

## Development and Evaluation of Removable Protective Coatings on Bronze

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### Abstract

Coatings are often used to help protect bronzes from destructive erosion caused by outdoor weathering. Experiments looking at improved coating systems for bronze have been a focus of research at North Dakota State University. Previous research has shown that the most protective coatings tend to be impervious to conventional solvent removal techniques and standard mechanical removal methods may damage bronzes and their patinas. This research has focused on viable coatings that afford protection to the underlying bronze surface while remaining removable under specific conditions not typically found in the outdoor environment. The preparation and evaluation of various unconventional coatings for bronze has been accomplished through synthesis and combinatorial methods. The results of the initial testing of the new coating will be discussed.

### Abstract

A menudo se aplican recubrimientos para proteger los bronzes de la erosión destructiva causada por los agentes atmosféricos. Ensayos a fin de desarrollar sistemas de revestimientos protectivos eficaces han sido un tema de investigación privilegiado en North Dakota State University. Experimentos llevados a cabo anteriormente probaron que los revestimientos que mejor protegen tienden a volverse impermeables a los medios convencionales de eliminación con disolventes y que los métodos de mecánicos de extracción pueden ser perjudiciales para los bronzes y sus patinas. Este trabajo de investigación se ha focalizado en desarrollar recubrimientos viables que protegen la superficie subyacente del bronce y que se pueden quitar en condiciones específicas atípicas de un ambiente exterior. La elaboración y evaluación de varios revestimientos no convencionales para bronce se han establecido por medio de síntesis y métodos combinatorios. Los resultados de la fase inicial de pruebas sobre el nuevo revestimiento serán discutidos.

### Abstract

Des revêtements sont souvent utilisés afin de protéger les bronzes de l'érosion destructrice causée par les agents atmosphériques. Des expériences visant à développer des systèmes de revêtements améliorés pour les bronzes ont été menées à North Dakota State University. Des recherches antérieures avaient démontré que les enduits protecteurs les

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plus efficaces sont souvent imperméables aux solvants par les techniques conventionnelles d'enlèvement, et que les techniques classiques mécaniques d'enlèvement peuvent endommager les bronzes et leur patine. Notre recherche a été de développer des revêtements viables qui permettent de protéger la surface sous-jacente du bronze tout en demeurant faciles à enlever dans des conditions spécifiques atypiques d'un environnement extérieur. C'est par la synthèse et les méthodes combinatoires que la préparation et l'évaluation de plusieurs revêtements non conventionnels pour le bronze ont été accomplies. Les résultats des essais préliminaires sur le nouveau revêtement seront discutés.

*Keywords:* removable, coating, reversible, film, paint, bronze, polyurethane

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## 1. Introduction

Removability is a property demanded of the materials used in the conservation of art. When a conservator works with a piece of artwork, there is a certain code of ethics that is maintained. It is the role of the conservators to help prevent future damage to the artwork they are treating. In this preventive process, the conservator must choose materials that will not further harm the object. It is often specified that the reversibility of a treatment is essential (Weil, 1981). The challenge presented by the conservation community is that everything applied to a piece of artwork must be *reversible*. In the case of a coating on bronze sculpture, the protective coating needs to be removable without damaging or changing the sculpture's surface. Although a protective *and* removable coating is a seemingly simple requirement of the conservator, from the perception of the coating scientist, they are opposing properties and it is difficult to achieve both.

Currently, the two common methods of removing a coating from a substrate are blasting abrasive materials (Djurovic et al., 1999) and solvent removal. Although blasting and stripping techniques have been used in the field of preservation, there are dangers of damaging the substrate, associated with these techniques (Grimmer, 1979). It has been proven that the reflection of sand particle off of a copper or brass substrate results is "considerable erosion" (Carter et al., 1991 and Fang et al., 1999). Water-blasting is also a method used to remove paint from a metal surface ("High-pressure water removes paint build-up", 1996; "Achieving surface preparation standards by waterjetting", 1998; Kierkegaard, 2000). When water-blasting is used on a bronze substrate, it is likely that water is forced into pores and will cause long term problems when trapped underneath a coating. When using solvents to remove a coating, they must be used in large quantities. This does not help the international drive to reduce the hazardous air pollutants (HAPs) and volatile organic compounds (VOCs). Laser removal of a coating on bronze holds much potential, but currently, the controlled irradiation of various coatings on bronze has not lead to universally positive results (Cooper, 2001). In conclusion, blasting, high-pressure water jet, and solvent removal methods not only can potentially damage the bronze surface, but these methods also present environmental hazards due to the resulting dust, dispersed liquid particles, and fumes. To avoid the necessity of solvent stripping or blasting methods, the synthesis of coatings that have inherent chemical decomposition mechanisms, which are different than their curing mechanisms are currently being studied (Van der Wielen et al., 2001; Olson et al., 2003; Shedlosky et al., 2004).

