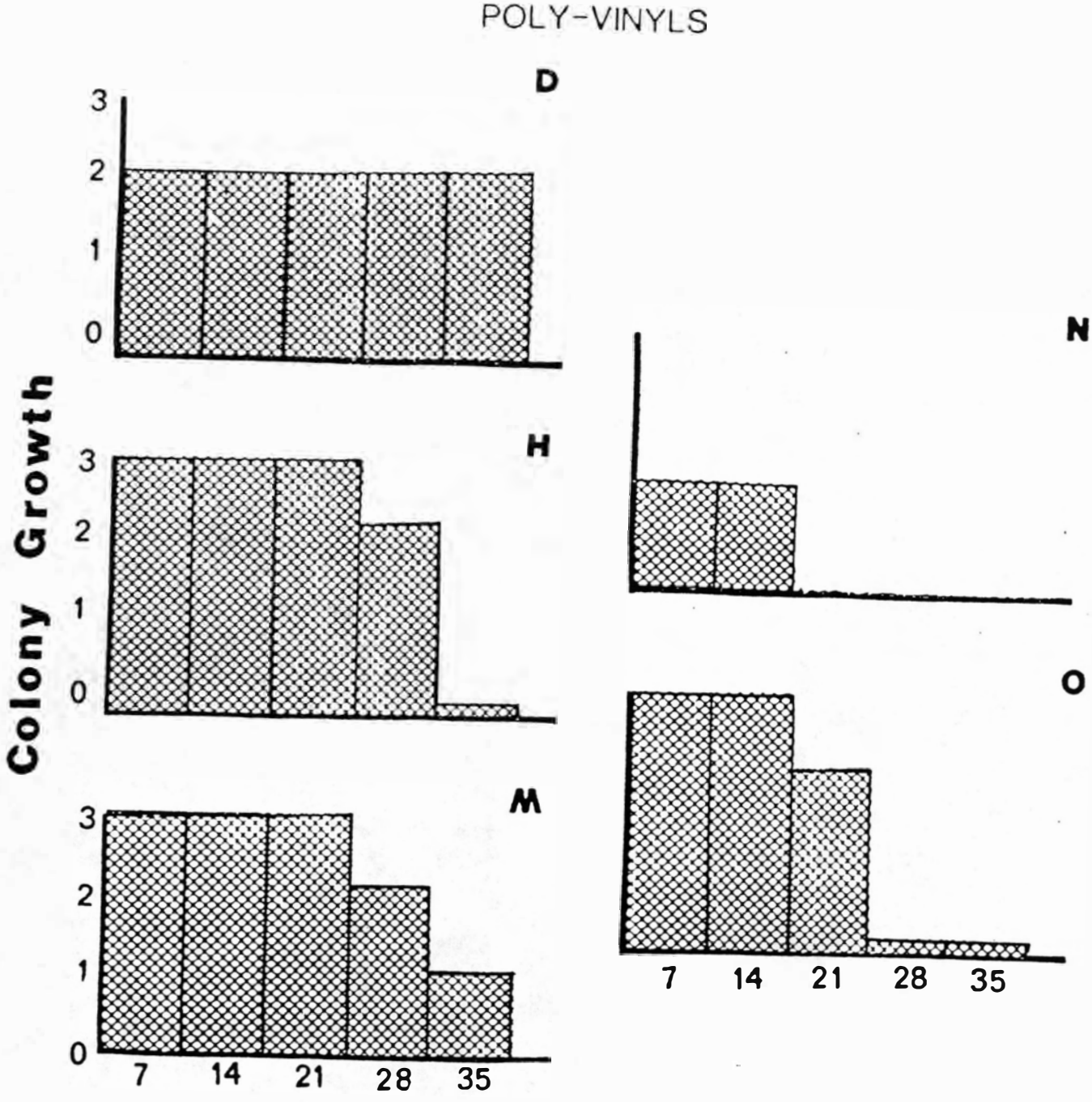


FIGURE 3.2-4

VISUAL OBSERVATIONS OF FUNGAL COLONY GROWTH ON SELECTED POLYMERS AND RESINS: (0)- 5% or less colony growth,(1)- 5 to 35% growth,(2)- 35 to 70% growth, (3) 70 to 100% growth.

ACRYLIC RESINS

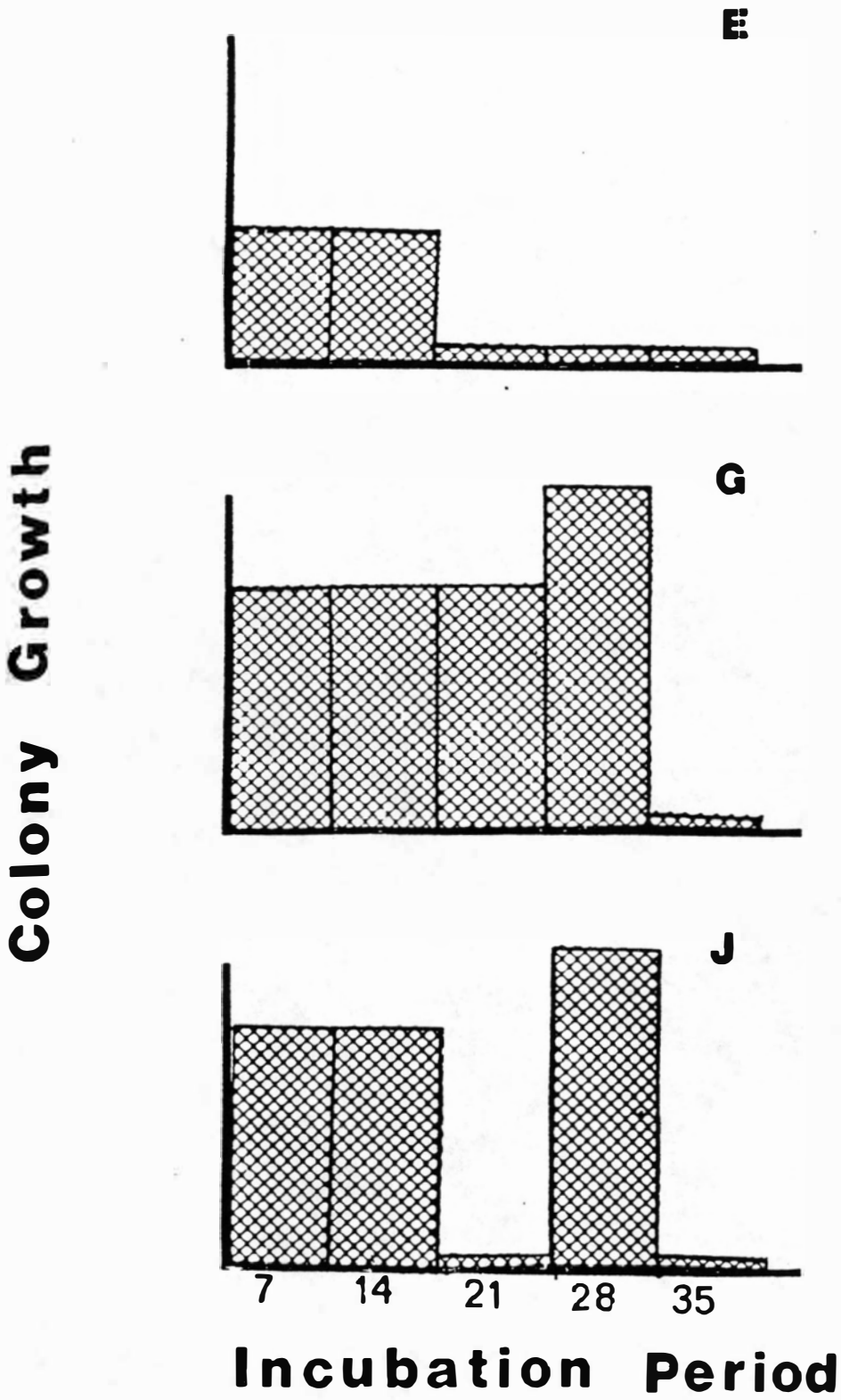


FIGURE 3.2-5

VISUAL OBSERVATIONS OF FUNGAL COLONY GROWTH ON SELECTED POLYMERS AND RESINS: (0)- 5% or less colony growth,(1)- 5 to 35% growth,(2)- 35 to 70% growth, (3) 70 to 100% growth.

POLYIMIDE

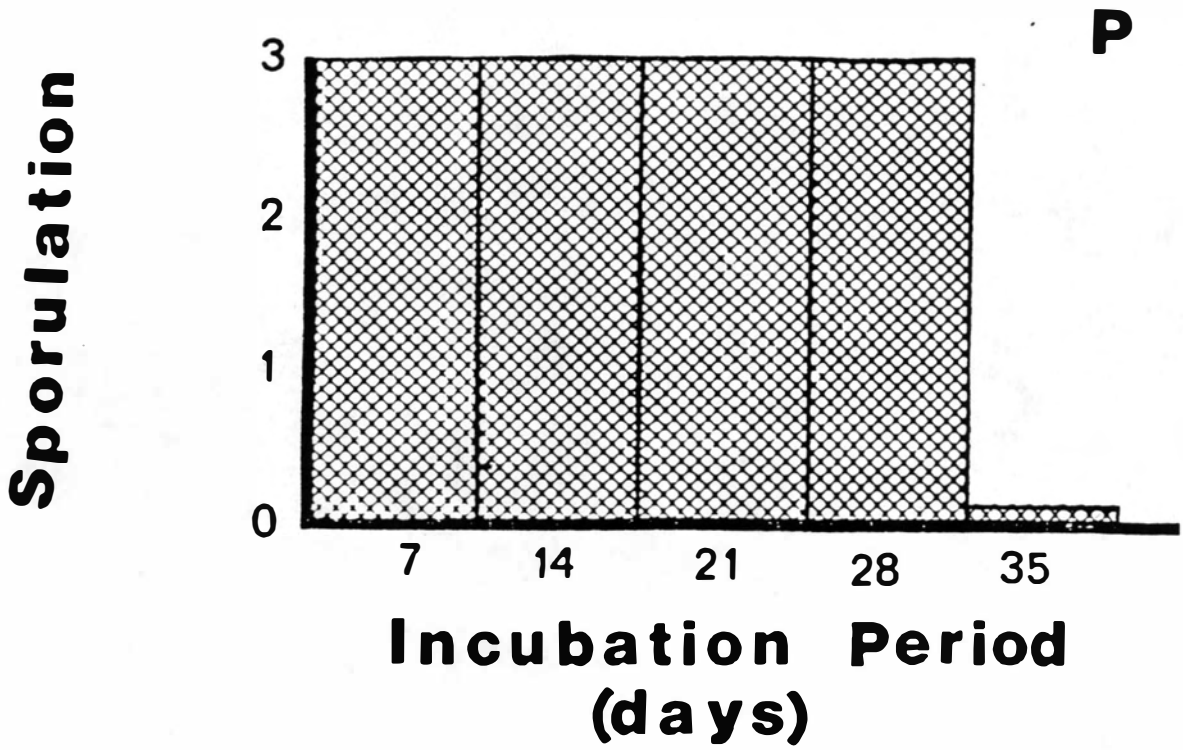


FIGURE 3.2-6

ASSESSMENT OF FUNGAL GROWTH ON SELECTED POLYMERS AND RESINS USING THE SPORULATION SCALE DEVELOPED BY SMITH AND NADIM (1983):(0)- no fruiting bodies present,(1)- few fruiting bodies present,(2)- average number of fruiting bodies present and,(3)- large number of fruiting bodies.

