Practical application of the Revolutionary Preservation (RP) System® for marcasite

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Abstract

This paper discusses the implementation of reduced oxygen environments for geological specimens at the Milwaukee Public Museum, Milwaukee, USA. In 2004, 400 marcasite specimens were re-housed using the Revolutionary Preservation (RP) System®, by Mitsubishi Gas Chemical Company. This system incorporates the RP-A oxygen absorber and Escal, a transparent barrier film, to produce low humidity and low oxygen microenvironments. This paper outlines the steps used to employ the RP System® and emphasizes the importance of documentation to evaluate the long-term effectiveness of the enclosures.

Keywords

geology, marcasite, iron disulfide, reduced oxygen environment, microclimate, RP System®, Escal, Ageless Eye®

Introduction

The marcasite specimens at the Milwaukee Public Museum were re-housed in microenvironments to improve storage conditions that contributed to their chemical and physical degradation. The presence of yellow and white oxidation products and fractures in the marcasite were evidence of the effects of improper storage conditions on vulnerable specimens. Newman (1998, 363) describes the breakdown of marcasite or ferrous disulfide (FeS_2) as a 'broad based oxidation process which results in a variety of ferrous–ferric–sulfate–hydroxide–hydrate phases and sulfuric acid'. These oxidation products cause internal stresses that can eventually destroy the specimen. Degradation is slowed considerably by maintaining a low relative humidity, below 30 per cent, and reducing oxygen levels in storage environments (Howie 1992). This is an effective and safe method for the long-term preservation of marcasite and pyrite in museum collections (Waller 1987, Howie 1992).

To obtain the recommended environmental conditions of low humidity and low oxygen, the Revolutionary Preservation (RP) System® was implemented. The RP System® combines oxygen absorbers and a silica-coated barrier film to produce a stable environment. Oxygen absorbers were introduced in conservation in the early 1990s for eradication of pests. It was then quickly adapted for the long-term storage of artifacts in reduced oxygen environments (Selwitz and Maekawa 1998). In addition, barrier films made it easier to create anoxic environments for storage due to their flexibility and good transmission rates (Burke 1992).

The predominant oxygen scavengers used in museum collections are Ageless® oxygen absorbers, produced primarily for the food industry by Mitsubishi Gas Chemical Company (Mitsubishi 1998). Mitsubishi now manufactures the RP agents, type A and K, which are specifically designed for the preservation of cultural material. There are several resources and published guidelines for implementing reduced oxygen environments for museum collections; these sources were consulted for the Milwaukee project (Daniel and Lambert 1993, Grattan 1993, Shashoua 1993, Burke 1996, Selwitz and Maekawa 1998, Carrio and Stevenson 2002).

Survey and long-term monitoring

One of the most important aspects of this project was to document and continue to monitor the re-housed specimens for future reference. Before re-housing, a general survey was conducted of the marcasite collection. A form was created for recording specific information about each specimen (Table 1). A specimen's condition was marked 'OK' if no oxidation products were observed, and the letter C, D, or F was assigned if there were signs of degradation. C was designated if the specimen showed some oxidation products but was structurally stable; D was given if there were oxidation products present and the specimen was cracking and/or crumbling; F was given if entire sections were crumbling and a predominant amount of sulfuric acid stains were present on the storage material. Extremely degraded specimens were moved to separate storage areas.

After the initial survey, 15 specimens were selected ranging in condition from good to poor. Condition reports were written for each of the 15 specimens, including a table that outlined specific information about the type of deterioration (Table 2). The specimens were photographed with colour and black and white film as well as digital photography. This information will be used for