Protective coatings are needed for outdoor bronze sculptures because the monumental alloy is especially susceptible to deterioration caused by atmospheric corrosion. Coatings put on any outdoor metal substrate, if not solely for aesthetic purposes, are meant to protect the underlying metal from corrosion. These coatings must endure a wide range of temperature conditions, ultraviolet radiation, pollutants, snow, acid rain, wind and particulate matter. Because of this considerable set of conditions, coatings, when used outside of conservation are typically developed to have the most robust properties possible. Such materials are usually made of crosslinked polymers. It has been found in previous studies, various coatings that are not removable with solvents outperform, in terms of coating protection and lifetime, those that are "removable" (Grimmer, 1979). It is also noted that crosslinked systems, offer a significantly higher protection and lifespan than that of their uncrosslinked counterparts. Because of the said restrictions, the sphere of material options in conservation has been diminished and crosslinked systems do not fit within the usable realm. The current procedure is to only apply coatings that are removable by solvents, as non-removable coatings have been interpreted as "adversely (affecting) cultural property or its future." (AIC) The primary coating used on bronze sculpture is wax (Kipper, 1996), but previous studies (Brostoff et al., 1997 and 1998; Bierwagen et al. 2001; Bierwagen et al. 2000 and 2001; Bierwagen et al., 2003) have shown less permeable coatings provide better protection and longer lifetimes between treatments.

The seemingly contradictory properties of removability and durability stand at odds with each other in coating design. When developing good protection of a metal from the coating, one needs adhesion and chemical stability to external stresses. When looking for removability, these properties must be decreased. Hence the ethics of conservation appears to run counter to normal coating design. The method in which this research project is attempting to get around this combination of incompatible requirements is to add a weak link within the coating that is activated within a manufactured set of conditions that is unlikely to occur in natural exposure.

## 1.2 Methods of Development

As stated previously, there are many robust coatings that cannot be considered when treating an outdoor bronze due to their irreversible nature. If this research is successful, it will free a set of high performance coatings from the removability restrictions. We aim to prepare clear protective coatings of controlled removability that have as little as possible impact on the bronze. Much of our development of removable coatings was based on the use of combinatorial synthesis and testing methodologies

The technique of combinatorial chemistry, new to the field of material science, is an incredibly useful tool for making minor formulation modifications of synthesized coatings, and for rapid and extensive screening of the coatings. The methodology is just being implemented in the field of coatings (Vratsanos et al., 2001; Schrof et al., 2001; Chisholm et al. 2002a and Chisholm et al. 2002b) and our studies have extended these methods into the specific area of formulating coatings with removability and high performance. The application of combinatorial chemistry, allowed this research to handle and screen many more materials than possible using standard practice. One is able to produce a large variety of products in a relatively short time frame. Coatings are multi-component systems that can have many complex interactions, (Pilcher, 2001) and, as such, are good candidates for the application of combinatorial

methods. This technique enables one to rapidly synthesize and characterize new coating polymers at a rate up to 100 times greater than standard practice

One of the challenges in using combinatorial chemistry is the design of the experiment. The method of analysis must be direct and have a clear pass or fail result. Our first analysis was to determine the removability of the coating. We used an increased pH to change the chemistry of the coating making it removable. We also tested the coatings in water to make sure the system was not so hydrophilic that the system would fail if exposed to water. This type of analytical measurement, when it can be miniaturized and automated, is ideally suited to use in combination with rapid synthetic methods for preparing new polymers of designed but unevaluated removability.

## 2. Experimental

### 2.1 Polyester synthesis

Typically polyurethane coatings are very durable and when applied to metals provide a high degree of protection (Koch et al., 1985; Wicks et al., 1999). The problem of using polyurethanes in an application on bronze sculptures is that they are permanent and only removable by mechanical methods. Through this research we are attempting to develop a polyurethane coating that is both protective and removable. Polyesters are synthesized by reacting a polyacid and a polyol as shown in Figure 1.

