Biodeterioration of Acrylic Polymers Paraloid B-72 and B-44: Report on Field Trials

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INTRODUCTION

Acrylic polymers have been widely used in the field of conservation since the 1930's. However, it is becoming increasingly apparent that under certain conditions, these synthetic polymers are subject to degradation through the activities of microbiological organisms. The biodeterioration of synthetic polymers is of particular concern to conservators when used for the long-term protection of archaeological collections and outdoor monuments, where stability with respect to biological attack is of critical importance. At the central Anatolian archaeological site Kaman-Kalehöyük, bronze and other copper alloy artifacts are routinely coated with a layer of acrylic followed by one of wax subsequent to treatment with Benzotriazole (BTA). A severe water leakage in the storage depot at Kaman during the winter of 2003 triggered profuse microbiological growth, and many of the acrylic and wax protective coatings suffered a significant degree of biological deterioration. As a direct result, N. Zaitseva conducted a field study during the excavation season of 2004 to assess the ability of wax and acrylic films to resist microbiological growth in conditions of high humidity. This project is an extension of her research, and will attempt to further characterize the susceptibility of two commonly encountered acrylic polymers, Paraloid B-72 and Paraloid B-44, to biological attack.

BACKGROUND LITERATURE

Both Paraloid B-72 and Paraloid B-44 are commonly encountered in conservation treatments. Paraloid B-72, in particular, is particularly favoured by conservators for its long-term stability under conditions of normal exposure. According to Horie (1987: p. 106), B-72 is a copolymer of ethyl methacrylate and methyl acrylate with a molar ratio of approximately 70:30%. First used as a lacquer for silver and other metals, B-72 quickly became one of the standards of conservation, functioning as a lining, coating, consolidant, adhesive, or in-painting media. Paraloid B-44 is a copolymer of methyl methacrylate with an unknown monomer. (Horie 1987: p. 107) Polymethyl methacrylate is known to form a hard coating that is extremely stable to degradation by heat, ultraviolet and oxidation. However, it has a very high glass transition temperature and thus separation from the substrate can sometimes be a problem. Nevertheless, it is one of the major components of Incralac, a commercial coating for metals.

A number of studies have been done in an attempt to further understand the biodeterioration of synthetic polymers. Studies that have involved acrylic polymers are briefly summarized below.

Nugari and Priori (1985) investigated the biodeterioration of Paraloid B-72 and several other acrylics through soil burial and agar plate tests. The extent of biodeterioration was assessed through weight loss determination. The researchers did not find a significant difference in the weight of inoculated samples and control samples, and concluded that the acrylics were not providing a source of carbon for the micro-organisms. However, they discovered that the fungal growth interfered with the structural properties of the polymer, modifying its water affinity.

Koestler and Santoro (1991) investigated the susceptibility of various synthetic resins used in stone consolidation. Fungal strains were inoculated onto film samples, without the use of agar medium or

additional nutrients. Assessment was made through microscopy, weight loss measurements, and Fourier Transform Infrared Spectroscopy, although the latter proved inconclusive. They concluded that many of the consolidants and adhesives, including Paraloid B-72, had poor resistance to fungal growth, and had the potential to act as a food source for microbes.

Heyn *et al*. (1995) experimented with microbial deterioration of some synthetic polymers commonly used in the conservation of wall paintings and art objects. Analysis of the level of deterioration was carried out through the use of Scanning Electron Microscopy. High Performane Liquid Chromatography and pH measurements were also used to investigate and measure any organic acids excreted by microorganisms. They determined that polyacrylates such as B-72, while more resistant when compared to cellulose derivatives, poly-vinylacetates and poly-vinylalcohols, nonetheless showed signs of microbial degradation. It was also established that bacteria and yeasts had a higher capability for polymer degradation than fungal strains.

