

*Final Report
to*

***SOUTHEAST ARCHAEOLOGICAL CENTER,
NATIONAL PARK SERVICE***

***Investigation into causes and mitigation of defective
object labels based on Acryloid/Paraloid B-72***

Pursuant to the cooperative agreement P15AC01488

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Executive Summary

The problems with object labeling encountered by the staff at the Southeast Archeology Center have been investigated. The problem of the bubbling defects in the B-72 applications has been attributed to moisture contamination of the acetone solutions. That pickup of moisture from ambient humidity, both into the B-72/acetone solutions or into the acetone used to make up those solutions, is rapid (although the rate will depend on humidity, air currents, and exposed surface areas versus volumes of the fluids). Without taking extraordinary steps, completely avoiding such moisture adulteration is not possible. A better strategy is to refresh the solutions when applied films begin to show bubbling defects; use smaller quantities of solutions so they are not in use over long periods and use containers presenting small surface areas to the air; and reduce the concentrations of the solutions (or add more acetone to solutions) to reduce the viscosity, which will make it more difficult for formed bubbles to be stable.

The loss of ink legibility was found to originate from two distinct problems. For “old” inks, the application of a protective topcoat solution causes the ink to disintegrate, probably from insufficient or partially aged shellac binder. Inks that demonstrate this defect should probably be replaced. For newer inks, which remain coherent with the application of the topcoat solution, the ink seems to lose adhesion to the B-72 underlayer, as though the underlying B-72 substrate is being redissolved by the acetone from the topcoat solution. High humidity ambient conditions during drying also seem to aggravate this condition by slowing the acetone evaporation and increasing the contact time of acetone with the solid B-72 substrate. To mitigate this problem, reducing the concentration of the topcoat solution, which creates thinner films that can release acetone more quickly, seems to be effective. Drying in lower humidity conditions, or other steps to speed solvent evaporation (hot air from a hair dryer, for example) might also be found helpful. As the dried films of dilute topcoat solutions will be thin, second coats may be needed. The ink will likely still be sensitive to the acetone solvent even beneath the initial dried topcoat film, so the same strategy to make thin films and dry them rapidly through the steps above should be followed.

Introduction

In 2015 conservation scientists at Yale University's Institute for the Preservation of Cultural Heritage (IPCH) entered into a collaboration with the conservation staff at the National Park Service's Southeast Archeological Center (SEAC), to explore the origins and possible mitigation of problems encountered in the application of accession number labels to their collection objects. Our primary contact at SEAC, Dr. Hillary Conley, described the problems as bubbling of an acrylic film that was the substrate for the ink labeling, and the disappearance of the ink numbers in the process of the labeling. Dr. Conley visited IPCH in September of 2015, and subsequently provided examples of the defective labels (applied to non-collection ceramic materials) as well as some of the acrylic resin, solutions, and inks that had been used to produce the problematic labels. These two defects, in the acrylic substrate and the ink, seemed to be separate problems in their nature and occurrence. As a result, we approached each problem as separate processes to be explored.

While the disappearing ink numbering was an unfamiliar one to us, the bubbles created in drying acrylic films cast from solution was in fact a familiar outcome, one which we had researched in our laboratory briefly some years previously. In that earlier work, we had succeeded in creating dried Acryloid/Paraloid B-72 films that were filled with air bubbles by adding water to the acetone solutions of that polymer. This admixture of a non-solvent to the solution is a well-known method for creating porosity in plastic films intentionally, for example in the fabrication of porous polymer membranes. The process at work is called "non-solvent induced phase separation," and the plastic films so created are "phase-inversion membranes" (Guillen et al. 2011). To produce these porous films, one simply adds a low-volatility non-solvent to the polymer solution. As a film cast from this solution dries, the solvent evaporates quickly, leaving the polymer in a solution with greater concentrations of the non-solvent. At a point in the drying, the phases "invert" – leaving the non-solvent in the matrix of polymer. The eventual evaporation of the non-solvent creates voids or bubbles in the polymer film. Another version of this fabrication technique simply allows a polymer solution to dry in an ambient of non-solvent vapor, a technique called "vapor-induced phase separation" (Menut et al. 2008). It was hypothesized that the effect encountered at the SEAC was analogous to this phase inversion membrane formation, with the low volatility non-solvent being water, absorbed unintentionally into the B-72/acetone solutions from ambient humidity. Our experimental directions were defined by this hypothesis that water content in the solutions was a determinant of the bubbling defect.

The problem of the disappearing ink writing, while not familiar, seemed easier to envision. The ink writing was disappearing with the application of a topcoat of B-72/acetone, the same solution used to create the B-72 substrate layer. It seemed plausible that either the ink was dissolving in the acetone of the topcoat application, or the substrate film was re-solubilizing from that topcoat solution and detaching the ink application, or both. A close examination of the ink reaction to the topcoat application was the starting point to diagnosing the origin of the phenomenon.

Methods and Materials

The majority of this study was performed using materials that were available in our laboratories. Solutions of Acryloid B-72 (Conservation Materials) in acetone (Sigma-Aldrich) were made and deposited dropwise onto glass microscope slides for visual examination. For the study of moisture pickup into the solutions, acetone dried over B₂O₃ and ultra-dry acetone (Acros) were used to make up the solutions. Solutions known to be prone to the bubbling defect were provided by SEAC, and these were used for occasional comparison to the solutions made in our laboratory.

Environments for drying the cast films were controlled as much as possible. It was found that results were erratic if solutions were allowed to dry on a bench in the laboratory, where humidity and air currents could not be controlled. Those controlled conditions were achieved either in our constant environment room (held at 23C and 50%RH) or in a glove bag with desiccant to create very low RH levels. Dried films were imaged with a USB microscope (Manhattan webcam 500).

Measurement of the relative B-72, acetone, and water contents of the solutions were performed in an attenuated total reflection (ATR) fluid cell, mounted in a Fourier transform infrared spectrometer (FTIR, Nicolet). For that test, aliquots of the B-72/acetone solution were introduced into the ATR cell at time indexes, and the absorbances at 2987 cm⁻¹ (attributed to B-72), 3001 cm⁻¹ (primarily deriving from acetone), and 3616 cm⁻¹ (water) were measured and ratioed to give relative abundances of each component.