Table 1. General survey form for marcasite specimens

Bag ID	Location no.	Condition	pH	Type	Spec. no.	Box size	Height	Rehoused	Turned pink	Notes	%RH	RP-A No.
A8	19503/C1869	F	n/a	LC/E	1	15 × 18	7.5	4/13/04	4/15/04	Acid stains on storage tissue	0%	5
B8	19503/C1869	D	n/a	LC/E	4	15 × 18	5	4/13/04	4/15/04	Acid stains on storage tissue	0%	4
C8	19503/C1869	D	n/a	LC/E	7	15 × 18	5	4/14/04	4/16/04	Acid stains on storage tissue	0%	5
D8	19503/C1869	3-OK 1-F	3	LC/E	3	9 × 15	5	4/14/04	4/15/04	Surveyed specimen	10%	4
E8	19503/C1869	OK	2; 3	LC/E	2	15 × 18	7.5	4/13/04	4/15/04	One eye not between blue and pink	0%	5
F8	19503/C1869	D	3	LC/E	2	15 × 20	9	4/14/04	4/16/04	Weight 2018 g / 2339 ml of air	0%	10
pulled	19503/C1869	F	n/a	LC/E	1	9 × 15	5					
OK	11869	OK	5.5	From.	1	9 × 15	5					

Table 2. Detail survey of selected specimens for future assessment

	Present	Quantity	Colour	Shape	Location
pH	0.0 4.5				Grey, brittle areas on nodule. Brown areas with no noticeable decay.
Oxidation products	Yes	Light	White	Fine needles that form in small domed clusters.	Found predominantly in the grey friable areas and along the perimeter of these areas. Some needles are interspersed with the yellow crust.
	Yes	Light	Light yellow	Crust	Yellow crust formed predominantly on the nodules that are grey and brittle.
	Yes	Very light	White	Powder	There is a small area where white powdery crystals formed and are pushing up a layer of the specimen.
Cracks	Yes	Medium			Cracks are located on grey nodules causing delamination and loss of those areas.
Fragile areas	Yes				Grey nodules.
Friable	Yes				Grey nodules.
Broken	Yes				Loss on grey nodules.
Liquid	No				
Stains	No				
Previous treatment	None apparent				

future assessment of the long-term effectiveness of the environments created with the RP System®. This detailed condition assessment was based on Shashoua's (1993, 1999) field study for re-housing rubber artifacts in reduced oxygen environments. Shashoua's article demonstrates the importance of documenting the condition of specimens to later evaluate the effectiveness of the enclosures. In addition, proper documentation of the specimens makes it easier to monitor the success of the environments.

The RP System®

Microenvironments are created with the RP System® using a multi-layered barrier film and sachets that absorb oxygen and/or moisture. The oxygen absorbers selected for this project are the RP agent type A (RP-A) which absorbs oxygen, moisture and corrosive gases. The chemical make-up of RP-A is given in the manufacturer's Material Safety Data Sheet as follows: 10–50 per cent mordenite; 10–45 per cent calcium oxide; 5–15 per cent unsaturated organic compounds; 10–30 per cent polyethylene; 5–15 per cent activated carbon (Mitsubishi Gas Chemical Company of Japan 1998).

Mordenite and activated carbon are included in the sachet to adsorb corrosive gases, such as hydrogen sulfide, hydrogen chloride, sulfur dioxide and ammonia (Mitsubishi Gas Chemical Company of Japan 1998). Calcium oxide is the primary desiccant in the system. Mitsubishi does not disclose detailed information on the role of the unsaturated organic compounds because of their proprietary nature, but they are part of the oxygen-absorbing reactions that occur in the sachets (Tsuyuki 2003). RP agents are recommended for long-term use and are more stable then Ageless®, which consists of iron oxide and a chloride salt (Burke 2001). Another distinct difference between the two absorbers is that RP agents do not require moisture to activate oxygen-absorbing reactions (Tsuyuki 2003). RP agents, like Ageless®, can be purchased in several different sizes depending on the volume of air within the microclimate.