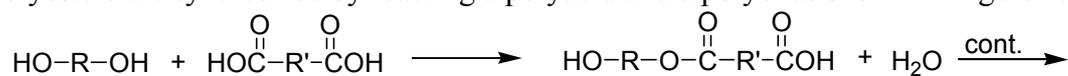


Figure 1. The reaction of a polyol and polyacid to form a polyester and water.

Commonly polyesters are formulated to have excess hydroxyl groups that are then used for crosslinking. The polyester urethane is made by crosslinking a multifunctional, hydroxyl-terminated polyester with an isocyanurate as seen in Figure 2.

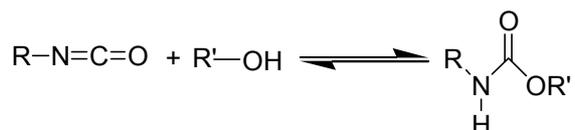


Figure 2. The crosslinking reaction of an isocyanate and a alcohol group.

Dimethylolpropionic acid (DMPA) was used as a monomer in the polyester synthesis. DMPA has two hydroxyl groups that are reactive and one protected acid group (see Figure 3).

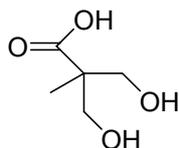


Figure 3. Structure of dimethylolpropionic acid.

Because of the hindered status of the acid group it is unlikely to react during the polymerization, and therefore does not need to be protected during the synthesis. This monomer is used in water-borne polyurethanes; once the polyester is synthesized the carboxylic acid can be neutralized with an amine, and it becomes water soluble

(Wicks et al., 1999). In the case of developing a removable coating, the polymer would not be neutralized until the coating is being removed. The means in which this occurs is the base catalyzed hydrolysis reaction, as seen in Figure 4. In this process the hydroxide attacks electrophilic carbon of the ester, the intermediate collapses reforming carbon-oxygen double bond, finally a fast acid/ base reaction, deprotonates the carboxylic acid.

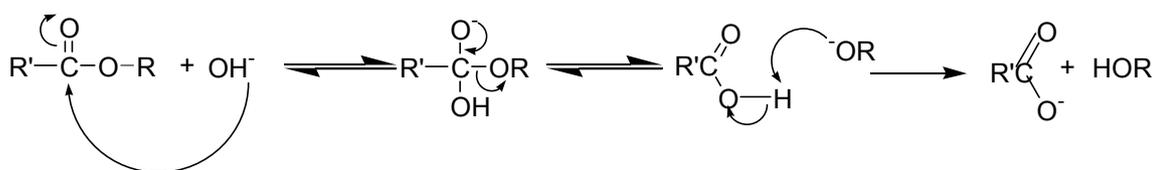


Figure 4. Based catalyzed hydrolysis reaction.

## 2.2 Crosslinking/ Formulations

The type of isocyanate and its crosslink density has a marked effect on the stability of the urethane system. Higher crosslink densities lead to more stable coatings and a smaller probability that the system will be removable. In addition a hydrophilic component within the coating could potentially help promote removability. All these variables were tested with each other in a series of factorial experiments with center points and star points to create a response surface for the different factors. The DMTA based polyester was then crosslinked and formulated varying the (1) crosslink density or the NCO:OH ratio, (2) the type of isocyanate, (3) the hydrophile content and (4) the type of hydrophile. Three separate isocyanates were used in the crosslinking reaction as well as 5 different hydrophilic additives. The three separate isocyanates were chosen for their specific properties.

*Isocyanate A* is a difunctional isocyanate with an aromatic component. This aromatic ring will increase the rigidity of the crosslinked system. *Isocyanate B* is trifunctional and is known to crosslink well with polyester polyols and result in a coating that has a high resistance to weathering. *Isocyanate C* is also a trifunctional molecule that has excellent adhesion and toughness.

A hydrophilic component was included in the study. Two hydrophilic molecules were chosen for their distinct properties and added in various amounts during the crosslinking reaction. By adding a hydrophilic molecule to the crosslinked structure, water uptake will be increased, increasing the degradation rate (Vogel et al. 2004). It was thought that this approach would also help the crosslinked polymers breakdown when exposed to the high pH material. *Hydrophile 1* had a molecular weight of 200 and is a very hydrophilic molecule. *Hydrophile 2* is composed of a hydrophilic chain sandwiched between two hydrophobic molecules. The molecular weight of this system is about 2000. A possible structure of the crosslinked system is found in Figure 5.