Ink samples studied were all Higgins Black Magic inks of various purchase dates supplied by SEAC. These inks were applied with a quill pen having a rounded nib to dried films of B-72 cast from 20% acetone solutions. These ink deposits were allowed to dry overnight before the dropwise application of the topcoat B-72/acetone solutions, made up as for the first investigation. Images of the ink response to the topcoat solution and the final outcomes were recorded with the USB microscope.

Project activity I: Origin and remediation of bubbling Acryloid B-72 films

Experiments, Results, and Discussion

1. Effect of water content in acetone solutions on quality of cast B-72 films

The initial series of experiments was aimed at confirming the correlation of the bubbling defect with water content of the acetone solution. Varying amounts of water were added to the solutions and films were cast. A solution of 20% (w/w) B-72 in acetone was made first. A series of sample solutions was made by adding different volumes of water (30 μ l, 90 μ l, 150 μ l, and 200 μ l) into 1ml of 20% B-72 solution. Then a film of the sample solutions was produced by dropping the sample solution on a clean glass slide, which was then allowed to dry in a constant environment (23°C and 50% RH). Results for these films are shown in Figure 1.

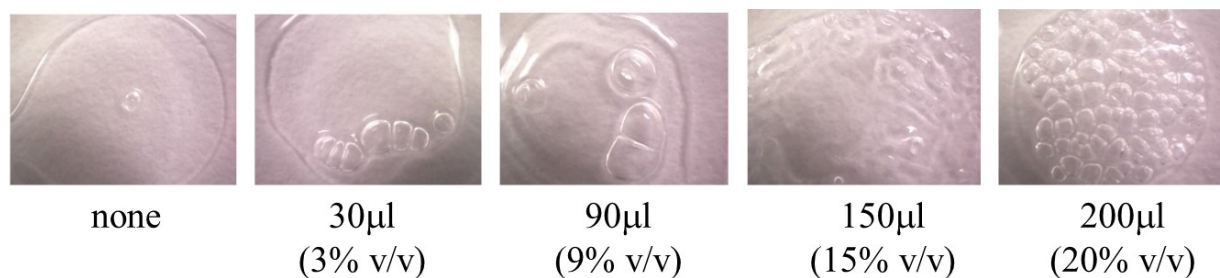


Figure 1. Dried B-72 films cast from 20% acetone solutions containing the indicated volume of water added to a 1 ml portion of solution.

Conclusion: Water in the B-72/acetone solutions causes the film to dry with bubbles, similar to the behavior of the defective object labels at SEAC. The greater the amount of water, the more numerous the bubbles.

2. Effect of B-72 solution concentration and viscosity on film quality

Two B-72/acetone solutions were made at lower concentrations of B-72, 15% and 10% w/w, to which varying amounts of water were added. These lower concentration solutions varied in viscosity as well. Photographs of the dried films cast from these solutions are shown in Figures 2 and 3.

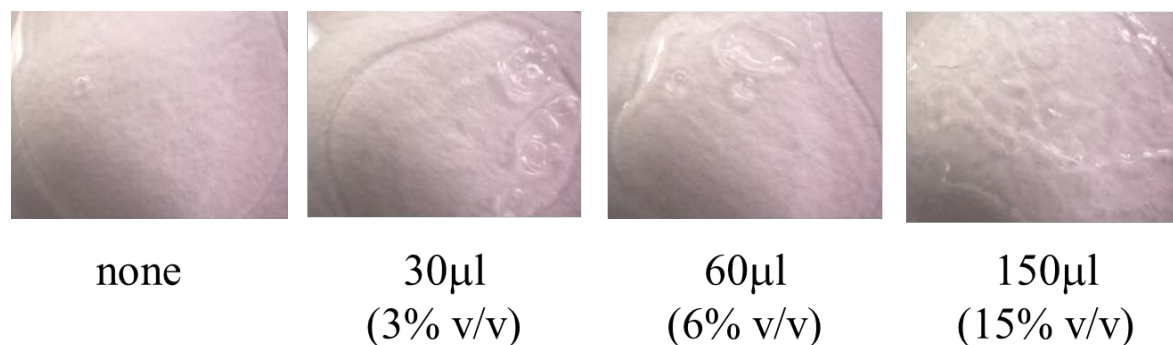


Figure 2. Dried B-72 films cast from 15% acetone solutions containing the indicated volume of water added to a 1 ml portion of solution.

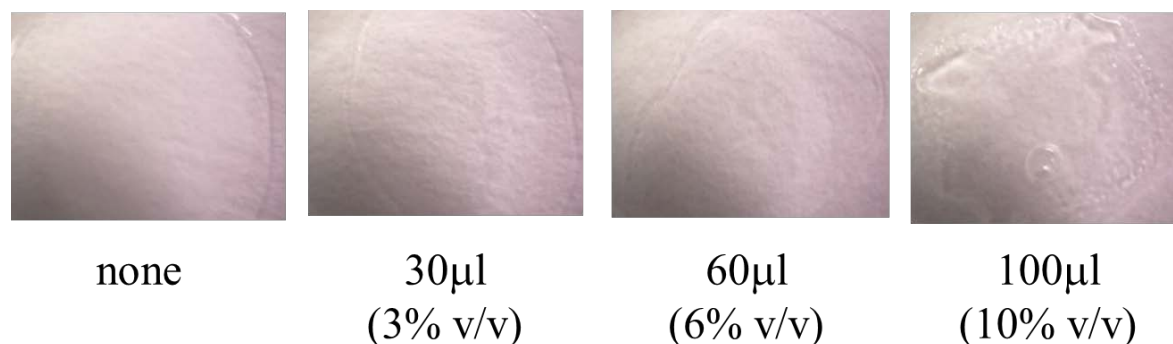


Figure 3. Dried B-72 films cast from 10% acetone solutions containing the indicated volume of water added to a 1 ml portion of solution.

Conclusion: It seems that the water content is not the only critical factor in the formation of defective bubbled B-72 films: the viscosity of the applied solution seems important in trapping the bubbles as the film dries. With equivalent water contents, the more dilute (and less viscous) B-72/acetone solutions seem to dry to films that are freer of bubbles than the more viscous solution. This dependence suggests a possible remediation strategy, which will be explored below.

