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CLEANING METHODS FOR THE REMOVAL OF LIMEWASH FROM PAINTED PLASTER SURFACES: UTILIZING ION EXCHANGE RESINS ON THE INTERIOR ARCHITECTURAL FINISHES OF THE CAPILLA DE NUESTRA SEÑORA DEL ROSARIO IN IGLESIA SAN JOSÉ, IN SAN JUAN, PUERTO RICO

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A THESIS In Historic Preservation Presented to the Faculties of the University of Pennsylvania in Partial Fulfillment of the Requirements of the Degree of MASTER OF SCIENCE IN HISTORIC PRESERVATION 2009

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Abstract

This project explores methods for the removal of limewash from overpainted plaster surfaces, testing whether ion exchange resins can be used to safely clean these historic materials. The study utilizes the interior architectural finishes of the Capilla de Nuestra Señora del Rosario in Iglesia San José in San Juan, Puerto Rico to investigate the properties and efficacy of ion exchange resins when applied to chalking matte paints on lime plaster. Built in the 16th century, Iglesia San José is considered the second oldest church in the Americas. In 1998, a loss of structural integrity forced the closure of the building to the public. Today, through support from the WMF and an international team of conservators, conservation and restoration efforts progress at the church. The 17th-century Capilla de la Virgen del Rosario possesses the most extensive of the church's remaining mural works. Current work in the chapel focuses on exposing the first mural campaign (Campaign A). Previous site work tested mechanical means of removal, which left behind a lime haze and proved aggressive on fragile plaster surfaces and powdering matte paints. Chemical methods, on the other hand, have not been tested. On fragile plaster surfaces, ion exchange resins may clean more effectively and cause less damage than mechanical methods. Current conservation literature shows little testing of ion exchange resins for their efficacy in removing limewashes or overpaintings, or their effects on calcium-rich substrates. This method requires further testing to determine if it is a cost- and time-effective restoration technique for large-scale applications.

Disciplines

Historic Preservation and Conservation

Comments

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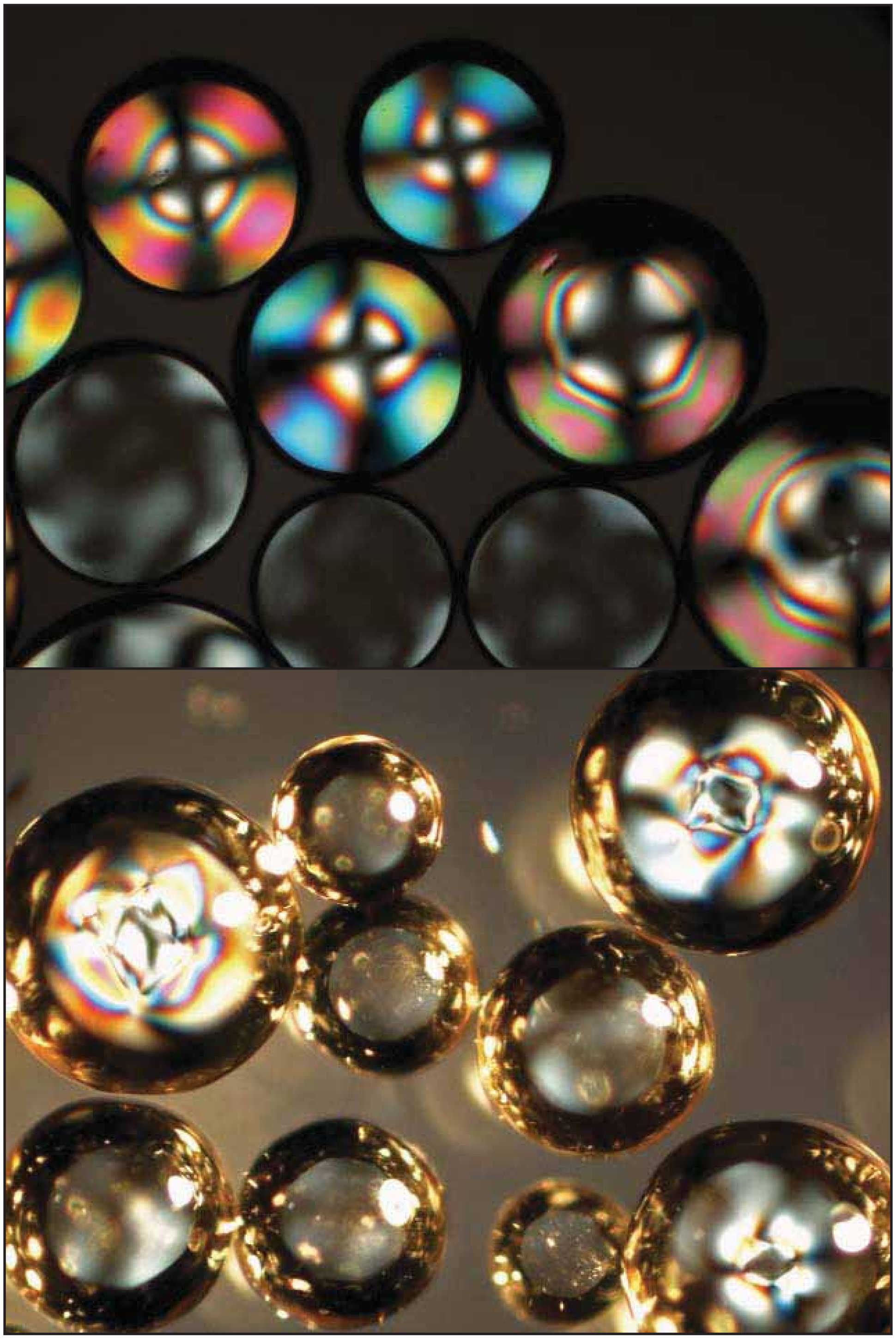

Ion exchange resin USF C-211 Na in water with (1) transmitted light, and (2) transmitted light with raking fiber optics. Viewed at 50x magnification on a Nikon Optiphot 2-Pol compound microscope, Koehler illumination 12 V 100 watt LL halogen lamp and Fiber Optic Specialties, Inc. 24 V 250 watt ELC bulb dual gooseneck fiber optic illumination. (Source: C. Smith, 2009)

To my Mother and Father,
whose good humor, sensibility,
loving natures, and commitment to quality
constantly inspire me.

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Few things in life are done alone; as such I must thank the family, friends, and colleagues that have made this feat possible. In particular, I would like to single out my mother and father, for teaching me that it is always better to challenge oneself…at least when you push your boundaries you'll have better stories to tell at the end of the day. To the entire familial unit, and especially my brothers, who keep me sane when I need it, and provide me with a little insanity when sanity has hit its breaking point. To my aunts and uncles who have provided unconditional and unwavering support throughout my academic career. To my UPenn and MaryWash families, for their willing hearts, hands, and ears throughout the past two years.

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perfer et obdura; dolor hic tibi proderit olim.

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CHAPTER ONE
INTRODUCTION

Revealing long-concealed and therefore long-forgotten works of the past requires a great degree of knowledge, precision and care. In this regard, contemporary architectural conservation strives to be "non-destructive," "non-invasive," and "sustainable." This "do no harm" philosophy is applicable for many forms of treatment but most notably for cleaning. When restoring architectural finishes covered with grime and multiple layers of overpaint, existing for long periods of time, and compromised by deterioration mechanisms, this task becomes more complicated. By what means can conservators clean surfaces, and in particular painted surfaces, so that they once again make sense visually, without causing physical or material damage, and allowing future conservators and curators the opportunity to revisit these actions?

Therefore, to advance the study of cleaning methods for the removal of overpainted limewash from painted plaster surfaces, this thesis proposes to explore the use of ion ex-

Figure 1.1: Mural in Capilla de Nuestra Señora del Rosario (Source: Johnston and Silva).

change resins as a targeted means of treatment. The study will focus on the seventeenth-century interior architectural finishes of the Capilla de Nuestra Señora del Rosario in Iglesia San José in San Juan, Puerto Rico to investigate the properties and efficacy of ion exchange resins as a means of removing limewash from friable mural painting on lime plaster.

The conservation literature contains little discussion or testing of ion exchange resins for their efficacy in removing limewashes or overpaintings. In addition, while the technique has been researched and used in Europe, it is not commonly utilized elsewhere. This method demands further testing to determine if it is a cost- and time-effective restoration technique for mural paintings and similar large-scale applications. If applied at the Capilla it could provide an interesting case study, as the scale would be much larger than previous paint cleaning studies suggest. This thesis proposes to evaluate whether ion exchange resins can offer a safer and more effective cleaning method than mechanical methods of limewash removal on fragile plaster wall surfaces.

1.1 RESEARCH TOPIC

This thesis begins with background information into the site and its conditions; a brief history of previous conservation efforts is also included. This is followed by an in-depth look at limewash characteristics and traditional methods of removal. The next chapter discusses ion exchange resins, including their chemical properties, history, current studies, and specific effect on limewash. Research into the resin types, formulations, and application techniques informed the methods chosen for this thesis. After these investigations, the report describes the mechanics of the resins in question through the analytical findings. A developed testing protocol evaluates the performance of four different ion exchange resins in their ability to remove limewash. The results of this work are summarized in the conclusions, along with recommendations for future research.

In-depth histories of Iglesia San José, documentation of the chapel murals, architectural archaeology or pathology of the chapel, and/or a conditions assessment of the chapel are not included. These subjects have been addressed in previous studies conducted by the Graduate Program in Historic Preservation of the University of Pennsylvania (UPenn), and the New School of Architecture of the Polytechnic University of Puerto Rico (PUPR).[1] Furthermore, as this thesis utilizes the Capilla de Nuestra Señora del Rosario for its case study, it does not discuss other locations within Iglesia San José.

1.2 SUBTOPICS

In addition to exploring the use of ion exchange resins as a means of safely removing limewash from overpainted surfaces, research and laboratory testing addresses a number of related subtopics. Foremost among these are the questions related to ion exchange resins and how they work: do they effectively remove limewash; do they have any adverse effects on the design layer and plaster substrate; will any residue or reactants be left behind; how do the ion exchange resins work chemically and to what extent? Prior to conducting laboratory trials, optimal performance for ion exchange treatments will need to be defined and an evaluation method developed from it.

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[1] See Lyles McBratney, "Emergency Stabilization of the Iglesia San José, Rosario Chapel Mural Paintings, San Juan, Puerto Rico" (Advanced Certificate in Architectural Conservation, Graduate Program in Historic Preservation, School of Design, University of Pennsylvania, August 2006); Cynthia L. Silva, "A Technical Study of the Mural Paintings on the Interior Dome of the Capilla de la Virgen del Rosario, Iglesia San José, San Juan, Puerto Rico" (master's thesis, University of Pennsylvania, 2006); Jill T. Verhosek, "Characterization and Assessment of Argamasa Applied as a Water-Resistant Masonry Surface Finish on the Dome of the Capilla de Nuestra Señora del Rosario, Iglesia San José, San Juan, Puerto Rico" (master's thesis, University of Pennsylvania, 2006); Kerry L. Johnston and Cynthia L. Silva, "La Capilla de Nuestra Señora del Rosario, Iglesia San José, San Juan, Puerto Rico: Interior Finishes Investigation and Conservation Treatment Plan" (Philadelphia, Pa.: The Architectural Conservation Laboratory, School of Design, University of Pennsylvania, September 2008).

1.3 ASSUMPTIONS

Several assumptions were made before deciding the feasibility and structure of this thesis project. In relation to the site, it was determined in previous studies that the first mural campaign (Campaign A) is the most intact and legible of the chapel's six campaigns. After trial on-site cleaning tests, conservators found that mechanical methods using wooden clay tools as well as strappo did not completely remove all limewash from the designated surfaces, leaving a residual haze that obscured the design layer. Based on related studies it is assumed that the resins can be used effectively to remove limewash, without damaging the painted surface and in a time- and cost-effective manner. As regards laboratory testing, it is assumed that adequate facsimiles can be created, so that on-site conditions can be simulated or projected, and results can be quantified.

1.4 LIMITATIONS

The limited time available for site visits combined with the distance of the site from and the University impose significant limitations on the amount and type of research this thesis can cover. As such, this thesis focuses on those tests and simulations that could be created in the laboratory, rather than on-site testing. The amount of sample storage and equipment available at the University of Pennsylvania restricts the quantity and type of testing that could be done. All tests were conducted in the University's Architectural Conservation Laboratory.

In reviewing the available literature, it became apparent that the most recent work involving ion exchange resins comes from Europe, much of it published in languages other than English. As a result some literature could not be accessed and was not included in this paper.

Finally, it is important to note that the actual degree of limewash remaining on the

Rosario Chapel's murals depends upon their location in the chapel, the materials present, the different factors acting on the walls, and the skill of the various cleaners working at the site. The result is variations in the amounts of limewash covering the original murals, which in turn make standardized testing more difficult. Similar issues arose in the laboratory, where the skill of the researcher, the type of substrate, and the type of paint affected results.

CHAPTER TWO
SITE INTRODUCTION:
LA CAPILLA DE NUESTRA SEÑORA DEL ROSARIO

2.1 HISTORICAL BACKGROUND

Built in the sixteenth-century, the convent church of Iglesia San José (see fig. 2.1), in San Juan, Puerto Rico (see fig. 2.2) is considered the second oldest church in the Americas.[1] The church has been attributed as both the "oldest surviving and first significant" architectural work in Puerto Rico, and the "earliest extant example of Gothic-influenced architecture in the New World."[2] Late in the twentieth-century, this significant site experienced a period of decline, until a loss of structural integrity forced the closure of the building to the public in 1998. By 2005, the church gained World Monuments Fund Watch (WMF) status. Today,

Figure 2.1: Exterior view of Iglesia San José (Source: Pantel del Cueto & Associates).

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[1] P. Emilio Tobar, *San Jose Church La Iglesia De San Jose: Templo Y Museo Del Pueblo Puertorriqueno* (San Juan: Imprenta la Milagrosa, 1963), 195. The church was built in phases between 1510 and 1540.

[2] Cynthia L. Silva, "A Technical Study of the Mural Paintings on the Interior Dome of the Capilla de la Virgen del Rosario, Iglesia San José, San Juan, Puerto Rico" (master's thesis, University of Pennsylvania, 2006), 1.

Figure 2.2: Map of Iglesia San José in Old San Juan, Puerto Rico (Source: The New York Times).

through funding from the WMF and the assistance of Pantel del Cueto and Associates, The Architectural Conservation Laboratory of the University of Pennsylvania, the San Juan Fortifications National Historic Site/National Park Service, and the New School of Architecture of the Polytechnic University of Puerto Rico (PUPR), conservation and restoration efforts progress at the church.[3]

The Capilla de la Virgen del Rosario (Chapel of the Virgin of the Rosary) is located within the Iglesia San José (see fig. 2.3). The Rosario Chapel was constructed sometime in the seventeenth-century, and it has not undergone any major structural alterations since the eighteenth-century.[4] The Chapel possesses the most extensive of the church's remaining mural works (a restoration from 1978-1981 removed all original plaster stucco in the church's lateral nave and main altar). The Chapel's interior mural works reflect changes in the church's

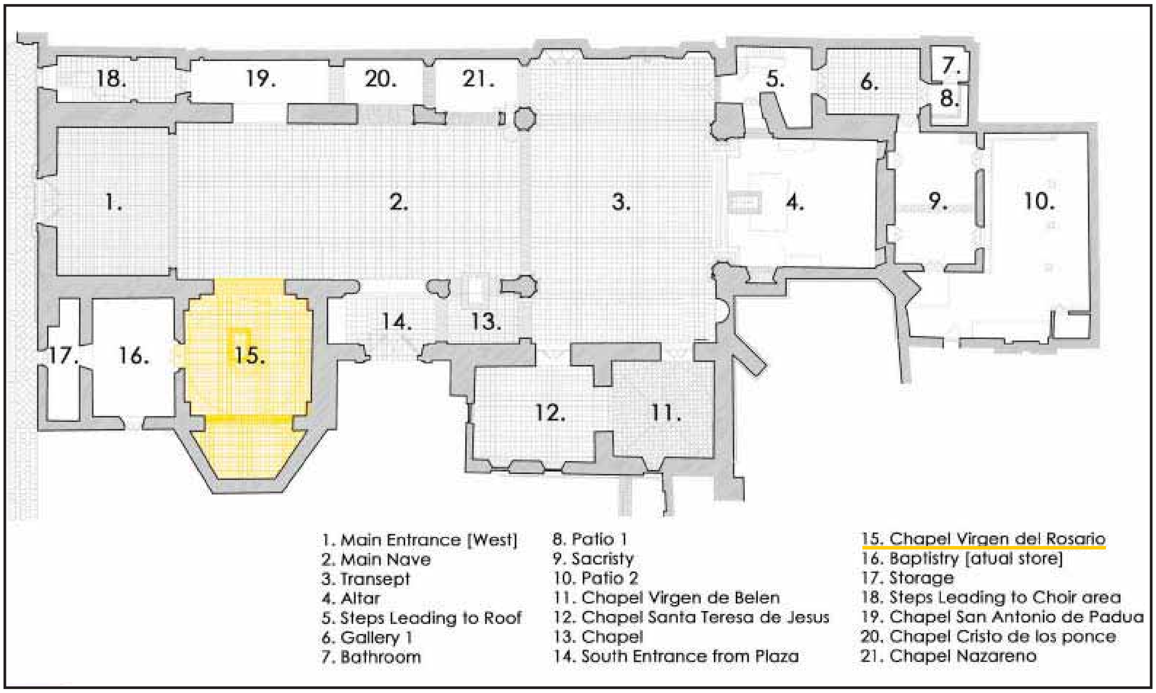

Figure 2.3: Plan view of Iglesia San José with the Rosario Chapel highlighted (Source: Pantel del Cueto & Associates).

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[3] Jill T. Verhosek, "Characterization and Assessment of Argamasa Applied as a Water-Resistant Masonry Surface Finish on the Dome of the Capilla de Nuestra Señora del Rosario, Iglesia San José, San Juan, Puerto Rico" (master's thesis, University of Pennsylvania, 2006), 1.

[4] Ibid., 2-3.

stewardship, including the Dominican, Jesuit, and Vincentian orders. Early wall paintings depict folkloric images of mer-creatures (*las sirenas*), while later nineteenth-century paintings display scenes from the 1571 Battle of Lepanto.[5]

2.2 ROSARIO CHAPEL: PREVIOUS RESEARCH AND SITE WORK

Initially, the conservation process at the Rosario Chapel consisted of two phases. The first phase addressed the architectural recording and emergency stabilization of the church. The second phase studied in detail the seventeenth-century Chapel of the Virgin of the Rosary (Rosario Chapel). Work in the Chapel included recording, analysis of its construction technology, a condition assessment of the masonry, murals and interior surface finishes as well as recommendations for intervention, including treatment and interpretation. After the study, the team undertook the emergency stabilization of the mural paintings in the Rosario Chapel using a system of injection grouting on the detached portions of the murals. Treatments began in the most severe areas, which were primarily located around areas of major loss.[6]

In 2006, research was conducted on the dome exterior,[7] the mural paintings themselves,[8] and the design and execution of an emergency conservation program.[9]

In 2008, The Architectural Conservation Laboratory revisited the interior, completed the study of the interior walls, and removed fragments of overpaintings for future conservation and display. From their laboratory and fieldwork, the team created a conservation treatment plan for the Chapel. The team focused its efforts on the conservation and restoration of the earliest (seventeenth-century) decorative paintings. A technique was needed

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[5] Silva, 2.

[6] Lyles McBratney, "Emergency Stabilization of the Iglesia San José, Rosario Chapel Mural Paintings, San Juan, Puerto Rico" (Advanced Certificate in Architectural Conservation, Graduate Program in Historic Preservation, School of Design, University of Pennsylvania, August 2006), 1-2.

[7] Verhosek.

[8] Silva.

[9] McBratney.

for effectively removing limewash overpaintings without damaging the original paintings underneath. Afterwards, the newly exposed and chalking original paint would need to be consolidated and stabilized.[10]

After this study, the Catholic Archdiocese of Puerto Rico made the decision to restore the Chapel back to the first paint campaign (Campaign A). Thus, the next step in the conservation process is to begin restoration of the paintings, along with several samples of the later campaigns. The 2008 study primarily tested mechanical means of removal, which left behind a lime haze and in areas proved aggressive on fragile plaster surfaces and powdering matte paints. Mechanical methods create greater opportunities for scratching the plaster surface and removing chalking and detached design layers. Chemical methods can also be aggressive and difficult to apply. On fragile plaster surfaces, ion exchange resins may afford more effective cleaning and cause less damage than previously tested methods.