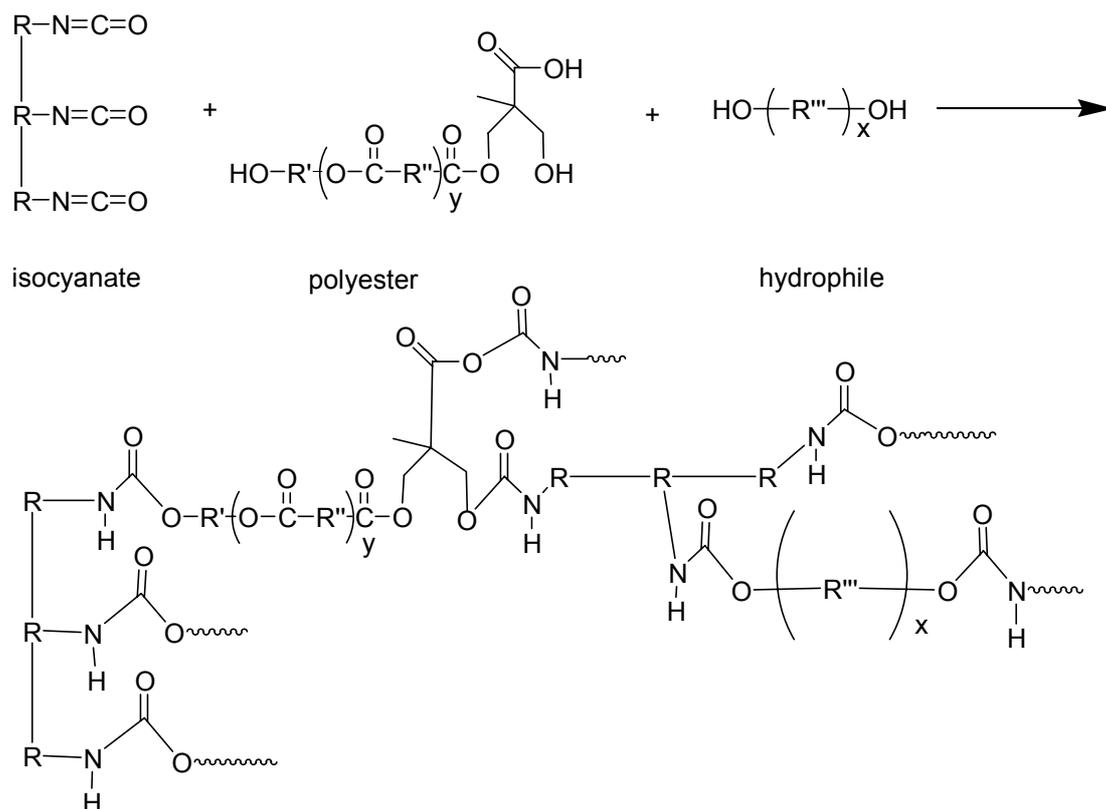


Figure 5. Possible structure of the crosslinked coating.

The isocyanates were crosslinked with a polyester in ratios of 0.295:1, 0.5:1, 0.589:1, 0.8:1, 0.995:1, 1.1:1, 1.304:1, 1.593:1 and 2.190:1. Additional samples were crosslinked in the same ratios with the hydrophilic additives 5, 10 and 13 wt.% of the polyester. Each of these samples were cast with a 37 $\mu$ m Sheen Cube film applicator onto polished, degreased spring loaded rolled bronze (Lubaloy Co.) with an alloy composition of 87.547% Cu, 0.005% Pb, 0.038% Fe, 10.6% Zn, and 1.76% Sn. These coatings were allowed to cure in ambient room temperature for 5 days and were evaluated for curing.