3. Changes in solution composition and increased risks of bubble defects in cast films from exposure of solutions to ambient humidity

The previous experiments indicated that the amount of water adulterating the B-72/acetone solutions is a primary factor in generating the bubble defect in cast films. Also implicated is the concentration of the B-72 itself, since that influences the viscosity and the ability of the drying film to trap the formed bubbles. But this latter concentration of B-72 in acetone is a changing quantity, since an open container will continuously concentrate the B-72 solution by the evaporation of the acetone. In a separate experiment we explored the uptake of water by and the simultaneous release of acetone from a B-72/acetone solution exposed to a high RH environment. By measuring the infrared spectrum of the resulting solution and isolating absorption features derived from B-72, acetone, and water, we could determine the relative amounts of those components. We also made the same infrared measurements of the B-72 solutions that had been provided to us by SEAC, which were reported to create bubbles in films when dried.

In the experiments, a solution of 20% (w/w) B-72 in dry acetone was prepared and placed in a jar containing 10ml water so that the entire solution was exposed to water vapor (100% RH) and the acetone in the solution was simultaneously allowed to evaporate. After a certain time, the exposed solution was taken out of the jar and a portion was injected into an ATR liquid cell in an FTIR spectrometer to measure the relative concentrations of the B-72, acetone, and water. The solution was then returned to the jar where it could continue to take up moisture and evaporate acetone. In addition to this solution that was allowed to pick up moisture from the ambient, three other solutions containing some amount of water were examined by this IR analysis: 1) a portion of the freshly prepared solution that was adulterated with 0.5% v/v water; 2) a nominal 20% B-72/acetone solution provided by SEAC that was reported to produce defective films; and a 20% B-72/acetone solution prepared for other aspects of the study and which had been aging for about 6 months since its initial preparation. Drops of each of these solutions were applied to glass slides and allowed to dry in a constant environment (23°C and 50% RH), to examine their tendency to form bubbles in the cast films.

In a typical FTIR spectrum of such a solution, a peak at 3616 cm^{-1} derives from an O-H vibration from water, a peak at 3001 cm^{-1} from $-\text{CH}_3$ is attributed to acetone (and some amount of methyl acrylic units in B-72), and a peak at 2987 cm^{-1} from $-\text{CH}_2$ vibration is attributed to B-72 in the solution. The ratio of absorbances at 2987 cm^{-1} and at 3001 cm^{-1} , A_{2987} / A_{3001} , indicates the relative concentration of B-72 in acetone. Similarly, the ratio of absorbances at 3616 cm^{-1} and at 2987 cm^{-1} indicates the relative amounts of water in the acetone. During the exposure, water is taken up and acetone is released, changing the composition of the solution. Those changes can be tracked over time and are represented in Figure 4.

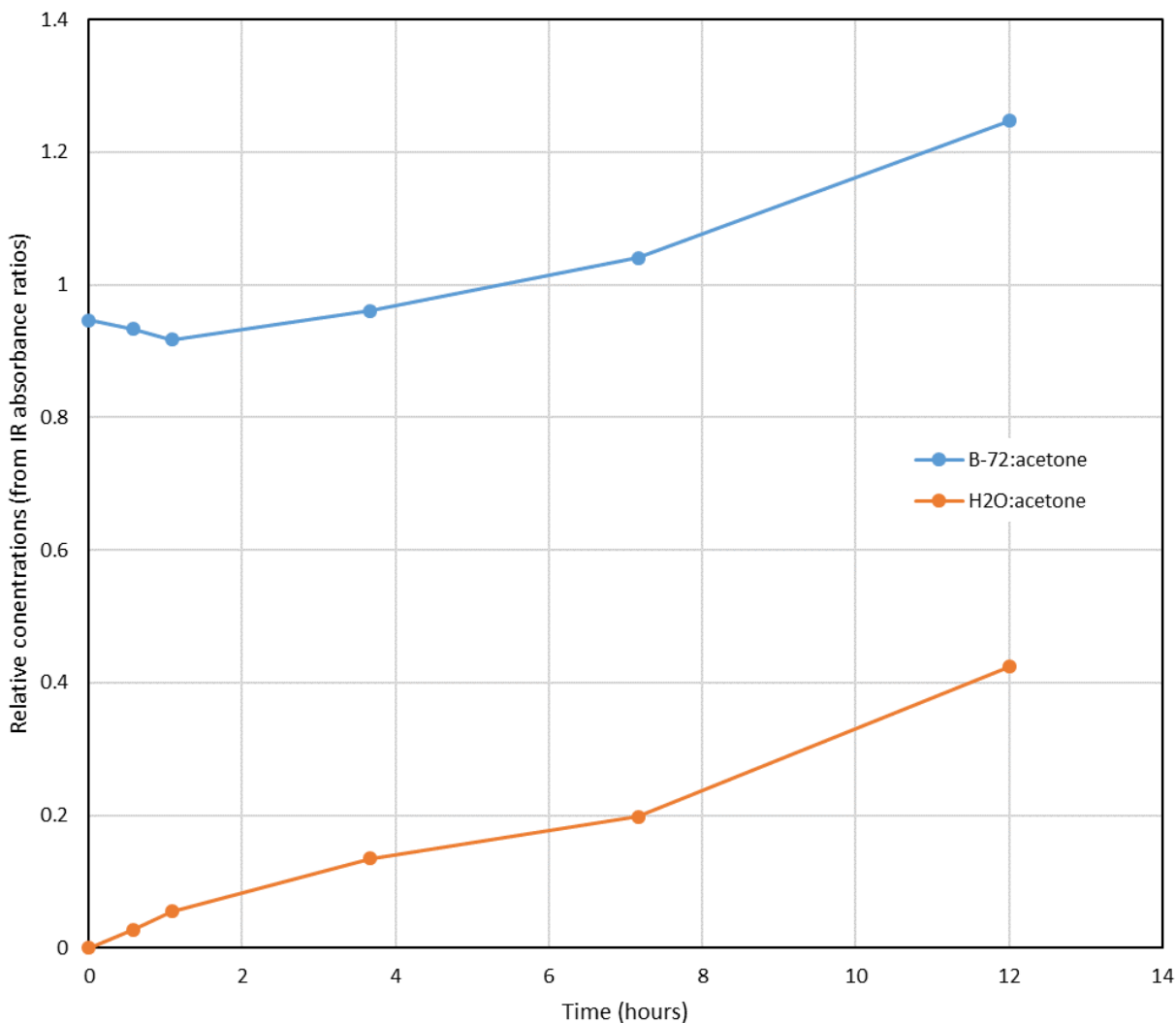


Figure 4. Change in relative concentrations (from the IR absorbance ratios) for 20% B-72/acetone solutions exposed to 100% RH ambient environment.