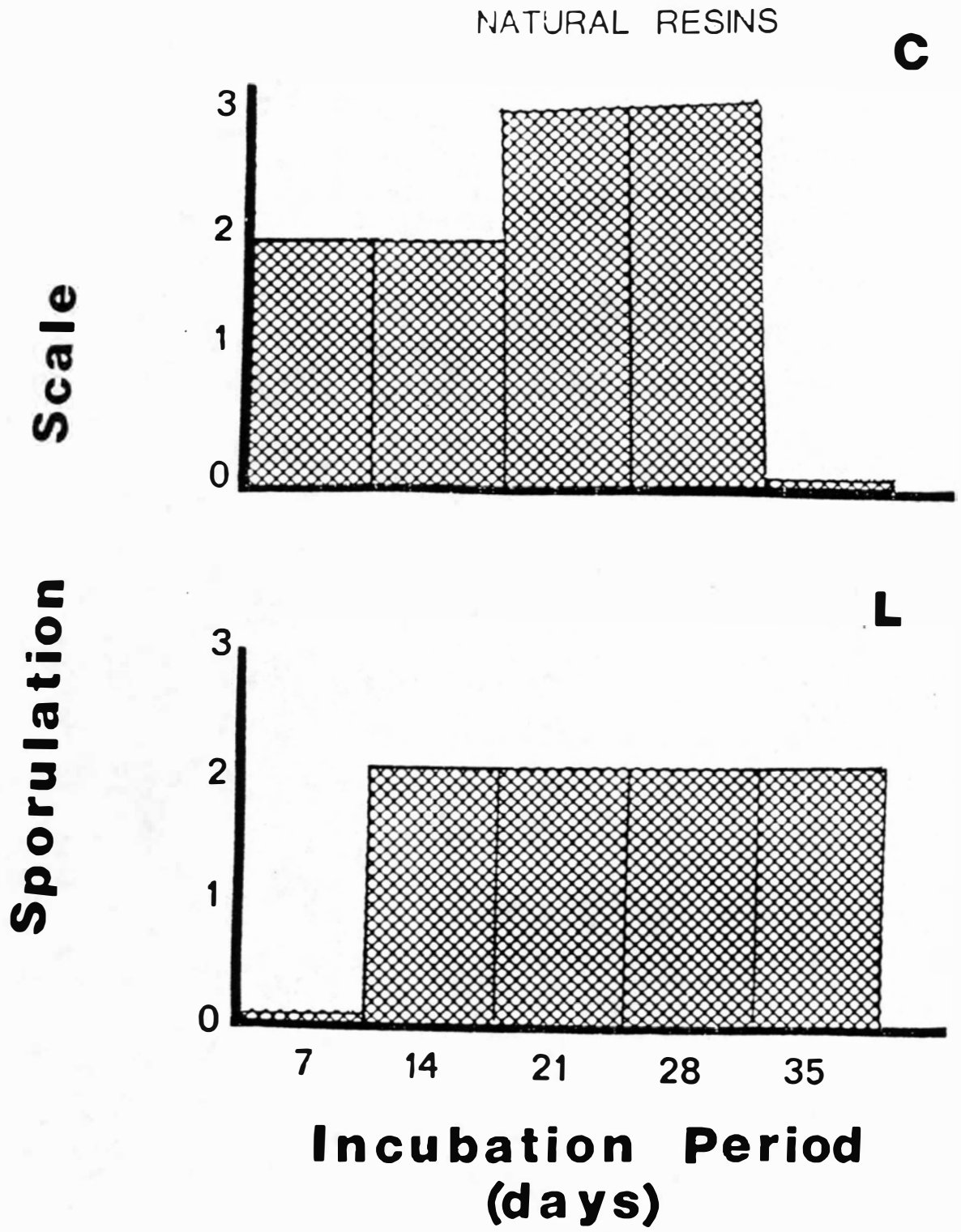


FIGURE 3.2-7 ASSESSMENT OF FUNGAL GROWTH ON SELECTED POLYMERS AND RESINS USING THE SPORULATION SCALE DEVELOPED BY SMITH AND NADIM (1983):(0)- no fruiting bodies present,(1)- few fruiting bodies present,(2)- average number of fruiting bodies present and,(3)- large number of fruiting bodies.

SILICONE-BASED RESINS

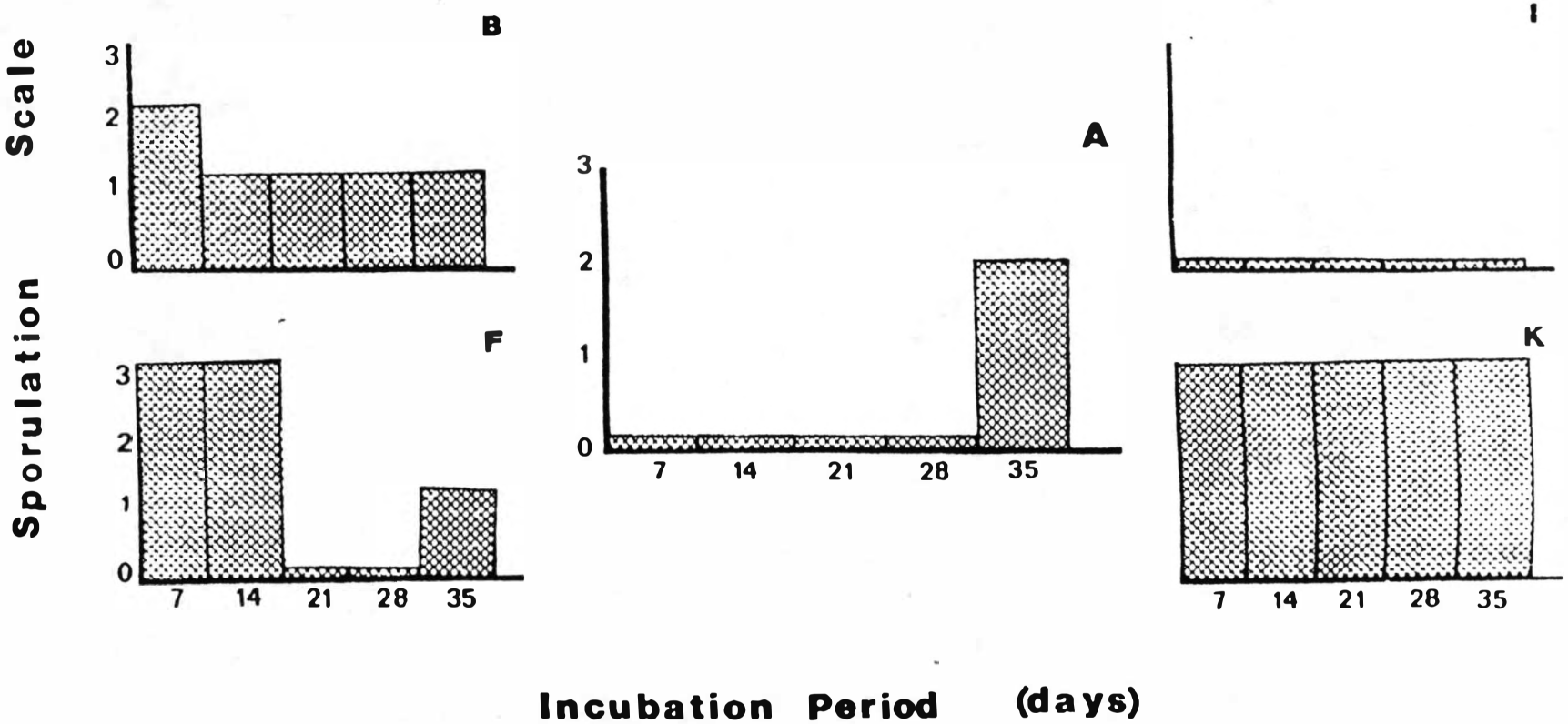


FIGURE 3.2-8

ASSESSMENT OF FUNGAL GROWTH ON SELECTED POLYMERS AND RESINS USING THE SPORULATION SCALE DEVELOPED BY SMITH AND NADIM (1983):(0)- no fruiting bodies present,(1)- few fruiting bodies present,(2)- average number of fruiting bodies present and,(3)- large number of fruiting bodies.

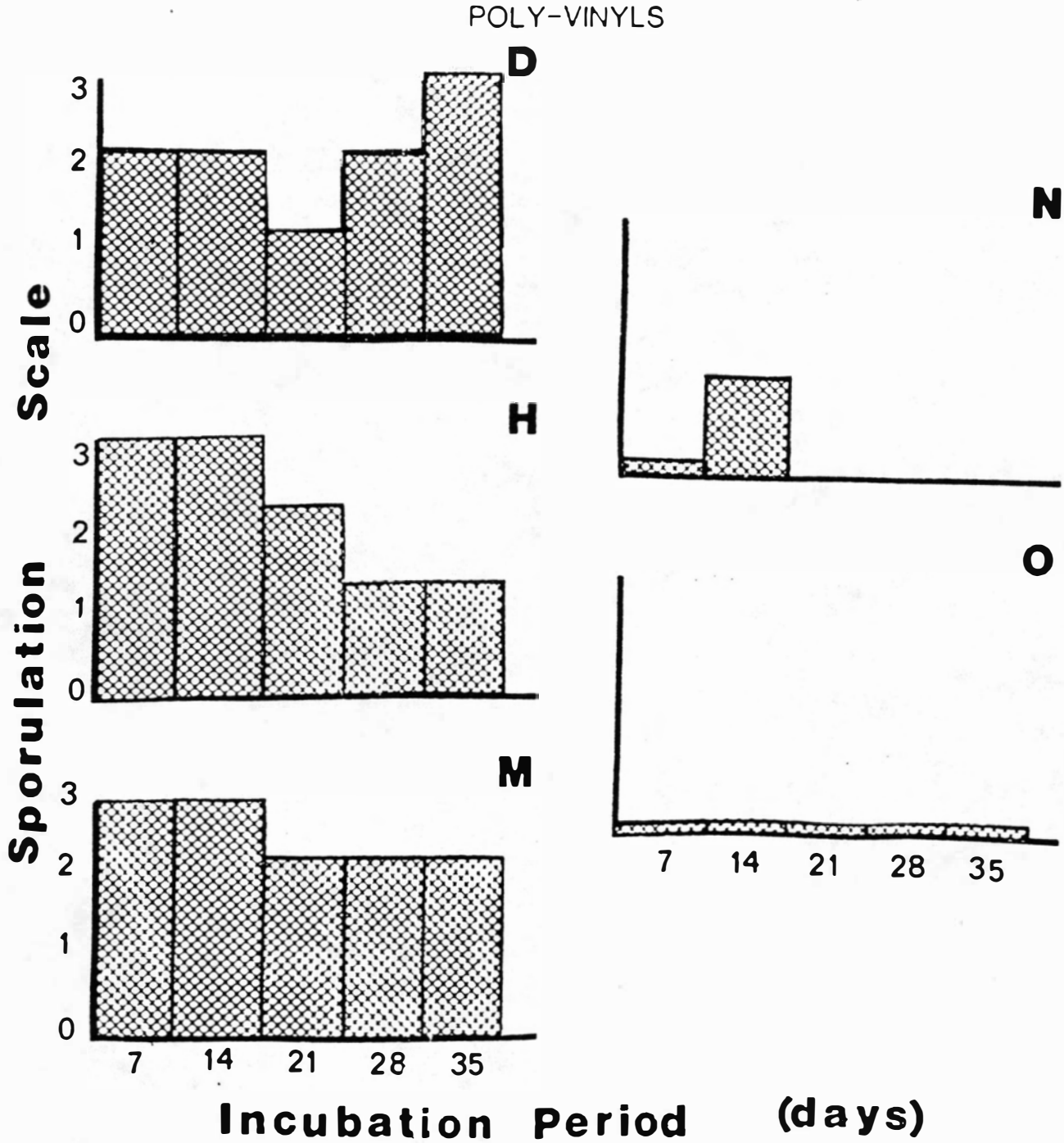


FIGURE 3.2-9

ASSESSMENT OF FUNGAL GROWTH ON SELECTED POLYMERS AND RESINS USING THE SPORULATION SCALE DEVELOPED BY SMITH AND NADIM (1983):(0)- no fruiting bodies present,(1)- few fruiting bodies present,(2)- average number of fruiting bodies present and,(3)- large number of fruiting bodies.