Escal was selected as the barrier film because it currently has the lowest transmission rates for oxygen and moisture compared to other transparent films (Collins 1999) (Table 3). Escal is a layered film composed of oriented polypropylene (OPP), silica coated poly(vinyl alcohol) (PVOH) and linear low-density polyethylene (LLDPE). Although transmission rates for Escal are slightly higher than for aluminized barrier films, such as Marvelseal 360, Escal was selected at the Milwaukee Public Museum for its transparency. Escal can be used in conjunction with aluminized barrier films when polyethylene is used as the heat seal layer. Escal was purchased in both tube and sheet form. Tube Escal was used for the majority of the specimens because it is sealed on two sides; therefore minimizing the work required during re-housing.

Table 3. Transmission rates for flexible barrier films (24h/atm)

Barrier Film	H_2O (g/m^2)	O_2 (c/m^2)
Polyethylene (4 mil) – (PE) (Getty Conservation Institute 1994)	200–900	170–850
Cryovac BDF-2001 (1 mil) – (EVOH/MDPE EVA/LDPE) (Maekawa and Elert 2003)	11	4
Escal (4 mil) – (OPP/Silica on PVOH/LLDPE) (Collins 1999)	0.01	0.05
MarvelSeal 360 (4 mil) – (PE/Aluminum foil/PE/PP) (GCI 1994)	~0	0.03

Figure 1. Individual package for Ageless Eye® with string across top

The system also incorporates an oxygen indicator, Ageless Eye®. Depending on the type of indicator purchased, the Eye® will change from blue (or purple) to pink when the oxygen level is between 0.1 and 0.3 per cent. This colour change is based on the azine dye methylene blue (Selwitz and Maekawa 1998). For environments that require a very low relative humidity Mitsubishi offers a type S Eye®, with a cotton string across the top of the cellophane package to help absorb and desorb moisture locally within the individual package (Yokouchi 2003). Type S is recommended for use with the RP-A agent and will become pink when the oxygen level is at or below 0.1 per cent (Figure 1).

Implementation

Preparing a staging area

A staging area is recommended to accommodate re-housing a large collection. It should be positioned close to the storage area due to the weight and fragility of the specimens. Specimen drawers should be vacuumed and lined with a non-abrasive material such as Ethafoam to prevent damage to the Escal bags. Escal, like other barrier films, is susceptible to damage from scratches, which will prevent an airtight package. Install the roll of Escal in an area that will allow easy access and prevent abrasion during use. A nitrogen tank should be installed close to the working area and the sealer may also need to be mounted to a table.

Preparing specimens for enclosure

Two sizes of acid-free paper specimen trays were selected to limit the variation of sizes for final enclosures. Sheet Ethafoam was used to line the trays and separate specimens from each other (Figure 2). Specimens that were marked 'OK' in the initial survey were tested with a pH indicator strip to determine if oxidation

Figure 2. Initial preparation of marcasite specimens

reactions had occurred. If the pH was at or below 4, the specimen was re-housed. Once the specimens were prepared, the entire tray was placed in a polyethylene bag to prevent the specimens from scratching and compromising the barrier film (Figure 3). Oxidation products were not neutralized or removed before re-housing, because in most cases stabilization can be achieved by re-housing in the proper microenvironment (Waller 2003).

Figure 3. Final preparation of marcasite specimens with polyethylene bags

Procedure for enclosure

Before implementing the reduced oxygen environments, the appropriate size RP-A agent had to be determined. Selection was based on the versatility needed, the cost effectiveness and approximate size of enclosures produced. RP-5A, which absorbs 100 ml of oxygen per 500 ml of air, was selected. To calculate the number of sachets to insert into a microclimate the following equation is used:

air volume (ml) = [total volume of bag and contents (H × W × D cm)] – [weight of the content (g) / specific gravity of content]

Marcasite has a specific gravity between 4.8 and 4.9 and often contains other minerals. For simplification, 5 was selected as the specific gravity. Average weights and volumes for enclosures were calculated based on the following sizes: 9 cm × 15 cm and 15 cm × 18 cm with the height ranging from 2.5 to 7.5 cm. This eliminated calculating the amount of RP-A agent needed for each enclosure; therefore increasing production speed. Double the amount of oxygen scavenger calculated for the air volume was placed in each enclosure. Excess scavenger acts as a buffer and ensures the longevity of the microenvironment (Burke 1996).