Conclusion: Exposure to a humid environment changes the composition of the B-72/acetone solution very rapidly. The fluid solution takes up moisture, increasing its water content, and it also releases acetone, which increases the concentrations of both the B-72 and the absorbed water in the solution. The rates of these processes will of course vary, depending on surface areas of solutions, volumes of solutions, air currents, and particular RH levels. Nevertheless, the reaction of the solution composition to ambient air conditions is expected to be rapid.

The resulting replicate films cast from the solutions exposed to high humidity are shown in the photographs in Figure 5.

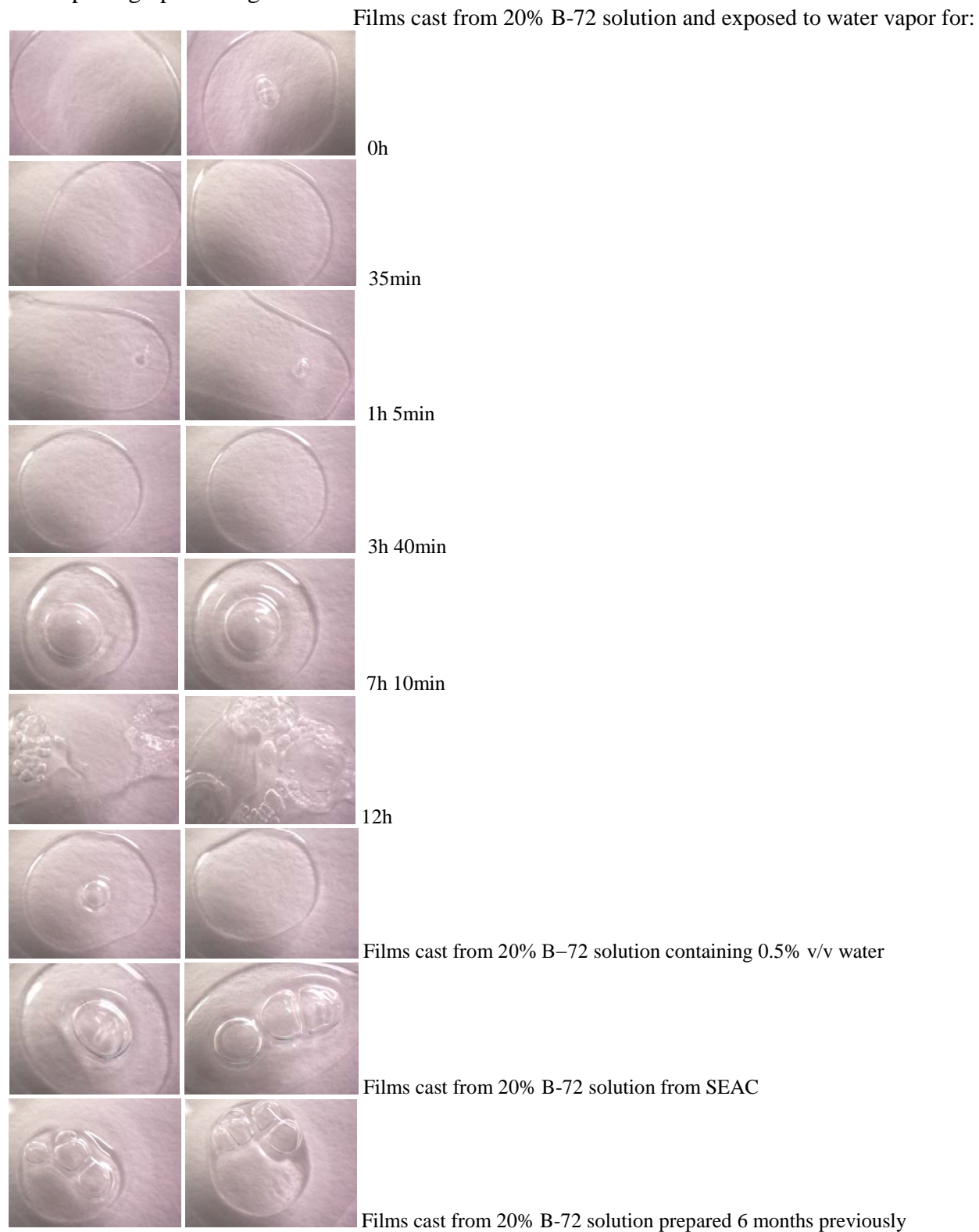


Figure 5. Photomicrographs of B-72 films cast from solutions as described in the labels.

The results for the films cast from the solutions of measured B-72/acetone/water composition are compiled in Figure 6. In that figure, the risk of cast films containing bubbles is shown to be greater at higher water content and at higher B-72 concentration (i.e., higher solution viscosity).