Abdel-Kareem (2000) studied the effect of biodeterioration on textiles that have been consolidated with synthetic polymers. The condition of the fabrics was monitored through measurement of the decrease in tensile strength. The results revealed that all synthetic resins tested, including Paraloid B-72, was affected by fungal growth, resulting in significant loss of tensile stress. Therefore, on substrates that are biodegradable, synthetic polymers were able to retard fungal attack but not impede it altogether.

Despite these studies, many factors still remain unknown. Furthermore, with the exception Paraloid B-72, few studies have been done on acrylic polymers and very little is known about the susceptibility of Paraloid B-44. The objective of the present study was to examine the biodeterioration of Paraloid B-72 and B-44, particularly focusing on their susceptibility to biodeteriogens when functioning as protective coatings (i.e. in thin film form). Field trials were conducted in an attempt to assess the rate and extent of biodeterioration, the influence of environmental control, as well as the effect of different solvents.

FACTORS AFFECTING BIODETERIORATION

Certain critical elements are necessary for biological growth to occur: these include a source of microorganisms, nutrients, water, and suitable temperature and pH. When all of these factors are present, the risk of biological activity becomes high. These factors are often difficult for conservators to control without the design and implementation of long term preventive conservation policies within storage and display facilities. When microbiological growth does occur, the extent of biodeterioration may range from merely surface growth all the way to mechanical failure and chemical breakdown of the polymer.

However, the extent and rate of biodeterioration may also be influenced by a number of other factors, one of which is the composition of the acrylic itself. The chemical composition of the polymer (molecular weight, solubility, stereoregularity, crystallinity, etc.) will have a direct bearing on its susceptibility to biodeterioration. (Allsop *et al*. 2004: p. 65) Furthermore, any additives present, including plasticizers, fillers, processing aids, remaining catalysts and residual monomers, will serve as an available carbon source for microorganisms even if the polymer itself is resistant to biological attack. The solvent used may also affect the rate of biodeterioration. Acrylic films, in particular, are known to have poor solvent release, due to the relatively rapid formation of touch-dry surfaces. Residual amounts of solvents can therefore remain trapped within the polymer film and this can also become a source of carbon for biodeteriogens.

Biodeterioration is also affected by physical factors, such as hydrophobilicity or hydrophilicity, film thickness, texture, and hardness. Hydrophobic coatings prevent intimate contact between the surface and the extracellular enzymes secreted by the biodeteriogen, making it less vulnerable to attack. A smooth and hard coating also discourages physical attachment and hence resists colonization by organisms.

Finally, biodeterioration can also act synergistically with photo, thermal, and chemical degradation. Physical and chemical deterioration processes causing alterations to the polymer films are often a prerequisite for microbial attack. Biological growth of one species may

Table 1 Experimental Variables

Resin	Solvent	Temperature	RH	Contamination
7% B-72	Acetone	High	High	High
7% B-44	Ethanol	Moderate	Moderate	Moderate/Low
	Toluene		Low	
	1:1 Acetone: EtOH			

also promote further colonization by other species, so that substrates that may otherwise have been resistant to attack may become vulnerable after colonization by another species. (Heyn *et al*. 1995: p. 74)

EXPERIMENTAL METHOD

Established lab protocols at Kaman-Kalehoyuk for stabilization and treatment of objects exhibiting overall outbreaks of bronze disease involves vacuum impregnation with 0.25M Benzotriazole under 40 cm HG vacuum. After BTA treatment, the artifact is then coated with a protective coating, consisting of a layer of 5-7% Paraloid B-44 in 1:1 acetone: ethanol, followed by a layer of 90% Be Square 195 and 10% Polywax 2000 in mineral spirits. However, 5-7% Paraloid B-72 is not uncommonly applied as a coating or a consolidant to artifacts that have not been treated with BTA. For these reasons, field trials were made with samples of 7% B-72 and 7% B-44 in various solvents.

Since this was a field study with limited resources and time frame, not all of the factors that affect biodeterioration could be isolated and examined in depth. Only the variables considered to be most important in terms of conservation were selected for testing; namely temperature, relative humidity (RH), and level of biological contamination.