2.3 ROSARIO CHAPEL: CONDITIONS

While minor and temporary interventions have improved roof drainage, ventilation, and stabilized detached plaster, moisture infiltration/condensation, chloride salts, and biological growth remain a chronic problem for the Chapel.[11] This leads to areas of detachment, between the plaster layers, and between the lime plaster and the wall structure (particularly in the Chapel sanctuary and arches).[12] Throughout the dome there are areas of loss and incompatible repair (both plaster and cement).[13]

Due in part to this deterioration, Campaign A remains the best-preserved and most

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[10] Kerry L. Johnston and Cynthia L. Silva, "La Capilla de Nuestra Señora del Rosario, Iglesia San José, San Juan, Puerto Rico: Interior Finishes Investigation and Conservation Treatment Plan" (Philadelphia, Pa.: The Architectural Conservation Laboratory, School of Design, University of Pennsylvania, September 2008), 2-3.

[11] Ibid., 41; Silva, 49.

[12] Johnston and Silva, 106; Silva, 49.

[13] Johnston and Silva, 2-3.

intact of the decorative layers. This is likely due to the fact that the design layer was applied directly onto the lime plaster substrate, and that it was protected for years under limewashes and later painting. These superimposed campaigns became heavily damaged and fragmented from salts, biogrowth, and loss (see fig. 2.4).[14]

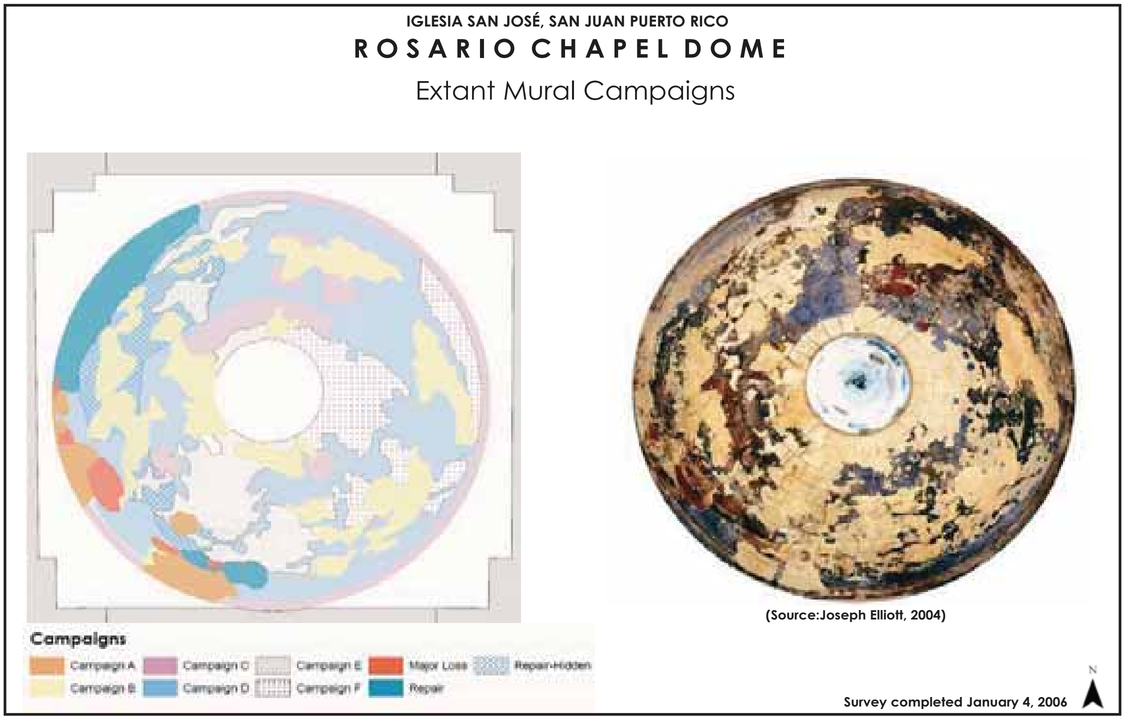

Figure 2.4: Painting campaign map for Rosario Chapel dome (Source: Silva, 113).

2.4 ROSARIO CHAPEL: INTERIOR FINISHES

The properties of the mural's materials and their condition determine the type of ion exchange resin and application methods necessary to break the bond between the limewash and the matte paints of Campaign A without damaging the paintings.

2.4.1 CAMPAIGN A

The 2006 and 2008 finishes studies of Rosario Chapel identified the original decora-

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[14] Ibid., 56.

tive wall painting scheme as Campaign A. This seventeenth-century scheme consists of three motifs: black banding, faux marbling, and figural paintings of mer-creatures (or *sirenas*).[15] This scheme is described in detail in both Silva's 2006 thesis, and in Johnston and Silva's 2008 "Interior Finishes Investigation and Conservation Treatment Plan."

Figure 2.5: Black banding and intersecting cross pattern on intrados of arch (Source: Johnston and Silva, 14).

The black banding, ranging between 2-3 inches, adorns the upper portions of the chapel. It either articulates the junctions of the architectural elements, or creates ashlar block and crossing X designs (see fig. 2.5). The painters incised lines in the wet enlucido to

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[15] Ibid., 11.

mark the placement and width of the black bands, before infilling these lines with carbon black paint.[16]

Figure 2.6: Faux marbling on sanctuary cornice (Source: Johnston and Silva, 17).

The faux marbling scheme appears on the original chapel cornice (see fig. 2.6). The painters used red ochre, yellow ochre, and green pigments in a freehand technique. Two fillets were painted in solid dark red and the cyma reversa received the same pigment in a pattern of semicircles.[17]

The chapel's four pendentives, located directly below the dome, each contain a sin-

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[16] Ibid., 11.
[17] Ibid., 17.

gle figure of a mer-creature, or *la sirena* (see fig. 2.7). These figures consist of carbon black, red ochre, yellow ochre, and green pigments. Carbon black banding outlines the pendentives, while wave-like black marks and greenish-blue wash surround the figures like water.[18]

Figure 2.7: Southwest pendentive, one of *las sirenas*
(Source: Johnston and Silva, 20).

2.4.2 CAMPAIGN A DESIGN LAYER

Silva's 2006 thesis identified the pigments present in Campaign A. The black pigment is charcoal black, which consists of carbon/graphitic black and lignite charcoal, a carbon black from wood coal. The yellow pigment is yellow ochre, a hydrous iron oxide ($Fe_2O_3 \cdot H_2O$).

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[18] Ibid., 20-21.

The red pigment is red ochre, or red iron oxide (Fe_2O_3). The copper green pigment is either verdigris, a copper acetate salt ($Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$), or malachite, a natural copper carbonate ($CuCO_3 \cdot Cu(OH)_2$), both of which contain copper, carbon, and oxygen.[19]

The painting technique appears to be *secco*, painted directly on the dry plaster.[20] No organic binders were identified with energy dispersive X-ray spectroscopy (EDS) or Fourier transform infrared spectroscopy (FTIR). EDS analysis found calcium, carbon and oxygen: all atomic constituents of calcium carbonate. FTIR analysis did not detect any organic binder, although it is possible that water infiltration, salt efflorescence, and bio-growth in the chapel degraded any previously existing organic media. Silva posited that if an organic binder was not used in the *secco* paintings, the artist could have instead applied limewater with pigments to a partially cured substrate.[21] This fact becomes important when considering methods for limewash removal.

2.4.3 PLASTER

The original dome plaster consists of two campaigns. The first is a leveling coat of a red mortar *enfoscado* applied directly to the structure's brick masonry; the second is a thin finishing coat of white plaster *enlucido*.[22]

The *enfoscado* plaster contains quartzitic sand, the feldspar mineral albite, magnetite, brick particles, and lime (calcium carbonate).[23] X-ray diffraction (XRD) analysis of the *enfoscado* determined the following semi-quantitative composition: 52% calcite ($Ca\ CO_3$) attributed to the lime binder, 29.3% quartz (SiO_2), 4% halite (NaCl) salt contamination, 10.01% albite ($Na\ Al\ SiO_3\ O_8$) attributed to low fired clayey brick, and 4.4% yagite ($(Na_3\ K)_3\ Mg_4\ (Al, Mg)_6\ (Si, Al)_{24}\ O_{60}$). Overall, the binder (lime) to non-binder (aggregate and brick dust) ratio

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[19] Silva, 62-64.
[20] Ibid., 15.
[21] Ibid., 62.
[22] Ibid., 11.
[23] Ibid., 55.

is a very lean 1: 7.5.[24] EDS mapping found chloride and sodium ions, indicating the presence of chloride salts, at the plaster surface and in the area of intra-layer detachment in the *enfoscado*.[25]

The *enlucido* contains quartz minerals, brick, and charcoal particles. XRD analysis found 83% calcite (Ca CO_3) attributed to the lime binder, 11.6% quartz (SiO2), and 5% halite (NaCl) from salt contamination. The mix is binder rich with a poorly sorted aggregate. The ratio of binder to aggregate is approximately 2:1 (by volume).[26] The *enlucido* provides the ground and background for Campaign A.[27]

2.4.4 LIMEWASH OVERPAINTING

The overpainting on Campaign A consists of several layers of calcium carbonate, also known as limewash or whiting.[28] During cleaning tests, Johnston and Silva found that the residual veils of limewash (lime haze) and thin, well-adhered gray limewash layers that lie directly on top of Campaign A are the most difficult of these layers to remove.[29]

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[24] Ibid., 56.
[25] Ibid., 57-58.
[26] Ibid.
[27] Ibid., 11.
[28] Ibid., 65.
[29] Johnston and Silva, 67.

CHAPTER THREE

LIMEWASH

3.1 COMPOSITION AND PROPERTIES

Limewash (also known as lime white and whitewash) is essentially a water-rich mixture of slaked (water-added) lime used as paint. The production of calcining (burning) and slaking lime has been practiced since the early Neolithic period, and it is still used today. Slaked lime is known for its alkaline (basic) properties and its abilities to neutralize acids. Lime is calcium oxide (CaO) obtained by burning, or 'calcinating,' limestone to temperatures of around 900°C. At this temperature the calcium carbonate (calcite, $CaCO_3$) disassociates to calcium oxide and carbon dioxide. In water, calcium oxide hydrates to calcium hydroxide. As it dries (cures), water is lost as carbon dioxide is reabsorbed from the atmosphere. This causes the lime to revert back to calcium carbonate. The curing process is extremely slow, and it can take several to many years for the reaction to complete depending on the environment.[1]

3.2 METHODS OF LIMEWASH REMOVAL

Conservators have long had to deal with the specific problem of cleaning thin veils of lime left behind after the removal of limewash overpaintings, particularly in church buildings.[2] This veil can obscure portions of the image, and from great distances, provides interference to the viewing audience. If it is more compact than the paint layer it covers, it may also cause their detachment. On the other hand, this may protect underpaintings for centuries.[3]

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[1] Nicholas Eastaugh, Valentine Walsh, Tracey Chaplin, and Ruth Siddall, *Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments* (Burlington, MA: Butterworth-Heinemann, 2008), 245.

[2] Isabelle Brajer, "Eigil Rothe, an Early Twentieth Century Wall Paintings Conservator in Denmark," *CeROArt*, no. 2 (2008), under "Introduction," http://ceroart.revues.org/index426.html (accessed January 23, 2009); P. Mora, L. Mora, and P. Philippot, *Conservation of Wall Paintings* (London: Butterworths, 1984), 213.

[3] P. Mora, L. Mora, and P. Philippot, *Conservation of Wall Paintings* (London: Butterworths, 1984), 213.

CHAPTER THREE - LIMEWASH

Superimposed limewash is a widespread problem throughout Western Europe, due to the large numbers of medieval church wall paintings that were covered with limewash during periods of religious upheaval and systematic iconoclasm (the deliberate destruction of symbolic icons), such as the Reformation of the sixteenth- and seventeenth-centuries. Nonetheless, the desire to overpaint sometimes stemmed from more general changes in ownership, taste, religious belief, or building alterations.[4] In Denmark, for example, a nineteenth-century nationalist revival led to renewed interest in these artworks and their uncovering. The first uncovering took place in 1826 in The Holy Three Kings' Chapel in Roskilde Cathedral, although restoration of the fifteenth-century wall paintings did not occur until nearly twenty years later.[5] In 1868 Lambach, Austria, eleventh-century Romanesque paintings that were painted over in the fifteenth-century were uncovered in the Benedictine abbey church underneath layers of limewash.[6] By the end of the Baroque period, the paintings in the convent church at Müstair were covered with limewash. The paintings were rediscovered between 1908 and 1909, and restored between 1947 and 1951.[7] In the nineteenth- and early twentieth-century, English medieval wall paintings that had been covered by limewash during the Reformation were rediscovered during restoration efforts.[8]

It was in the first half of the twentieth-century that wall painting restoration became a professional field that required experienced conservators. In turn, the uncovering process

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[4] Kirsten Trampedach, "Introduction to Danish Wall Paintings – Conservation Ethics and Methods of Treatment," http://www.natmus.dk/cons/walls/chrchpnt.htm (accessed January 22, 2009).

[5] Ibid.

[6] Ivo Hammer, "The Conservation in Situ of the Romanesque Wall Paintings of Lambach," in *The Conservation of Wall Paintings Proceedings of a symposium organized by the Courtauld Institute of Art and the Getty Conservation Institute*, ed. Sharon Cather (London: The Getty Conservation Institute, July 13-16, 1987), 43-45.

[7] Andreas Arnold and Konrad Zehnder, "Monitoring Wall Paintings Affected by Soluble Salts," in *The Conservation of Wall Paintings Proceedings of a symposium organized by the Courtauld Institute of Art and the Getty Conservation Institute*, ed. Sharon Cather (London: The Getty Conservation Institute, July 13-16, 1987), 110.

[8] Ann Ballantyne and Anna Hulbert, "19th and Early 20th Century Restorations of English Mediaeval Wall Paintings: Problems and Solutions," in *Les Anciennes Restaurations en Peinture Murale* (Paris, France: International Institute for Conservation of Historic and Artistic Works. Section Française, 1993).

gained more importance.[9] This is particularly evident in the work of Eigil Rothe, "the Father of wall painting conservation in Denmark." From 1916 to early 1930, Rothe formulated his own mixture for impregnating and clarifying images otherwise obscured by a veil of calcium carbonate. His "Preparation" consisted of an alkaline soap solution, mixed with an oil resin varnish and an aqueous solution of casein dissolved in borax. This mixture was emulsified, thinned with turpentine, and finally mixed with a siccative, wax, and camphor. Rothe did not design the "Preparation" with limewash removal in mind, rather, he aimed to saturate the pigments and bring out enough detail in the wall paintings so that they appeared clearly. He wanted a colorless, lusterless treatment that imitated the appearance of aged paint, rather than one that restored the paintings to their original appearance. He also designed his surface treatment to protect the paint layer, allowing for water cleaning of dirt without dissolving the paint pigments.[10]

Figure 3.1: Figures on the wall paintings in Undløse Church (ca. 1425) treated with the Carlsberg Preparation in 1920 (Source: Brajer).

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[9] Trampedach.

[10] Brajer, under "The Carlsberg Preparation."

CHAPTER THREE - LIMEWASH

Rothe's work represents an early foray into preventative conservation treatment. However, the treatment does have its drawbacks. It is not easily reversible and dust attracts to treated areas (see fig. 3.1).[11] Furthermore, when conservators selectively treated moisture and salt-damaged areas years later, they discovered that untreated portions of the paintings experienced ruptures and flaking. This resulted from migration of moisture and salt solutions from the treated areas, where they could not penetrate the "Preparation" barrier, to the comparatively porous untreated areas, where they crystallized.[12]

By 1984, Paolo and Laura Mora and Paul Philippot explored the value of the *strappo* technique, the use of non-polar solvents, and mechanical means for separating superimposed limewash layers from original paint. In the *strappo* technique a mural painting is removed from a wall by detaching only the paint layer. It involves coating a facing with an adhesive based on animal glue. The technique is fast to use, large areas can be recovered as one piece, it can be used on curved surfaces, and it should not damage underdrawings and paintings when they are covered by multiple limewash layers. On the other hand, it does expose the painting to high risk, as the stripping action can tear off the original paint, and it rarely removes the total thickness of the paint layer, often leaving portions behind. Needless to say the technique is a last resort when emergency salvage is the only option. For mechanical techniques small files, chisels, rubber hammers, and scalpels are employed to detach layers. The limewash can be dampened with water, if the original paints are insensitive to water, or non-polar solvents, If they are sensitive to water. Finally, a mixture known as AB 57 (containing slightly basic salts reinforced with surfactants and fungicides) is sometimes used to remove the final lime layers. Acids are not to be used; they act indiscriminately upon all paint layers. If during the cleaning process the paint layer is pulled off with the lime, a fixative must be applied to the original paint layer and the pigments reapplied to the wall.[13]

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[11] Ibid.

[12] Ibid.

[13] P. Mora, L. Mora, and P. Philippot, 257-258, 297-298, 328.

CHAPTER THREE - LIMEWASH

A 1996 study from India on the exposure of wall murals covered with limewash recommended trying mechanical removal with palette knives, wooden mallets, scalpels, emery paper, and wire brushes. Hydrochloric acid and acetic acid were used on rare occasions by a skilled conservator. Alcoholic water was used to soften limewash layers and to dry the original paintings after cleaning.[14]

In 2000, scientists used a pulsed Nd:YAG laser to remove layers of limewash, plaster, glue, and dirt from a medieval wood paneled chamber in the Tetzelhouse in the Saxon town of Pirna. The laser removed all of these layers without damaging the wood substrate. This was considered a successful technique as the process is self-limiting, there was no health hazard, and the results were visually uniform.[15]

By 2005, a team of European scientists were testing laser techniques for the uncovering of polychromed works of art. The SALUT Project utilized existing laser systems to remove superimposed layers of paint on secco wall paintings. Success was determined through optical microscopy (OM), electron probe microanalysis (EPMA), colorimetry, micro-Raman (µRaman), and Fourier transform infrared spectroscopy (FTIR) analysis. This particular study found that Q-switched Nd: YAG lasers emitting at 1,064 nm could remove oil paint and limewash layers, although this required a computer-controlled X-Y-Z station to control the process as it caused certain pigments (cinnabar, yellow ochre, and burnt sienna) to discolor, the texture of the pictorial layer was modified, and it was not effective when the limewash layer exceeded 25 µm.[16]

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[14] I. K. Bhatnagar, C. B. Gupta, and Mamta Pandey, "Exposing of Hidden Treasure (Wall Painting) and their Preservation—Two Case Studies," *Conservation of Cultural Property in India* 29 (1996): 206.
[15] Günter Wiedemann, Markus Schulz, Jan Hauptmann, Hans-Günter Kusch, Sabine Müller, Michael Panzner, and Hendrik Wust, "Laser cleaning applied in the restoration of a medieval wooden panel chamber at Pirna," *Journal of Cultural Heritage* 1, no. Supplement 1: LACONA III (August 1, 2000): S247.
[16] G. Van der Snickt, A. De Boeck, K. Keutgens, and D. Anthierens, "The SALUT Project: Study of Advanced Laser Techniques for the Uncovering of Polychromed Works of Art," in *Lasers in the Conservation of Artworks: LACONA VI Proceedings, Vienna, Austria, Sept. 21–25, 2005*, ed. J. Nimmrichter, W. Kautek, and M. Schreiner (Springer Berlin Heidelberg, 2007), 151.