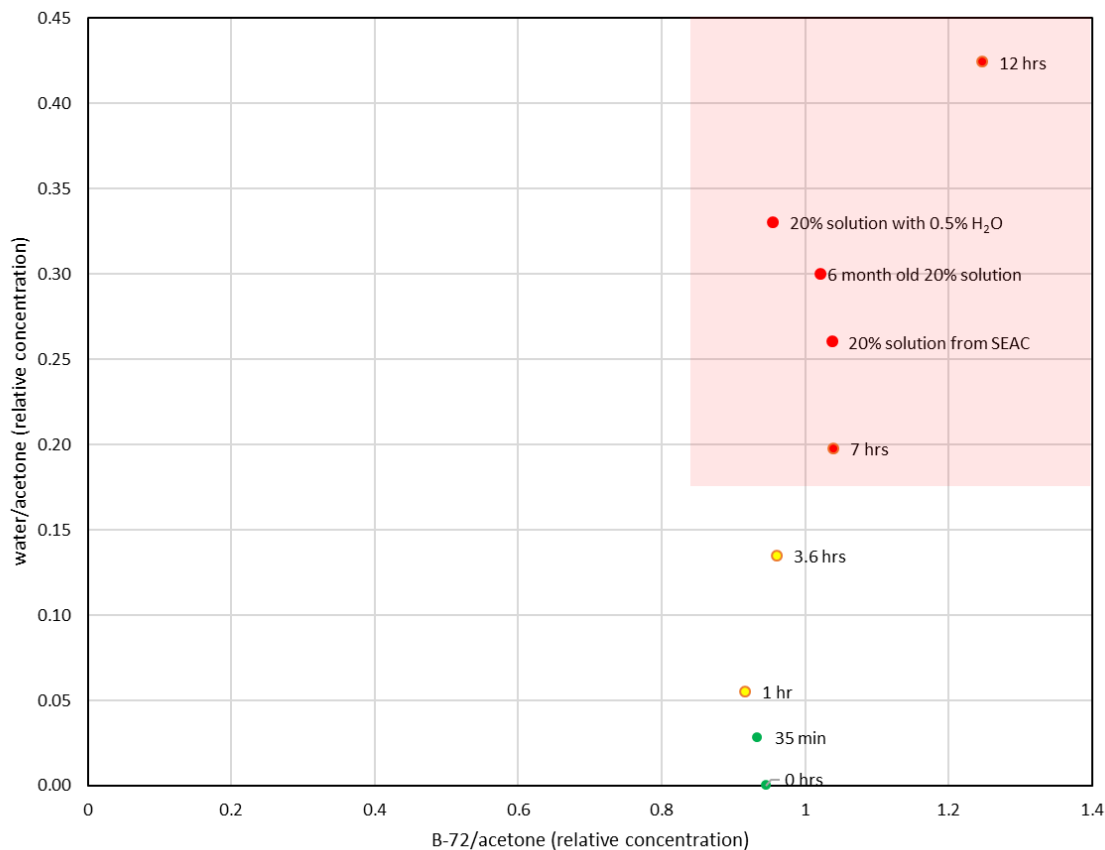


Figure 6. Graph showing relative composition of B-72/acetone/water solutions, as measured from ratios of IR absorbances derived from each constituent. The labels next to the data points denote the solution that was studied (time labels identify the 20% B-72/acetone solution exposed to 100% RH for the periods indicated). The colors of the data points indicate the quality of the films cast from these solutions: green for films that dried with no apparent bubbles, yellow for films having a few or small bubbles, and red for films with large numbers of larger bubbles. The shaded pink area is the region where bubbles in the cast films are likely due to high water content and high solution viscosity.

Conclusion: These experiments strengthen the overall sense that water content and solution viscosity combine to create conditions that are likely to result in films plagued by bubbles. In very humid conditions, water absorption into the solutions occurs in very short periods of time, but even moderate humidity conditions (such as the lab space in which this study was done) can result in significant water absorption into the solution in a few months.

4. Mitigation of bubbling defect in B-72 films cast from acetone

The findings of these experiments suggest a number of possible strategies to mitigate the problems associated with B-72/acetone solutions that suffer the bubbling defects. Since the principal problem is the presence of water in highly viscous fluid solutions, the strategies are mainly aimed at minimizing the amount of absorbed water, or reducing the solution viscosity. Removal of water from solutions that have become adulterated is not particularly easy to do. Some more practical measures that might be considered are:

- 1) Once the films begin showing signs that they are drying with bubbles, stop using the solution and instead prepare a fresh B-72 solution. Use acetone that has not been exposed to ambient humidity for a significant time, preferably from a bottle that has been opened relatively recently.
- 2) Protect the B-72 solution from exposure to ambient humidity as much as possible. If a large volume of the solution was prepared, fill smaller bottles or vials (10-20ml) with a small amount of solution, so it might be used up before absorbing a lot of water or evaporating a lot of acetone. Using a container with a narrow mouth, and which provides the solution with a small surface area of contact with air, may help minimize its moisture uptake from ambient humidity.
- 3) If the bubbles start forming in the cast films, adding more acetone to the solution might decrease the viscosity enough to avoid bubble formation. Films cast from these dilute solutions will be thinner, so multiple coats may become necessary.

Project activity II: Origin and remediation of impermanent ink writing

Experiments, Results, and Discussion

1. Examination of ink alteration with applied B-72 topcoat

In order to better understand the processes causing the eradication of legible ink writing with the application of the final topcoat of B-72/acetone solution, photomicrographs were taken of the ink before and after topcoat application. It became clear that we were observing different behaviors, illustrated in Figure 7.