Slides were prepared by measuring 0.12 mL of the acrylic solution with a micropipette, and dispensing the liquid onto a marked area measuring 3 cm by 2 cm. The liquid was then smeared with a glass rod or tip to produce as even a surface as possible. The approximate film thickness was 0.2 mm or 20 microns. There were 13 sets of 7 slides each, making a total of 91 samples. In addition 7 samples of modern bronzes were coated with

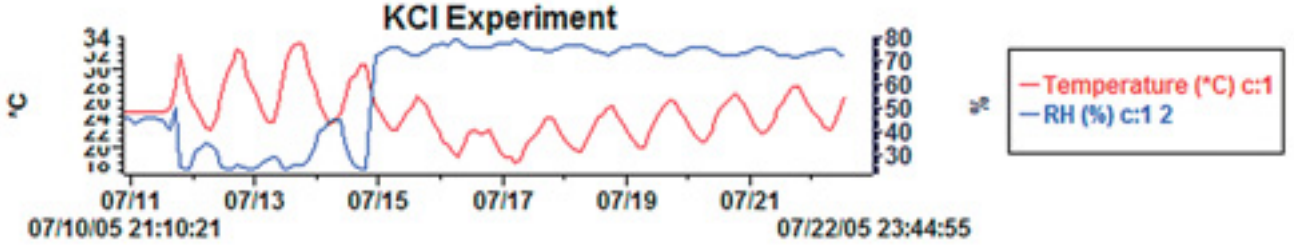

Fig. 1 Relative Humidity Control with Saturated KCl Solution

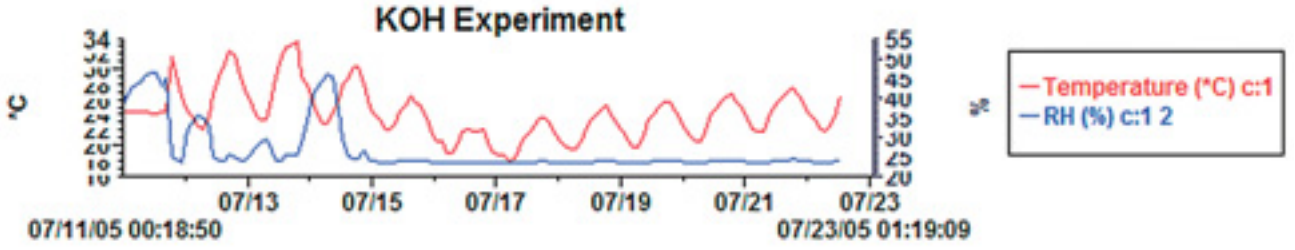

Fig. 2 Relative Humidity Control with Saturated KOH Solution

the various coating formulations; these were numbered 1 to 7. For each set, different exposure levels, relative humidity, and temperature were tested.

Relative humidity was controlled through the use of saturated salt solutions. The selected salts were Potassium Hydroxide (KOH) for low humidity conditions and Potassium Chloride (KCl) for high humidity conditions. According to literature, the former gives an RH of 8% at 25˚C, while the latter gives an RH of 80% at 25˚C. A mixture of the two was used to maintain a moderate RH level. The salt solutions were prepared by measuring 30 mL of salt into a container. Water was added slowly until half of the salts were dissolved. High temperature sets were placed in the Doğu depot, a temporary aluminum shelter with a very hot and stuffy interior atmosphere. For moderate temperature, sets were placed inside the Beton depot, the current storage facility. This depot is a concrete structure located beneath the dighouse, and is thus protected from the sun, creating a moderate temperature environment. Temperature and RH levels were monitored through the use of dataloggers.

The sources of biodeteriogens were swatches of cloth storage bags exhibiting active mould growth, found in the storage depot underneath a leak. The bags were cut into smaller pieces and placed into small plastic containers. For high levels of contaminations, large swatches of highly contaminated cloth samples were used. For low level contamination, small swatches of less contaminated cloth were used.