### 2.3 Removability evaluation

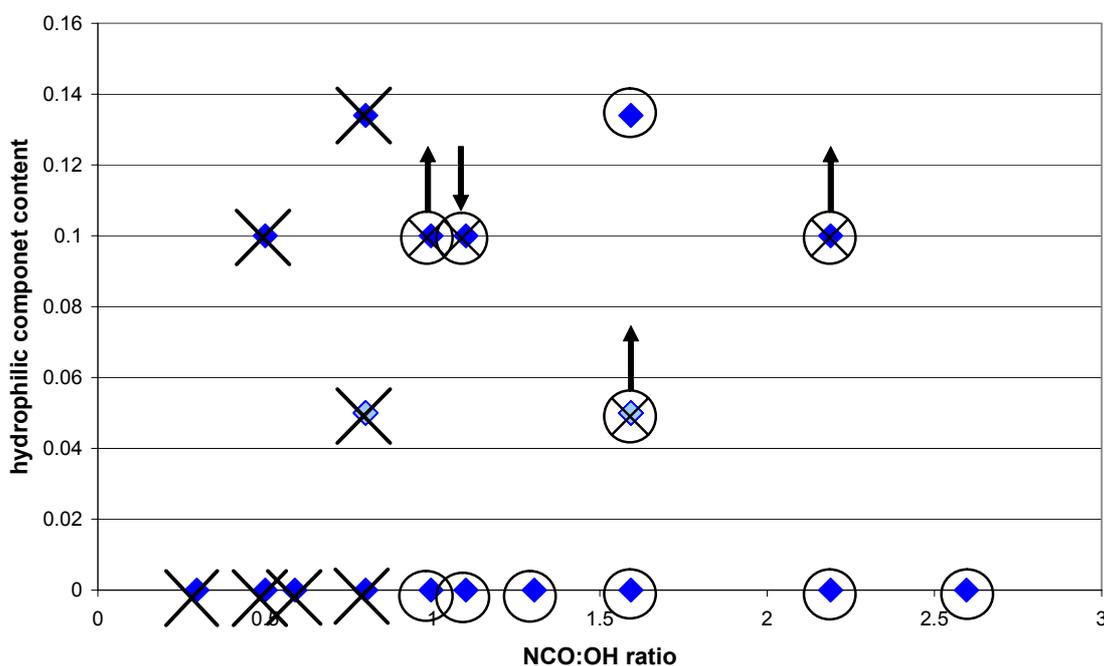
Each coating was exposed to the 3M varnish remover, Safest Stripper™ modified to a pH of 9 for 30 minutes. The system was lightly abraded with a plastic scraper and rinsed with deionized water. Each urethane was evaluated visually to see if the coating was removed after the exposure. Subsequently the urethanes were immersed in a water bath for 30 minutes, and the coatings were analyzed to determine if the coating was adversely affected by the water exposure.

### 3. Results

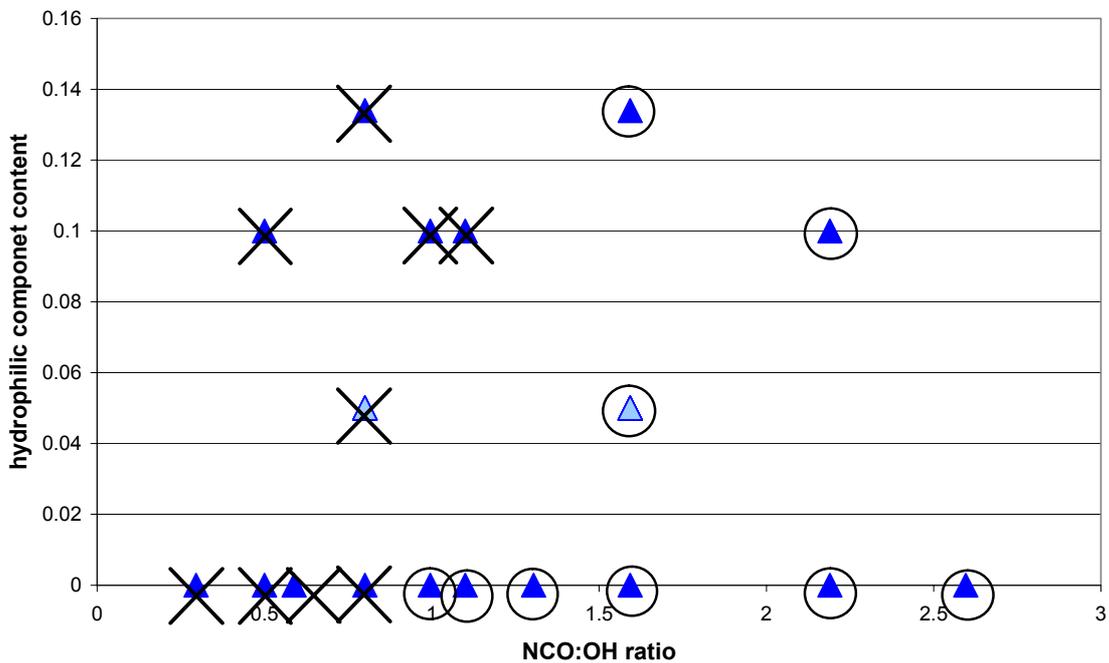
The response surfaces, Figures 6-11, display the durability and removability of each of the coating as a function of the variables. By analyzing the response surface, one can identify the areas of water resistance and removability. The following symbols have been used to represent the coating properties. The  $\bigcirc$  represents that the coating was not affected by the water immersion, and was removed after the exposure to the high pH paste. The X through the point indicates that the system did not cure, and