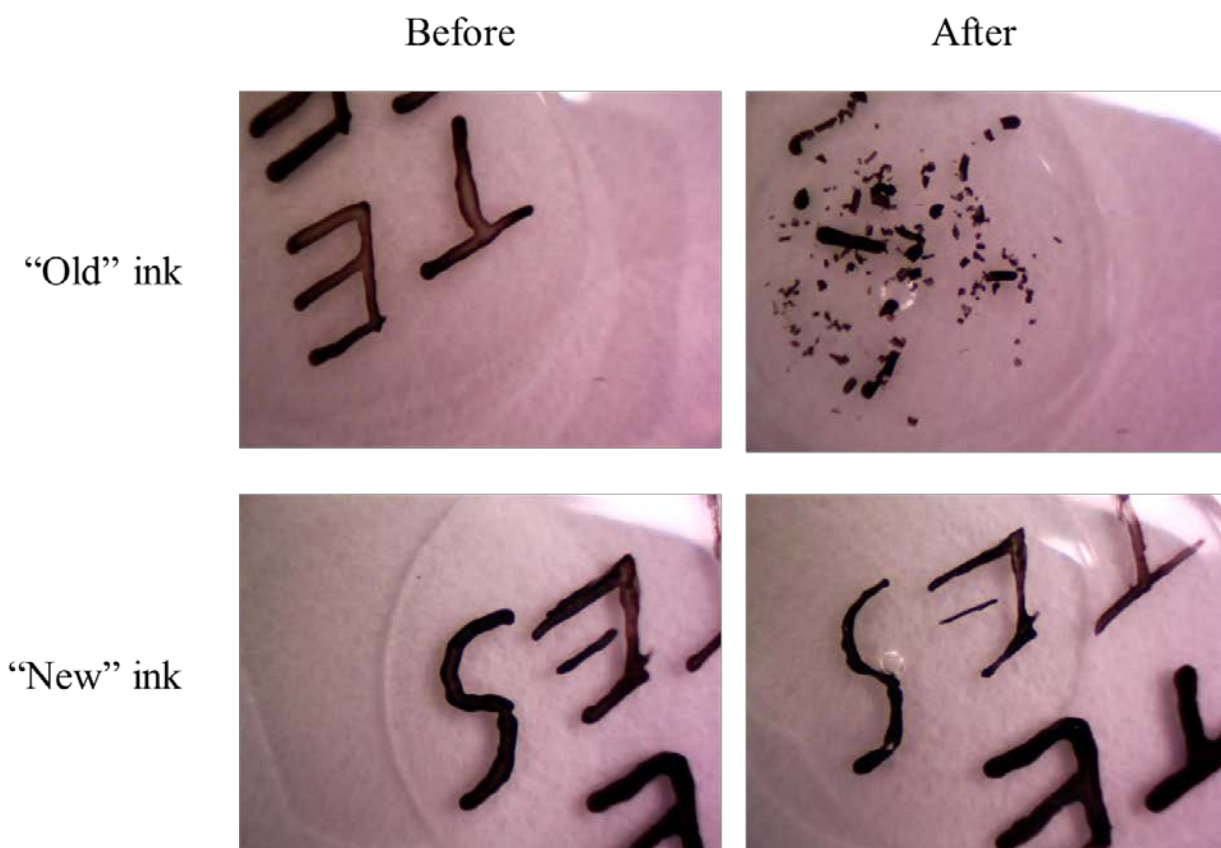


Figure 7. Photomicrographs of writing on dried B-72 films, before and after application of a topcoat of 20% B-72/acetone. Two behaviors are apparent for the “old” ink (used by SEAC for some period of time and supplied for this study) and the “new” ink (two samples were purchased by SEAC in 2014 and 2015 and provided for this study – both of these newer samples behaved similarly).

Time-lapse videos clarify the effect of the topcoat solutions on the old and new ink lines. These videos are shown in Figure 8.

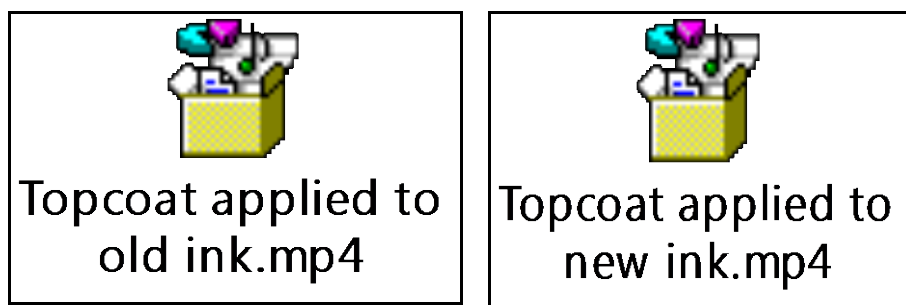


Figure 8. Time-lapse videos of magnified view of dried inks on B-72 films as a drop of 20% B-72/acetone topcoat solution is added.

Conclusion: It is clear in the videos how the ink is disrupted upon topcoat solution application. The old ink fractures into jagged islands that are then swept around in the fluid topcoat solution, and those fragments appear to also redissolve. This total loss of cohesion (as well as adhesion) is indicative of a dried ink deposit that lacks sufficient binder to resist the slightest disruption of solvent exposure or fluid movement. It is likely that, over time, the fluid ink has aged in the bottle in a way that reduces the amount of binder (in this case, shellac, according to the manufacturer) in the applied ink films. This might be a result of crosslinking of the shellac binder, a known problem in the long-term storage of shellac solutions, or coagulation of the suspended pigment into clumps having little binder. The reported absence of a chemical smell in the old ink probably suggests the evaporation of a stabilizing agent, often ammonia.

The erosion of the legible ink line in the application of new ink is fundamentally different. In this case, the ink line does not disintegrate: it retains its cohesion, presumably because of the greater content of shellac binder, but it loses its adhesion to the substrate layer. These integral ink strokes then lift up into the fluid solution, move about, and sometimes twist to present only the very thin profile of the depth of the ink line. The written line shifts, narrows, and becomes indistinct. The detachment of the ink layer may also reflect slight dissolution of the substrate B-72 layer upon contact with acetone.

The apparent ink defects can be attributed to the acetone solvent being applied with the topcoat layer. The following experiments examined the influence of environmental conditions during the drying of the topcoat, the concentration (i.e., acetone content) of the applied topcoat, and the barrier afforded by a thin topcoat towards subsequent applications.

2. Influence of ambient conditions during drying of topcoat application

Samples of ink writing on dried B-72 films were coated with a drop of 20% B-72/acetone and allowed to dry under two different RH levels: very low and 50%RH. The changes in the ink lines were recorded with images, typical ones shown in Figure 9, which were dried at very low RH, and Figure 10, samples dried at 50% RH.