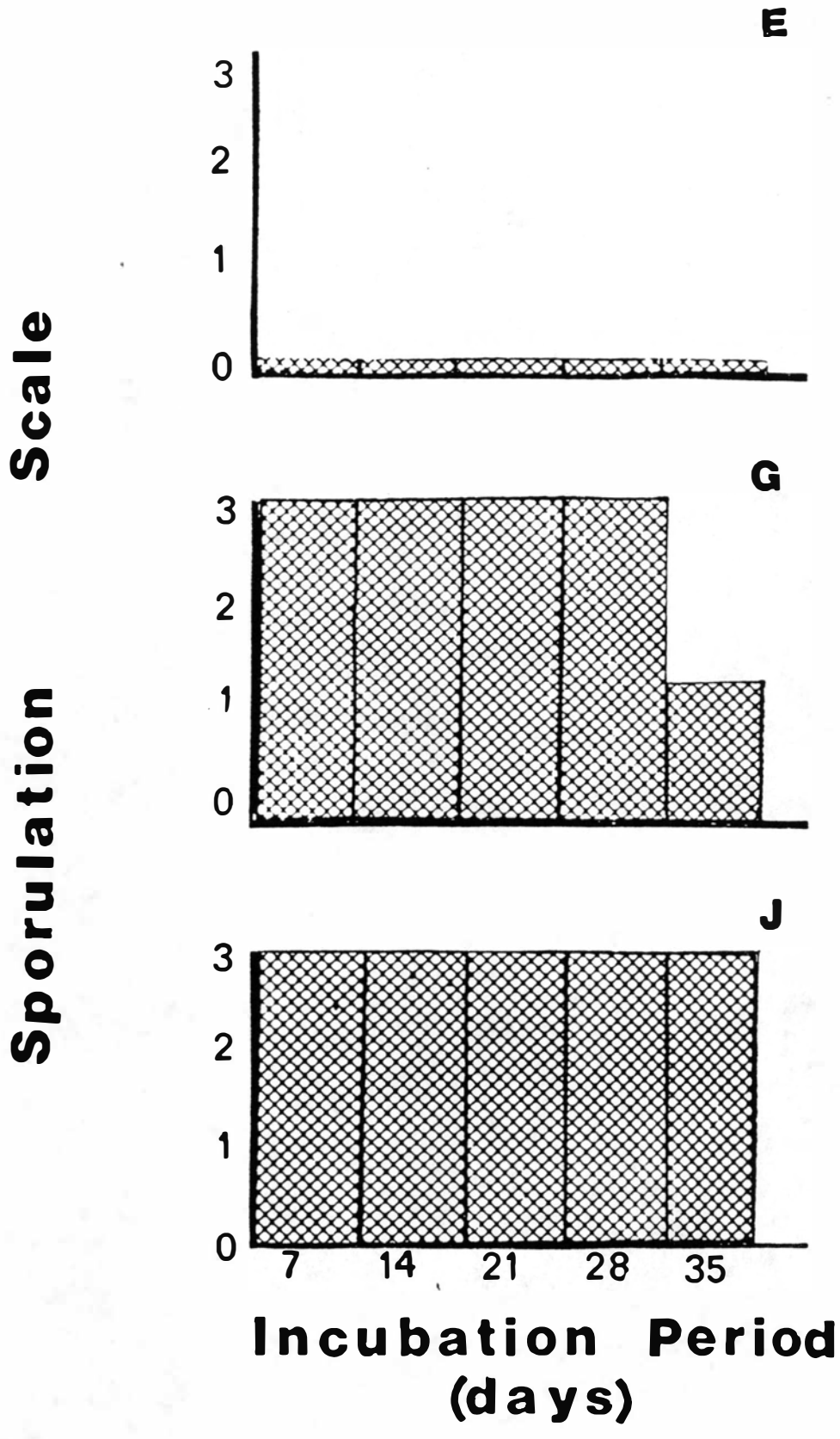


FIGURE 3.2-10

ASSESSMENT OF FUNGAL GROWTH ON SELECTED POLYMERS AND RESINS USING THE SPORULATION SCALE DEVELOPED BY SMITH AND NADIM (1983):(0)- no fruiting bodies present,(1)- few fruiting bodies present,(2)- average number of fruiting bodies present and,(3)- large number of fruiting bodies.

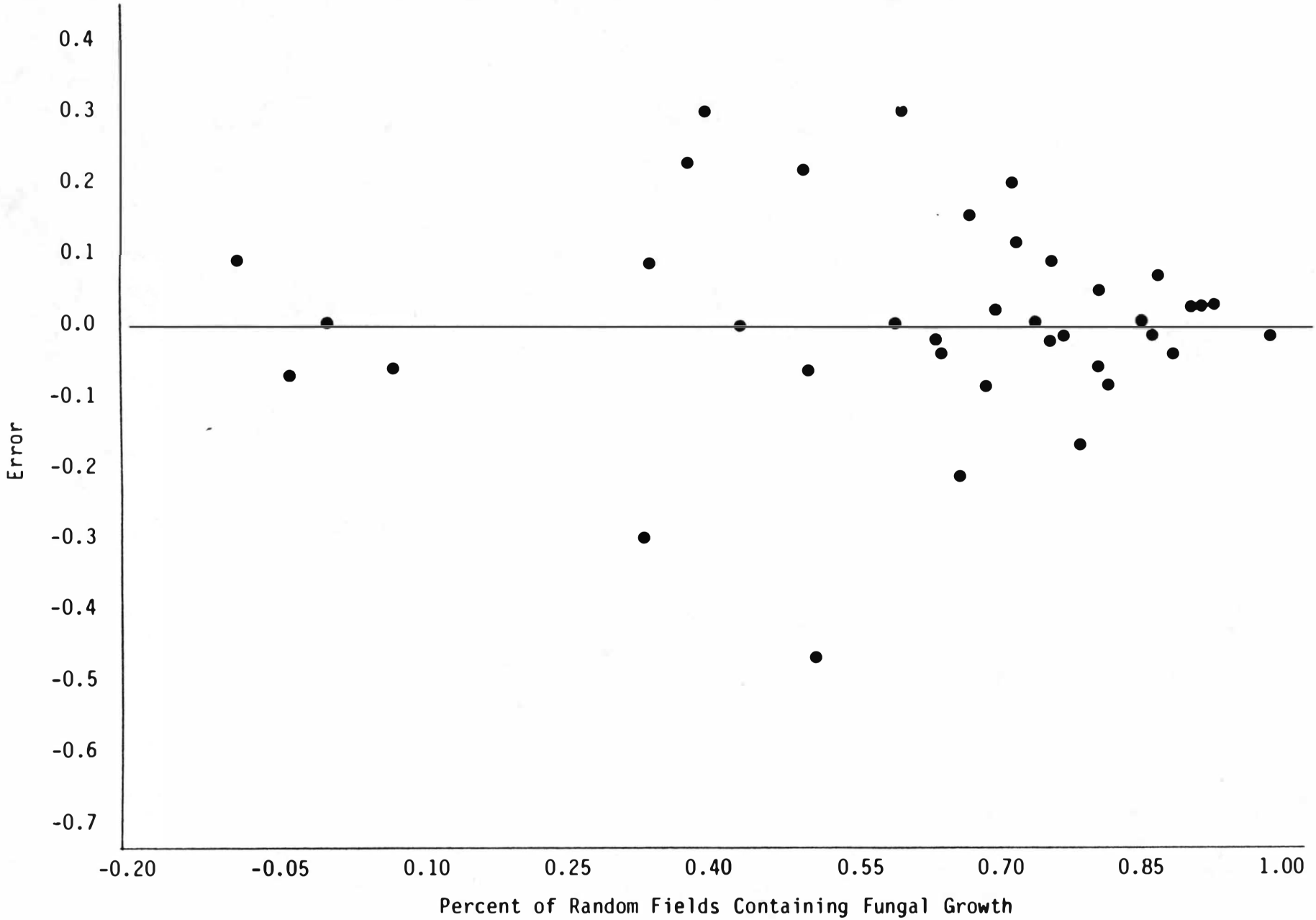


FIGURE 3.2-11 Residuals Plot of Square Root Transformed Random Field Data

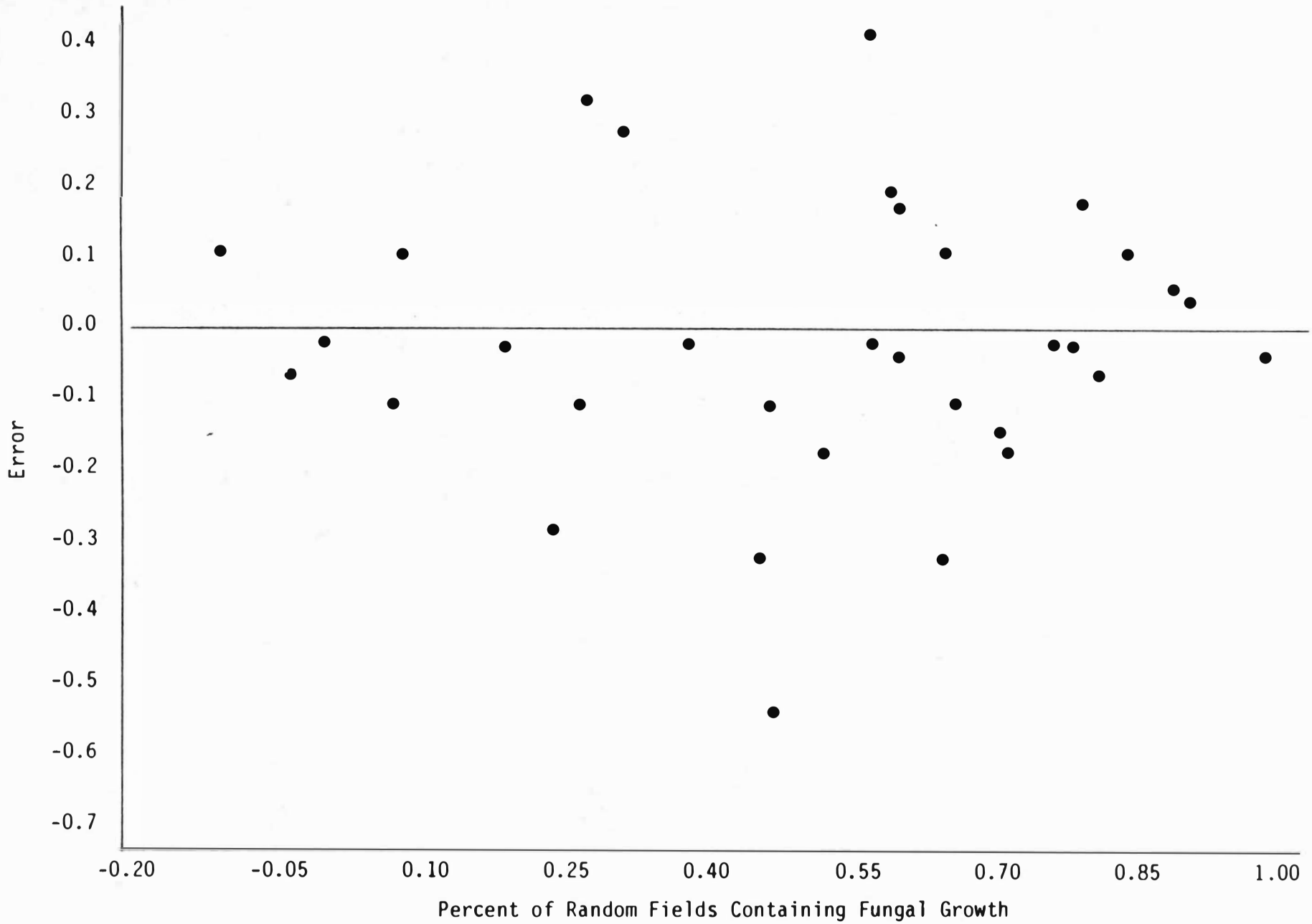


FIGURE 3.2-12 Residuals Plot of Untransformed Random Field Data

TABLE 3.2-1 WILCOXON'S TWO-SAMPLE TEST GROUPINGS OF GROWTH AND SPORULATION SCALE DATA

SPORULATION SCALE

CONSOLIDANT	A	E	I	O	B	F	C	D	H	L	M	G	J	K	P
MEDIAN			0			1			2					3	
SPORULATION SCALE															

GROUPINGS

GROWTH

MEDIAN GROWTH	A	E	I	B	F	G	H	J	O	D	L	M	C	K	P
			0		1				2					3	

GROUPINGS

A=G.E.Silicone B=Tegovakon V C=Dammar D=Mowital E=Rhoplex F=Conservare H G=Acryloid B-72 H=AYAF I=Conservare OH J=Acryloid F-10 K=Conservare H40 L=Shellac M=AYAT O=AYAA P=Imron Note: Experimental samples of N (AYAC) did not survive until the 5th week of incubation; control samples were not affected over the interval.

3.2.3. RANDOM FIELD OBSERVATIONS

3.2.3.1 Homogeneity of Random Field Data

Comparisons of residual plots of untransformed RFP observations (Figs. 3.2-11 and 3.2-12) with square root transformed data and untransformed RFP data, respectively, typically associated with binary data of this type show that the untransformed data are more homogeneous (error distributed about the mean is normal) than the transformed data. This is not uncharacteristic for data sets of this type, since transformation of the data is usually better (i.e., more homogeneous) when the data are more limited to the ends of the spectrum (Steel and Torrie, 1960). In our study that would mean at either low or high percentages of cover, but since our data was spread over the interval, we were able to use untransformed data in our subsequent analyses.

3.2.3.2 Multiple Range Tests

3.2.3.2.1 Duncan's Multiple Range Test

These tests are of use in comparing each sample set (sets within each time interval) and in comparing the closeness of the means, after ranking, to data from other consolidants. Thus these tests illustrate which polymers or resins are significantly different from each other.

The Duncan's Multiple Range Test for mean fungal growth performed at the conclusion of the experiment is presented in Table 3.2-2. Based upon that ranking, five groupings occur. In the group having the least biodeterioration effect (group C-G-B-O-E, bottom line of Table 3.2-2) only two, O and E (**AYAA** and **Rhoplex AC-234**, respectively), were significantly different from all other groupings.