remained tacky five days after it was cast. The symbol  $\bigcirc$  with an upward arrow represents a system that was removable after the water immersion. The symbol  $\bigcirc$  with a downward arrow indicates that the system was not removable in the water bath or when the high pH paste was applied. The points represented by a lighter shade are the center points and were duplicated 6 times.

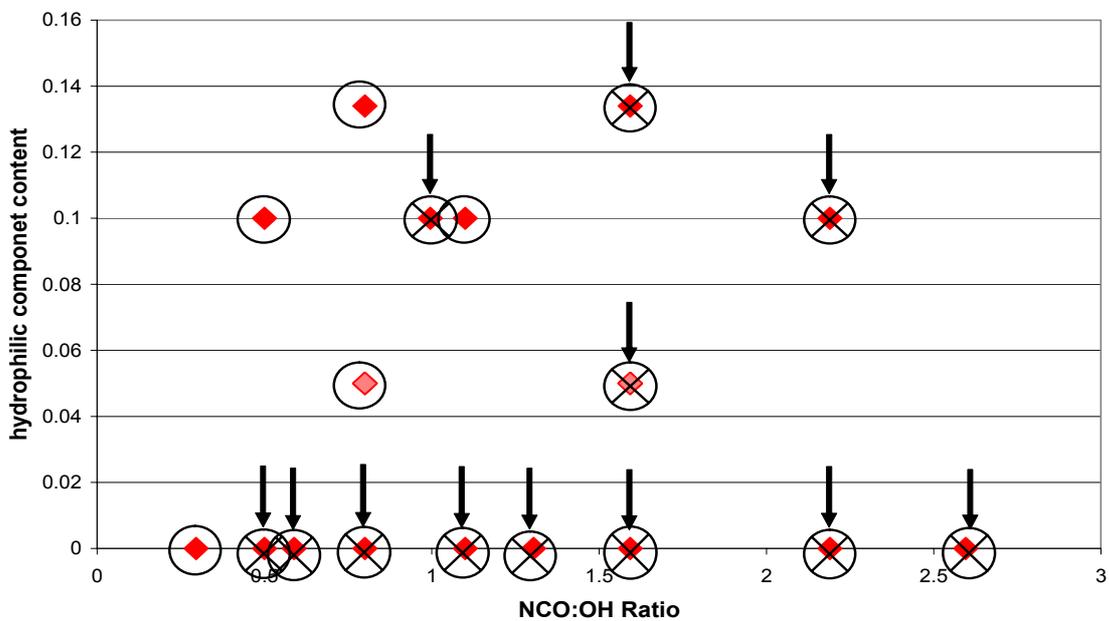
Figure 6. Isocyanate A + Hydrophilic Component 1



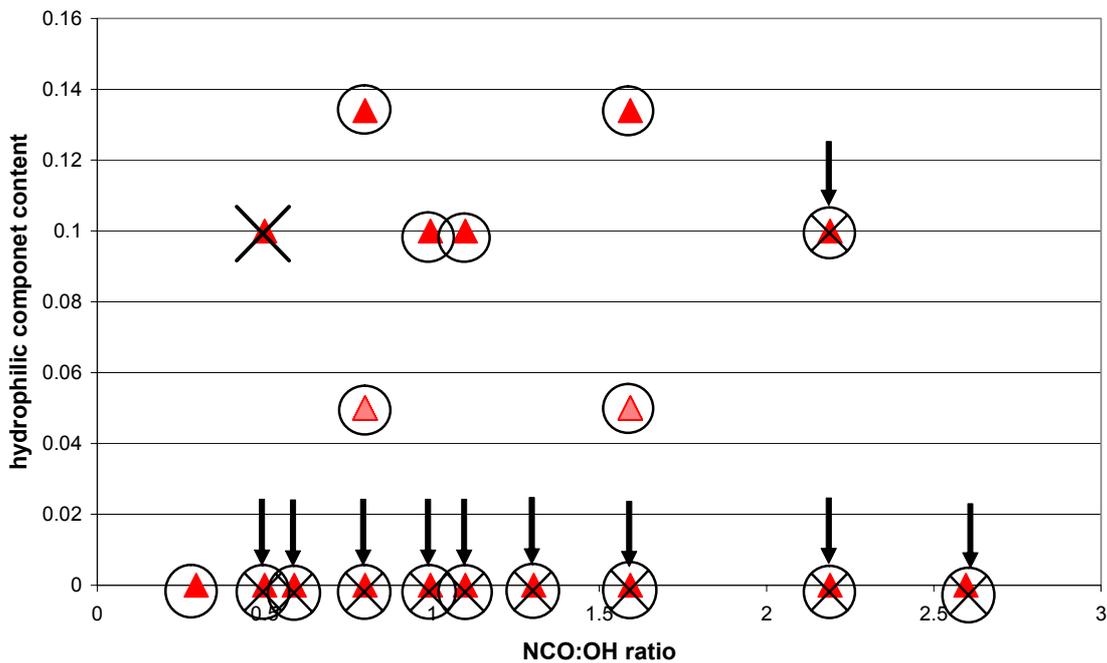
**Figure 7. Isocyanate A + Hydrophilic Component 2**