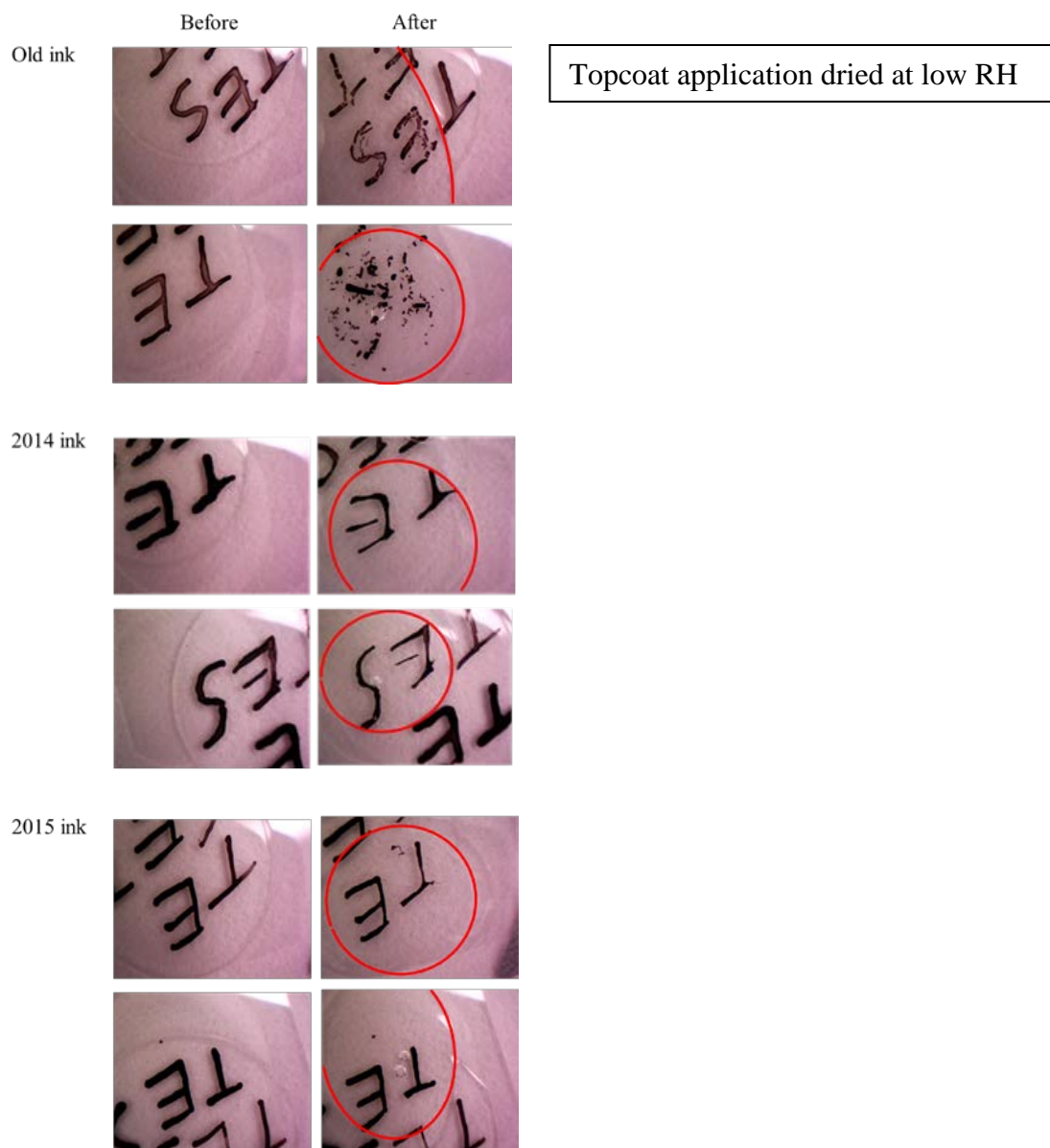


Figure 9. Photomicrographs of samples of the three inks, applied to B-72 films, before and after application of a topcoat of 20% B-72/acetone. Films dried at very low RH. Red outlines indicate the approximate extent of the drop of topcoat film.

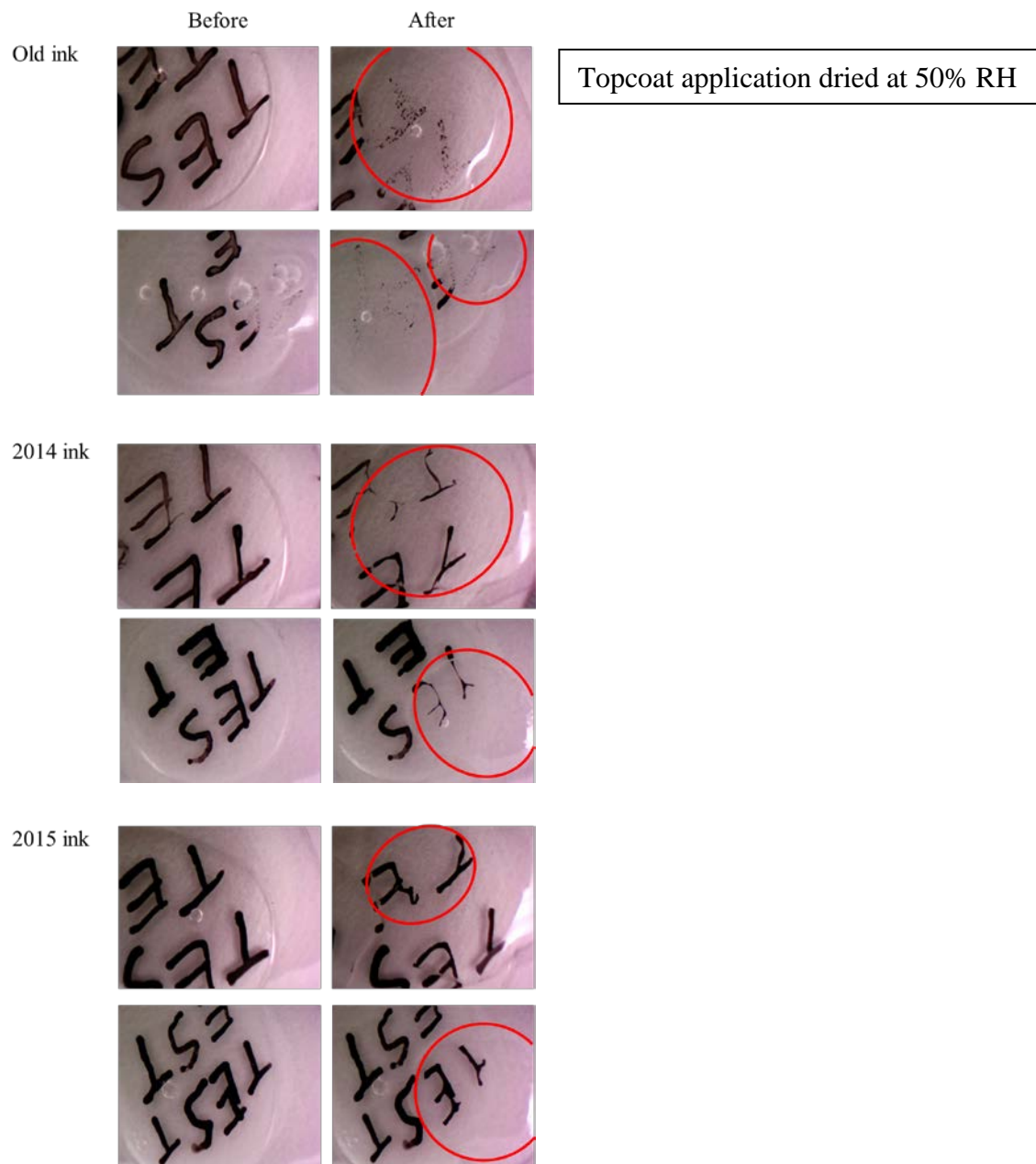


Figure 10. Photomicrographs of samples of the three inks, applied to B-72 films, before and after application of a topcoat of 20% B-72/acetone. Films dried at 50% RH. Red outlines indicate the approximate extent of the drop of topcoat film.

Conclusion: In addition to the age of the ink, the conditions of the drying of the topcoat seem to affect the integrity of the ink line, with somewhat more disruption evident when drying occurs in moderate humidity. This relates to the acetone evaporation rate, which is slowed in humid air (de Vrieze et al. 2009). Slower evaporation increases the contact time of the acetone with the ink and with the B-72 substrate film upon which the ink sits.