This 2005 study also noted that "current practice for the removal of superimposed layers involves use of solvents and/or mechanical action using a scalpel." The researchers chose laser techniques over these for several reasons. For one, they found that solvents were costly, time consuming, damaging to the original surface, high in retention and toxicity, and results varied depending upon the experience of the conservator. They hypothesized that lasers, on the other hand, could provide a quick, safe, and quality-assured alternative.[17]

3.3 METHODS EMPLOYED AT ROSARIO CHAPEL

Johnston and Silva's 2008 study found that relatively little published literature exists on past and current treatment methods for limewash removal. The literature that does exist does not go into enough detail to provide a sample methodology; most simply recommends mechanical removal with a scalpel. As such, research into alternative sources is necessary. Two sources, Sophie Stewart's dissertation "The Uncovering of Wall Paintings: Ethics and Methods,"[18] and *The Conservation of Wall Paintings* by Paolo and Laura Mora and Paul Philoppot,[19] provided the basis for the techniques employed at Rosario Chapel.[20]

The methods employed in the 2008 study fall into three categories: dry mechanical, chemical + mechanical, and *strappo*. Two dry mechanical methods were tested: manual scalpel removal and microabrasion. Three chemical + mechanical methods were tested: misting spray, sponge / paper towel compress, and methylcellulose poultice. The *strappo* tests employed several different combinations of cotton, gauze, muslin, solutions, glue recipes, and methods of removal.[21]

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[17] Ibid., 151-152.

[18] Sophie Stewart, "The Uncovering of Wall Paintings: Ethics and Methods" (Diploma Research Project, Courtauld Institute of Art / Getty Conservation Institute, 1991).

[19] P. Mora, L. Mora, and P. Philippot, *Conservation of Wall Paintings* (London: Butterworths, 1984).

[20] Kerry L. Johnston and Cynthia L. Silva, "La Capilla de Nuestra Señora del Rosario, Iglesia San José, San Juan, Puerto Rico: Interior Finishes Investigation and Conservation Treatment Plan" (Philadelphia, Pa.: The Architectural Conservation Laboratory, School of Design, University of Pennsylvania, September 2008), 57.

[21] Ibid., 59-62.

CHAPTER THREE - LIMEWASH

The results of the combined laboratory and field tests led the conservators to list dry mechanical cleaning as the most effective method for bulk limewash removal and haze mitigation. Thin, well-adhered limewashes required softening with either a spray, compress, or poultice treatment, followed by picking or scraping with wooden tools (see fig. 3.2). By comparison, strappo proved more time-consuming and expensive. It did, however, prove useful in removing the fragments of subsequent painting campaigns from the walls, which were saved for later display.[22] The skill of the operator proved to play a significant role in a treatment's ultimate effectiveness.[23]

When cleaning lime haze, Johnston and Silva found that complete removal was not possible on painted areas. Instead, it could only be mitigated, as complete removal "could result in significant loss of original material." Through the application of bamboo skewers, wood cuticle pushers, stiff stencil brushes, and water-moistened cotton swabs, the conservator gradually reduces the opacity of the lime haze.[24]

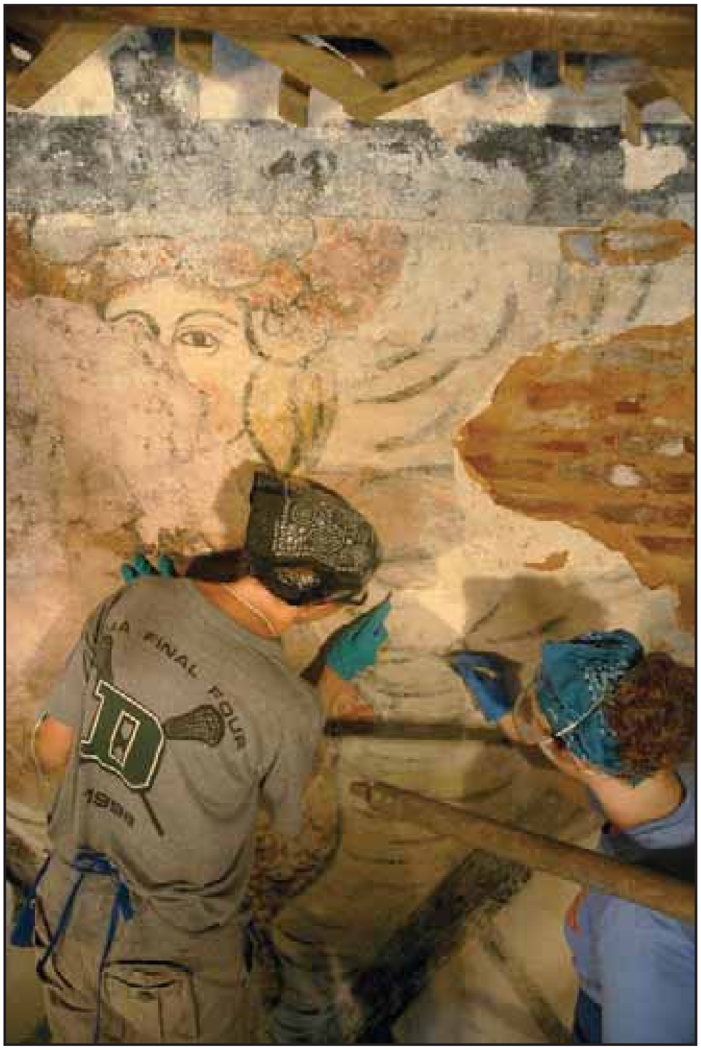

Figure 3.2: Mechanical cleaning of ***la sirena*** **in Rosario Chapel (Source: Johnston and Silva, 96).**

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[22] Ibid., 82.
[23] Ibid., 79, 99.
[24] Ibid., 97.

CHAPTER FOUR

LITERATURE SURVEY: STUDY AND TESTING OF ION EXCHANGE RESINS FOR CONSERVATION

4.1 INTRODUCTION TO ION EXCHANGE RESINS

Since their invention in the 1930s, synthetic ion exchange resins have become widely used in the fields of medicine, water treatment, and food processing. In the second half of the twentieth-century, cultural heritage professionals began to adapt ion exchange technology for their own purposes.[1] Researchers found that the resins' ability to exchange ions made them useful in cleaning and desalination operations.

4.2 PROPERTIES OF ION EXCHANGE RESINS

Ion exchangers can be natural or synthetic, inorganic or polymeric, but they are all activated by aqueous solutions. They can appear in many forms: woods, papers, sands, clays, glauconites, zeolites, functional resins, and living organisms.[2] Today, commercial distributors sell them as microspheres.[3]

Ion exchange resins are insoluble organic polymers that can take up the positive and negative ions of compounds they come into contact with, exchanging them for cations (e.g., hydrogen ions) or anions (e.g., hydroxyl ions). Mixed ion exchange resins (a combination of cationic and anionic resins) can take up cations and anions simultaneously. A resin's exchangeable ions are traded stoichiometrically, meaning it is an even exchange where an amount of ions removed from a material are replaced with the same amount of ions of a dif-

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[1] Stephen F. Percival, Jr., Everett D. Glover, and Lee B. Gibson, "Carbonate Rocks: Cleaning with Suspensions of Hydrogen-Ion Exchange Resin," *Science*, n.s., 142, no. 3598 (December 13, 1963): 1456-1457.

[2] Andrei A. Zagorodni, *Ion Exchange Materials Properties and Applications* (Oxford, UK: Elsevier BV, 2007), 1.

[3] P. Fiorentino, M. Marabelli, M. Matteini, and A. Moles, "The Condition of the 'Door of Paradise' by L. Ghiberti. Tests and Proposals for Cleaning," *Studies in Conservation* 27, no. 4 (November 1982): 150; Zagorodni, 18.

ferent type (ionic form) but the same charge.[4]

All exchangers fall into one of three categories: cationic, anionic, or mixed type (cationic + anionic). The exchange type is determined by the type of ion (which are classified by electrical charge) that the material exchanges.[5] They are also classified as either weak or strong, based on the strength of the acid or basic groups present in the polymer chain.[6]

The basic chain (polymeric matrix) structure of ion exchangers is what makes the exchange reaction possible. The chain contains fixed ionic groups in equilibrium with counterions of an opposite charge, each attached to the chain with covalent links (see fig. 4.1). The counterion, or contro-ion, is the exchangeable part of the structure and, according to its electrical charge, is classified as either cationic (positive) or anionic (negative). The reaction mechanism for cations and anions is as follows:[7]

Cationic Exchange Resin in Hydrogen Form $– R–A^- H^+ + \text{Cation}^+ \rightarrow – R–A^- \text{Cation}^+ + H^+$
Where $– R–A^-$ is the fixed group and H^+ is the exchangeable counterion.

Anionic Exchange Resin in Hydroxyl Form $– R–C^+ OH^- + \text{Anion}^- \rightarrow – R–C^+ \text{Anion}^- + OH^-$
Where $– R–C^+$ is the fixed group and OH^- is the exchangeable counterion.

From these equations it is apparent that counterions are always the opposite charge of the fixed groups or sites. In other words, these counterions compensate for the fixed charge.[8]

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[4] Fiorentino, 150; Zagorodni, 18.

[5] Nicola Berlucchi, Ricardo Ginanni Corradini, Roberto Bonomi, Edoardo Bemporad, and Massimo Tisato, "'La Fenice' Theatre – Foyer and Apollinee Rooms – Consolidation of Fire-Damaged Stucco and Marmorino Decorations by Means of Combined Applications of Ion exchange Resins and Barium Hydroxide," in *Proceedings of the 9th International Congress on Deterioration and Conservation of Stone, Venice, June 19-24, 2000*, vol. 2, ed. Vasco Fassina (Amsterdam, The Netherlands: Elsevier Science B.V., 2000), 24.

[6] Viviana Guidetti and Maciej Uminski, "Ion Exchange Resins for Historic Marble Desulfatation and Restoration," in *Proceedings of the 9th International Congress on Deterioration and Conservation of Stone, Venice, June 19-24, 2000*, vol. 2, ed. Vasco Fassina (Amsterdam, The Netherlands: Elsevier Science B.V., 2000): 328.

[7] Berlucchi, 24.

[8] Zagorodni, 424.

CHAPTER FOUR - LITERATURE SURVEY

Cation exchange materials are materials that possess negatively charged fixed groups or sites and exchangeable ions of the opposite charge (cations). Anion exchange materials possess positively charged fixed groups or sites and exchangeable ions of the opposite charge (anions).[9] During cation resin exchange action there is a gradual increase in free acidity, while during anion resin exchange action there is a gradual increase in alkalinity.[10] In both types the exchange groups are randomly dispersed throughout gel-like particles of exchange resin.[11]

A resin's ionic form is determined by the counterions that are present. For example, an ion exchanger in sodium form contains exchangeable Na^+ ions. In the following example a cation exchanger in Na^+ form is converted to the K^+ form:[12]

$$\mathbf{R{-}Na^+ + K^+ \rightarrow R{-}K^+ + Na^+}$$

Ion exchange resins are insoluble in water. They gain this ability through cross-linking, usually interconnections of short hydrocarbon bridges, between polymeric chains. Together these form a three-dimensional polymeric matrix (see fig. 4.1).[13] Divinylbenzene (DVB) is the most common cross-linking agent used to prepare ion exchange resins.[14] When the resins are dry, their functional groups are non-ionized but polar, making them hydrophobic. When surrounded by water, cross-linked functional polymers become ionized and swell to hold the high water content, thereby allowing water molecules and ions to migrate within the resin's swollen polymeric network.[15] Swelling occurs due to the higher concentration of internal solution in the ion exchanger, which in turn creates enough of an osmotic pressure difference between the interior of the material and the external solution to cause

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[9] Ibid., 422.

[10] Berlucchi, 24.

[11] Robert Kunin, *Ion Exchange Resins* (Malabar, Florida: R.E. Krieger Pub. Co., 1985), 48.

[12] Zagorodni, 16.

[13] Ibid., 15, 425.

[14] Ibid., 427.

[15] Ibid., 15.

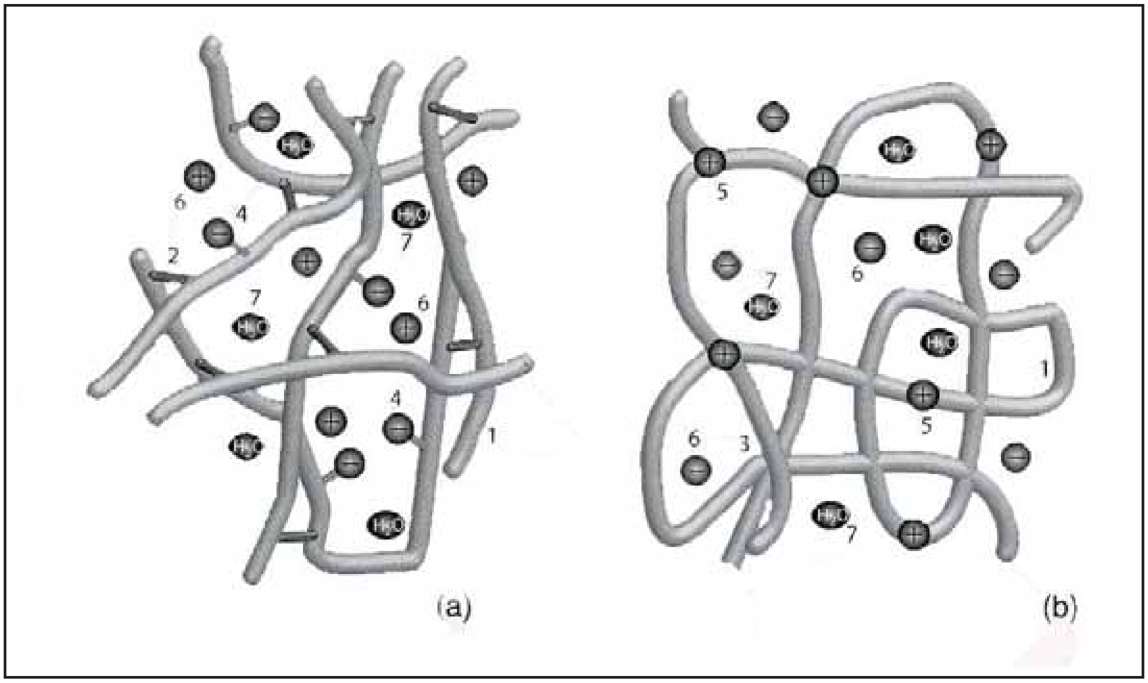

Figure 4.1: Illustration of two polymeric ion exchangers: (a) cross-linked cation exchange material; (b) anion exchange material with unrecognizable cross-links. Parts of the structure are labeled: (1) polymeric chain; (2) cross-link; (3) physical knot; (4) negatively charged cation exchange group attached to the chain; (5) positively charged anion exchange group incorporated in chains; (6) counterion; (7) water. (Source: Zagorodni, 20).

water molecules to transfer in. Water is also "pumped" into the polymer when ionized fixed functional groups, which are positioned next to each other along the same matrix chain, repel one another electrostatically and stretch the matrix.[16] For these reasons, almost all ion exchange processes take place when the material is swollen or contains a certain amount of water.[17] As resins swell, the efficiency of the ion exchange process increases. Swelling opens up the polymeric matrix, thereby allowing more of the exchanger's functional groups to be accessed and to participate in ion exchange reactions.[18]

The overall exchange process consists of five stages (see fig. 4.2): (1) diffusion of ions through the external solution to the surface of the exchange particles, (2) diffusion of these ions through the surface of the gel particle, (3) the exchange of these ions with those already

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[16] Ibid., 138.
[17] Ibid., 134.
[18] Ibid., 15.

in the exchanger, (4) diffusion of the displaced ions out through the exchanger, and (5) diffusion of these displaced ions through the external solution.[19]

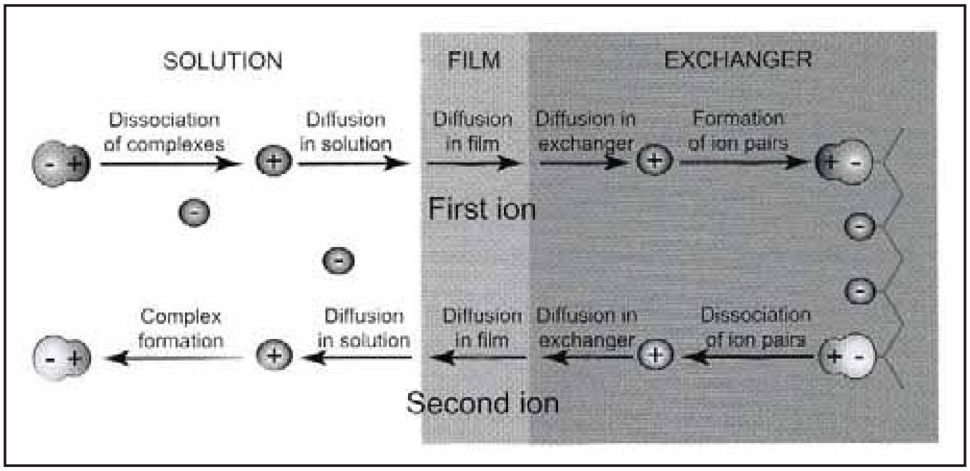

Figure 4.2: Overview of the ion exchange process (Source: Zagorodni, 223).

Today most of the ion exchangers in use are synthetic resins sold in spherical granules (100-400 mesh). These resins can be used repeatedly, as the resins are insoluble and they can be regenerated back to their original form.[20] This property may help to explain their popularity as a conservation treatment, as it allows for both long-term use and re-use of the resins.

4.3 The Scientific Study of Ion Exchange Resins

The groundwork for ion exchange research was first laid in the middle and late eighteenth-century, when Michael Faraday developed the concept of ions and Svante Arrhenius the theory of electrolytic solutions. The latter theory is of import because ion exchangers are essentially polyelectrolytes, or consisting of two ions of opposite charge.[21]

Still, it was not until the nineteenth-century, while conducting soil experiments, that

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[19] Kunin, 48.

[20] Berlucchi, 24.

[21] Zagorodni, 2.

scientists first discovered the exchange of cations. In 1848 two English agricultural chemists, H. S. Thompson and J. Thomas Way, found that when treating a soil with either ammonium sulfate or ammonium carbonate, most of the ammonium was adsorbed and lime was released. After several years of study, they determined the following: [22]

1. The exchange of calcium and ammonium ions in soils was verified.
2. Ion exchange in the soils involved an exchange of equivalent quantities.
3. Certain ions were more readily exchanged than others.
4. The extent of exchange increased with concentration, eventually reaching a "leveling off" value.
5. The temperature coefficient for the rate of exchange was lower than that of a true chemical reaction.
6. The aluminum silicates present in the soils were responsible for the exchange.
7. Heat treatment destroyed the exchange properties of the silicates.
8. Exchange materials could be synthesized from soluble silicates and alum.
9. Ion exchange differed from true physical adsorption.[23]

In 1876, E. Lemberg further advanced the field by demonstrating the stoichiometry and reversibility of ion exchange. Lemberg used sodium chloride to transform leucite into analcite, and then reversed the process with a solution of potassium chloride.[24]

Ion exchange technology, while popular with soil chemists and geochemists, was not widely used before the beginning of the twentieth-century. At this point, industrial water softening became the first widespread industrial use for the technology. R. Gans was one of the first to employ natural and synthetic aluminum silicates to soften waters and treat sugar solutions. Still, much of the work during the early twentieth-century focused on the nature of the ion exchange process in clays, soils, and other silicates. Through this work, sci-

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[22] Kunin, 2.
[23] Ibid.
[24] Ibid., 3.

entists began to understand the relationship that existed between ion exchange and crystal structure.[25]

So it was that natural cation exchangers had been known for almost a century before the first organic ion exchangers were ever created. However, increasing commercial exploitation of the siliceous ion exchangers was quickly revealing their limitations. Between the growing knowledge of crystal structure and the growing need for higher capacity exchangers, the stage was set for the discovery of synthetic resins, a breakthrough that would quickly revolutionize the field.[26]

In 1935-1936, Basil Albert Adams and Eric Leighton Holmes discovered sulfonated coal cation exchangers. From this they determined that certain synthetic (artificial) resinous materials were capable of ion exchange, that stable and high-capacity cation exchangers could be prepared as a sulfonic acid resin, and that polyamine-type resins exhibited anion exchange properties.[27] Unlike cation exchangers, which scientists had known occurred naturally, no effective anion exchangers were available before the invention of synthetic organic resins in 1935.[28] Since then, laboratories the world over have made vast amounts of synthetic ion exchange materials commercially available.[29]

Some of the first research with these materials focused on the application of anion exchanger and cation exchanger resins with simple solutions of inorganic milk constituents. The results allowed scientists to modify the mineral constituents in milk (M.I.E., or mineral-ion exchange), including decreases in calcium ions for softer curd and stabilization of evaporated milk to prevent coagulation.[30] Three methods were used to modify the milk's mineral

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[25] Ibid.
[26] Ibid., 3-4.
[27] Ibid.
[28] Zagorodni, 2.
[29] C. W. Gehrke and E. F. Almy, "The Action of Mineral-Ion Exchange Resins on Certain Milk Constituents," *Science, New Series* 110, no. 2865 (November 25, 1949): 556.
[30] Ibid., 556-557.

components, either by removal of certain ions, by substituting other ions for normal ions present, or by both operations.[31]

By the 1940s, investigations moved on to the use of ion exchange substances in the separation of cations from anions, in the separation of amino acids, purine, and pyrimidine bases, alkaloids, and so on.[32] By this point the typical laboratory set-up had become that of the ion exchange column.