Specimens prepared in the 9 × 15 cm trays received four or five sachets and specimens prepared in the 15 cm × 18 cm trays received five or six sachets.

Escal bags, with three sealed sides, were made before inserting the specimens. A relative humidity (RH) indicator card was inserted into each bag for later verification of the RH. The appropriate amount of RP-5A sachets were then inserted into each bag. This should be done as quickly as possible because their oxygen absorbing capacity will be exhausted. The manufacturer states that the agent should not be exposed for more than 30 min (Mitsubishi Gas Chemical Company of Japan 1998). If any RP-A remains, immediately seal it before moving onto the next step. The RP-5A is supplied in a quantity of 1000, where individual sachets are bagged in groups of 25; therefore five or six specimen trays were sealed in one session. The Ageless-Eye® is the last material inserted into the bags because they are easily compromised upon exposure to air. It is recommended that at least two Eyes® be placed in each enclosure in case one is faulty (Burke 2001). Care should be taken to ensure that the Eyes® are kept out of the light and refrigerated when not in use. Refrigeration should only occur after the Eyes® have turned pink, because low temperatures affect their reaction rates. The indicators are placed in the bag where they can be viewed easily, then the final side of all the bags are sealed leaving a small hole at one corner. Any remaining oxygen indicators are sealed immediately with an oxygen absorber before addressing the enclosed specimens. The Ageless-Eye® should be blue initially, if not, then note this on the survey report as a faulty indicator. The bags are then purged individually with nitrogen for approximately 30 s, followed immediately by a tracer gas that is sprayed into the bag before final sealing. The bag is kept inflated after purging to minimize the decompression that occurs upon absorption of oxygen.

Creating a good seal is vital to the long-term stability of reduced oxygen environments, and can be one of the more difficult aspects of the project. The recommended width is approximately 10 mm but there is recorded success with narrower seals (Shashoua 1999, McPhail et al. 2003). Mitsubishi recommends 10 mm wide seals using a thermal sealer or the RP Clip, which creates a reversible seal using pressure. Clamp and impulse thermal sealers are available with a number of different seal widths and lengths. For the project at the Milwaukee Public Museum a combination of an impulse foot sealer and a bench mounted clamp sealer were used to make a seal approximately 10 mm in width. A good seal was determined by comparing the seal to the Mitsubishi seal on tube Escal. It was difficult to eliminate bubbles and uneven patterns entirely on every enclosure. In retrospect, an impulse sealer with the appropriate width and length to yield a single seal in one pass is highly recommended. Additionally, the person implementing the project should be aware that the final seal can be problematic because of the additional height of the specimen and inflation of the bag (Figure 4).

Figure 4. Example of final enclosure of marcasite specimen in the RP System

Initial evaluation

After sealing approximately 15 environments, most of the Ageless Eyes® indicated that the microenvironments were not oxygen free. This could be caused by insufficient oxygen absorber, poor seals and/or faulty indicators (Burke 1996, Selwitz and Maekawa 1998). To locate the source of the problem, test environments were sent to Mitsubishi for analysis. It was eventually determined that the indicators were compromised.

Ageless Eyes® are sensitive to exposure to air, light and extreme changes in temperature and relative humidity. Conservators have reported problems with the colour-changing properties of the indicators and it has been shown that Ageless Eyes® do not perform well at low RH levels (Maekawa and Elert 2003). The indicators sent to the Milwaukee Public Museum were most likely compromised before reaching the museum, and were made worse by storage in low humidity environments using the RP-A agent. Simple tests were done using microenvironments at 0–10 per cent RH and 70–80 per cent RH. The Eyes® did not change in the low humidity environments but did change in the high humidity environments after several days.