3. Effect of B-72 concentration of topcoat solution

It was expected that more dilute concentrations of B-72 in the topcoat solution would help mitigate the ink reaction to the acetone solvent. While containing more acetone per volume, a more dilute solution would be less viscous and create a thinner layer (since the solids content is lower), which could allow for a more rapid drying of the topcoat film. That thinness of film, however, may not provide sufficient protection to the ink lettering, and a second application of topcoat solution might be needed. In this experiment we examined the ink reaction to application of a topcoat that was 5% B-72/acetone, rather than the 20% concentration used above. We also examined the changes in the ink upon application of a second topcoat after drying the first topcoat. Both 20% B-72/acetone and 5% B-72/acetone solutions were examined as the second topcoat application applied over the dried film cast from 5% B-72/acetone.

The inks on B-72 layers coated with 5% B-72/acetone are shown in Figure 10. The inks coated with 5% B-72/acetone, dried, and recoated with 20% B-72/acetone or 5% B-72/acetone are also shown in Figure 11.

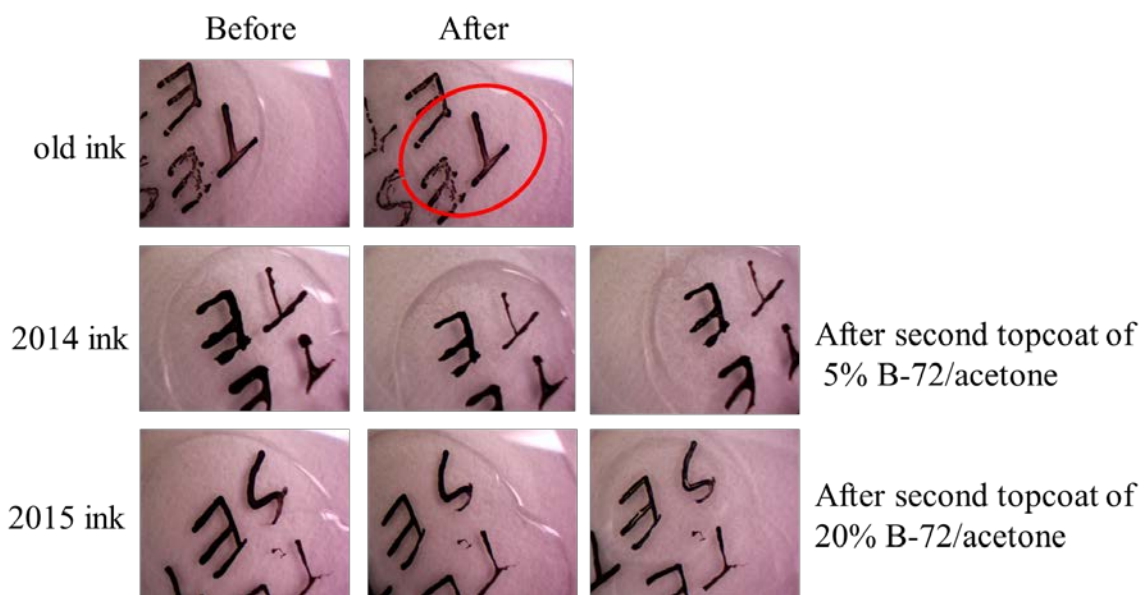


Figure 11. Photomicrographs of three inks, applied to B-72 layers, before and after application of a topcoat of 5% B-72/acetone, and after a second topcoat of 5% B-72/acetone (for the 2014 ink) or 20% B-72/acetone (for the 2015 ink).

Conclusion: A 5% B-72/acetone topcoat solution seems to greatly reduce the deformation of the ink line, even for the old ink that disintegrated from application of 20% B-72/acetone (Figs. 7-10). Even with a thin topcoat, though, subsequent application of a second topcoat of 20% B-72/acetone (2015 ink) still seems to affect the ink slightly, even underneath the dried first topcoat. The second topcoat of 5% B-72/acetone (2014 ink) did not seem to significantly affect the ink.

4. Mitigation of ink defect

Based on these findings, several recommendations can be made to reduce the incidence of problems with applying legible ink labels:

1. Use new bottles of ink. If the quality of an ink is in question, a quick test would be to check the effect of a 20% B-72/acetone topcoat on an inked text. Ink that disintegrates upon application of that topcoat may no longer be usable.
2. Reduce the concentration of the topcoat solution. A 5% B-72/acetone solution seems to dry quickly, and because of its thinness, multiple coatings may be needed to fully protect the label.
3. Dry the topcoat application as rapidly as possible, to minimize the dwell time of the acetone on the ink and its B-72 support layer. Avoid drying the topcoat application in high humidity conditions, which will slow acetone evaporation.

Summary

The problems with object labeling encountered by the staff at the Southeast Archeology Center have been investigated. The problem of the bubbling defects in the B-72 applications has been attributed to moisture contamination of the acetone solutions. That pickup of moisture from ambient humidity, both into the B-72/acetone solutions or into the acetone used to make up those solutions, is rapid (although the rate will depend on humidity, air currents, and exposed surface areas versus volumes of the fluids). Without taking extraordinary steps, completely avoiding such moisture adulteration is not possible. A better strategy is to refresh the solutions when applied films begin to show bubbling defects; use smaller quantities of solutions so they are not in use over long periods and use containers presenting small surface areas to the air; and reduce the concentrations of the solutions (or add more acetone to solutions) to reduce the viscosity, which will make it more difficult for formed bubbles to be stable.

The loss of ink legibility was found to originate from two distinct problems. For “old” inks, the application of a protective topcoat solution causes the ink to disintegrate, probably from insufficient or partially aged shellac binder. Inks that demonstrate this defect should probably be replaced. For newer inks, which remain coherent with the application of the topcoat solution, the ink seems to lose adhesion to the B-72 underlayer, as though the underlying B-72 substrate is being redissolved by the acetone from the topcoat solution. High humidity ambient conditions during drying also seem to aggravate this condition by slowing the acetone evaporation and increasing the contact time of acetone with the solid B-72 substrate. To mitigate this problem, reducing the concentration of the topcoat solution, which creates thinner films that can release acetone more quickly, seems to be effective. Drying in lower humidity conditions, or other steps to speed solvent evaporation (hot air from a hair dryer, for example) might also be found helpful. As the dried films of dilute topcoat solutions will be thin, second coats may be needed. The ink will likely still be sensitive to the acetone solvent even beneath the initial dried topcoat film, so the same strategy to make thin films and dry them rapidly through the steps above should be followed.

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