G. F. D'Alelio's work between 1945 and 1952 led to the synthesis of extremely stable and versatile ion exchange resins derived from styrene and acrylics. Chemists could now create "tailor-made" synthetic ion exchange resins with the physical and chemical properties needed for specific applications. Around this time, large investments were made into ion exchange technologies due to the early development of the nuclear industry, which applied them in isotope separation.[33]

C. Whalley noted in 1956 that by that point ion exchange water-softeners had been popular for years. The first came from natural zeolites and clays, which did not possess specific groups. These would come later in the form of sulphonated coal and phenol-formaldehyde condensates, which possessed bifunctional carboxyl and hydroxyl groups. The first stable unifunctional resins were based on styrene-divinylbenzene copolymers.[34]

By 1990, ion exchange resins were regularly used for commercial processes, including water softening, chemical purification, separation of ionic from non-ionic forms and analytical applications.[35] Today most commercial ion exchange materials are sold for use as water softeners in water-treatment technologies. They are used in separations, recover-

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[31] Ibid., 558.

[32] Ibid., 557.

[33] Kunin, 4.

[34] C. Whalley, "Recent Advances in Methods of Analysis of Oils and Fats with Special Reference to Microanalytical Procedures," *Paint Technology* 20, no. 222 (March, 1956): 87.

[35] H. M. Premlal Ranjith, Mike J. Lewis, and David Maw, "Production of calcium-reduced milks using an ion exchange resin," *Journal of Dairy Research* 66 (1999): 139.

ies, deionization, and catalysis.[36] Ultrapure water production is the principal application for ion exchangers, the major consumers of which are the semiconductors manufacturing, electronics, and nuclear industries.[37] The pharmaceuticals and food industries, meanwhile, value the chemically active nature of ion exchange resins, in addition to a chemical and physical stability that prevents product contamination. In hydrometallurgy, the technology is used to create highly selective separation systems that can extract uranium or noble metals. In biochemistry and biotechnology, scientists are designing methods and technologies for obtaining desirable products and by-products from biochemical mixtures. In medicine, ion exchange materials are used to control drug release in a patient's body, and the high chemical stability ensures that the polymers do not cause harm or discomfort. In chemical analysis, scientists use the exchangers to obtain or improve analytical signals.[38] Scientists continue to explore the possibilities, creating resins for a variety of specific tasks, ranging anywhere from recovering antibiotics to sugar refining.

4.4 THE APPLICATION OF ION EXCHANGE RESINS IN CONSERVATION

Since their invention in the 1930s, synthetic ion exchange resins have become widely used in the fields of medicine, water treatment, and food processing. By the 1950s, cultural heritage professionals had also begun to experiment with these versatile materials.[39]

4.4.1 ARCHAEOLOGY AND CERAMICS

Researchers found that the resins' ability to exchange ions made them useful in cleaning operations, particularly in the cleaning of metal and stone. In 1953, for example, the British Museum's Research Laboratory employed a simple water circulator with ion ex-

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[36] Kunin, 4.
[37] Zagorodni, 2-3.
[38] Ibid.
[39] H. Barker and R. M. Organ, "A Simple Water-Circulator for Museum Use," *Studies in Conservation* 1, no. 2 (June 1953): 84.

change column. This connected to a water jet to soak out soluble salts in concentrated areas on historic objects.[40]

Stephen Koob and Won Yee Ng's 2000 research continues a long tradition of research into methods for the desalination of historic artifacts. Their study focused on the development of a faster and less laborious method than water soaking for the removal of soluble salts from ceramics. In turn, they devised a washing station that recycles wash water through a deionizing column.[41]

4.4.2 METAL

J. Patscheider and S. Vepřek undertook a metals cleaning project in 1986. They used an ion exchange column as part of an ion chromatography test to measure the removal of chlorides from iron artifacts they were conserving.[42] A few years later, Lorna Green wrote one of the few published reevaluation studies on ion exchange as a conservation treatment. Her 1989 study reexamined treatments performed by the British Museum on lead objects in the early 1960s. She described the technique as requiring the immersion of a lead artifact in an ion exchange solution, usually Amberlite IRA 400. She noted that while this treatment stabilized the lead and dissolved corrosion from metal surfaces, it may also lead to the loss of surface details otherwise preserved in corrosion layers.[43]

It was in the 1980s that conservators first began to test the possibility of using ion exchange resins for cleaning artwork. P. Fiorentino, M. Marabelli, M. Matteini and A. Moles published a 1981 study that tested a mixed-bed ion exchange resin called Rm, among oth-

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[40] Ibid.

[41] Stephen P. Koob and Won Yee Ng, "The Desalination of Ceramics using a Semi-Automated Continuous Washing Station," *Studies in Conservation* 45, no. 4 (2000): 265.

[42] J. Patscheider and S. Vepřek, "Application of Low-Pressure Hydrogen Plasma to the Conservation of Ancient Iron Artifacts," *Studies in Conservation* 31, no. 1 (February 1986): 31.

[43] Lorna Green, "A Re-evaluation of Lead Conservation Techniques at the British Museum," in *Conservation of Metals: Problems in the Treatment of Metal-Organic and Metal-Inorganic Composite Objects: International Restorer Seminar, Veszprém, Hungary, 1-10 July 1989*, ed. Márta Járo (Központi Muzeumi Igazgatóság (Hungary): István ÉRI, 1990), 121, 123, 125.

er solvent-reagent systems, to remove a buildup of atmospheric dust particles and surface corrosion products from the gilded surfaces of Lorenzo Ghiberti's bronze 'Door of Paradise.' From 1979 through 1981, laboratory and in situ tests in Florence, Italy demonstrated the efficacy and safety of the resin mixture in conservation work.[44]

4.4.3 STONE

Desulfatation

In 1995, a team of Italian conservators evaluated the use of ion exchange resins for cleaning and desulfating architectural surfaces. On-site tests were performed on different oxalate films mixed with gypsum and black gypsum crusts. Testing utilized thin section microscopy, color measurements by a CIELab system, and chemical identification of extracted ions by liquid chromatography to monitor and evaluate the results.[45]

In 2000, Viviana Guidetti and Maciej Uminski took the desulfatation process one step further. They developed a mixture, containing both strong anionic and weak cationic resins, for removing calcium sulfate from calcareous encrustations on marble objects. The conservators tested formulas containing various additive mixtures designed to improve the ease of use and water uptake. Tests were conducted on sulfated marble plates at one hour intervals. The final formula included cellulose fibers for water retention and thickening, attapulgite clay for water retention, a pH indicator to monitor the chemical reaction, and acrylic latex to prevent moisture escape.[46] The resin formulates and the marble were evaluated by ionic chromatography to determine initial and residual amounts of SO_4^{2-}.[47] The researchers found that all of the mixed-exchanger formulates tested were efficient in removing calcium sulfate

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[44] Fiorentino, 145.

[45] R. Quaresima, A. Pasanisi, and C. Scarsella, "Patine ad ossalati e croste nere: indicazioni su possibili interventi conservative," in *La pulitura delle superfici dell'architettura; atti del convegno di studi, Bressanone, 3-6 luglio 1995*, vol. 11 of *Scienza e beni culturali*, ed. Guido Biscontin and Guido Driussi (Padova, Italy: Libreria Progetto, 1995), 179.

[46] Guidetti, 327.

[47] Ibid., 329.

(removing between 95 and 100 percent of sulfate ions), but chose one formulate for application on historic marble samples covered by "black crusts."[48]

Today, the Italian restoration company Syremont states that it sells three types of ionic exchange resins specifically for restoration cleaning: a strong cationic resin SK50, a weaker cationic resin with oxy-hydrogen functions SK 10, and an anionic resin Akeogel. Conservators utilize SK50 for the removal of dullness and calcium encrustations, SK10 for more delicate calcium removals, and Akeogel for the desulfating cleaning of stone surfaces, particularly carbonic ones.[49]

One of the most common targets for desulfatation is calcium-containing salts, like calcium sulfate. Conservators concern themselves with these materials for several reasons. Salts like calcium sulfate are partially soluble in water, causing them to cycle through periods of solubility and re-crystallization within masonry exposed to external moisture sources. In stones with low porosity, the salts may accumulate on the surface and mix with atmospheric particles to form dark grey excretions. In stones with a higher porosity, the salts migrate through the surface. When they crystallize, the force of the expansion causes mechanical compression, and can eventually lead to break-up of the stone surface.[50] Environmental pollution is a major contributing factor to this sulfatation process, particularly in urban areas. Sulfur dioxide in the air reacts with moisture, oxygen, and calcium carbonate (limestone and marble) to create calcium sulfate dihydrate (gypsum). Due to the higher specific volume and solubility of calcium sulfate in comparison to calcium carbonate, calcium sulfate has the ability to incur a lot of damage in a relatively short period of time.[51]

Traditionally, salt removal involves free migration of soluble salts into compresses

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[48] Ibid., 330.

[49] "Key experiences - Restoration products," Syremont, http://www.syremont.it/index.php/component/ content/article/63-key-experiences-restoration-products/161-key-experiences-restoration-products.html (accessed January 7, 2009).

[50] Berlucchi, 25.

[51] Guidetti, 327.

made of cellulose dust, cellucotton, or cotton wool, soaked in de-ionized water or ammonium carbonate compresses. Ammonium carbonate compresses produce calcium carbonate and soluble ammonium sulfate. This can lead to an overly white patina, with morphological and cohesion properties different from that of the original material, and salt migration into the stone.[52] Large-scale operations may consider nebulized water, sanding, or high pressure water cleaning, although the latter two are comparatively aggressive.[53] Regardless of which method conservators consider, in places that possess a high level of soluble salts or elements composed of gypsum, treatments containing large amounts of water are inappropriate.[54]

Thus since the end of the twentieth-century, conservators have employed ion exchangers to remove sulfates and oxalates from stone surfaces, including efflorescence and

Figure 4.3: Limestone sample with black encrustation compared to sample cleaned with ion exchange resin (Source: Martínez-Arkarazo, 515).

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[52] Guidetti, 327.

[53] Berlucchi, 23; Guidetti, 327; Wieslaw Domaslowski and Alina Tomaszewska-Szewczyk, "Desalting of Stones by Means of Ion Exchangers," in *8th International Congress on Deterioration and Conservation of Stone, Berlin, 30 Sept. - 4 Oct. 1996: Proceedings*, vol. 3, edited by Josef Riederer (Berlin, Germany: S.N., 1996).

[54] Berlucchi, 23.

black crusts (see fig. 4.3).[55] The resins work without any mechanical action, thereby avoiding water saturation and morphological changes to the surfaces.[56] When the resins are applied to an object contaminated with salts, they react with the surface layer (to a depth of approximately 70-100 µm). The resins do not penetrate deeply enough into the object to adversely affect its porosity, or to further contaminate the object by introducing new materials. Ideally, the exchange reaction substitutes ions that are harmful to the stone with innocuous ones, and only at the contact interface between the exchanger and the surface to be cleaned.[57] The chemical reaction for treating calcium sulfate is as follows:[58]

$$\mathbf{2R^{+}{-}{-}OH^{-} + Ca\ SO_4 \rightarrow R^{+}_2 {-}{-}SO_4^{2-} + Ca\ (\ OH\ )_2}$$

Nonetheless, the reaction does not end there. After the sulfate ion in the stone is substituted by the hydroxyl ion in the ion exchange resin, calcium hydroxide is formed. This new ion is then either washed away or acted upon by carbon dioxide in the atmosphere, forming calcium carbonate:[59]

$$\mathbf{Ca\ (\ OH\ )_2 + CO_2 \rightarrow CaCO_3 + H_2\ O}$$

Therefore, in addition to removing salts from the stone surfaces, this process has the additional benefit of acting as a consolidant. Calcium carbonate forms a stable crystalline aggregate, which conservators may prefer to use in place of synthetic consolidants.[60]

There are several limitations to note when considering the use of ion exchange resins for desulfation. In particular, conservators must monitor cationic resins when carbonate

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[55] I. Martínez-Arkarazo, A. Sarmiento, A. Usobiaga, M. Angulo, N. Etxebarria, and J.M. Madariaga, "Thermodynamic and Raman Spectroscopic Speciation to Define the Operating Conditions of an Innovative Cleaning Treatment for Carbonated Stones Based on the Use of Ion Exchangers—A Case Study," *Talanta* 75, no. 2 (2008), 511.

[56] Guidetti, 328.

[57] Berlucchi, 24.

[58] Ibid., 25; Guidetti, 328.

[59] Berlucchi, 25; Guidetti, 328.

[60] Berlucchi, 25.

rocks are being cleaned, as they may be damaging to the surface. Wherever the resins come into contact with $CaCO_3$, the compound decomposes and calcium ions migrate into the surface of the resin compress.[61]

Encrustation Removal

Many of the encrustations that form on stone surfaces, be they from pollution, salts, or other deterioration mechanisms, are calcareous in form. As such, conservators have found that the same properties that make ion exchange resins useful in removing salts, make the resins effective in removing other calcium-rich layers. At present, studies focus on dealing with limestone, marble, and gypsum features that require calcium-extraction without causing excessive damage to the calcareous substrates.[62] They find that this can work when an encrustation, like carbonated lime, has microcrystals with a higher specific surface and higher porosity than the substratum, such as marble.[63] See Section 4.5 for examples of calcareous encrustation removal.

Biological Growth

M. E. Young and D. C. M. Urquhart are part of the Masonry Conservation Research Group at Robert Gordon University. In the late 1990s, they studied a variety of chemical means for removing biological growths (including algae, lichens, bacteria, fungi, and mosses) from sandstone buildings. After identifying the factors that lead to biological growth on sandstone, the authors examined current methods of removing the growth and the effect that these methods have on re-growth. In their experiments, they used ion exchange resins

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[61] Wieslaw Domaslowski and Zyzik Malgorzata, "Badania nad zastosowaniem jonitow do odsalania kamiennych obiektow zabytkowych," in *Acta Universitatis Nicolai Copernici* 52, no. V (1973): 226.

[62] A. Giovagnoli, C. Meucci, and Marisa Tabasso Laurenzi, "Ion Exchange Resins Employed in the Cleaning of Stones and Plasters: Research of Optimal Employment Conditions and Control of their Effects," in *Deterioramento e Conservazione della Pietra: Atti del 3 Congresso Intemazionale, Venice, October 24-27 1979* (Padova, Italy: Instituto di Chimica Industriale, Università degli Studi di Padova, 1982).

[63] Giovagnoli, 508.

to extract water soluble phosphate (and other soluble ions) from the stones. Nonetheless, ion exchange treatments are described as a cleaning mechanism that may cause alteration and dissolution of rock-forming minerals.[64]

Consolidation and Stabilization

A study from the United States, conducted in 1997, employed ion exchange resins to stabilize Egyptian limestone from Naga el-Deir, in the Abydos/Thebes region. The conservators noted that delamination is a common problem with this stone, and that it is presumably caused by the presence of clays along the bedding planes. A series of tests examined the role clay minerals play in the stone's decay. Within this, ion exchange resins are mentioned as one of several "unconventional" methods available for stabilizing the clay structure. By replacing sodium ions with calcium and/or magnesium ions, cation exchange reduces the swelling capacity of the clay.[65]

4.4.4 MURALS

Around 1986, Italian conservators adapted ion exchange resins for mural painting conservation. In the Brancacci Chapel in Florence, a later application of whole egg varnish from buon fresco was removed by swelling it with an ion exchange resin poultice specially designed by the company Montedison.[66] Researchers were interested in finding a cleaning method that would not alter or attack the pigments or paint layers, while chemically removing organic materials applied in previous restorations.[67]

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[64] M. E. Young and D. C. M. Urquhart, "Algal growth on building sandstones: effects of chemical stone cleaning methods," *Quarterly Journal of Engineering Geology and Hydrogeology* 31 (1998): 315, 319.

[65] Carlos Rodriguez-Navarro, Eric Hansen, Eduardo Sebastian, and William S. Ginell, "The Role of Clays in the Decay of Ancient Egyptian Limestone Sculptures," *Journal of the American Institute for Conservation* 36, no. 2 (Summer, 1997): 151, 159.

[66] Marion Alof, "Brancacci chapel," *Conservation News* 33 (1987): 11.

[67] Ornella Casazza and Sabino Giovannoni, "Preliminary Research for the Conservation of the Brancacci Chapel, Florence," in *The Conservation of Wall Paintings: Proceedings of a symposium organized by the Courtauld Institute of Art and the Getty Conservation Institute, London, July 13-16, 1987*, ed. Sharon Cather (London: The J. Paul Getty Trust, 1991), 17.

Probably the best-known and most-documented exploitations of ion exchange technology in conservation occurred in the aftermath of the "Munich Dürer Attack." Credited as being the first large-scale application of the mural cleaning method, researchers note that before this point ion exchange resins were rarely used in the field of conservation, except for a number of stone, metal, and paper projects.[68] In April 1988 five panel paintings by A. Dürer located in the Alte Pinakothek, Munich were severely damaged by sulfuric acid (see fig. 4.4). The acid affected the wooden panel, the calcium carbonate ground, and the pigments. An ion exchange resin was chosen to soften crusts caused by the acid, ad-

Figure 4.4: 'Lamentation of Christ' after attack and during treatment with ion exchange resin (Source: Heimberg, color plate).

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[68] Bruno Heimberg, "Die Restaurierung de Münchner Dürer-Gemälde nach dem Säure-Attentat von 1988," in *Die Kunst der Restaurierung: Entwicklungen und Tendenzen der Restaurierungsästhetik in Europa: Internationale Fachtagung des Deutschen Nationalkomitees von ICOMOS und des Bayerischen Nationalmuseums, München, 14.-17. Mai 2003*, ed. Ursula Schädler-Saub (München: ICOMOS, Nationalkomittee der Bundesrepublik Deutschland, 2005), 278; A. Burmester, J. Koller, and H. Kawinski, "The Munich Dürer Attack: the Removal of Sulphuric Acid and Acid Compounds by Use of a Conditioned Ion exchange Resin," in *Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture: Preprints of the Contributions to the Brussels Congress, 3-7 September 1990*, ed. John S. Mills and Perry Smith (London: The International Institute for Conservation of Historic and Artistic Works, 1990), 181.

sorbing the acid products and neutralizing what acid remained on the painting. The conservators chose the resin Lewasorb A50 in hydroxyl form. The strongly alkaline exchange material was washed with water before use to remove any alkaline impurities. 100 g of resin were stirred in 400 mL of water for 30 minutes, allowed to settle, decanted, and then repeated three times. This caused the pH of the washing water to decrease approximately from 11 to 6. The wet resin was then ground into a fine powder in an agate mortar. Afterwards the resin was charged with carbonate ions by pouring it into a solution of 50 g sodium carbonate (Na_2CO_3) in 200 mL of distilled water. Three times the resin was stirred, decanted, and liquid allowed to adsorb. The carbonate-charged resin was then rinsed again (approximately seven times) until the pH of the wash was between 6 and 7.[69] This technique is not entirely new, the work builds off of a similar but less successful study from 1978, when the Kassel Rembrandt paintings were attacked.[70]

The Munich conservators chose to use resins over more conventional treatments, such as dry mechanical removal, dry chemical adsorption in combina-

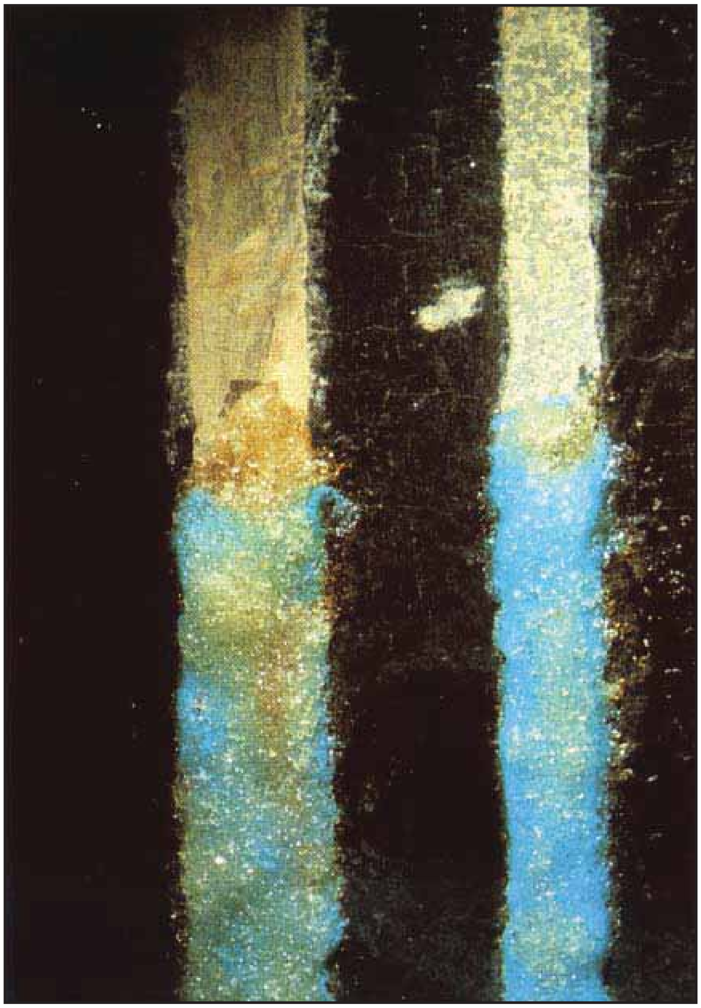

Figure 4.5: Detail of painting containing azurite. Upper part undergoing ion exchange resin treatment, lower part after removal of dried resin (Source: Heimberg, color plate).