Photomicrographs of all samples were taken prior to exposure. One container with the saturated salt solution and one container with a contaminated cloth sample were placed into each polycarbonate box. A sheet of gauze held in a coroplast frame was then placed over top and the slides placed on top of the gauze. The containers were then sealed and placed into either the Doğu depot or the Beton depot. Observations and photomicrographs were taken weekly.

OBSERVATIONS AND DISCUSSION

After 14 days of exposure, no perceptible mould growth could be found on any of the samples. The samples were placed into an accelerated growth environment, with very high levels of humidity created by sheets of paper towel saturated with water. This accelerated growth environment was maintained for 1 week.

After 1 week of exposure to the accelerated growth environment, and 21 days of exposure in total, there appeared to be active mould growth on some samples. Condensation and water damage to the coating was also visible on some samples. The samples were allowed to air-dry and replaced into their relative humidity chambers.

The samples were left in their relative humidity chambers for an additional 15 days, then observed under high magnification transmitted light microscope (refer to Figures 3-9 below). It was very apparent that within each set of slides, the toluene samples exhibited the highest concentration of mould spores and supported the fastest rate of mould growth. Samples prepared with acetone were most susceptible to water damage from high relative humidity environments, resulting in swollen and cloudy films, and occasionally in the case of B-44, the lifting of the film from the glass slide.

A significant amount of bubbles could be seen within the films under microscope. These are suspected to be pockets of residual solvent, trapped within a dried surface film. These bubbles appear to be more conducive to biological growth, as there is frequently concentrated growth within these areas, particularly in the case of toluene and 1:1 acetone: ethanol.

Slides that were subjected to high relative humidity conditions supported a faster rate of growth than slides of the same composition that had been placed in low relative humidity environments. There were more germinated spores and reproductive structures present on these samples. There was little noticeable difference in the growth rates between the high and moderate temperature environments; this may be due to the fact that accurate temperature control was lacking.

Figs. 3-9 Photomicrographs of Selected Slides

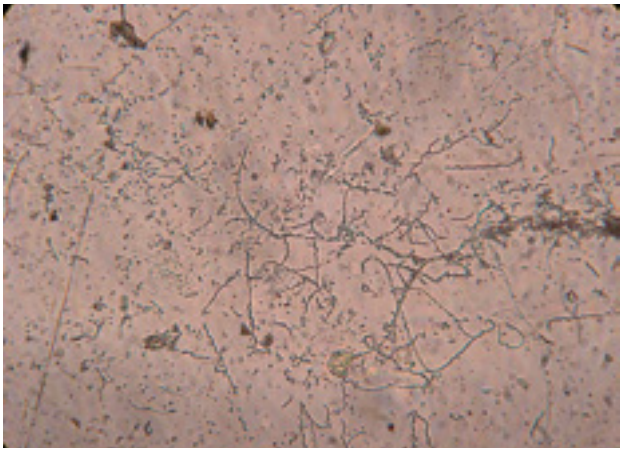

Fig. 3 7% B-72 in toluene
This sample contains many germinated spores and particulates. (200x)

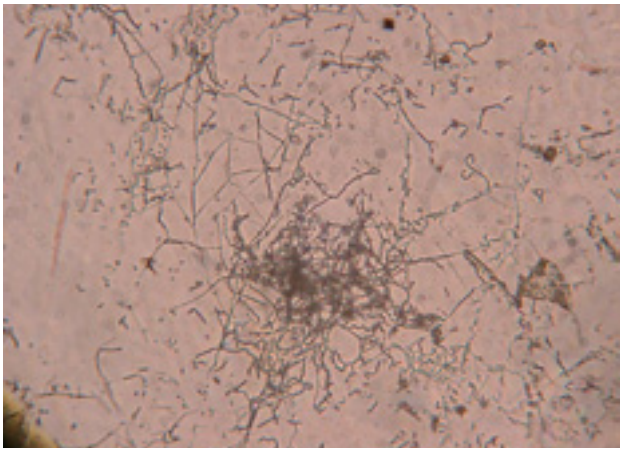

Fig. 4 7% B-44 in toluene
Many spores have germinated on this sample. (200x)