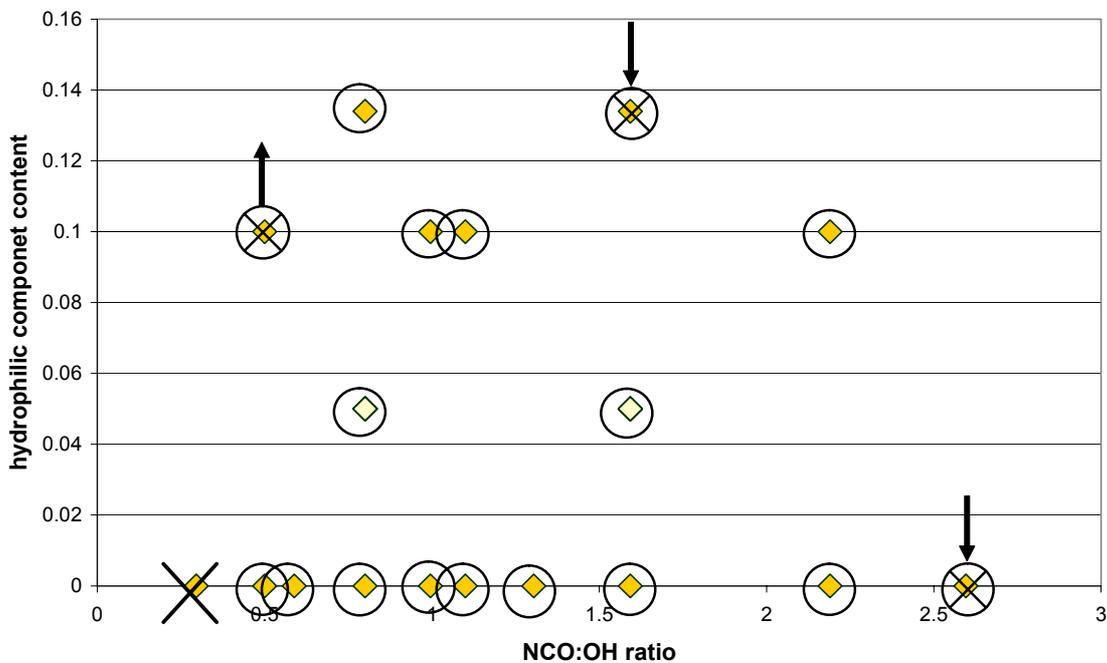
**Figure 8. Isocyanate B + Hydrophilic Component 1**