3.2.3.2.2 Student-Neuman-Keuls Test

The Student-Neuman-Keuls test (SNK) is a multiple range test similar to Duncan's that is considered to be more conservative since it generally provides fewer significant groupings for the same data. Utilizing the same random field data in Table 3.2-2, Table 3.2-3 was constructed with the SNK test.

This test presents three significantly different groupings for the data as compared with five from the Duncan's procedure. However, with regard to the least biodeteriorated polymers, the results are the same, with **AYAA** and **Rhoplex AC-234** being the only polymers significantly different from other groupings in growth effect.

3.3 CHEMICAL OBSERVATIONS

3.3.1 FTIR RESULTS

3.3.1.1 FTIR Results of the Special Washing Study

To ensure that chemical changes did not occur to the test samples after peroxide washing, a special study was undertaken prior to inoculation of the test strips with fungi. In this washing study, samples of each of the 16 polymers and resins were washed, scraped and weighed, as presented in section 2.4.1, and sent to the Getty Conservation Institute for FTIR analysis.

The results of this special study noted that of the 16 polymers and resins tested, only **Rhoplex AC-234** (consolidant E) and **Imron 192S** (consolidant P) showed a chemical change after H_2O_2 washing. In the case of **Rhoplex AC-234**, change was noted in the 15% H_2O_2 wash but not in lower concentrations. **Imron 192S** showed more chemical changes associated with high concentrations of H_2O_2 and less at lower concentrations--a linear decrease with concentration was noted. Based on these observations, a 5% solution of H_2O_2 was chosen as the wash solution to remove the fungi.

TABLE 3.2-2 DUNCAN'S MULTIPLE RANGE TEST GROUPINGS OF RANDOM FIELD OBSERVATIONS

POLYMERS/RESINS	K	J	A	P	L	F	I	M	H	D	C	G	B	O	E
	DUNCAN'S MULTIPLE RANGE TEST[a]														
Mean % of Growth	100	90	80	80	73	60	60	60	60	60	40	30	20	0	0

A=G.E.Silicone B=Tegovakon V C=Dammar D=Mowital E=Rhoplex F=Conservare H G=Acryloid B-72 H=AYAF I=Conservare OH J=Acryloid F-10
K=Conservare H40 L=Shellac M=AYAT O=AYAA P=Imron

[a]Duncan's Multiple Range Tests were performed on data after analysis of variance (ANOVA) detected significant differences at <0.05 (the mean values were calculated from the data collected at week 5 of sampling). The mean concentrations of the underlined stations are not significantly different at the 0.05 level.

Note: Experimental samples of N (AYAC) did not survive through the 5th week of incubation; control samples were not affected over the interval.

TABLE 3.2-3 STUDENT-NEUMAN-KEULS TEST GROUPINGS OF RANDOM FIELD OBSERVATIONS OF FUNGAL GROWTH ON TEST MATERIALS

POLYMERS/RESINS	K	J	A	P	L	F	I	M	H	D	C	G	B	O	E
	STUDENT-NEUMAN-KEULS TEST[a]														
Mean % of Growth	100	90	80	80	73	60	60	60	60	60	40	30	20	0	0

A=G.E.Silicone B=Tegovakon V C=Dammar D=Mowital E=Rhoplex F=Conservare H G=Acryloid B-72 H=AYAF I=Conservare OH J=Acryloid F-10 K=Conservare H40 L=Shellac M=AYAT O=AYAA P=Imron

[a]SNK tests were performed on data after analysis of variance (ANOVA) detected significant differences of a<0.05%. The mean values were calculated from the data collected at week 5 of incubation. The mean concentrations of the underlined groups are not statistically different at a=0.05.

Note: Experimental samples of N (consolidant AYAC) did not survive to the fifth week of incubation; control samples were not affected over the testing interval.

3.3.1.2 FTIR Organism Exposure Results

To ascertain chemical changes that may have occurred after fungal exposure, the control and experimental samples were analyzed by the GCI using Fourier transform infrared spectroscopy. Comparison of experimentals (exposed to fungal organisms) and controls (exposed to identical conditions, except no fungal inoculation) showed that very little chemical change occurred. The overall results for FTIR must be considered inconclusive. The following provides a brief synopsis of the GCI's findings:

- Spectra obtained from inoculated versus control samples produced no conclusive results on the type or degree of polymeric degradation.

- No new spectral bands were observed in any samples.

- Differences in the relative heights of existing hydroxyl, carbonyl, and carbonyl and hydrocarbon absorbence bands were observed for some sample/control pairs. The GCI called the differences "slight," but did note that these changes may be due to the hydrolysis of the polymers by enzymatic activity of the fungi.

- The GCI report also noted that there was "no systematic or consistent pattern produced in the related sample sets or between similar polymer types."

- The GCI report concluded that: "Although the interpretation of spectral differences may be subjective, it is clear that the biological activity of the fungi, under the condition of this analysis,

do not produce significant chemical deterioration products for the polymers examined."

An overview of the GCI results, organized by polymer and resin type, is presented in Table 3.3-1.

The conclusion of the GCI study noted the following reasons why the FTIR results may have been inconclusive:

- The polymers may be resistant to fungal attack.
- The chemical changes may be below the sensitivity limit of FTIR, which is a 5% change.
- The fungal growth on the samples was inhomogeneous, thus resulting in inhomogenous portions being analyzed.

The FTIR results provided by the GCI were by themselves inconclusive. They did not support or refute the biological effects observed in the other parts of the study.

TABLE 3.3-1
FTIR RESULTS FROM THE GCI STUDY*

Polymer Class	Sample Tested	Study Results
Silicone Resins	A--**G.E. Silicone** B--**Tegovakon V** F--**Conservare H** I--**Conservare OH** K--**Conservare H40**	Most of the silicone resins show stronger OH absorption than the controls, indicating a higher degree of hydration.
Polyvinyls Acetates	H--**AYAF** M--**AYAT** N--**AYAC** O--**AYAA**	Each of the PVACs showed different patterns of changes. However, these changes seem to be consistent within the individual polymer sets. The apparent difference in carbonyl intensities needs to be verified by other methods or replication.
Butryl	D--**Mowital**	Polymer unaffected by fungal growth.
Acrylics	E--**Rhoplex** G--**Acryloid B72** J--**F-10**	Samples of **Rhoplex** showed variations in peak heights ratios of C-H stretch bonds that corresponds to a chain breaking pattern. Samples of **Acryloid B72** do not exhibit these changes. While sample J--**F10** showed slight and inconsistent changes.
Natural Resins	C--**Dammar** L--**Shellac**	**Dammar** appeared to be unaffected by fungal exposure. Changes in spectra for **Shellac** are slight, but consistent with patterns that are expected for hydrolysis and chain scission. These changes may be real but should be verified by other methods.
Polyamide	P--**Imron**	Experimental shows higher OH peak, indicating sample hydration.

*Valentin, N., and M. Derrick. Infrared analysis report for susceptibility of stone consolidants to microbiologically induced deterioration. The Getty Conservation Institute. January 12, 1988.

Section 4

4 DISCUSSION

4.1 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. 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.

In all cases of treatment, the objects should be regularly inspected to assess their state and to judge the effectiveness of the particular treatments applied. Maintenance after treatment is also necessary to prevent any further damage. This often involves replacement or repair of the protective coating system.

A good consolidant should, typically:

- Penetrate easily into the substrate
- Result in similar thermal properties for treated and untreated layers
- Not cause a reduction in porosity and pore size distribution of the substrate
- Be compatible with the substrate to form a durable composite
- Not alter the appearance of the substrate.

4.2 RATIONALE FOR TESTING

Devising a reproducible test for evaluation of an effect is difficult and fraught with several types of bias. In the present project we were attempting to screen 16 consoliants or potential consolidants for their susceptibility to microbiological deterioration. By definition, a screening test is typified by an assay that is easy to set up and run, and that will provide meaningful reproducible results.

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. This study was designed as a way of measuring on a macro scale the relative durability of polymers and resins.

The most important step in designing a screening program for consolidants is to define the objectives of the program. The broad objective of such a program is to provide information to enable the conservator to make a more informed selection of a polymer or resin based upon 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 (consolidant) is important in assessment of microbiological attack (Hueck et al., 1969). 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. Therefore, the stability of the coating over time is an important factor in evaluating its efficacy in preventing biological attack.

It has been observed by Kempten et al. (1963) after analysis of soil burial processes, that breakdown of fungicide-protected cotton by biotic attack occurs only after a nonbiotic process lowers the concentration of the inhibitory compound. Two distinct phases have been associated with the breakdown of protection: (1) the leaching out of active agents and (2) the settling of organisms.

As pertaining to the leaching effect, a full scale assessment of the volatility of active agents associated with this assessment was outside the purview of the study. However, some assessment of effects of washing and leaching as related to weight loss were noted and are presented in the results section of the present study.

4.3 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 formaldelhyde, 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.

4.4 POLYMER AND RESIN COMPOSITE SCORING

The present study has developed physical and chemical methods with which to describe deterioration associated with fungal contact 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 (high, medium and low) and numbers were assigned (a 1, 2, or 3) to consolidants/resins within the groups. Afterwards a factor weighting was applied to give greater value to those factors 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; 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 physico-chemical changes such as 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 Table 4-1.

From the results section, 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.).

TABLE 4-1 POLYMER AND RESIN COMPOSITE SCORING RANKINGS

Polymer/Resin	Sporulation[a] Scale	Weight[b] Change	Colony[c] Growth	Multiple[c] Range Test	FTIR[a]	TOTALS
E RHOPLEX AC-234	1	3	2	3	2	**11**
O AYAA	1	3	4	3	2	**13**
B TEGOVAKON V	1	6	2	3	1	**13**
A G.E. SILICONE 1048	1	6	2	6	1	**16**
H AYAF	2	3	4	6	2	**17**
D MOWITAL B-20-H	2	3	6	6	1	**18**
F CONSERVARE H	2	6	4	6	1	**19**
G ACRYLOID B-72	2	9	4	3	1	**19**
M AYAT	2	3	6	6	2	**19**
L SHELLAC	2	3	6	6	2	**19**
I CONSERVARE OH	1	9	2	6	2	**20**
C DAMMAR	2	9	6	3	1	**21**
P IMRON 192S	3	6	6	6	1	**22**
J ACRYLOID F-10	3	6	4	9	1	**23**
K CONSERVARE H40	3	3	6	9	2	**23**
N AYAC[d]						**>23**

[a]Based upon a factor weight of 1.

[b]Based upon a factor weight of 3.

[c]Based upon a factor weight of 2.

[d]Final composite rank not computed since fungal treatment resulted in complete breakup of samples.

For example, the table shows that silicone-based polymers are both resistant to fungal attack (**G.E. Silicone 1048**) and poorly resistant (**Conservare H40**). Due to a lack of company-supplied product data and failure of the FTIR to detect any 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.

The acrylic polymer class also showed divergent behavior. **Acryloid F-10** showed poor resistance to microbial growth while **Acryloid B72** showed moderate resistance. **Rhoplex AC-234** ranks as the best overall in resistance to biodeterioration effect.

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 breakup 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.**

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**, **AYAA**, and **Tegovakon V**, with composite scores of 11, 13, and 13, respectively. **G.E. Silicone 1048**, **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 **AYAA**, **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**, **AYAT**, and **Shellac**) fell between the extremes, with composite scores of 19 (see Table 4.1).

Section 5

5 CONCLUSIONS

5.1 MAJOR FINDINGS

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

- **Rhoplex AC 234**, **Tegovakon V**, and **AYAA** had high resistance.
- **AYAC**, **Conservare H40**, **Acryloid F-10**, **Imron 192S**, **AYAA** and **Dammar** all showed poor resistance.
- **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 with these products and of any environmental controls that may reduce their susceptibility to attack; and (2) attempts be made either to replace these products with more resistant products or to include a biocide within them. If a biocide is added to these products, further testing should be carried out.

5.2 SUGGESTIONS FOR FUTURE RESEARCH

The screening test developed and tested in this study represents a first attempt in the conservation field to rank consolidants based upon statistically valid objectives using short-term laboratory testing.

It is not the object of this screening test to supplant full-scale field testing, but rather to present a more limited number of polymers and resins for a field test. In addition, it is hoped that those polymers or resins shown to be more resistant to biodeterioration may be re-evaluated with appropriate addition of biocidal agents, which should presumably lengthen their service life as consolidants or coatings.

This short-term test is meant as an adjunct to durablity testing of consolidants and coatings and should be performed in concert with such testing. A field study is the next logical step in these studies. Key objectives of a field study would be to test the microbiological susceptibility of a polymer or resin with and without the addition of a biocide in mixed environmental conditions, and to test for any resultant alteration in the physical properties of the underlying matrix/polymer combination using standard materials testing methodology. Another area of importance to development of better consolidants is the quantification of the effects of various environmental factors on the physical degradation of the matrix/polymer system (e.g., acid rain or extreme exposure conditons).