A new set of type S Eyes® were sent to the Milwaukee Public Museum and tested in low humidity environments using the RP-A agent. This set performed well, but after exposure to air three times in combination with low RH they did not change pink. Additionally, these tests indicated that a low RH, less than 10 per cent, could be produced in a microenvironment that is not airtight; therefore one cannot rely on the humidity indicator card to establish if the environment is working correctly.

To ensure the accurate response of the indicators, the new set of type S Eyes® were repackaged in smaller units using an oxygen absorber that did not lower the relative humidity. Additionally, air exposure was kept to a minimum. Originally 500 Eyes® were sent to the museum in a single package with several Ageless® oxygen absorbers. The second set of indicators was repackaged by Mitsubishi in smaller units of 20 with two to four Ageless® oxygen absorbers per packet. A concerted effort was made to use all 20 Eyes after opening the packet. When this was not possible, the exposed Eyes® were marked and sealed carefully with an Ageless® absorber. Eyes® that were exposed to the air were used alongside a fresh Eye® in the specimen enclosure to reduce the chance of failure.

There have been no problems with the new set of type S Eyes®. More research is necessary to determine how well the type S indicators respond to repeated exposure to air and storage at low RH levels. The problems noted here may not occur with all type S Eyes®, but maintaining a strict procedure for minimizing air exposure and storage at moderate RH levels ensures their success rate in low humidity environments.

Conclusion

Once appropriate procedures were established, the RP System® was relatively easy to implement and was successful at creating low humidity (less than 10 per cent) and low oxygen microenvironments. Implementation of reduced oxygen environments is not as straightforward as it may seem, and when failure occurs it is sometimes difficult to determine the cause. Mitsubishi is supportive in achieving successful results and should be contacted if problems occur. Low humidity can influence the colour change of Ageless-Eyes®. These indicators should be immediately placed in smaller packages with oxygen absorbers that do not lower the relative humidity. When careful control is maintained over the exposure and storage of Ageless-Eyes®, they are an accurate indicator of the oxygen levels in the microenvironments.

In addition, a survey should be conducted of all specimens to determine the general condition of the collection. Individually selected specimens should have proper photographic and written documentation, including a description of oxidation products and determination of pH. This survey can be used to establish the effectiveness of the environments overtime by comparing the condition before re-housing and upon removal from the environment. Future monitoring and testing of the environments at the Milwaukee Public Museum will continue to ensure that the specimens are stable and the materials used to re-house the collection do not adversely affect the marcasite.

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Materials

Escal (270 mm/250 mm × 100 m tube and 1000 mm/100 m sheet)
RP Agent (A type)
Ageless-Eye®
Mitsubishi Gas Chemical America, Inc.
520 Madison Avenue
17th Floor
New York
NY 10022-4213, USA
Tel: +1 (212) 752 4620

Humidity Indicator Cards (Standard)
Talas
20 West 20th Street
New York
NY 10011
USA
Tel: +1 (212) 219 0770

Archival Specimen Trays (3.625 × 5.85 × 1″ and 5.85 × 7.25 × 1″)
University Products Inc.
517 Main Street
PO Box 101
Holyoke
MA 01041
USA
Tel: +1 (800) 628 1912

Polyethylene zipper bags (2mil – 8 × 10″ and 10 × 12″)
Associated Bag Co.
400 West Boden Street
Milwaukee
WI 53207, USA
Tel: +1 (800) 926 6100

Dow Ethafoam (1/2″ sheet PE)
Clark Foam Products
655 Remington Blvd
Bolingbrook
IL 60440
USA
Tel: +1 (630) 226 5900

Bench Mounted Sealer (Model: 250)
Clamco Corporation
12900 Plaza Drive
Cleveland
Ohio 44130
USA
Tel: +1 (800) 299 1655

Impulse Foot Sealer (Model: AIE 450FI)
American International Electric Inc.
2835 Pellissier Pl
Whittier
CA 90601, USA
Tel: +1 (800) 732 5377