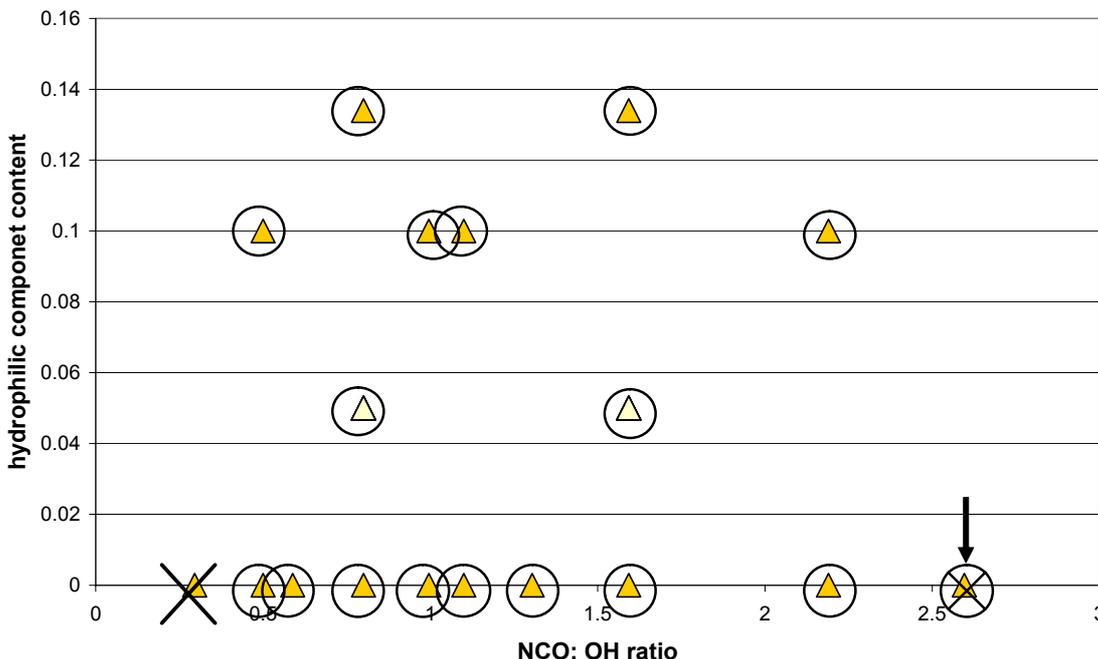
**Figure 9. Isocyanate B + Hyrophlic Component 2**



**Figure 10. Isocyanate C + Hyrophlic Component 1**



**Figure 11. Isocyanate C + Hydrophilic Component 2**



**4. Discussion**

Without the hydrophilic additives, the three isocyanates perform differently at the various crosslinking ratios. *Isocyanate A* did not cure at the lower crosslink densities, but above a crosslinking ratio, of 1:1 (NCO:OH), the system was cured and removable when the high pH paste was applied. *Isocyanate B* formed a very stable system above a ratio of 0.3:1 (NCO:OH), and was found not to be removable. *Isocyanate C* was not cured at the very low crosslink densities, and formed a non-removable coating at the highest crosslink density, but between the two extremes, formed a coating that was stable verse water exposure, but removable when exposed to the high pH paste.

The hydrophilic additives did have an effect on the removability of *Isocyanate A*. *Hydrophile 1* increased the hydrophilicity of the coating, so when it was added in higher quantities, the coatings were removed with water. *Hydrophile 2*, which is the system that contains the hydrophilic component within a sandwich of the hydrophobic entities, was not affected by the water immersion and proved to form a removable coating at the higher crosslink densities.

*Isocyanate B* with the addition of *Hydrophile 1*, was very stable, and was not removable, except at a very low crosslinking density. With the addition of the *Hydrophile 2* the system was removed with the high pH paste at crosslinked ratios between 0.8:1 and 1.593:1 (NCO:OH). In both cases the increase in the hydrophile component did not change the results.

Overall the removability of *Isocyanate C* with the high pH paste was very successful. The addition of the hydrophilic components did not have a marked effect on the performance, as the system was already removable.

## 5. Conclusions

Polyurethanes have been identified as a durable and potentially long life coating system. This research has developed a series of polyurethanes based on a DMPA polyester. This resultant crosslinked system was tested for its removability with a high pH material and water. *Isocyanate A* and *C*, when fully crosslinked, formed coatings that were removable with the high pH paste. The *Hydrophile 1* added too much hydrophilicity to *Isocyanate A* and caused the systems to be removable with water. *Isocyanate B* gained increased removability with the *Hydrophile 2* versus *Hydrophile 1*. The fully crosslinked systems that do not have any hydrophilic additives are expected to form the most durable coatings.

## 6. Future Work

The next stage of the research will consist of using the most durable formulas from this research and incorporating paint additives such ultraviolet light absorber, a hindered amine light stabilizer, leveling agent, and a fungicide. Other possible additives may be investigated if they seem beneficial to the coating. The successful candidates from this stage of the research will be applied to bronze substrates and will be tested to determine their resistance to weathering via electrochemical and accelerated methods.

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