In view of their apparent strong resistance to microbial degradation, in addition to their good consolidant properties, the alkoxy silanes or other new derivatives of the silanes are worthy of further study to answer a number of questions: first, What components of the silanes are resistant and which are sus-

ceptibile to microbial attack? How important is chain length or molecule complexity in resistance to microbial attack? Would the presence of a biocide alter a polymer's physical resistance to attack or its consolidating ability?

To provide a better understanding of chemical changes in the polymers and resins after fungal attack, microscopical FTIR of in-situ thin films may be warranted. Other techniques that may aid in understanding the chemical transformations involved are gas phase chromatography and liquid chromatography.

Section 6

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Appendix A

APPENDIX A

LITERATURE REVIEW OF CONSOLIDANTS

A. Silanes and Siloxanes

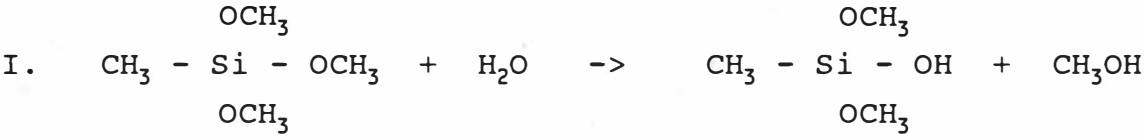
Silanes are simple monomeric molecules based on the tetravalent silicon atom, and may contain many different substituted groups. Siloxanes are polymers of silanes containing silicon-oxygen bonds (Seymour and Carraher, 1981). In the conservation of stone, two types of siloxanes are used. These include the various prepolymerized polyorganosiloxanes, more commonly called silicones, which are used as stone sealants and water repellents, and the alkoxysilanes, which are polymerized in situ, and are used as consolidants. (The term silicone is an inaccurate name for the siloxanes in general. The name silicone was first used in the 1920's and has continued to be used for prepolymerized siloxane polymers). Siloxanes were first experimented with as stone consolidants in the 19th century. The silicones soon replaced compounds such as wax or natural oils as weatherproofing compounds, but initial experiments with alkoxysilanes as consolidants were discouraging (Amoroso and Fassina, 1983; Lewin and Wheeler, 1985). In recent years, however, alkoxy silanes have performed well in experiments as stone consolidants (Bradley, 1985; Hanna, 1984). The silicones, being applied in a polymerized form, lack the penetrating ability of the silanes, which are applied as monomers.

The basis of siloxane chemistry is the oxygen-silicon backbone:

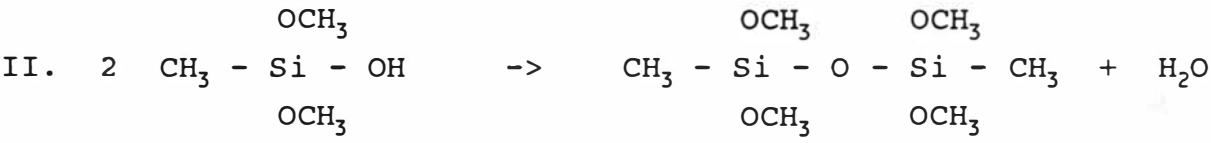
```
        R       R       R
- - Si - O - Si - O - Si - -
        R       R       R
```

The oxygen-silicon bond system is very stable. Unlike the carbon-carbon bonds, such as in organic polymers, the oxygen-

silicon bonds do not tend to form conjugated double bonds which can lead to chain scission. The siloxane polymers, or polysiloxanes, polymerize in a two step reaction process (Eaborn, 1960). The monomeric units of the siloxane chain, silanes, are hydrolyzed with water to form silanol molecules. A condensation reaction between two silanol molecules then leads to the formation of a siloxane polymer with Si - O - Si linkages. This is illustrated with the stone consolidant compound methyl trimethoxy silane (MTMOS):



I. $CH_3 - Si(OCH_3)_3 + H_2O \rightarrow CH_3 - Si(OCH_3)_2 - OH + CH_3OH$



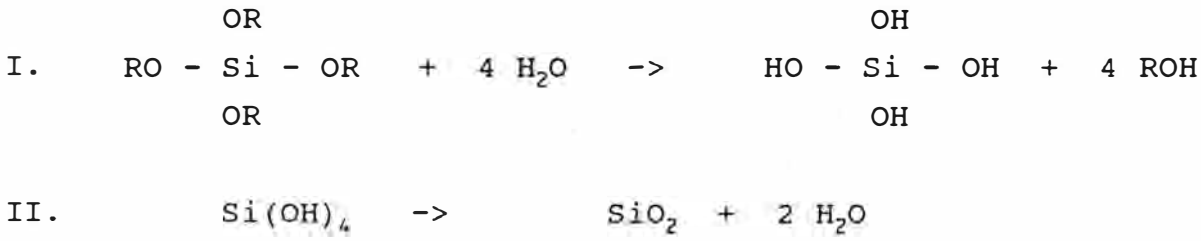
II. $2\ CH_3 - Si(OCH_3)_2 - OH \rightarrow CH_3 - Si(OCH_3)_2 - O - Si(OCH_3)_2 - CH_3 + H_2O$

Further hydrolysis and condensation can lead to a longer chain polymer, and the formation of a three-dimensional network by cross-linking between the polymer chains. The hydrolysis reaction is catalyzed by bases and acids. The polymerization and the evaporation of the liquid monomers of silanes such as MTMOS, and the silicone resins, was found to be dependent on the relative humidity (Mavrov, 1983; Charola et al., 1984).

The silanes are highly regarded as possible consolidants because after polymerization they form a binder similar to that in siliceous sandstone. Laboratory evaluations of alkoxysilanes have shown them to have good penetrating ability in stone, but to vary greatly in their ability to consolidate stone. In general, the silanes alone do not consolidate stone as well as epoxies or acrylic copolymers. The siloxanes were, however, found: To be very stable in the presence of acid and ultraviolet; to have in-

creased water repellency; allow the removal of salts; to have decreased porosity but did not fill the pores of stone; and did not substantially alter the appearance of treated stone (Bradley, 1985; Clifton, 1984; Sramek and Kralova, 1981; DeWitte, Charola and Sherryl, 1985). Recent experiments showed that the addition of a small amount of acrylic copolymer to an alkoxy silane greatly increased the extent of consolidation (Bradley, 1985).

Recent experiments with another form of silane have yielded very favorable results. These are the silicic acid esters, which have the general form of $Si(OR)_4$. The silicic esters are catalyzed in situ in the presence of water to form silicic acid, which forms a silicic gel of silicon dioxide and water:



I. $RO-Si(OR)_2-OR + 4\,H_2O \rightarrow HO-Si(OH)_2-OH + 4\,ROH$

II. $Si(OH)_4 \rightarrow SiO_2 + 2\,H_2O$

Like the alkoxysilanes, polymerization of the silicic esters is dependent on relative humidity. The silicic esters can be used for waterproofing and consolidating, and have all the advantages of the alkoxysilanes, while providing more effective consolidation of the stone (Bradley, 1985; Charola and Koestler, 1986; DeWitte et al., 1985).

B. Acrylic Resins

Acrylic resins in various forms have found a wide use in different fields of conservation, being used for such varying purposes as a varnish for paintings to a consolidant for stone and concrete. Acrylics are used in the form of monomers polymerized in situ, or more commonly, in the form of a copolymer

which is applied dissolved in any one of a number of organic solvents. The clarity of acrylic resins, good adhesive properties, reversibility and excellent aging properties have made them a popular weapon in the modern conservators arsenal. A mixture based on Acryloid B72 and a silicon resin has also been used with some success as a consolidant and water repellent (Rossi-Manaresi, 1981).

Acrylic monomers can be produced by esterification of acrylic acids with various alcohols. Acrylic esters are also prepared from ethylene, acetylene, or acetone. Acrylic monomers have the general form $CH_2CR_1COOR_2$, such as methyl acrylate, $CH_2CHCOOCH_3$, or in the form of methyl methacrylate, $CH_2C(CH_3)COOCH_3$. Polymerization of these monomers occurs at the double-bonded carbons, called the vinyl groups. The reaction begins with the addition of a free radical, generated by an initiator, to the double bond of a monomer. This compound then attaches to another monomer, which attaches to another and so on in a series of chain propagating steps. This is an example of chain-reaction polymerization called vinyl polymerization (Seymour and Carraher, 1981). Polymerization of the unsaturated monomers of this type yields a saturated polymer backbone, with the different pendant groups attached. Polymethylmethacrylate has the form:

$$
\begin{array}{c}
\qquad\qquad CH_3 \qquad\quad CH_3 \qquad\quad CH_3 \\
- - CH_2 - \underset{COOCH_3}{C} - CH_2 - \underset{COOCH_3}{C} - CH_2 - \underset{COOCH_3}{C} - CH_2 - -
\end{array}
$$

Polymerization can occur under the influence of heat, U.V., and gamma radiation, or with chemical initiators such as azobis (isobutyronitrile) or benzoyl peroxide. Monomers can be applied solvent-free to porous stone and polymerized in place using an initiator compound or by heating with a thermal blanket (Kwiat-

kowski, 1985). Polymerization by radiation in stone is more difficult, and is more common in the consolidation of less dense substances such as wood.

The most common use of acrylic resins in conservation today is in the form of a prepolymerized copolymer. A copolymer is a mixture of two or more different monomers which is allowed to polymerize. Copolymerization allows the production of materials with very different properties from that of either monomer. The addition of ethyl acrylate to methyl methacrylate, for example, can increase hardness and improve weathering ability. A common type of copolymer is polymerized from methacrylate and ethyl-methacrylate. These are supplied in the form of small pellets which are dissolved in an organic solvent to the desired dilution and applied to the stone. Ketones, esters, aromatic hydrocarbons, partially chlorinated aliphatic hydrocarbons and cyclic ethers are in general good solvents for acrylics. Aliphatic hydrocarbons can also be used for butyl and higher ester polymers.

Acrylics polymers in general are atactic polymers (the side groups attached to the polymer backbone are randomly distributed) and have an essentially amorphous structure. They are extremely transparent, and transmit light in the visible as well as the ultra-violet. Polymethylmethacrylate, however, absorbs light in the region of 280-320 nm. Acrylics have very good resistance to oxidative photodegradation; most stable of all is PMMA. PMMA can undergo chain scission under the influence of normal U.V. light by the formation of radicals, while polymethyl acrylate forms cross-links and becomes insoluble (Sramek and Kralova, 1981). The presence of monomers or catalysts can significantly reduce the stability of acrylic polymers. Acrylics can resist weak acids well, and has been shown to slow down the damaging effects of acidic attack on stone (Tucci et al., 1985). Acrylics, and

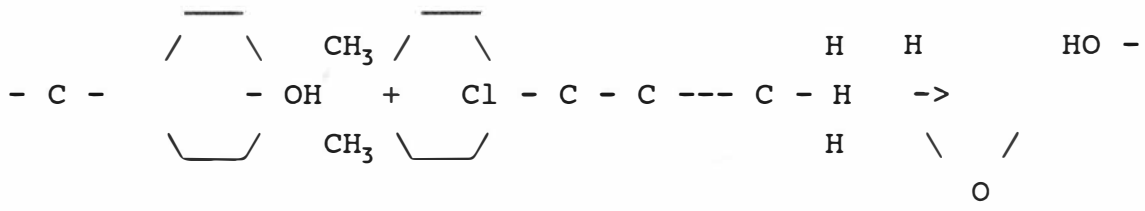
PMMA in particular, are only slightly susceptible to alkalis, but can become soluble in alkali at higher than normal temperatures. Acrylics are also susceptible to many organic solvents.

Acrylic copolymers are thought to be generally resistant to microbiological deterioration, and not able to be used as a food source by microorganisms (Nugari and Priori, 1985; Pankhurst et al., 1972). Studies with some acrylic textiles exposed to fungal cultures, however, showed local erosion and cleavage of the fibers with certain Penicillium and Aspergillus species (Watanabe, 1985).