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[69] Burmester, 177-178.
[70] Ibid., 181.

tion with wet or dry neutralization, cleaning with solvents or pouring water, encapsulation by inert media, and wet chemical neutralization. Dry mechanical removal of acid crusts was recommended, but the authors suggested that this be followed with dry adsorption, as any remaining layers were still acid. There are several disadvantages associated with these treatments, including the possibility of leaving behind difficult to remove non-transparent masses, uncontrolled 'one-way' displacement of wetting agents into undamaged areas, the transformation of dry crusts into dissolved soluble compounds, the introduction of new chemicals, and uncontrollable reactions.[71] Conversely, the ion exchange resin leaves no harmful products and neutralizes the pH. Sulfate ions in the acid are exchanged with carbonate ions in the resin to form carbonic acid (H_2CO_3), which decomposes instantly into CO_2 and water. Neutralization protects both the wall paintings and the conservators applying the treatment. Grinding the resin and conditioning it with carbonate ions optimized the exchange process. The resin paste's high surface tension made it easy to apply and easy to restrict to intended portions of the murals. After drying, the resin can be safely removed with a vacuum (see fig. 4.5). Alternately, the limitations may include alterations to the appearance of treated areas and paste water mixing with existing materials to cause a blanching effect.[72]

In 1994, a team of conservators from the Central Institute for Restoration included anionic ion exchange resin tests in the cleaning phase of their project on the wall paintings of the Scrovegni Chapel in Padua. The goal was to capture and remove destructive sulfates on the inner wall of the façade and on two detached wall paintings with Syremont's Akeogel. In order to quantify the amount of residual soluble salts, conservators used a cellulose pulp pad which could be examined before and after the tests with SEM to verify the effective removal of the sulfates. The resin was mixed with distilled water and applied as a pack. Conservators placed a protective sheet of Japanese paper between the paper pulp pad and the surface of the painting, allowing a dwell time of approximately twenty minutes. SEM-EDS

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[71] Ibid., 180.
[72] Ibid., 181.

analysis found that before the treatment, sulfur was found in two test samples to a depth of ± 100 microns and ± 25 microns. After the applications, the analysis found a complete removal of sulfur.[73]

A 1996 project in Romania, funded by the Japanese Trust Fund for the Preservation of the World Cultural Heritage and implemented by UNESCO, employed ion exchange resins to remove overpainting from the original sixteenth-century interior murals at Probota Monastery. The original paintings were done *a fresco*, where the artist painted directly on the wet lime-based rendering plaster. However, during a restoration effort between 1844 and 1848, the monastery's interior was overpainted in a *secco* technique, which utilized an egg white protein binder. Conservators applied resins through Japanese paper (see fig. 4.6) wherever delicacy was required; otherwise they utilized ammonium carbonate compresses. Any lime drops and mortars were removed mechanically with a combination of

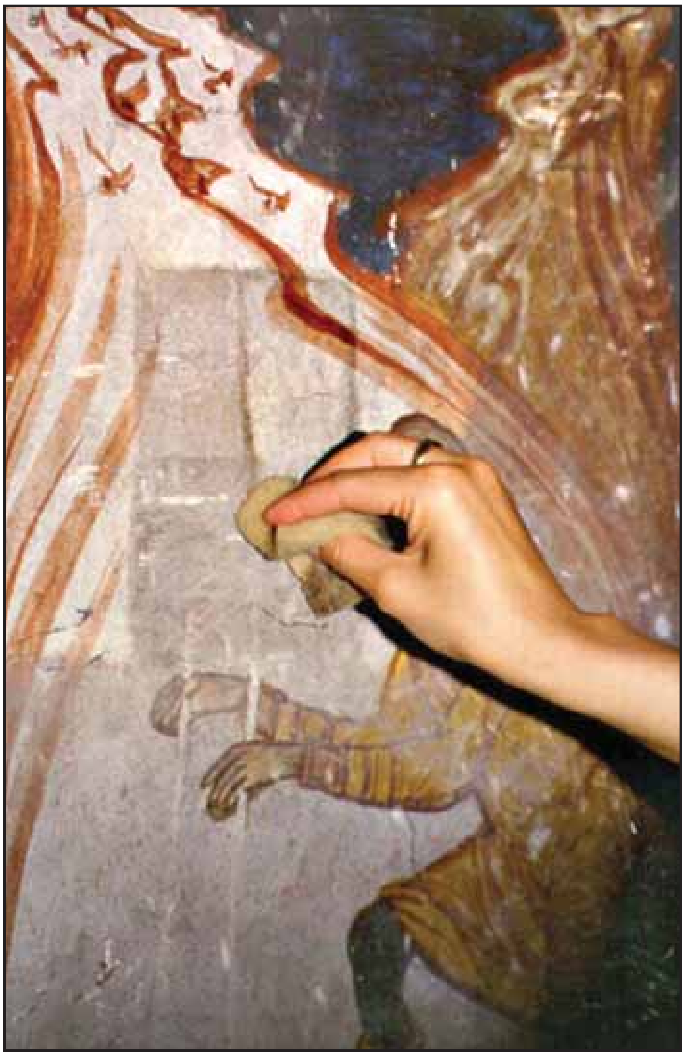

Figure 4.6: Cleaning mural with ion exchange resin through Japanese paper (Source: Metaneira).

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[73] E. Borrelli, M. Marabelli, and P. Santopadre, "The Scrovegni Chapel: Studies on State of Conservation and Cleaning Procedures," http://www.giottoagliscrovegni.it/eng/resta/santo_p/sant_doc.htm (accessed January 24, 2009).

scalpels, wooden blades, and fiberglass brushes.[74]

An unpublished dissertation in 2005 tested methods for the desalination of wall paintings in Valletta, Malta. Of the methods tested, anion exchange resin Akeogel (manufactured by Syremont) proved the most effective and safe desalination method. The resin was applied by a brush and as a poultice. Results of the test were evaluated visually and with scanning electron microscopy.[75] A similar study one year later, this time with the Università degli Studi di Siena in Italy, also chose to use Akeogel for the removal of sulfur compounds found in and under the paint film. The Akeogel was applied to the painted surface through Japanese paper for twenty minutes. The resin treatment was then followed by the application of pulp cellulose packs to allow for quantification of sulfur removal with an electron microscope SEM/ISIS.[76]

A different 2005 study, this time in Ljubljana, Slovenia, once again employed ion exchange resins for the chemical cleaning of wall paintings. In this instance, researchers designed a chemical cleaning method to transform calcium sulfate dihydrate (gypsum) back into calcium carbonate and to remove the casein layer on the painting's surface. The study found that $(NH_4)_2CO_3$ (ammonium carbonate) and NH_4HCO_3 (ammonium bicarbonate) were the best reagents, and that cellulose pulp and a mixture of cellulose pulp and silicate absorber made the best poultices with good adhesion to the wall surface. Each of the reagents was added to an absorber before being applied to the surface over Japan paper. Dwell times depended on the depth of the transformed calcium sulfate, lasting either fifteen minutes,

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[74] Metaneira Books, "The Mural Paintings," http://www.metaneira.com/probota_webpage/mural.html (accessed January 25, 2009).

[75] Joanna Hilli Micallef, "A Study on the Desalination of Paintings on Globigerina Limestone: the Wall Paintings at the Former Jesuit's College, Valletta" (B.Cons. diss., University of Malta, Heritage Malta, Institute of Conservation and Management of Cultural Heritage, 2005).

[76] Claudio Milanesi, Mauro Cresti, Franco Baldi, Rita Vignani, Fabrizio Ciampolini, and Claudia Faleri, "La Cappella del Sacro Chiodo, studio dello stato di conservazione ed ipotesi di intervento conservative," Università degli Studi di Siena , Dipartimento Scienze Ambientali 'G. Sarfatti', 15 January 2006, http://www.unisi.it/ricerca/dip/dba/labcm/S.M.S/web/index.html (accessed January 25, 2009).

thirty minutes, one or two hours. After the removal of the poultice, the wall surface was washed with a moist sponge. A similar test was conducted to measure the transformation of sulfate to carbonate using an anionic Akeogel resin (OH form).[77] The treatment consisted of one part resin mixed with one part deionized water (w/w). Researchers applied this surface treatment for either fifteen or thirty minutes.

Samples collected before and after the cleaning test allowed for analysis of the wall paintings. All told, twenty-five different areas were tested and their samples analyzed using SEM/EDS mapping analyses. This involved optical microscopy recorded by JVC 3-CCD video camera and scanning electron microscopy (SEM). In this case, low-vacuum SEM was used because it does not require samples to be coated with a conductive gold or graphite film. Energy dispersive X-ray spectroscopy (EDS) using INCA software allowed for qualitative, quantitative, and mapping analyses of the samples. The results of the analyses showed that the ion exchange resins required more than a half hour of surface contact to be fully effective, meanwhile the effect of cleaning was worse than applications of ammonium carbonate and bicarbonate for the same period of time.[78]

4.5 ION EXCHANGE RESINS FOR REMOVING CALCIUM

A variety of methods exist for employing ion exchange resins in the removal of calcium ions. One of the first well-documented cases, a 1949 study by C. W. Gehrke and E. F. Almy, focused on the action of mineral-ion exchange resins on milk constituents. This study found that in cation exchangers, the type of opposite ion present in test solutions was a factor. When the anion present was citrate, calcium ions were removed more completely then

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[77] All of the commercial products tested in this study came from C.T.S. C.T.S. is a European producer and distributor of art restoration and conservation products, tools and equipment for art restoration and conservation. "Back Matter," *Studies in Conservation* 43, no. 2 (1998).

[78] Polonca Ropret and Peter Bukovec, "Chemical Cleaning of Quaglios' Mural Painting in the Cathedral of Saint Nicholas in Ljubljana," ZVKDS Restavratorski Center, http://www.rescen.si/upload/Clanki_2005/ 1132645098.pdf (accessed January 25, 2009).

when the anion present was chloride.[79] They also noted that researchers need to take care not to overuse the cation exchanger, as the cations present in various complex solutions are absorbed at different rates. Those absorbed in the first part of the exchange run (through an ion exchange column) were released later by the regeneration effect of the other cations in the solution which were preferentially adsorbed. In other words, the hydrogen ions from the exchanger do not exchange every time a cation enters the exchanger, as the entering cation sometimes replaces a previously adsorbed cation. The cation exchanger used in these experiments was Zeo-Karb-H, manufactured by Permutit Company in New York City.[80]

A. Van Kreveld and G. van Minnen reported in 1955 a method for the determination of Ca^{2+} and Mg^{2+} activity in milk using an ion exchange resin. Included in the study was the use of resins to exchange Ca and Mg from micelles[81] by using Na^+ or K^+.[82]

H. Bergseth and Sh. L Abdel-Aal's 1974 study focused on the use of a mixed bed resin containing a cation and an anion exchanger to determine the cation exchange capacity (C. E. C.) of calcareous and gypseous soils.[83]

In 1976, M. Anderson, G. C. Cheeseman, and R. Wiles used cationic resins of the Zerolit 236 type to produce Ca-reduced single cream.[84]

One of the first documented cases of masonry cleaning by ion exchange resins comes from Italy in 1979. This study follows up previous work on the use of ion exchange resins for removing calcareous encrustations on marble surfaces, particularly in fountains,

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[79] Gehrke, 557.

[80] Ibid.

[81] Micelles are aggregates of amphipathic molecules in water, meaning containing both polar and nonpolar domains, where the nonpolar portions are in the interior and the polar portions at the exterior surface, exposed to water. Mark Lefers, "Life Science Glossary," http://www.biochem.northwestern.edu/ holmgren/Glossary/Definitions/Def-M/ micelle.html (accessed January 8, 2008).

[82] Ranjith, 139.

[83] H. Bergseth and Sh. L Abdel-Aal, "Ion Exchange Removal of Calcium Carbonate and Gypsum from Mineral Material Prior to Determination of Cation Exchange Capacity using 89Sr++," *Colloid & Polymer Science* 253 (1975): 322.

[84] Ranjith, 139.

exposed to the flow of hard waters. The discussion focuses on a series of laboratory experiments undertaken to measure the exchange action of four different resins over time, their ability to remove lime layers, and to check their effects on a calcareous substrate (in this case Carrara marble, selenitic gypsum, and calcite crystals).[85] Resin mixtures were applied in 3mm thick layers to marble plates coated with a lime layer less than 1mm thick. Tests ran for 24 hours, with applications at pre-determined intervals.[86] The study found that the treatments dissolved calcium carbonate incrustations, gave conservators good control, and worked without leaving by-products behind on the substrate.[87] Alternately, the resins did cause etching on the interface between the calcite crystals. In some cases this causes an increase in intercrystalline porosity.[88] This study best supports the aims of this thesis by proving that ion exchange resins can be used in a reasonably safe manner to remove lime layers from a calcareous substrate.

The 1981 study of P. Fiorentino, M. Marabelli, M. Matteini and A. Moles used ion exchange resins to remove, among other things, calcium sulfate, calcium nitrate, gypsum ($CaSO_4.2H_2O$), and calcite from Lorenzo Ghiberti's bronze 'Door of Paradise.'[89] The mixed-bed ion exchange resin used was Rm, a mixture with a moist weight ratio of 1:1.6 of cationic Biorad Dowex 50W-X4 (in H^+ form, 100-200 mesh) to anionic Biorad Dowex AG1-X8 (in OH^- form, 100-200 mesh). The pH of the washed mixture was 5.5.[90] The resin was chosen because it was not as damaging to the bronze surface as mechanical cleaning, it did not detach the gold gilding, and it allowed for optimal cleaning in a short time and under controlled conditions.[91] Before conducting cleaning tests, laboratory testing evaluated the effect of the cleaning agents on the bronze substrate. Samples were taken from the panels, embedded

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[85] Giovagnoli, 499.
[86] Ibid., 500.
[87] Ibid., 499.
[88] Ibid., 505-506.
[89] Fiorentino, 148.
[90] Ibid., 150.
[91] Ibid., 152.

in resin, polished, and then subjected to the actions of the reagents for dwell times of one to forty minutes. After each time, the sections were examined under the metallographic microscope at 500x magnification. Once researchers determined that the resins did not in any way damage the bronze, they proceeded to cleaning tests on one of the gilded door panels.[92] Cleaning took place in three stages. First, preparation of the test area required degreasing with xylene-acetone. Next, researchers applied a reagent pack in a vertical position to a 7 x 7 cm area. Application of the resin packs, consisting of 7 g dry resin in 17 ml of water, occurred twice for ten minutes each. After each application's removal, they then washed the area with distilled water.[93] The resin required three washes, each of 150 ml of water.[94] Researchers tested the wash-water to determine the amount of cupric ion dissolved, the pH, and the conductivity.[95]

The 1997 study of H. M. Premlal Ranjith, Mike J. Lewis, and David Maw investigated the use of ion exchange to reduce Ca in milk, with a focus on understanding the exchange of salts in Ca-reduced milk and the changes to its physical properties.[96] In these experiments researchers used Duolite C433, a weakly acidic cation exchange polymer with a matrix of crosslinked polyacrylic acid, held in a mesh basket in a stainless steel tank connected to a centrifugal pump. This is a batch system rather than an ion exchange column. The resin's functional group is COO^-, the total ion exchange capacity is 4.2 equiv./l and the particle size is 0.3-1.1 mm in diameter.[97] To facilitate ion exchange, researchers treated the resin with NaOH or KOH. Treatment is complete when it converts to the Na^+ or K^+ form and the pH of liquid passing through the resin changes from neutral to alkaline.[98] The results of the ion exchange process were evaluated by withdrawing several 10 ml liquid samples throughout

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[92] Ibid., 150.
[93] Ibid.
[94] Ibid., 151.
[95] Ibid., 150.
[96] Ranjith, 139.
[97] Ibid.
[98] Ibid., 140.

the ion exchange process and analyzing for total percent calcium reduction using EDTA titration with Solochrome black dye as indicator. They were also analyzed for protein, lactose and salts. Researchers waited about two hours after the ion exchange treatment, to allow the ions to equilibrate, before measurements were taken to analyze the compositional changes.[99] A laboratory Camlab pH meter measured pH. The atomic absorption spectrophotometry method measured the Na, K, Ca and Mg within a known quantity of milk or permeates obtained after ultrafiltration. A chloride analyzer measured Cl^-. Changes in color were determined using a Minolta CR310 Chromameter, which measures the reflection spectrum and prints out the CIELab values.[100] It should be noted that this study found that the loss in Ca was accompanied by a loss in luminosity and a change in color.[101]

As noted before, in 2000 conservators began testing the abilities of ion exchange resins to remove calcium sulfate from calcareous encrustations on marble objects. Viviana Guidetti and Maciej Uminski tested formulas containing various mixtures of strong anionic and weak cationic exchange resins, along with additives designed to improve the ease of use and water uptake. The final formula included a pH indicator and acrylic latex.[102]

A more recent study, by Theodōros Skoulikidēs in 2002, describes ion exchange resins as a damaging cleaning method. Concerned with the conservation of Pentelic marble, the author reported the resins' damage and/or removal of gypsum films, damage to the marble surface, and removal of Ca^{2+} as the reasons for its poor rating.[103]

An article in the 2008 edition of the *Chemical Engineering Journal* describes in detail the use of Amberlite IR–120, a strong acidic cation in hydrogen form, as an effective low cost ion exchange resin for the removal of calcium impurities in wastewater treatment. The

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[99] Ibid.
[100] Ibid.
[101] Ibid., 143.
[102] Guidetti, 327.
[103] Theodōros Skoulikidēs, *Methodoi synteöreöseös tou Pentelikou marmarou* (Athens: Hypourgeio Politismou, Epitropē Syntērēseōs Mnēmeiōn Akropoleōs, 2002).

experiments required synthetic Amberlite IR-120 from Fluka Co., and $CaCO_3$ and H_3BO_3 from Merck. The experimental setup utilized a batch stirred system, consisting of a glass reactor, a magnetic stirrer, a thermostat, and a WTW inolab pH/ion level 2 model pH meter to measure solution pH and temperature. An atomic absorption spectrometer provided quantitative analysis of the calcium concentration. Thus, the experiments here took into account solution pH, resin-to-solution ratio, temperature, and resin contact time. The conclusion of this study was the determination that optimum operation occurred when the mixture possessed a pH 1.5, a resin-to-solution ratio of 6.174g/250mL, temperature 303° (K), and a contact time of twenty minutes. In those cases maximum calcium removal was 99 percent.[104]

4.6 SELECTION CRITERIA

From the conservation literature, some conclusions can be drawn as to what properties are commonly sought in an ion exchange resin mixture: [105]

1. Maximum ion exchange/removal efficiency.
2. Neutrality towards the substrate, making it safe to use on historic objects.
3. Good rheological properties (solid- and liquid-like behavior).
4. Good adherence to substrates when wet, and easy to remove when dry (low adherence when dry ensures that the substrate is left free of formulate traces.)
5. A lack of fissurations in the dried mixture hinders water evaporation and improves removability.
6. Maximum capacity to uptake and retain water without decreasing the rheological characteristics (such as resistance to flow during vertical applications).
7. Ease of application.
8. Low cost, particularly for large-scale applications (a higher ratio of inert additives

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[104] C. Özmetin, Ö. Aydın, M.M. Kocakerim, M. Korkmaz, and E. Özmetin, "An Empirical Kinetic Model for Calcium Removal from Calcium Impurity-Containing Saturated Boric Acid Solution by Ion Exchange Technology using Amberlite IR–120 Resin," *Chemical Engineering Journal* (2008), doi:10.1016/j.cej.2008.09.021: 1, 4, 11.