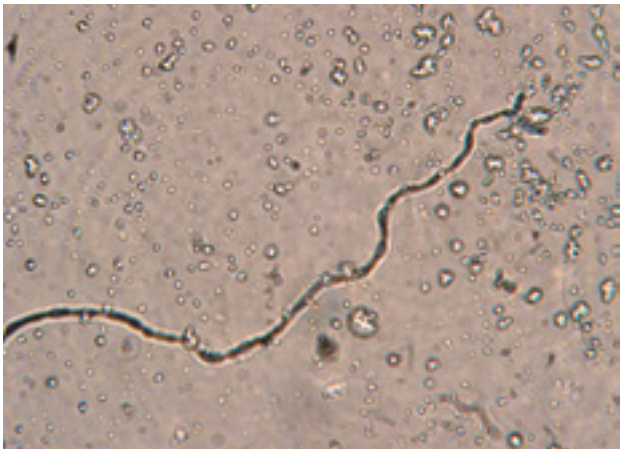

Fig. 5 7% B-72 in 1:1 acetone: EtOH
This sample shows some spores present and a single germinated spore. (40x)

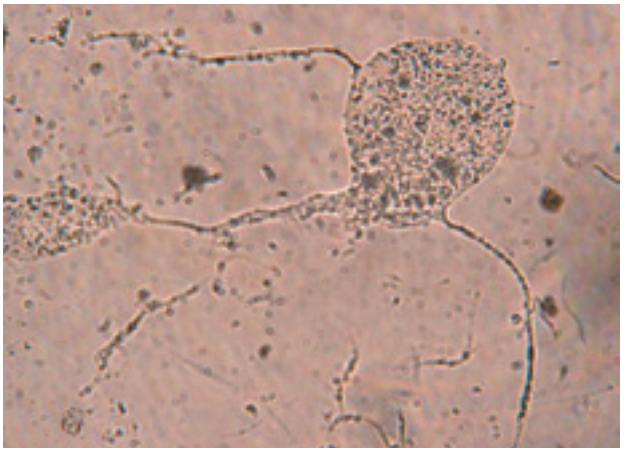

Fig. 6 7% B-44 in 1:1 acetone: EtOH
Germinated spores and particulates are contained in this sample. Spores are concentrated in bubbles of residual solvent in the film. (40x)

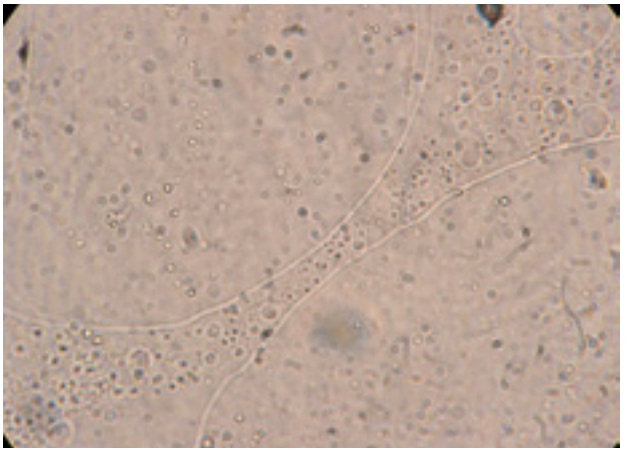

Fig. 7 7% B-72 in EtOH
There are many spores on the film but few have germinated. Spores are concentrated in areas outside of the bubbles. (40x)