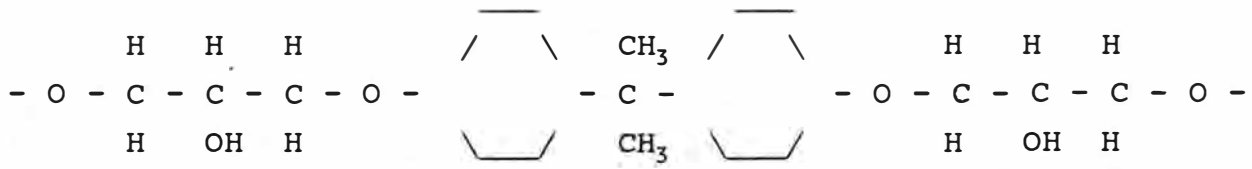
C. Epoxy Resins

Epoxy resins are usually considered in stone conservation only in difficult restoration cases, such as when consolidation of a stone element that is to be put under compressive stress is required, or the joining of large pieces of stone. Only epoxy resins may provide the mechanical strength to ensure success. Epoxy resins are usually used in conservation only when absolutely necessary, however. After they set they are irreversibly set in place. Other disadvantages include high viscosity, a darkening of the appearance of the stone, low stability in ultraviolet radiation with a tendency to yellow, and fair to low resistance to oxidative degradation and to acids (Gauri, 1974; Hawkins, 1982; Rossi-Manaresi, 1981; Kotlick et al., 1983).

Epoxies are formed by cross-linking of epoxy resins in the presence of a curing agent (Seymour and Carraher, 1981). The most common epoxy resins are polymers based on monomers of bisphenol A and epichlorhydrin. These polymerize in the presence of hydroxide to form a viscous liquid resin:



Bisphenol A Epichlorohydrin

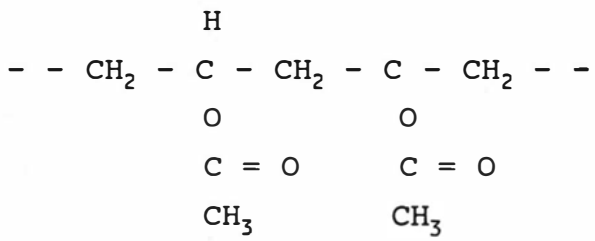


This epoxy resin, or epoxy prepolymer, is mixed with a curing agent, often an amine or polyamine, which forms cross-links between the resin chains, producing a tough, clear epoxy with generally excellent adhesion properties. The curing time can be regulated by the choice of curing agent and setting temperature.

The high viscosity of epoxy resins can lead to inadequate penetration of the stone, however,and the formation of a sharp interface between the unconsolidated and consolidated parts of the stone. This can be controlled somewhat with the addition of a solvent or solvent mixture containing an aromatic hydrocarbon, often methyl ethyl ketone, to dilute the resin before applying it with the hardener to the stone. More recently, solutions of aliphatic epoxy resins have been studied which have lower viscosities, good color stability along with the strong consolidating and adhesive abilities associated with epoxies (Bilinski, 1978). Some studies have indicated that these aliphatic epoxies adsorb more SO_2 than the bisphenol-A type epoxy, and have more physical adsorption versus chemisorption, leading to enhanced calcite-SO_2 reactivity and the formation of gypsum (Laukhuf et al., 1982).

D. Vinyl Polymers

Vinyl polymers are amorphous, atatic polymers similar to poly vinyl acrylate polymers. They are many type of vinyl compounds, including poly vinyl chloride, poly vinyl alcohols, poly vinyl acetate, and others. The most important for stone conservation is poly vinyl acetate or PVAC (Bilinski, 1978). The chemical composition of PVAC is similar to the poly acrylics:



PVAC films are highly transparent, very resistant to cracking and yellowing due to U.V. light, are very permeable to water vapor, resistant to abrasion, and can be diluted to attain low viscosities for good penetration. The low concentrations needed for good penetration, however, may mean that several coats may be needed for sufficient protection. Pure PVAC and poly vinyl chloride films are also very resistant to deterioration by microorganisms, but PVC has been shown to be vulnerable to the action of enzymes produced by many types of fungi (Inoue, 1983). The addition of plasticizers to these types of polymers has been shown to support the growth of some microorganisms (Hamilton, 1983; Roberts and Davies, 1986; Pankhurst et al., 1972). It has also been theorized that ultraviolet light may produce degradation of some PVC components which are more susceptible to biological attack (Hamilton, 1983).

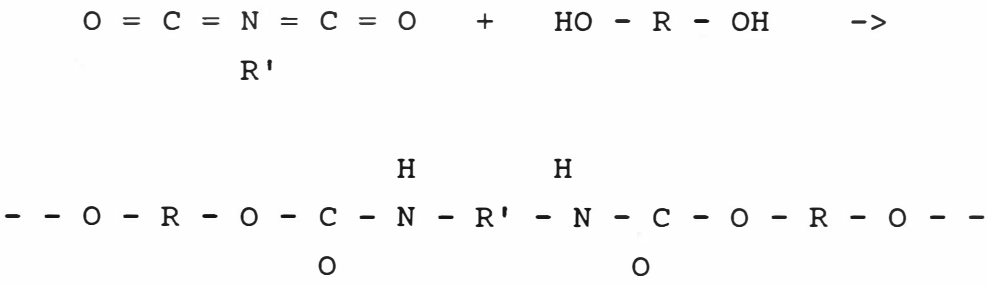
PVAC can be applied either dissolved as a solution in an organic solvent such as toluene, acetone, or an alcohol, or in an

aqueous emulsion, with the addition of surface active agents. PVAC polymers and copolymers may lack the adhesive strength necessary for consolidation, especially on siliceous surfaces. It has also been found to produce a glossy looking surface, and if not carefully applied, may produce impermeable layers which can trap moisture and salts underneath (La Fleur, 1976). Poly vinyl chloride and the other chloride polymers may release chlorides due to photochemical processes, which could damage the stone (Ochrona Zabytkow, 1961; Davis and Sims, 1983).

E. Polyurethanes

Polyurethanes are another form of artificial organic polymer used for the protection of stone, but is more commonly used as a sealant for outdoor metal and wooden objects, a consolidant for wooden objects, and for the casting of replicas (Kalberg, 1978; Naylor, 1983). The polyurethanes are applied to stone prepolymerized, dissolved in an organic solvent, and are used as sealants, but not as consolidants.

Polyurethanes are formed by a step-reaction polymerization process with dihydroxy alcohols and diisocyanates (Seymour and Carraher, 1981):



Studies with polyurethanes on stone show them to have little penetrating and consolidating ability, but have good water-repellency properties, and may be useful as sealants, but some

have found them to produce unacceptable darkening of the stone (Clifton, 1984; DeWitte et al., 1985). Exposure and natural weathering tests on the polyurethanes have given mixed results. Some have found them to have resisted weathering after 10 years exposure, with little yellowing, blistering or loss of gloss (Naylor, 1983). Others report poor aging qualities, with loss of protective capability and embrittlement (Steen, 1971; Sharman et al., 1983).

Unlike many other synthetic polymers, polyurethanes have frequently been shown to be subject to direct attack by micro-organisms, especially by fungi (Seal and Pathirana, 1982; Pathirana and Seal, 1985; Pankhurst et al., 1972). Fungi cultivated on polyurethanes have been shown to produce weight loss, tensile strength loss, and elongation changes, most notably with the polyester polyurethanes. It has been theorized that non-specific protease and esterase enzymes produced by certain fungi may catalyze hydrolysis at susceptible sites on the polymer chains.

F. Inorganic Materials

Inorganic consolidants of various types were extensively used throughout the 19th century and the first half of the 20th century, but because of the problems with their performance have generally been superseded today by the use of synthetic polymers or silanes. Most inorganic consolidants produce a white insoluble phase in the pores of the stone by precipitation or by a chemical reaction with the stone. In theory, the new phase developed inside the stone should be similar in composition to the original stone itself, and act to bind together deteriorated stone. In practice, little success has been achieved with these materials, and in some cases they have accelerated the rate of decay. Inorganic consolidants have tendencies to produce hard

and shallow crusts because of poor penetration ability, form soluble salts as a by-product of their reactions, promote the growth of damaging precipitated crystals, and have poor binding ability (Torraca, 1975; Torraca, 1976; Warnes, 1926).

Alkai silicates are one type of inorganic consolidant. Known since ancient times as 'silica juice', its industrial manufacture was begun in the nineteenth century, and called 'wasserglas'. Alkai silicates are dispersions of silica in sodium hydroxide, or are water soluble preparations of silica and sodium or potassium. (Ex. $SiO_2 \cdot Na_2O + (n + 1)H_2O$) After application to the stone, a silica gel ($SiO_2 \cdot n\ H_2O$) can be precipitated from the reaction of the alkalai silicate with an acid, or by reaction with a salt such as calcium chloride. The precipitated silica can then crystallize to bind the stone.

If sodium hydroxide is not removed by washing, it can lead to effluorescence and salt crystallization damage by the formation of sodium carbonate or sodium sulfate. The formation of crystalline soluble salts such as sodium chloride or calcium arsenate may also result from a reaction of the alkalai or the stone with the precipitating agent.

Flurosilicon compounds such as hydrofluorosilicic acid (H_2SiF_6) have also been used to consolidate stone since the nineteenth century as an alternative method to the alkalai silicates (Kessler, 1883). Fluorosilicic acid is applied in an aqueous solution, and reacts readily with carbonates, oxides or hydroxides to form metal salts of Na, K, Al, Mg, and Pb. On limestones, however, it reacts vigorously to form calcium silicofluoride and carbonates, at the expense of the calcium carbonate. This reaction occurs upon contact with the limestone so as to produce a shallow crust with little consolidating ability. It reacts more slowly with siliceous stone to form a cementlike

material, but again consolidation occurs only near the surface. The acid also has a tendency to discolor some stone, especially iron containing stone.

Different types of soluble silicofluorides, containing magnesium, zinc, or aluminum, have also been applied. These result in the formation of silica, insoluble fluoride salts and carbon dioxide. Again, only the surface is hardened, which may eventually exfoliate. Damaging soluble salts are also formed when these are applied to limestone or calcareous sandstone. Evaluations of these types of fluoro-silicon compounds determined that these were not effective consolidants (Penkala, 1964). Deterioration caused by this type of consolidant was seen during the examination of the Donatello Pulpit from the Prato Cathedral, which had been treated with magnesium fluorosilicate in 1941 (Franchi et al., 1978). Although recent evidence (Gale et al., 1987) suggests silicofluodride treatment may in fact result in good protective layer with no evidence of exfoliation of the treated layer or deterioration of the underlying stone.

Several types of hydroxide solutions have been used to treat stone. Calcium hydroxide, or limewater, has been used for many centuries in an attempt to protect or restore limestone. Calcium hydroxide in solution reacts with atmospheric carbon dioxide to form calcium carbonate, which may help to bind calcareous stone. Calcium hydroxide is fairly insoluble though, so repeated treatments are necessary. The effectiveness of this technique in consolidation is debatable, but most conservators feel that at least it should not be harmful to the stone. The new calcium carbonate is, however, susceptible to the same weathering processes as the original stone, and as such probably offers little protection against further weathering. The use of newly slaked lime (calcium oxide in water) has also been investigated and seems to show some consolidating ability.

Barium and strontium hydroxides have also been studied as consolidants. Like calcium hydroxide, these react with carbon dioxide to form insoluble carbonates. These, however, if they react with sulfates form insoluble compounds, unlike calcium sulfate which is fairly soluble, and may help protect the stone in sulfide containing urban environments. Initial work with these compounds found them to have good consolidating abilities, but they were also found to produce only surface hardening, which can lead to exfoliation due to the formation of a dense surface layer and crystal growth.

Lewin developed a method to precipitate barium carbonate and sulfate deep within the stone by the addition of urea (Lewin and Baer, 1974). The urea slowly undergoes hydrolysis within the stone producing ammonia and carbon dioxide. These form ammonium carbonate which raises the pH of the solution. When the proper pH is reached, the hydroxide reacts with the carbonate and precipitates out. By this method the reaction rate can be controlled to produce an even crystalline solid solution. This method is still somewhat experimental, and more needs to be learned about the long-term benefits or problems.

G. Waxes

Waxes were among the first products applied to stone for protection or consolidation of the stone (Lauri, 1969; Rossi-Manaresi, 1972). These included the natural waxes such as beeswax, which are made of fatty acids, waxy acids, esters, alcohols and hydrocarbons, or the petroleum-derived waxes such as paraffin or microcrystalline waxes, which are pure hydrocarbons (Mills and White, 1977). Synthetic waxes consist of polymerized hydrocarbons, esters, and oxidized hydrocarbons, such as the polyethylene and the polyethyleneglycol waxes (Werner, 1957). Waxes can be

applied dissolved in a number of organic solvents, or by applying in a molten state.

Waxes have been found to have a protective effect on stone, and are effective in increasing water repellency, and can increase the tensile strength of porous stone. The disadvantages of waxes include a tendency to soften at relatively low temperatures, and to remain sticky, and trap dirt on the surface. They often cause yellowing and dulling of the surface, and may even form soaps in the presence of calcium carbonate and high humidity. They can also lose their water repellency with time and allow blisters to form underneath the wax layer, and become increasing insoluble (Gutin, 1969). Penetration of the surface is usually fairly shallow, and if not carefully applied may form a nonporous layer which could lead to spalling of the treated stone surface. Waxes are thought to be very durable materials, but even by 1926 several species of the fungus **Aspergillus niger** were identified which were able to degrade wax (Gorlenko, 1983).