[105] Guidetti, 327-331; Giovagnoli, 499.

to ion exchange resins can be beneficial).

9. A cleaning action easily controlled by the operator.

For example, one such system was developed in 1989 to evaluate a desulfating treatment applied to the marble surfaces of the fifteenth – eighteenth-century funerary monument of Giovanni and Pietro de' Medici by Andrea del Verrocchio. Here the desirable properties were determined to be: (1) a creamy mixture whose rheology allows it to adhere to surfaces oriented in any direction, (2) easy application with a broad knife or brush, (3) a fluid form that can reach into narrow recesses of sculpted objects, (4) a high degree of chemical inertia towards the historic materials, (5) high exchange capacity and retention of ions from the pollutants, and (6) easy removal of dried resin.[106]

When applying resin treatments, conservators must work to prevent water evaporation. The exchange action ends once the resin dries out, even when the exchange power is not exhausted.[107] Various additives can be included in the formulations to retard water evaporation: cellulosic thickeners increase water uptake and retention, inorganic attapulgite clay increases water content without decreasing rheological properties, and an exterior layer of acrylic latex hinders water escape (this also makes it easier to remove large slabs of dry mixtures without loss of resin powder).[108] Efficacy can also be improved by saturating the resin and treatment areas with water.

When treating an element, conservators should be prepared to apply more than one resin compress. Once the ions have exchanged, they do not migrate from the resin's contact surface towards the inner layers. This decreases the amount of time it takes to saturate the

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106 P. Ruschi, V. Massa, and G. Pizzigoni, "Funerary monument of Giovanni and Pietro de' Medici by Andrea del Verrocchio: cleaning of stone surfaces," in *Science, technology, and European cultural heritage: proceedings of the European symposium, Bologna, Italy, 13-16 June 1989*, ed. N.S. Baer, C. Sabbioni, and André I. Sors (Oxford: Butterworth-Heinemann Publishers, 1991): 754-755.

107 Guidetti, 328.

108 Ibid., 330-331.

packing and render it ineffective.[109]

In addition to the mixture properties, there are certain properties conservators should be aware of when choosing a resin type appropriate for their purposes:[110]

> 1. At low concentrations (aqueous solutions) and ordinary temperatures, the extent of exchange increases with increasing valency of the exchanging ion ($Na^+ < Ca^{+2} < Al^{+3} < Th^{+4}$).
>
> 2. At low concentrations (aqueous solutions), ordinary temperatures, and constant valence, the extent of exchange increases with increasing atomic number of the exchanging ion ($Li < Na < K < Rb < Cs$; $Mg < Ca < Sr < Ba$).
>
> 3. At high concentrations, the differences in the exchange "potentials" of ions of different valence (Na^+ versus Ca^{+2}) diminish and, in some cases, the ion of lower valence has the higher exchange "potential."
>
> 4. At high temperatures, in non-aqueous media, or at high concentrations, the exchange "potentials" of the ions of similar valence do not increase with increasing atomic number but are very similar, or even decrease.
>
> 5. The relative exchange "potentials" of various ions may be approximated from their activity coefficients—the higher the activity coefficient, the greater the exchange "potential."
>
> 6. The exchange "potential" of hydrogen (hydronium ion, H_3O^+) and hydroxyl ions varies considerably with the nature of the functional group and depends on the strength of the acid or base formed between the functional group and either the hydroxyl or hydrogen ion. The stronger the acid or base, the lower the exchange potential.
>
> 7. Organic ions of high molecular weight and complex metallic anionic complexes exhibit unusually high exchange potentials.
>
> 8. As the degree of cross-linking between the polymer chains (reticulation) or the fixed ion concentration of an ion exchange material is lowered, the exchange equilibrium constant (an equivalence of rates for forward and backward processes[111]) approaches unity.[112]
>
> 9. The lower of the degree reticulation (cross-linking), the higher the porosity of the

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[109] Giovagnoli, 508.
[110] Kunin, 32.
[111] Zagorodni, 427.
[112] Kunin, 32.

polymer.[113]

10. Sieve action is a phenomenon whereby large counterions cannot enter narrow pores of dense, highly cross-linked materials during the exchanger phase, while smaller counterions are free to reach functionionl groups. This leads to slow diffusion rates.[114]

11. In most cases, the rate of exchange in ion exchange resins increases with decreasing particle size and increasing temperature.[115]

4.7 CLEANING EVALUATION

When evaluating treatments, conservators often test resin formulations for their rheological properties, adhesion to the substrate, fissuration on drying, water retention, and to quantify the amount of ions removed.[116]

When evaluating the efficiency of the exchange reaction, scientists often use ion chromatography to analyze an exhausted resin (one that can no longer exchange ions) through either combustion or the eluate produced by cleaning and regenerating an exhausted resin.[117] Powder from treated and untreated samples can also be analyzed and compared.[118] Ion chromatography chemically identifies and quantifies the extracted ions present.[119] An atomic absorption spectrometer can also provide quantitative analysis of the ion concentration.[120]

Energy dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) examination of sample cross sections allows researchers to compare substrates before and

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113 Giovagnoli, 507.

114 On the other hand, sieve effects can be exploited to fulfill separation needs. Sieve action allows operators to select which ions they want to separate from a substance based on the size-discrimination phenomenon. Zagorodni, 84-85.

115 Kunin, 52, 69.

116 Guidetti, 327.

117 Ibid., 329; Martínez-Arkarazo, 515.

118 Guidetti, 329.

119 G. Gobbi, G. Zappia, and C. Sabbioni, "Anion Determination in Damage Layers of Stone Monuments," *Atmospheric Environment* 29, no. 6, (1995), 703; Quaresima, 179.

120 Özmetin, 4.

after cleaning.[121] Alternately, the resin or the resin carrier (such as a cellulose pulp pad) can be examined before and after the tests with SEM/EDS (or SEM/ISIS) to verify the effective removal of the ions.[122] In the case of masonry samples, a metallographic microscope is often used to check surface morphologies before and after treatment.[123]

Water absorption tests are used to measure changes in a treated stone's permeability. Conservators want to know if the treatments are having any negative side effects, such as increasing the porosity of the surface stone layers.[124]

Color measurements can be used to supplement these techniques, to monitor undesirable changes to surfaces and finishes, and occasionally to monitor changes in pH. Changes in color may be gauged using photography, the Munsell system, spectrophotometers, and tristimulus colorimeters. The Minolta CR310 Chromometer is one example of a tristimulus colorimeter, an instrument that measures reflection spectrum and then presents the data as a series of CIELab values.[125]

A variety of pH indicators are available, both electronic and chemical, for monitoring both the resin and the substrate. These are useful for determining the strength of a resin application, its after-effects, and for gauging the length of a reaction.

4.8 DISCUSSION

Research shows that much of the conservation work with ion exchange resins occurs in Europe. As such, a number of studies are not readily available in English. Furthermore,

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[121] Berlucchi, 26.
[122] Borrelli; Ropret.
[123] Giovagnoli, 505.
[124] Berlucchi, 26.
[125] Premlal, 140; Quaresima,179; Michael R. Schilling, Li Jun, Li Tie Chao, Guo Hong, Li Zuixiong, and Duan Xu Xe, "Color Measurement at the Mogao Grottoes," in Conservation of Ancient Sites on the Silk Road: Proceedings of an International Conference on the Conservation of Grotto Sites, ed. Neville Agnew (Los Angeles: The Getty Conservation Institute, 1997), 341-342.

the lack of American research and use means that American companies do not supply ion exchange gel resin for conservation purposes. Instead, work in the United States focuses on agricultural, water, and pharmaceutical uses. These resins are more expensive, because they are sold in industrial-size amounts, and they may not suitable for topical applications; their chemical reactivity requires water immersion. Commonly, this is achieved through the utilization of an ion exchange column, which filters liquids and occasionally provides for material submersion, thereby cleaning the specified item.

Nonetheless, it is apparent that conservators have begun to study the particular question of calcium removal with ion exchange resins. In addition, a number of European companies that specialize in conservation carry ion exchange resins, in gel form, that are appropriate for topical treatment and cleaning of wall paintings. Ironically, the bulk of the conservation research currently being conducted on ion exchange resins focuses on carbonate stones, a material that is comparatively sensitive to aggressive exchange reactions. Nonetheless, this work may prove to be useful when treating other sensitive substrates, such as lime plaster.

Conservators continue to fine-tune ion exchange applications for architectural conservation. This requires inquiries into gels, poultices, and other applications that can withhold the water necessary for ion exchange to occur, and also facilitate application to the varied surfaces and materials found in building construction. Testing of rheological properties will continue to be important, as will resources detailing the types of ions, acids and bases suitable for conservation. Currently, conservators have little precedent to follow, and they are adapting materials not yet meant for such small, delicate operations. Yet, the history of ion exchange technology is one of increasing specificity. If resins can be made to target specific sugars and minerals, then why not specific historic compounds? Resins are already used for stabilization, to replace undesirable ions with innocuous ones. It is simply a matter of choosing the proper combination of ions to achieve the proper combination of by-products.

A great deal more testing and re-evaluation needs to occur before conservators can claim that ion exchange resins are consistently suitable and safe for cleaning wall paintings. However, it does appear that the gradual nature of resin treatments, in addition to their ease of use and control, make it an promising tool for the cleaning of fragile plaster finishes.

CHAPTER FIVE
ION EXCHANGE RESIN TESTING

The goal of the literature review was to determine the types of ion exchange resins, resin formulations, and testing that were appropriate given the project's parameters. Very few studies were found that dealt with plaster substrates, limewash removal, and wall paintings. Those that did lacked in-depth explanations of the methodology, materials, and testing utilized. While this study makes use of many sources, two were of particular assistance when designing tests and formulations: A. Giovagnoli, C. Meucci, and Marisa Tabasso Laurenzi's work on "Ion exchange resins employed in the cleaning of stones and plasters: research of optimal employment conditions and control of their effects,"[1] and Viviana Guidetti and Maciej Uminski's study of "Ion exchange resins for historic marble desulfatation and restoration."[2] Giovagnoli's work was one of the few to focus on cleaning lime incrustations on a calcareous substrate. The testing model examines the exchange action of four different resins over time, their ability to remove lime layers, and their effects on the calcareous substrate. Guidetti's piece also works with calcareous substrates; although this time the variables had more to do with formulate additives to improve both the exchange reaction and the physical rheology.

5.1 SELECTION CRITERIA

Four different ion exchange resin samples were obtained for laboratory testing and material analysis. While there are several conservation-specific resins sold by the Europe-based companies C.T.S., InSitu, and Syremont, it was deemed important to acquire an American-made product, in the interest of cost-effectiveness and efficiency. It is assumed that

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[1] A. Giovagnoli, C. Meucci, and Marisa Tabasso Laurenzi, "Ion Exchange Resins Employed in the Cleaning of Stones and Plasters: Research of Optimal Employment Conditions and Control of their Effects," in *Deterioramento e Conservazione della Pietra: Atti del 3 Congresso Intemazionale, Venice, October 24-27 1979* (Padova, Italy: Instituto di Chimica Industriale, Università degli Studi di Padova, 1982): 499-510.

[2] Viviana Guidetti and Maciej Uminski, "Ion Exchange Resins for Historic Marble Desulfatation and Restoration," in *Proceedings of the 9th International Congress on Deterioration and Conservation of Stone, Venice, June 19-24, 2000*, vol. 2, ed. Vasco Fassina (Amsterdam, The Netherlands: Elsevier Science B.V.): 327-333.

most conservators will choose a local product over one that will cost more to ship and take longer to obtain.

A total of six chemical companies with U.S. branches and ion exchange resin products were contacted.[3] Of these, products from two companies, Lanxess Sybron Chemicals, Inc. and Siemens Water Technologies Corp., were selected for participation in laboratory trials. These companies were chosen for their willingness to submit samples for testing and to provide some technical assistance. The resins tested are Lewatit CNP 80 and Lewatit TP 207 from Lanxess, and USF C-211 and USF C-211 H from Siemens.

When selecting the resins, a basic list of criteria was discussed with representatives from Lanxess and Siemens. Together, the author and the corporations determined which products best fulfilled these requirements. The criteria fell into the following categories:

- ✓ The product must not be aggressive so that it damages the decorative finishes and lime plaster below the limewash layers.
- ✓ The product should be selective enough to target calcium ions.
- ✓ The resin matrix needs to be large enough to take in and hold calcium ions.
- ✓ The calcium ions should be replaced with an innocuous product.
- ✓ The exchange reaction should not result in a strong acid.
- ✓ Enough calcium ions should be removed to cause degradation of the limewash layer/layers and facilitate limewash removal with either the actual dried poultice, or a minimal amount of mechanical means.
- ✓ The resin should be applicable as a gel or poultice treatment.
- ✓ The resin should be able to mix with additives and still be effective.
- ✓ The pH should be close to neutral.

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[3] The six companies were Dow Chemical Company, Lanxess Sybron Chemicals, Inc., Merck, Mitsubishi Chemical USA, Inc., Rohm & Hass, and Siemens Water Technologies Corp.

- ✓ The resin should have a high exchange capacity, necessitating a matrix that can take a large number of calcium ions.[4]

From this, two ion exchange products were chosen from each company. Lewatit CNP 80 and Lewatit TP 207 were identified from Lanxess after conversations with the Technical Services department and Phil Fatula, Market Manager, Chemical Processing Market Segment of Sybron Chemicals Inc., a Lanxess Company. The CNP 80 is meant to be the more aggressive of the two options, as it forms carbonic acid when the calcium ions in the calcium carbonate exchange with the hydrogen ions in the resin. The TP 207 is meant to be less aggressive than the CNP 80 and pH neutral. It is in the sodium-form, meaning that sodium bicarbonate is formed when the calcium ions in the calcium carbonate exchange with the sodium ions in the resin. Both are cation exchange resins capable of exchanging calcium ions.[5]

USF C-211 and USF C-211 H were chosen from Siemens Water Technologies Corp. after conversations with the Technical Support department and Greg Bachman, Director of Operations for Siemens Water Technologies. A mixed bed resin (cation and anion) was considered first, as it would remove all cations (including Ca, Mg, and K) and replace them with sodium. However, the mixed bed resin has a more limited exchange capacity. It also creates pure water as a byproduct, which attacks all materials except stainless steel and plastics. USF C-211 was chosen for its capacity to exchange Ca^+ ions. Both the H^+ and Na^+ forms were requested to allow for comparisons to be made between resins of the same type, but with different exchangeable counterions. The H^+ form would be more acidic, and the Na^+ form closer to neutrality.[6] Bachman was concerned that while the hydrogen-form might clean

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[4] Commercial ion exchange resins are largely designed for the treatment of aqueous solutions, they are not meant to be placed in direct contact with a substance. Thus the concentration of calcium in the limewash is comparatively higher than what is normally encountered in these operations.

[5] Technical Services of Lanxess Sybron Chemicals Inc., interview by author, telephone, 21 February 2009; Phil Fatula, “Re: Ion Exchange Resin Testing,” personal e-mail, 20 February 2009.

[6] Technical Support of Siemens Water Technologies, interview by author, telephone, 19 February 2009; Greg Bachmann, interview by author, telephone, 25 February 2009.

the $CaCO_3$ quicker than the sodium-form, it may also have a greater chance of damaging the substrate.[7]

5.2 MATERIAL DESCRIPTIONS

5.2.1 LEWATIT CNP 80

Lewatit CNP 80 is the proprietary name of a high capacity,[8] macroporous[9] weak[10] cation exchange resin manufactured by Lanxess Corporation – Sybron Chemicals, Inc.[11] Chemically it is a copolymer from acrylic acid,[12] divinylbenzene[13] and aliphatic diene with carboxy-

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[7] Greg Bachman, "RE: Request for Sample," personal e-mail, 27 February 2009.

[8] The capacity of an ion exchange resin is defined by the number and availability of its functional groups or sites. This in turn determines the quantity if ions the sorbent (resin) can accumulate. Andrei A. Zagorodni, *Ion Exchange Materials Properties and Applications* (Oxford, UK: Elsevier BV, 2007), 422.

[9] Macroporous resins have a matrix with a heterogeneous structure consisting of two phases: (1) gel regions containing high-density polymer chains and a minor amount of solvent, and (2) macroscopic permanent pores containing solution similar to the surrounding medium. In this instance, the solvent is acrylic acid, divinylbenzene, and aliphatic diene. The macropores have diameters between 20-200 nm. This distance is much larger in comparison to the distance between adjacent hydrocarbon chains of gel-type materials (0.5-20 nm). Furthermore, macropores do not collapse when they lose water, while gel pores only appear when swollen with water. This makes macroporous resins better-suited for operations limited by slow diffusion of exchanged ions in the gel phase, the exchange of ions takes place on the surface of macropores or close to the surface, the molecules never enter the dense gel regions. The macropores make the resins more chemically stable, allow for faster diffusion in the liquid phase, and the open-pore structure allows larger molecules to diffuse. Andrei A. Zagorodni, *Ion Exchange Materials Properties and Applications* (Oxford, UK: Elsevier BV, 2007), 46, 47, 431.

[10] Ion exchange resins are also classified as either weak or strong based on the strength of the acid or basic groups present in the polymer chain. Viviana Guidetti and Maciej Uminski, "Ion Exchange Resins for Historic Marble Desulfatation and Restoration," in *Proceedings of the 9th International Congress on Deterioration and Conservation of Stone, Venice, June 19-24, 2000*, vol. 2, ed. Vasco Fassina (Amsterdam, The Netherlands: Elsevier Science B.V., 2000), 328. Strong cation exchangers have groups that are completely ionized in the internal solution of the material. Weak ion exchangers have working pH ranges and can only exchange ions if pH allows for ionization of their functional groups. Andrei A. Zagorodni, *Ion Exchange Materials Properties and Applications* (Oxford, UK: Elsevier BV, 2007), 26.

[11] Sybron Chemicals Inc., "Lewatit CNP 80," Product Information, http://www.sybronchemicals.com/products/cations/cnp80.pdf (accessed April 13, 2009).

[12] Acrylic acid is a monomer used to prepare polymeric networks. The structure is *CH2=CH—COOH*. Andrei A. Zagorodni, *Ion Exchange Materials Properties and Applications* (Oxford, UK: Elsevier BV, 2007), 422.