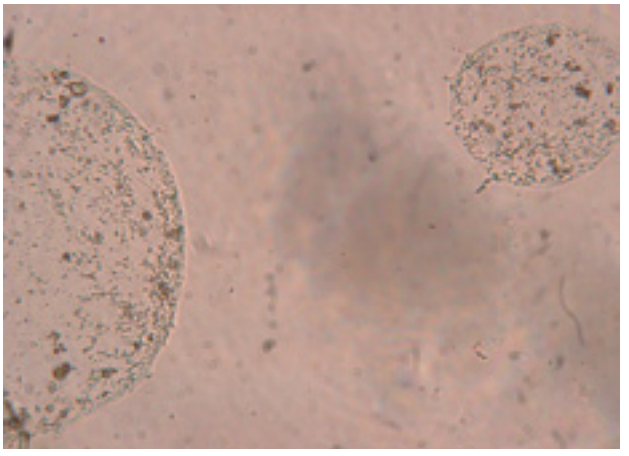

Fig. 8 7%B-72 In acetone
Spores present in higher concentrations inside bubbles. (40x)

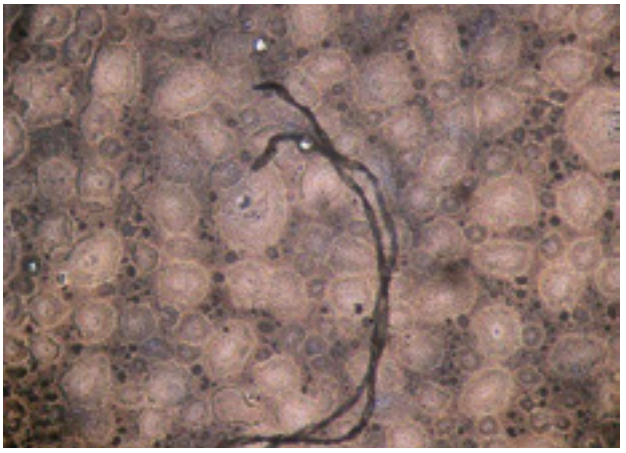

Fig. 9 7% B-44 in acetone
Germinated and non-germinated spores present amongst a heavily water damaged film. (80x)

GENERAL TRENDS AND RESULTS

Since this was a field trial based on relatively short experimental period, and lacking many experimental controls, no firm conclusions can be drawn. However, these field trials appear to reveal some preliminary trends and results. Of the solvents tested, toluene appeared to be by far the most susceptible, and hence, despite its ability to form very even and smooth films, would be most unsuitable as a solvent for the application of coatings. Paraloid B-44 was far more susceptible to moisture damage than B-72, but in general, films prepared in acetone, and to a lesser extent, 1:1 acetone: ethanol, were all susceptible to water damage, becoming swollen and cloudy. Based solely on these trials, it was not possible to draw definitive conclusions regarding the susceptibility of Paraloid B-72 versus Paraloid B-44 to biological attack; however, Paraloid B-72 performed better in terms of moisture resistance. The field trials revealed that Paraloid B-44 in 1:1 acetone: ethanol, the coating recommended by the treatment protocols at Kaman-Kalehöyük, has medium resistance to biological growth, but is very susceptible to moisture damage.

Further experimentation would be necessary to characterize the biodeterioration of acrylic polymers. A more precise method of environmental control would be beneficial, as well as more accurate methods of exposure to mould contamination to ensure even exposure between the different samples. Experiments may be expanded to determine the effect of other variables, such as concentration, light, and pH. Experiments may also be repeated with artificially aged samples to characterize the rate of biodeterioration when acting synergistically with photo and thermal degradation.

The biodeterioration of acrylic polymers is as yet not clearly understood; however, it is clear that these polymeric materials are susceptible to some form of biological attack. Even in situations where the polymer chain itself is not being assimilated as a source of carbon, it may still be damaged chemically and physically by the secretion of the organisms and by their physical growth. Therefore, preventive measures, such as the control of relative humidity in the storage environment, are essential for the prevention of biological growth.

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