H. Natural Resins

Natural resins such as dammar and shellac, although chiefly used as paint mediums or protective coatings, have been used in the past as adhesives and consolidants for many types of objects, including stone monuments (Laurie, 1969; Lewin, 1966; Rossi-Manaresi, 1972; Mills and White, 1977). These were often not applied alone, but as a mixture with waxes and other resins, or with calcareous or siliceous materials. Some stones examined with an ancient treatment of resins and wax showed some protection (Rossi-Manaresi, 1972), but these resins are generally not used today in stone consolidation.

Dammar is a triterpenoid resin derived from the **Dipterocarpaceae** family of trees which grow mainly in the Malay states and the East Indies. It is very light in color, lustrous

and adherent when new, and is completely soluble, when new, in solvents such as white spirits, turpentine or toluene. With aging and oxidation the resin becomes yellow and darker and becomes progressively more insoluble (Feller, 1985: Gettens and Stout, 1966).

Shellac is a resinous secretion of the lac insect, **Coccuslacca**, and comes mainly from India. It has been widely used as an adhesive, consolidant or protective surface coating since antiquity, and is still used in some places such as Greece or Turkey in the conservation of archaeological material, especially ceramics and bone. When new, shellac can easily be dissolved in alcohol to make a quick setting adhesive. With aging, however, shellac becomes very brittle, and can cause stress and separation of a join. Shellac also darkens with age and becomes very hard to remove, requiring a solvent like pyridine to soften or dissolve it. Due to the many artificial polymers with much better aging characteristics and ease of use, shellac is not often used today in modern conservation treatments (Koop, 1979, 1984), except in wood conservation.

Weathering and Degradation of Polymers

With the increased use of synthetic polymers and plastics in the field of conservation, there has been an increased concern for the long-term stability of these materials. Although plastics are generally thought of as being very resistant to change ,they are subject to many types of weathering processes which can alter their properties in different ways and degrees, depending on the chemistry of the polymer (Schabel, 1981: Davies and Sims, 1983). In general use, the initial inherent characteristics of a polymer are what decides its use in a particular situation. The conservator, however, must be aware of the possibilities of changes in these characteristics, and make his

choice of materials on as fully informed basis as possible. Information on these changes have often in the past been gained from observations of alterations in place on artwork and monuments. Experiments in artificial weathering can help the conservator identify possible problems with a particular choice of material and avoid their use in a situation where they might cause more harm than good.

'Degradation' is a very general term. In a strict sense, polymer degradation refers only to chain scission within the macromolecules. In a more general use, polymer degradation refers to any change in polymer's properties. These may be optical changes, such as yellowing or loss of transparency, physical changes such as reduction in adhesion or elasticity, mechanical changes such as cracking or shrinkage, or chemical changes such as a loss in molecular weight or alteration of crystalline structure. There are many causes of these types of alterations, The most important being photochemical or radiation induced, chemical, thermal, mechanical, and biological. These various modes of degradation should not be thought of as completely separate, but often closely interact to simultaneously cause deterioration of a polymer. This simplest case of this is the accelerated action of chemical deterioration in the presence of high temperatures.

Light- or radiation-induced degradation concerns the physical and chemical changes which may occur as a result of irradiation. Light-induced deterioration occurs as a result of absorption of visible, infrared or ultraviolet light by the polymer or one of its additives. This requires the presence of wavelength specific chromophores or light absorbing groups in the compound. Photochemically important chromophores generally absorb light in the ultraviolet range resulting in chemical processes that can severely deteriorate polymers. High energy radiation such as X-rays, gamma-rays or particle radiation does not require the exis-

tence of chromophoric groups to induce changes since all parts of the molecule are capable of interacting with these forms of radiation. Radiation damage is caused by the formation of highly reactive intermediates such as free radicals and ions which can lead to chain-scission or cross-linking of polymers.

Chemical degradation is a very broad term referring to changes induced with acids, bases, solvents, etc. Chemical deterioration of polymers used for stone conservation may occur from acids formed by the reaction of various atmospheric pollutants, most notably sulfuric acid from sulfur dioxide. Various damaging chemicals may also be present in the form of soluble salts within the stone. Chemical degradation can also refer to oxidative damage, interaction with water, or even biological caused deterioration.

Thermal degradation occurs at elevated temperatures when chemical changes are induced without the simultaneous involvement of another compound. Polymeric compounds are rarely pure and it is often hard to distinguish between purely thermally induced changes or chemical changes due to impurities. Elevated temperatures also accelerate the rate of most chemical reactions, and minor impurities may have important effects at higher than normal temperatures.

Mechanical deterioration generally refers to macroscopic effects produced under the influence of shear forces. These stress-induced damages generally are accompanied by bond breakage in the polymer main chains. This sort of physical damage can occur from vibration, striking of the surface, sand-blasting, scratching, freeze-thaw damage, etc.

Biological deterioration is closely related to chemical deterioration of polymers. Various microorganisms are capable of

producing a wide variety of acids, solvents and enzymes which can alter the chemical structure of polymers. These may be produced merely as a byproduct of the organisms metabolism, or may be produced directly as a result of the organisms use of the polymer as a food source. For either case, many different fungal and bacterial organisms have been found which serve to deteriorate polymers. Biodeterioration of polymers may cause staining, etching of the surface, loss of opacity, changes in weight or flexibility, and other changes, which may or may not be important to the specific application of the polymer (Klausmeier and Andrews, 1981).

Many synthetic polymers seem to be fairly resistant to direct microbial deterioration, possibly due to hydrophobic characteristics which reduce enzymatic activity (Calley, et al., 1973). Still, there have been studies reporting microbial growth and effects on almost every type of synthetic polymer. This may sometimes be due to the presence of additives such as plasticizers, lubricants or light stabilizers, many of which can serve as nutrients for the growth of microorganisms (Hueck van-der-Plas, 1960; Potts, 1978; Strzelczyk, 1981; Pankhurst et al., 1972, Sudesh Kumar, 1982-3). The additive which usually represents the most bulk is a plasticizer. This is defined as a material which is mechanically mixed into a plastic formulation to increase flexibility, workability or extensibility, making the plastic or resin mixture softer, more flexible and easier to process. Compounds used as plasticizers include fatty acids or oils containing fatty acids such as tung or linseed oil. These were found to be especially susceptible to attack. Other materials include various carboxylic straight chain esters, which were slightly more resistant, tricarboxylic acid derivatives, which showed good resistance, and phtalic acid esters, which were generally inert, although at least several species of bacteria have been shown to be able to utilize dioctyl phtalate as their

sole carbon source (Williams and Dale, 1983). Most plasticizers are esters, and some studies have shown that the breakdown of these compounds is initiated by extracellular esterases, which enable microorganisms to cleave the ester fraction from the compound, and utilize the acid fraction of the compound. These esterases, like most enzymes, are usually very specific, and production of one type does not provide the ability to utilize all types of ester plasticizers.

Deterioration of polymers by actual breaking of the polymeric chains into smaller, water soluble units which may be utilized by the organism or may be leached out of the substrate may proceed in one or both of two ways. Extracellular enzymes can split the polymers into large pieces by random attack along the chain or deterioration may proceed by end group attack, with single two carbon units removed one at a time. Polyester urethanes and some polyesters have shown breakdown with large chain weight loss, probably by the action of esterases. Other polymers appear to mainly suffer attack at end groups, with subsequent small weight losses. These probably proceed with oxidase enzymes, and the stepwise oxidative removal of the end one or two carbons of a long chain. This has been seen with some hydrocarbons, polyethylenes, and polystyrenes.

Most plastics and polymers in dry, clean environments that do not contain plasticizers or other additives may be quite resistant to microbial contamination. However, these same materials in outdoor use often show effects which can be attributed to biological causes. The natural environment may provide the nutrients for fungal, bacterial or algal growth, in the form of inorganic soils, salts, or organic materials. This film of contaminants may support only initial germination, or even the entire growth of colonizing microorganisms which may damage the polymer. In order to prevent or minimize deterioration, biocides

are frequently incorporated into polymer formulations. These should be effective against a wide variety of organisms, fungal, bacterial and algal, non-toxic to humans at the concentration used, low in cost, compatible with the other elements of the formula and uses of the polymer, and effective for the life of the product. Some biocides in use in plastic formulations include different mercury containing compounds, such as phenyl mercury salicylate, other metal compounds, such as copper quinolinate and tributyl tin oxide, quaternary ammonium compounds such as dodecyl dimethylbenzyl ammonium napthenate, and various sulfur or halogen containing compounds.

Consolidants Used in Current Study

Product	Area/Sample	Manufacturer
Natural Resins:		
1. Dammar	1596	AF Suter
2. Shellac	1575	AF Suter
Polyvinyl Acetates:		
3. AYAA	1540	Union Carbide
4. AYAC	1575	Union Carbide
5. AYAF	1539	Union Carbide
6. AYAT	1596	Union Carbide
7. Mowital B-20-H	1564	American Hoescht
Acrylic Resins:		
8. Acryloid B-72	1657	Rohm and Haas
9. Acryloid F-10	1550	Rohm and Haas
10. Rhoplex AC-234	1554	Rohm and Haas
Polyurethane:		
11. Imron	1615	Dupont
Silicone Resin:		
12. Silicone 1048-283	1490	General Electric
Silane:		
13. Conservare H40	1950	ProSoCo
Silicate Esters:		
14. Tegovakon V	1672	Goldschmidt
15. Conservare H	1431	ProSoCo
16. Conservare OH	1653	ProSoCo

Product Claims:

PVA AYAA

Polyvinyl acetate resin. Clear thermoplastic, without a sharp melting point, but which becomes progressively softer with increasingly temperatures above 97° C. Not suitable for continued exposures above 65° C, although reported color stable after 4.5-5 hours at about 58° C. There is some cold flow seen even at room temperatures, which is intensified by the addition of plasticizers, retained solvents or moisture. Resistant to light, weak acid, alkali or salt solutions. May be modified with plasticizers to improve flexibility. Readily soluble in solvents such as ketones, esters and lower alcohols. Insoluble in hydrocarbons, higher alcohols and water, although continued immersion in water will soften and swell PVA's, particularly the lower viscosity grades. Excellent adhesive for cloth, papers, ceramics, metal, plastics, glass, wood and stone. Refractive index 1.4665. Specific gravity 1.18. Molecular weight 83,000. Inherent viscosity of 0.42. Sold in the form of pellets. Cited in FDA regulations as acceptable materials for use as adhesives in food packaging or as coatings for any material for use in processing food. However, they may contribute to nuisance dusts, causing slight, temporary irritation.

PVA AYAC

Same as above, except has a softening point of 71° C, a molecular weight of 12,800, an inherent viscosity of 0.12, and is sold in the form of solid blocks.

PVA AYAF

Same as above, except has a softening point of 114° C, a molecular weight of 113,000 and an inherent viscosity of 0.52.

PVA AYAT

Same as above, except has a softening point of 141° C, a molecular weight of 167,000, and an inherent viscosity of 0.68.

Acryloid B-72

Ethyl methacrylate copolymer. Stable, durable and transparent polymer. General purpose resin, compatible with vinyl, cellulosics, chlorinated rubbers and silicone resins. Sold as solid or as a 50% solids solution in toluene. May be brushed or sprayed on.

Acryloid F-10

Butyl methacrylate polymer. Softer and more elastic than B-72. Good adhesion and elongation. Transparent and resistant to discoloration, but less resistant to acid and alkali than B-72. Supplied as a 40% solids solution in mineral spirits, and soluble in all petroleum hydrocarbons. Especially useful for application over oleoresinous or other solvent sensitive finishes. May be applied with a brush or as a spray.

Rhoplex AC-234

Acrylic resin emulsion. Forms a durable, tough, flexible adherent film, resistant to alkali and water.

Imron

Polyurethane enamel. Formulated for use over prepared metal, or fiberglass surfaces. Activated with isocyanate activator and hardener. Sold as ready to use solution containing methyl ethyl ketone, toluene, ethyl acetate, xylene, naptha, propylene glycol, monomethyl and ether acetate, butyl acetate, N-butyl alcohol, aromatic hydrocarbons and mineral spirits. Sold as clear or pigmented coatings. Provides a 'wet-look' finish, with good chemical resistance and durability. Drying time 15-30 minutes.

Silicone 1048-283

Experimental protectant and sealant--not a consolidant. Prepolymerized silicone resin polymer mixture. Sold as a 10% active solids solution in mineral spirits. Formulated for concrete and all types of stone. Developed as a water repellent and stain guard against spray-paints, etc. Application by spraying, or misting lightly to prevent color change. Reportedly is acid resistant, and somewhat alkali resistant. After setting, is reportedly resistant to solvents such as methylene chloride (used for the removal of graffiti). In company de-icing and scaling tests, it exceeded 300 freeze-thaw cycles without failure (Personal Communication, Dwayne Merril, General Electric).