[13] Divinylbenzene (DVB) is the most common cross-linking agent used to prepare ion exchange

lic acid functional groups. It is shipped in hydrogen (H^+) form. The matrix is a crosslinked polyacrylate. It is sold as solid, opaque yellow-white beads, U.S. mesh 12-50 (see fig. 5.1).[14] It releases a slight naphthalene odor. It poses little or no hazard if spilled, as it does not contain any hazardous components, however the beads may make surfaces slippery. The resin is slightly flammable. It is safe for operators to handle, although it may cause mechanical irritation if introduced into the eyes. Even so, it is not expected to cause any adverse acute or chronic health effects. It is not carcinogenic. Its transportation is non-regulated. The pH for CNP 80 is neutral to slightly acidic.[15]

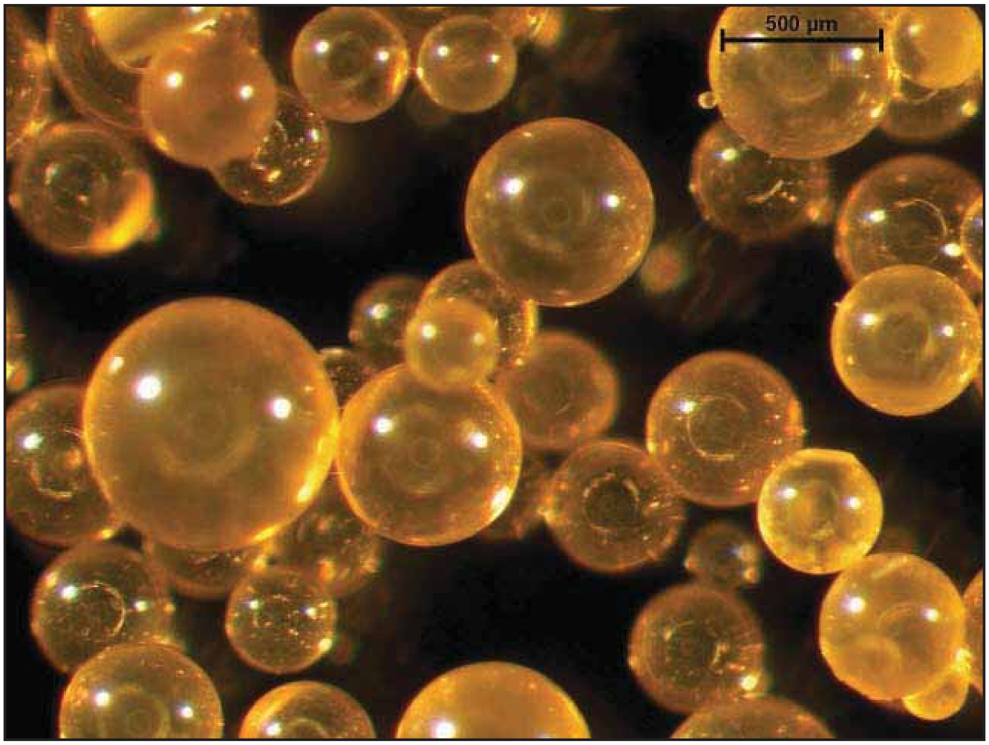

Figure 5.1: Lewatit CNP 80, viewed at 115x magnification on a Leica MZ16 stereomicroscope, with quartz-halogen illumination using a Leica KL2500 LCD, 3200 K, and additional Volpi Intralux 5000-1 dual gooseneck fiber optics (Source: C. Smith, 2009).

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resins. Cross-links are interconnections (hydrocarbon bridges) between the polymeric chains of a resin's matrix. By using a cross-linking agent like DVB, the ion exchange polymer (resin) becomes insoluble. Andrei A. Zagorodni, *Ion Exchange Materials Properties and Applications* (Oxford, UK: Elsevier BV, 2007), 427, 425.

[14] Over 90 percent of the resin is U.S. mesh 12-50, which is equivalent to 0.3-1.6 mm.

[15] *Lewatit CNP 80 (5851B)*; MSDS No. 000000003835; Lanxess Corporation: Birmingham, NJ, December 29, 2008.

CNP 80 is traditionally used for dealkalization, demineralization in combination with a strong acid resin, removal of heavy metals from aqueous solutions, high solids softening where low hardness levels are necessary, and as a cation polisher following a strong base resin. Its water retention capacity is 45-50 percent.[16]

When considering placing CNP 80 in a formulate, it is important to note that it is stable in pH ranging from 0-14 and temperature ranging from 34-170°F. It can be stored for up to two years in temperatures ranging from 34-104°F. Its optimal operating conditions are at a maximum temperature of 158°F, pH 5-14. After saturation, the resin can be regenerated with HCl and H_2SO_4 and reused. CNP 80 should not be mixed with strong oxidants, like nitric acid, as violent reactions can occur.[17] The cost per cubic foot is $165.00.[18]

5.2.2 LEWATIT TP 207

Lewatit TP 207 is the proprietary name of a high capacity, weakly acidic, macroporous cation exchange resin manufactured by Lanxess Corporation – Sybron Chemicals, Inc.[19] Chemically it consists of a styrene-divinylbenzene copolymer matrix with iminodiacetic acid functional anchor group in the form of salt. It is shipped in sodium (Na^+) form. It is sold as solid, opaque beige beads, mean size 0.61 mm (see fig. 5.2). It is odorless. It poses little or no hazard if spilled, as it does not contain any hazardous components, however the beads may make surfaces slippery. The resin poses slight health, reactivity, and physical hazard. It is safe for operators to handle, although it may cause mechanical irritation if introduced into the eyes. Still, it is not expected to cause any adverse acute or chronic health effects. It is not carcinogenic. Its transportation is non-regulated. The pH for TP 207 is approximately 9 in aqueous suspension.[20]

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[16] Sybron Chemicals Inc., "Lewatit CNP 80."

[17] Sybron Chemicals Inc., "Lewatit CNP 80."

[18] Lanxess Sybron Chemicals Inc., interview by author, telephone, 21 April 2009.

[19] Sybron Chemicals Inc., "Lewatit MonoPlus TP 207," Product Information, http://www.sybronchemicals.com/products/selective/tp207.pdf (accessed April 13, 2009).

[20] *Lewatit TP 207, Sodium Form (5348B)*; MSDS No. 000000004007; Lanxess Corporation: Birmingham,

The chelating iminodiacetate groups[21] in TP 207 are for the selective extraction of heavy metal cations from aqueous solutions. It is traditionally used to remove divalent cations from neutralized water. They are removed in the following order: copper > vanadium (VO) > uranium (UO2) > lead > nickel > zinc > cadmium > iron (2) > beryllium > manganese > calcium > magnesium > strontium > barium > sodium. This is useful when removing metal contaminants from processing baths, recovering useful metals from electroplating rinse water, removing heavy metals from contaminated ground water, selectively removing trace heavy metals from metal surface finishing industry and extraction of heavy metals from hydrometallurgical solutions. Its water retention capacity is 55-60 percent.[22]

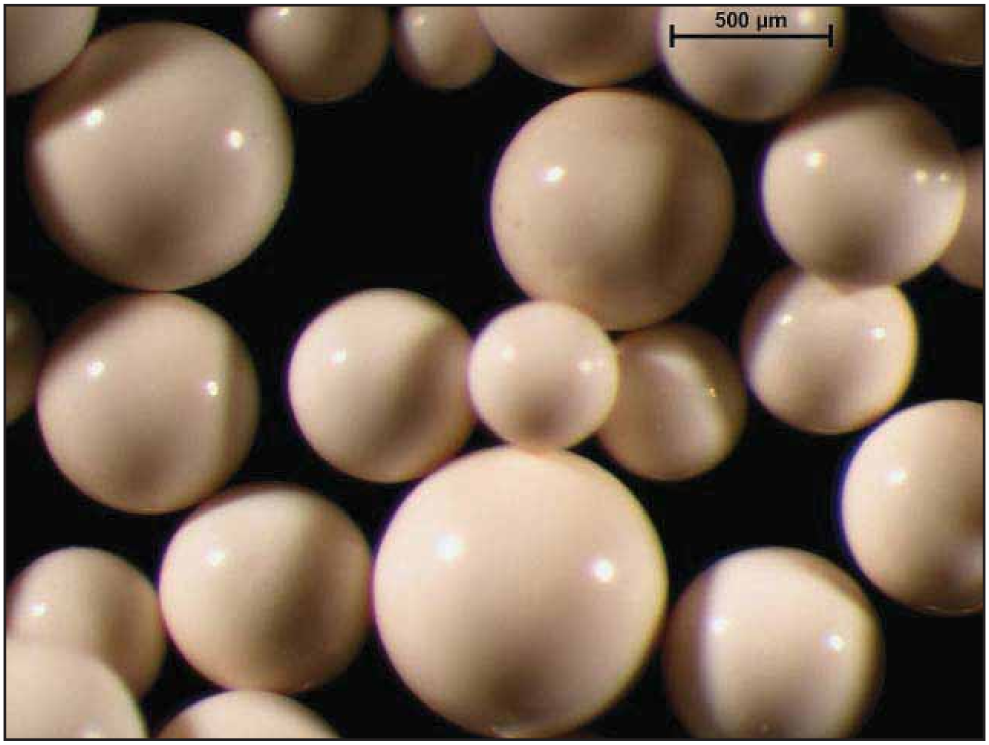

Figure 5.2: Lewatit TP 207, viewed at 115x magnification on a Leica MZ16 stereomicroscope, with quartz-halogen illumination using a Leica KL2500 LCD, 3200 K, and additional Volpi Intralux 5000-1 dual gooseneck fiber optics (Source: C. Smith, 2009).

NJ, December 29, 2008.

[21] Chelating materials possess fixed groups that can form chelate rings with metal ions, or rings made through the connection of a large ligand molecule to a metal ion. Andrei A. Zagorodni, *Ion Exchange Materials Properties and Applications* (Oxford, UK: Elsevier BV, 2007), 55-56.

[22] Sybron Chemicals Inc., "Lewatit MonoPlus TP 207," Product Information, http://www.sybronchemicals.com/products/selective/tp207.pdf (accessed April 13, 2009).

When considering placing TP 207 into a formulate, it is important to note that it is stable in pH ranging from 0-14 and temperature ranging from 34-176°F. It can be stored for up to two years in temperatures ranging from 34-104°F. Its optimal operating conditions are at a maximum temperature of 176°F, pH 1-9. After saturation, the resin can be regenerated with the mono-sodium and di-sodium forms of NaOH and reused. TP 207 should not be mixed with strong oxidants, like nitric acid, as violent reactions can occur.[23] The cost per cubic foot is $400.00.[24]

5.2.3 USF C-211

USF C-211 is the proprietary name of a high capacity, eight-percent cross-linked gel[25] strong acid cation exchange resin manufactured by Siemens Water Technologies Corp. Chemically it consists of a sulfonated copolymer matrix of styrene and divinylbenzene with sulfonic acid functional groups. It is shipped in sodium (Na^+) form.[26] It is sold as solid spherical beads (see fig. 5.3). It releases either no odor or a slight amine odor. It poses little or no hazard if spilled, however the beads may make surfaces slippery. It is safe for operators to handle; it does not have any acute or chronic health effects except when in introduced into the eyes. C-211 can temporarily cause severe eye irritation and short-term corneal injury.[27] Transportation of C-211 is unregulated.[28] It is traditionally used for deionization and chemi-

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[23] Ibid.

[24] Lanxess Sybron Chemicals Inc., telephone interview, April 21, 2009.

[25] Gel-type resins possess a matrix with homogenous polymer density. Different ion exchange polymers have different chemical properties based off of the different density distributions of their gels. While the molecular- and nano-scale open areas between the hydrocarbon chains are referred to as pores, there is no well-defined pore structure. When the gel is swollen, the micropores between its hydrocarbon chains contain the imbibing solvent. When dry, the pores collapse. Andrei A. Zagorodni, *Ion Exchange Materials Properties and Applications* (Oxford, UK: Elsevier BV, 2007), 429, 46.

[26] Siemens Water Technologies Corp., "USF C-211 Cation Resin," Technical Data Sheet, http://www.water.siemens.com/SiteCollectionDocuments/Product_Lines/Industrial_Process_Water/Brochures/C_211_Na.pdf (accessed April 13, 2009).

[27] Gloves and protective eyeglasses should always be worn as a precaution.

[28] *C-211 Ion Exchange Resin*; MSDS; Siemens Water Technologies Corp.: Warrendale, PA, May 15, 2000, rev. September 19, 2003.

cal processing applications.[29]

When considering placing USF C-211 into a formulate, it is important to note that it operates in pH ranging from 1-14 and a maximum temperature of 250°F.[30] It can be stored at temperatures between 35-100°F. USF C-211 should not be mixed with strong oxidants, like nitric acid, as violent reactions can occur, and it should not be burned as toxic fumes/vapors will be released. It will auto ignite at temperatures above 900°F. Hazardous decomposition begins at temperatures over 194°F.[31]

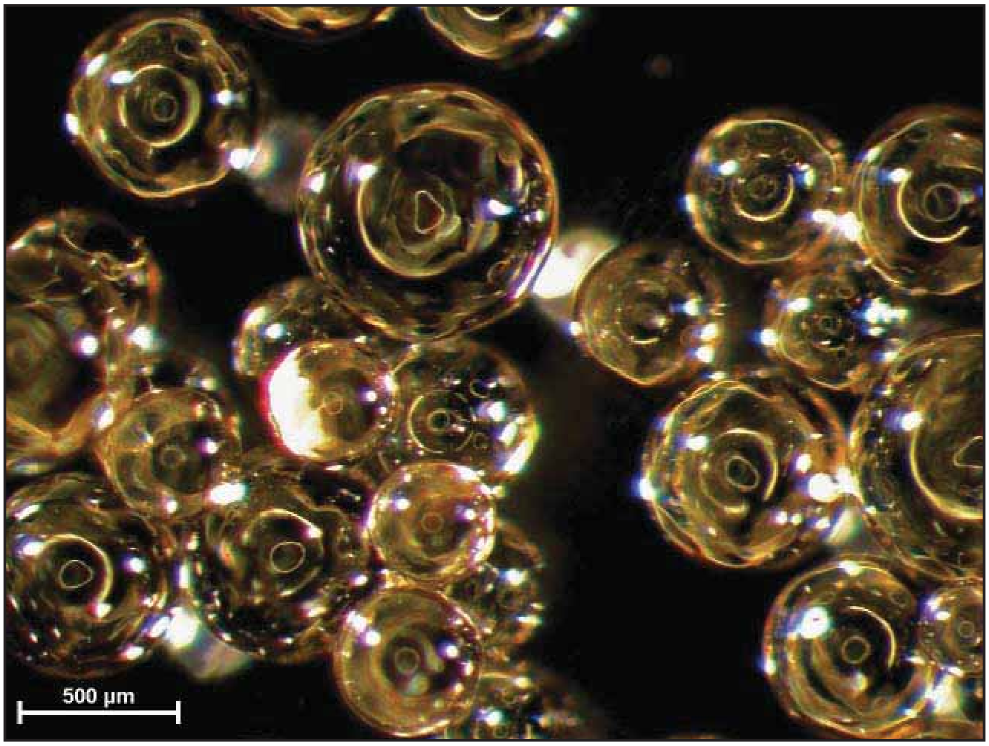

Figure 5.3: USF C-211, viewed at 115x magnification on a Leica MZ16 stereomicroscope, with quartz-halogen illumination using a Leica KL2500 LCD, 3200 K, and additional Volpi Intralux 5000-1 dual gooseneck fiber optics (Source: C. Smith, 2009).

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[29] Siemens Water Technologies Corp., "USF C-211 Cation Resin."
[30] Ibid.
[31] *C-211 Ion Exchange Resin*; MSDS.

5.2.4 USF C-211 H

USF C-211 H is the proprietary name of a high capacity, eight-percent cross-linked gel strong acid cation exchange resin manufactured by Siemens Water Technologies Corp. Chemically it consists of a sulfonated copolymer matrix of styrene and divinylbenzene with sulfonic acid functional groups. It is shipped in hydrogen (H^+) form.[32] It is sold as solid spherical beads (see fig. 5.4). It releases either no odor or a slight amine odor. It poses little or no hazard if spilled, however the beads may make surfaces slippery. It is safe for operators to handle; it does not have any severe acute or chronic health problems associated with it. C-211 H can temporarily cause a mild irritation and redness of the skin, and it may cause se-

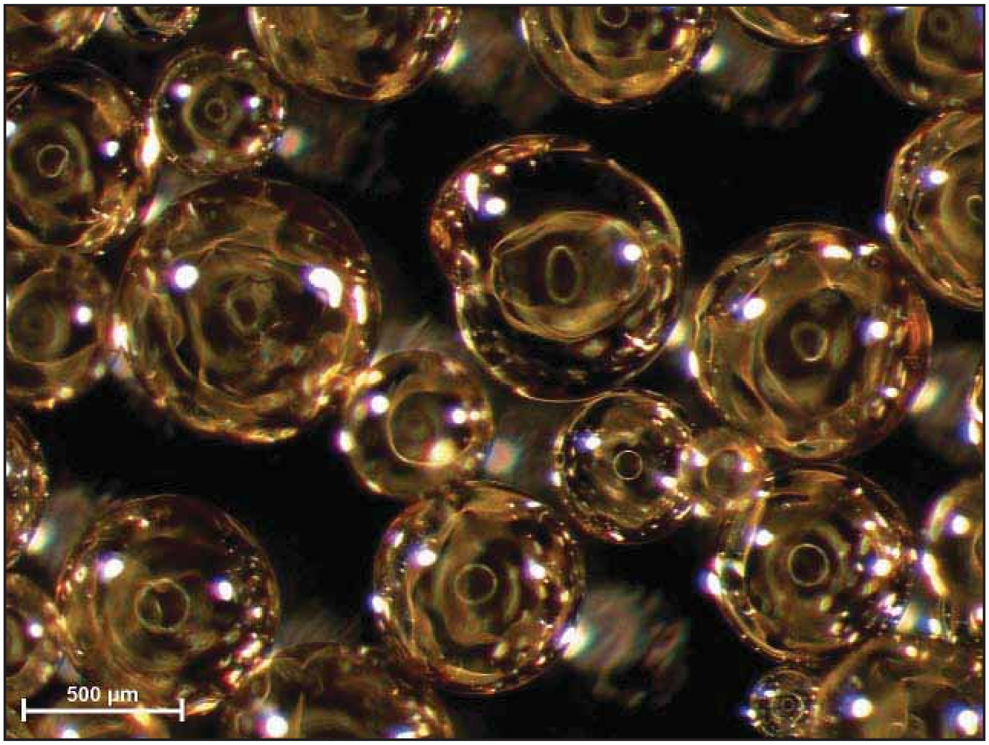

Figure 5.4: USF C-211 H, viewed at 115x magnification on a Leica MZ16 stereomicroscope, with quartz-halogen illumination using a Leica KL2500 LCD, 3200 K, and additional Volpi Intralux 5000-1 dual gooseneck fiber optics (Source: C. Smith, 2009).

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[32] Siemens Water Technologies Corp., "USF C-211 (H) Cation Resin," Technical Data Sheet, http://www.water.siemens.com/SiteCollectionDocuments/Product_Lines/Industrial_Process_Water/Brochures/C_211_H.pdf (accessed April 13, 2009).

vere eye irritation and short-term corneal injury.[33] Transportation of C-211 H is unregulated.[34] It is traditionally used for deionization and chemical processing applications.[35]

When considering placing USF C-211 H into a formulate, it is important to note that it operates in pH ranging from 1-14 and a maximum temperature of 250°F.[36] It can be stored at temperatures between 35-100°F. USF C-211 H should not be mixed with strong oxidants, like nitric acid, as violent reactions can occur, and it should not be burned as toxic fumes/vapors will be released. It will auto ignite at temperatures above 900°F. Hazardous decomposition begins at temperatures over 194°F.[37]

5.3 ION EXCHANGE RESIN ANALYSIS

5.3.1 OBJECTIVES

Preliminary testing of the four ion exchange resins was designed simply to determine whether or not the resins have any effect on limewash. By simultaneously testing the four resins and a control, direct comparisons could be made between the materials. For the purposes of this study, any changes to the limewash need to be significant enough to cause degradation of the limewash layers. As such, the changes should be visible with the naked eye or under low microscopic magnification.

At this point questions of substrate, formulation, and additives were taken out of the equation. Without confirmation that the resins have any effect on calcium carbonate molecules, further testing becomes unnecessary. Pure resin mixtures, containing only resin, water, and pH indicator, were created. All other additives were omitted. Just enough water was

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[33] Gloves and protective eyeglasses should always be worn as a precaution.
[34] *C-211 H Ion Exchange Resin*; MSDS; Siemens Water Technologies Corp.: Warrendale, PA, April 1, 2000.
[35] Siemens Water Technologies Corp., "USF C-211 (H) Cation Resin."
[36] Ibid.
[37] *C-211 H Ion Exchange Resin*; MSDS.

used to keep the resins saturated and to activate the exchange reaction, but no more water than they could absorb. The Universal Indicator Solution was included to monitor changes in pH. Changes in pH should indicate whether reactions are taking place (causing an active change in pH), whether exchange actions have stopped (no change in pH), and whether the reaction product is acidic, basic, or neutral.

5.3.2 METHODOLOGY

All sample preparation, testing, and microscopy were completed in the Architectural Conservation Laboratory of the University of Pennsylvania's Department of Historic Preservation.