Conservare H

Silicate ethyl ester compound, containing a silane water repellent. Manufactured especially for strengthening and consolidating stone and masonry, based on formulas and technology developed by Wacker-Chemie of Munich, Germany. Most of the silicate ester will transform into SiO_2 after two weeks under average conditions of 68° F and 50% relative humidity. Temperature and humidity conditions are critical for proper performance of the

material, usually restricting application to a certain time of the year for outdoor applications. Low viscosity and good penetration. Tack-free drying. Neutral pH dibutyltin dilaurate catalyst. Acid resistant material. Treated material has good vapor permeability. Mixture contains organic solvents, including methyl ethyl ketone. Surface must be clean of salts, dirt, etc., to assure good penetration. Materials are best treated by dipping applications, but good results can be obtained with brush or spray applications. Coverage varies depending on the type of material being treated and its condition. Consumption rate usually between 10 to 80 square feet per gallon. Material should be applied until excess material remains visible for 30 minutes after treatment. Has a limited shelf life, but should remain stable in storage in closed containers for approximately one year. Not suitable for application to some types of marble. Density approximately 0.9 and refractive index about 1.38 at 25° C.

Conservare OH

Same as Conservare H, except that no silane water repellent is incorporated in the mixture. If water repellency is desired, impregnation of the stone with a water repellent is suggested after consolidation treatment.

Appendix B

APPENDIX B

MORPHOLOGICAL CHARACTERISTICS OF FUNGAL ISOLATES

The Genus **Penicillium**

1. Colonies bluish green, somewhat velvety with white center and reverse cream color.

2. Colonies wrinkled bluish green exudate.

3. Colonies with restricted growth, rich blue-green, often on a background of yellow to orange, reverse bright orange to red.

4. Sulfur light to greenish colony with yellowish reverse side.

5. Whitish colony with exudate.

6. Very dark bluish green colonies.

Microscopic examination revealed septate conidiophores terminating in broom-like whorl of branches, the latter consisting of a single whorl of conidia-bearing organs, Each isolate must be further characterized.

The Genus **Aspergillus**

1. Small colonies, non-spreading with tough texture, white periphery and center with light orange and grayish center.

2. White fuzzy periphery with center that starts as sulfur yellow and then becomes light green and latter dark green.

3. White fuzzy periphery with cottony center that remains yellow with a grayish tint to it.

Microscopic examination revealed non-septate conidiophores enlarging towards the apex and terminating in a swelling bearing phialides which themselves bear conidia. Each isolate must be further characterized.

The Genus **Fusarium**

Colonies appear white to off white to a light gray. Microconidia are oval and some curved while macroconidia appear septate and sickle-shaped. Some chlamydospores were also present.

The Genus **Cladosporium**

Thick velvety colonies with deep rich green color and a reverse black color. Spores occur in large, tree-like clusters. Conidia are distinctly verruclose with scars at one or both ends.

The Genus **Curvelaria**

Dark colored colonies that appear velvety. Dark colored conidia produced at the apex of the conidiophores. The conidia have 3 or 4 septa and appear curved or bent. Although this organism was only isolated from sample # 4B, original samples 1A, 2A, 3A, 4A, and 4C, all appeared to have had this organism. The colony is difficult to maintain in culture and becomes sterile after one or two transfers.

Yeast

Several samples resulted in yeast isolation. Colonies appeared cream white and cells were unicellular, egg-shaped, or cylindrical with buds.

Unidentified organisms

1. Lemon yellow colony with exudate. Periphery has an ultra light bluish gray color. The colony causes the media to buckle. Microscopic examination revealed branched hyphae with conidiophores and conidia. It appears to be related to **Penicillium**.

2. Whitish colony with exudate causes media to buckle.

3. Black colony on top and bottom, causes media to buckle, non-spreading.

4. White colony with heavy exudate, non-spreading, with cream reverse side.

5. Hat-shaped colony with white top and side with exudate, causes media to buckle.

6. Colony with bluish-green center and wrinkled and raised sides, causes media to buckle.

Conclusions:

Six different organisms belonging to the genus **Penicillium** were isolated as well as three different organisms belonging to the genus **Aspergillus**. other representative genera were **Fusarium**, **Cladosporium**, and **Curvularia**. Several other mold isolated need further identification. (References for this section: Barnett and Hunter, 1972; Cooke, 1963; Golman, 1957; Onions et al.., 1981; Pitt, 1979; and Raper and Fennel, 1977.)

Appendix C

APPENDIX C

SUMMARY OF IN-SITU LIQUID PARTICLE COUNT DATA*

Organism	Unit	<4μm	+ 1-4μm	Total Counts
Penicillium	0.1ml	4.52×10^6	1.228×10^7	1.68×10^7
Penicillium	"	5.75×10^6	1.105×10^7	1.68×10^7
Fusarium	"	7.10×10^6	1.216×10^7	1.926×10^7
Cladosporium	"	1.552×10^7	1.768×10^7	3.31×10^7
Aspergillus	"	6.80×10^6	1.34×10^7	2.02×10^7
Aspergillus	"	4.32×10^6	1.28×10^7	1.712×10^7

*Model ILI1000 Spectrex Corporation.

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Am J Hosp Pharm 33:150–151 (Feb) 1976

PROTOTRON PARTICLE COUNTER* MODEL ILI 1000

FEATURES

- Makes in-situ, quantitative particle counts of bottled liquids
- Reads any bottle with a 20 to 200 mm inside diameter
- Uses scanning laser beam with all solid state electronics
- Provides automatic digital readout after a scan of 10 cc in approximately 15 seconds
- Detects the number of particles above a manually set threshold between 1 and 100 μm
- Can be used to count particles in liquids flowing through transparent pipes

APPLICATIONS

- Quality control of hydraulic fluids & oils
- Particle count of air filters
- Monitoring continuous flow operations through glass pipe
- Inspection of pharmaceutical solutions
- Water quality testing for semiconductor industry
- Quality control for bottled beverages

.... and many other applications.

GENERAL DESCRIPTION

The standard Prototron Particle Counter includes both diffuse vertical illumination for visual identification of large particulates, and a scanning laser beam for detection of small particulate matter.

The 31 pound, compact unit (12" X 24" X 18") houses the laser tube, scanner and photo detection electronics. A front panel knob allows setting of a particle size threshold limit between 1 and 100 μm. Particle counting and illumination are controlled by front panel pushbuttons. A simplified schematic of the instrument is shown in Figure 1. The laser beam focuses inside the bottle in a 2 cm long "sensitive zone" as shown in Figure 2.

The secondary lens picks up scattered light (in the annulus around the target) from all particles in the path of the scanning laser beam. However, the photo detection electronics only registers those particles in the "sensitive zone", which are larger than the size specified by the threshold setting. Usually, dust particles on the bottle wall do not affect the count, as long as the wall is not in the sensitive zone. However, optical discontinuities should be avoided.

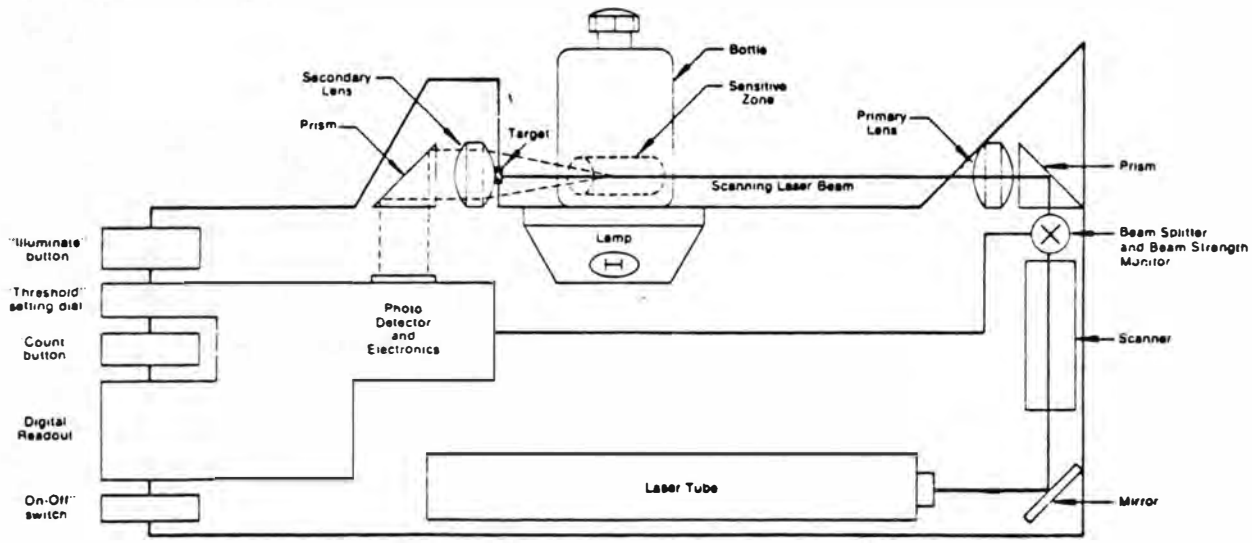

Fig. 1 Schematic of Particle Counter

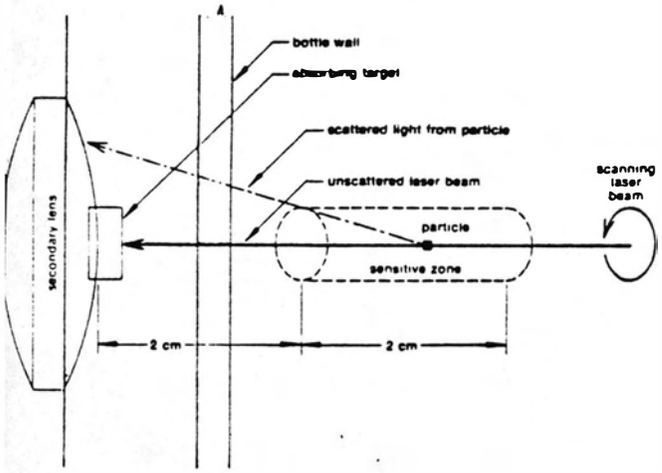

Fig. 2: Laser Beam Optics.

Once the count button is pushed, the revolving laser beam scans a total volume of 10 cc in 15 seconds, and the digital readout displays the average number of particles with sizes above the threshold limit in one cc of liquid.

By taking sequential measurements, qualitative size distribution data can be developed, or the threshold selector can be locked to provide statistical quality control data at one setting.

MAINTENANCE

The Prototron Particle Counter is fully covered by a one year warranty and the laser life is rated at 10,000 hrs. The warranty includes replacement of the illumination lamp and the laser tube. Other than such normal replacement, the unit is virtually maintenance free.

OPERATION

The operation of the Prototron Particle Counter consists of three steps: (1) Gently agitate the sample of bottled liquid to produce a uniform suspension; (2) Place bottle in the "V" notch and rotate to a point where the laser beam enters and leaves unobstructed; (3) Press the "Count" button. Within 15 seconds, the total particle count per cc is displayed on the digital readout.

In addition, by pressing the "Illuminate" button, a light table may be used to visually detect particles larger than 40 microns. The light table goes off when the "Count" button is pressed.

SAFETY

The laser used in the Prototron Particle Counter is rated at one milliwatt, and even less energy is emitted from the primary lens. Virtually all laser beam energy is fully absorbed by the target. The Electronics Industry Association has recommended that the Bureau of Radiological Health and OSHA accept lasers with energies of 5 milliwatts, or less, for relatively unrestricted usage. Therefore, the Prototron Particle Counter is well within the specified safety regulations.

SPECIFICATIONS

Size	18" (45.72 cm) high; 12" (30.48 cm) wide; 24" (60.96 cm) deep
Weight	31 pounds (14.06 kg)
Power	115 volts; 60 Hz (can be modified to 230 volts; 50 Hz on special order)
Display	3 digits
Outputs	Connections provided for external alarm, printer, oscilloscope, or pulse height analyzer
Bottle Size	20 to 200 mm inside diameter
Bottle Material	Transparent, scratch-free glass or plastic
Read-Out Volume	1 cubic centimeter
Detectable Particle Size	Continuously adjustable from 1 to 100 μm
Warranty	One year on parts and labor

ORDERING INFORMATION

The Prototron Particle Counter may be ordered direct from Spectrex Corporation. It may also be leased (with an option to buy plan). To arrange a lease, call collect (415) 365-6567. Quantity discounts are available. For more information, write or call Spectrex Corporation.

SPECTREX

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