First, limewash paint chips were taken from samples prepared thirteen days earlier. A limewash mixture consisting of approximately 12 ¾ cups of Graymont Type S hydrated lime was mixed with approximately 13 ½ cups hot water in a stainless steel bucket using a Milwaukee brand Magnum heavy duty 3/8-inch drill. This wash was left to stand for at least 12 hours before use.[38] Terracotta pavers were chosen as the substrate to both provide a porous base for the wash to adhere to while at the same time removing lime substrates from the initial testing equation. The 6-inch by 6-inch handmade terracotta tiles were rinsed with water and left to dry for at least 12 hours. The pavers were then divided into ten even sections using Polyken® brand tape. The sections measured roughly 1-inch wide by 2 7/8-inch long. The tiles were next sprayed with water and painted with one coat of limewash, using a Shur-Line seven-inch pad painter. After one hour this process was repeated so that the tiles possessed two applications of white limewash that formed one finish coat. After 24 hours, another two coats of limewash were added, also one hour apart. This time, however, the limewash was mixed with lamp black pigment to differentiate it from the first white coat (see fig. 5.5). This was done to make it easier to visually quantify the amount of exchange

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[38] Limewash formula adapted from an article by Sarah Marie Jackson, Tye Botting and Mary Striegel, "Durability of Traditional and Modified Limewashes," *APT Bulletin* 38, no. 2/3 (2007): 21. Ratio tripled from original 4 ¼ c. hydrated lime to 4 ½ c. hot water.

Figure 5.5: Materials used in sample preparation, including Polyken tape, terracotta tiles, limewash, drill, lamp black, and pad painter (Source: C. Smith, 2009).

and deterioration. After eleven days one of the painted terracotta tiles was scoured with a razor blade and five paint flakes were obtained for testing. The flakes ranged in size from about 1-1.5 cm.

The resins were prepared by first placing each into a ceramic mortar and pestle and grinding them into a fine powder. As noted by Kunin, the rate of ion exchange can be increased by finely grinding the resins or otherwise increasing the surface area.[39] Seven grams of each ground resin were measured out and placed into separate 50 mL plastic beakers labeled with the resin name and a number. One mL of universal pH indicator and two mL of distilled water were added to each beaker, except for the no. three beaker containing CNP 80. This mixture required 4 mL of distilled water for the resins to swell and gel like the other samples. A fifth beaker held a control, consisting of 2 mL of water and 1 mL of universal pH

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[39] Robert Kunin, *Ion Exchange Resins* (Malabar, Florida: R.E. Krieger Pub. Co., 1985), 69.

indicator.

Each sample was examined with reflected light under the Leica MZ16 stereomicroscope at 12.5x and 115x magnification with quartz-halogen illumination using a Leica KL2500 LCD, 3200K, and additional Volpi Intralux 5000-1 dual gooseneck fiber optics to monitor changes in appearance. The samples were also examined under fiber optic raking light alone, to better examine topographical changes (such as pitting and disaggregation). If the samples display different degrees of deterioration, it can be assumed that the unique component in their treatment (in this case the ion exchange resin) is contributing to this change. The purpose of these examinations is to determine whether or not the resins have any effect on limewash deterioration, whether the type of resin has an effect (i.e. different resins exchange differently), and to determine whether or not the resins have more effect than water (the control).

Photomicrographs (see Appendix A) were taken with a Nikon DSFi1 digital camera and NIS Elements computer software. Images were taken of both sides of the paint chips, in raking and non-raking light, and of the resins themselves (at 7.1x magnification). They were taken at regular intervals: 0, 0.5, 1.5, 13.5, and 37.5 cumulative hours. At each interval the resins were photographed before removing the paint chips, rinsing them with distilled water, and photographing both sides. The resins were then stirred, sprayed with distilled water if they had dried out, and the paint chips were returned to the middle of the resin or water mix. The beakers were then covered with Parafilm to inhibit evaporation. In each instance the dwell time was increased (0.5 hr, 1 hr, 12 hrs, 24 hrs) to allow the resin more time for ion exchange. Stirring the mixture should have put the paint chips into contact with resins that had not previously exchanged.

Appendix B contains additional product and supplier information. Appendix C contains the Material Safety Data Sheets for the ion exchange resins used.

5.3.3 RESULTS

See Tables 5.1, 5.2, 5.3, 5.4, and 5.5 in Appendix A for sample comparisons over time. In the tables the grey top coat is considered side one, while the white base coat is considered side two. The base coat may contain traces of terracotta substrate.

SAMPLE 1: C-211 H

The resin remained a deep reddish-pink throughout the experiment, indicating a pH between 4.0 and 5.0. After half an hour, hints of yellow appeared, indicating a pH between 5.0 and 5.5.[40]

The paint sample decreased in dimension throughout the experiment. The shape went from angular and irregular to smooth and round. The texture on sides one and two evolved from the initial grooved surface to something smoother (see 0-1.5 hours), and finally pitted (see 13.5 to 37.5 hours). Side one showed the most drastic changes in color, from a dark grey at the start, to a lighter grey after the first half hour, and finally a range of greys and black. (See table 5.1).

SAMPLE 2: C-211 NA

The resin started blue-green, indicating a pH around 8.5, and became progressively more purple throughout the experiment, indicating a pH between 8.5 and 10.0.

The paint sample decreased in dimension throughout the experiment. The sample largely retained its initial grooved surface on side one and the both grooved and grainy texture on side two. Some degree of pitting was displayed throughout the samples; it did not increase significantly over time. The change in color in sample two was not significant

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[40] The pH was determined by referencing the Universal pH Indicator Chart, cat. no. I-180, provided by Fisher Scientific with the Fisher Universal Indicator. The chart is meant to be used with samples of aqueous solutions placed in test tubes and mixed with indicator solution. The samples in this experiment contain a larger percentage of solids, and as such they do not provide clear pH results. The pH values are approximations made after considering the effect opaque resins have on the solutions.

enough to draw any conclusions from. (See table 5.2).

SAMPLE 3: CNP 80 H

The resin remained an orangey-pink color throughout the experiment, indicating a pH between 4.0 and 5.0.

The paint sample experienced a comparatively small decrease in dimension throughout the experiment. The sample largely retains its initial grooved surface on side one, although the character changed greatly. From the first half hour on, side one became much lighter in color. At the first half hour, side one appeared to be almost bleached of color, with hints of grey underneath a white layer. From 1.5 to 13.5 hours, side one showed signs of increased microcracking and flakes. By 37.5 hours, the grooves were much less pronounced, the flakes were gone, and more grey appeared on side one. On the other hand, while side two did not experience much color change, its grainy texture did increase over time. From the first half hour on, the surface developed into increasingly larger flakes. By 37.5 hours, however, the flakes had disappeared and the surface appeared relatively smooth. (See table 5.3).

SAMPLE 4: TP 207 NA

The resin remained a very pale purple with off-white inclusions that lightened very gradually over time. The off-white areas appeared to come from active reactions. The color indicates a pH between 9.0 and 10.0.

The paint sample decreased significantly in dimension throughout the experiment. The sample largely retained its initial grooved surface on side one, and the grainy texture on side two. From the first half hour on, side one became lighter in color. At 1.5 hours, side one displayed severe microcracking and flakes. Between then and 13.5 hours, the flakes disappeared and the side regained its smoothly grooved appearance. At 37.5 hours, there were hints of a darker grey layer under the lighter grey top layer. Meanwhile, side two did not experience much color change but its grainy texture did increase over time. By 1.5 hours, side two displayed microcracking, flakes, and pitting. At 37.5 hours, however, the flakes disappeared and the surface appeared relatively smooth with a partial layer of white material on top. (See table 5.4).

SAMPLE 5: CONTROL

The control started as a dark olive green, indicating a pH of 6.5, moved to a dark purple by the first half hour, indicating a pH between 9.5 and 10.0, and finally became increasingly green, indicating a pH between 7.0 and 8.5.

The paint sample decreased in dimension throughout the experiment. The sample largely retained its initial grooved surface on side one, and the grainy texture on side two. From the first half hour on, side one became lighter in color and both sides became increasingly purple. From the first half hour on the first side displayed some pitting, the second side began to show pitting from 13.5 hours on. Overall, the textures did not change over time. (See table 5.5).

5.3.4 DISCUSSION

Resins 1 (C-211 H) and 3 (CNP 80 H) both proved to be acidic throughout the ion exchange process. This is not unexpected, as they are both hydrogen-form resins whose by product should be carbonic acid. In talking with various resin manufacturers, it was universally agreed that the hydrogen resin form would be more aggressive than the sodium-form. Thus, the sodium-form resins 2 (C-211 Na) and 4 (TP 207 Na) proved to be highly alkaline throughout the ion exchange process. The control, meanwhile, remained relatively neutral, occasionally moving towards the basic end of the spectrum as the limewash deteriorated. From this and the slight color change in all the resins, it seems likely that interaction with the limewash actually causes the formulates to become more basic.

Very little of the dimensional change during the experiment came from interaction with the treatments. The paint chips were often broken during handling, most often with tweezers. This is due to a combination of operator error and weakening of the material. In light of this fact, it is not possible to determine the degree of dimensional loss caused by the treatments, although it appears that the width and length would have changed very little if not for the handling.

The greatest change in texture occurred in samples 1, 3, and 4. Again, this is not surprising to see in samples 1 and 3, as these were submerged in the hydrogen-form resins. Sample 1 became the most rounded, and the degradation of the grey lime layer is severe. The appearance of black areas could be from a breakdown of the limewash revealing the lamp black pigment particles contained in the mix. This deterioration took longer to appear than in samples 3 and 4. As mentioned earlier, the diffusion process is slower in gel resins than in macroporous resins like CNP 80 and TP 207. Nonetheless, the C-211 H gel resin will eventually achieve results comparable to the two macroporous resins as it is a strong acid and the Lewatit products are categorized as weak strength resins. While both of the Lewatit resins induced flaking, CNP 80 H proved to be stronger. Both are stable, efficient exchangers that can exchange large molecules owing to their macroporous matrices. The CNP 80, nevertheless, created larger flakes and in greater quantities than did the TP 207. There are at least two possible explanations for this. For one, as mentioned before the CNP 80 is in hydrogen-form and is therefore more acidic. Secondly, it has the greatest exchange capacity of all the resins tested. The exchange capacity of the two sodium-form resins is approximately 2.0 meq/mL minimum.[41] The exchange capacity of C-211 H is 1.8 meq/mL minimum.[42] In contrast, the exchange capacity of CNP 80 (H^+) is 4.3 eq/L minimum, more than twice the capacity of any of the other resins.[43]

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[41] Siemens Water Technologies Corp., "USF C-211 Cation Resin"; Sybron Chemicals Inc., "Lewatit MonoPlus TP 207."

[42] Siemens Water Technologies Corp., "USF C-211 (H) Cation Resin."

[43] Sybron Chemicals Inc., "Lewatit CNP 80."

When compared to the results of the ion exchange resins, the control mixture did not produce such drastic results. If it can be compared to any of the resins, then its results best resemble those obtained with resin 2, the C-211 in Na^+ form. The pitting is not quite as pronounced, but neither formula caused flaking of the limewash layers. The resin results may be explained by the fact that it is both a gel resin (slow diffusion) and in a sodium form (less acidic).

5.4 FORMULATE EFFICACY

5.4.1 OBJECTIVES

The experiment scale was increased to test various formulations and to see what effect they had on limewash applied to a substrate. The goal was not to create a mixture that would remove large quantities of limewash; rather it was to lay the groundwork for later testing by determining a mixture that would be both suitable for building conservation and for maximizing ion exchange. The mixture needed to retain water so that the resins would stay activated. It needed to have appropriate rheological properties, including a resistance to flow, good adhesion to substrates, good adhesion to inclined surfaces, easy application, and it needed to be easy for an operator to control.

After examining the resin's physical properties at a small scale, it was necessary to apply the resins to a substrate. This would help to determine if large-scale testing was feasible, and to give a preliminary look into how ion exchange resins perform in a less-optimal environment (i.e. one where the sample is exposed to the air, they are not surrounded by resin, additives are involved, and the substrate dries out quickly).

5.4.2 METHODOLOGY

All sample preparation, testing, and microscopy were completed in the Architectural Conservation Laboratory of the University of Pennsylvania's Department of Historic Preservation.

For the first part of the experiment, four resin formulas were adapted from Guidetti and Uminski's discussion of ion exchangers for marble desulfatation (see table 5.6). Due to either availability or ease of use, Vitacel L 601 FCC took the place of Arbocel BE600, Attagel 40 was substituted with Attapulgite E 1890, Fisher Universal pH Indicator was used in place of a mixed pH indicator, and Saran Wrap replaced Latex AL8:[44]

Table 5.6: Composition of Resin Comparison Formulations (weight parts)

Formula	Cation Exchange Resin	Cellulose Thickener Arbocel BWW40	Cellulose Thickener Vitacel L 601 FCC	Inorganic Additive Attapulgite	Water	Universal pH Indicator
1	70	4.25	12.75	-	110	0.5 mL for every 10 mL of water
2	35	4.25	12.75	-	110	Same as above
3	70	4.25	12.75	13	125	Same as above
4	35	8.40	25.60	10	165	Same as above

* Resin applications are wrapped in Saran Wrap to inhibit moisture loss.

Arbocel BWW40 and Vitacel L 601 FCC are powdered cellulose thickeners that improve a formulation's mechanical performance, making it easier to apply and increasing water uptake and retention. Water uptake and retention is especially important for maximizing and sustaining the ion diffusion process.[45] Attapulgite is an inorganic additive from clay that increases the water content in a formulation without decreasing its rheological properties, such as wet adhesion.[46] Fisher Universal pH Indicator Solution allows researchers to monitor pH changes during the ion diffusion process. As the pH changes, so does the mixture's color. When new applications do not change color, the researcher knows that the process is com-

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[44] Guidetti, 330.
[45] Ibid.
[46] Ibid.

plete and that no more ions can be removed.[47] Wrapping the samples in Saran Wrap places them in a polymeric barrier that hinders water escape. This decreases the rate of formulate drying by about 30%, maximizing the ion diffusion process.[48]

A small batch of each formula was mixed in a 50 mL plastic beaker with ion exchange resin C-211 Na. As in the last experiment, the resin was prepared by first placing it into a ceramic mortar and pestle and grinding it into a fine powder. After mixing the treatments, several things were apparent. For one, all of the formulas were spongy and cake-like in consistency, enough so that they adhered to an upturned trowel, were easy to spread onto a substrate, and would retain a controlled shaped and area chosen by the operator. Secondly, in formulas 1, 2, and 3, water was separating from the mixtures and settling on top of the solid components. Formula 4 not only had the best consistency, it was the only mixture that retained its moisture over time. Based on these observations, a modified version of formula 4 was chosen for the second part of the experiment (see table 5.7). In this formulation, the high resin and Attapulgite content of sample 3 were added to formula 4:

Table 5.7: Composition of Resin Efficacy Formulation (weight parts)

Formula	Cation Exchange Resin	Cellulose Thickener Arbocel BWW40	Cellulose Thickener Vitacel L 601 FCC	Inorganic Additive Attapulgite	Water	Universal pH Indicator
4.2	70	8.40	25.60	13	165	0.5 mL for every 10 mL of water

For this experiment five versions of the formula were made, one for each type of resin in addition to a control. The control formula included everything but an ion exchange resin. Each went into a labeled 400 mL plastic beaker.

Also for the second part of the experiment, a limewash mixture had been prepared

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[47] Ibid., 328-329.
[48] Ibid., 330-331.

seven days earlier, consisting of approximately 12 ¾ cups of Graymont Type S hydrated lime was mixed with approximately 13 ½ cups hot water in a stainless steel bucket using a Milwaukee brand Magnum heavy duty 3/8-inch drill. This wash was left to stand for at least 12 hours before use.[49] Terracotta pavers were chosen as the substrate to both provide a porous base for the wash to adhere to while at the same time removing lime substrates from the initial testing equation. The 6-inch by 6-inch handmade terracotta tiles were rinsed with water and left to dry for at least 12 hours. The pavers were then divided into ten even sections using Polyken® brand tape. The sections measured roughly 1-inch wide by 2 7/8-inch long (see figure 5.6). The tiles were next sprayed with water and painted with one coat of limewash, using a Shur-Line seven-inch pad painter. After one hour this process was repeated so that the tiles possessed two applications of white limewash that formed one finish coat. After 24

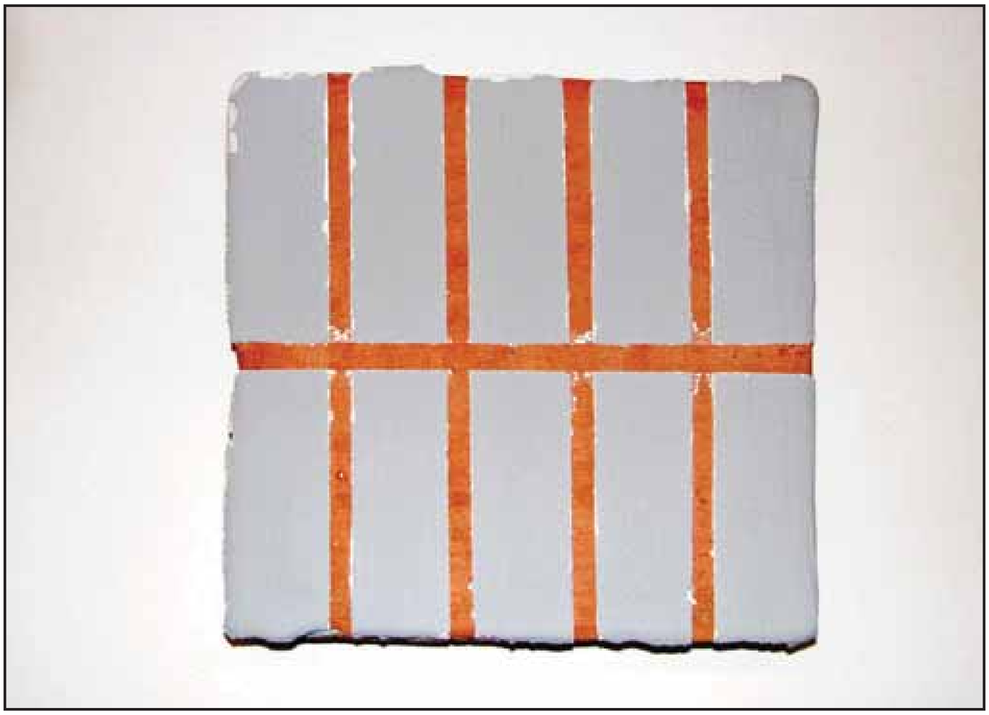

Figure 5.6: 6-inch by 6-inch terracotta tile covered with white limewash base and lamp black top coat. Tape removed to reveal ten sections (Source: C. Smith, 2009).

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[49] Limewash formula adapted from an article by Sarah Marie Jackson, Tye Botting and Mary Striegel, "Durability of Traditional and Modified Limewashes," *APT Bulletin* 38, no. 2/3 (2007): 21. Ratio tripled from original 4 ¼ c. hydrated lime to 4 ½ c. hot water.

hours, another two coats of limewash were added, also one hour apart. This time, however, the limewash was mixed with lamp black pigment to differentiate it from the first white coat. This was done to make it easier to visually quantify the amount of exchange and deterioration. After drying for four days, one terracotta tile was chosen. The tape was removed, leaving ten separate spaces available for testing (see figure 5.6). Five spaces were labeled for application of the five mixtures.

The formulas were applied five times, at one hour intervals (see figures 5.7 and 5.8). Hence every hour the terracotta tile was (1) unwrapped from the Saran Wrap, (2) photographed, (3) the moist resin was removed with a wooden clay tool, (4) the used resin was placed in a plastic sample holder and sealed with electrical tape for testing at a later date, (5) the exposed surface photographed, (6) the surface was sprayed with water, (7) a new application of the same resin applied to the same tile section, (8) photographed, and (9) resealed in Saran Wrap. Multiple applications should ensure that increasing quantities of ions are removed, rather than leaving a resin on so long that the resin's ion exchange capacity is expended. This is particularly important for ion exchangers, as the reaction occurs on the surface in contact with the substrate, ions do not travel throughout the treatment application. Once an application's surface is full of ions, it will not exchange anymore and the resin is considered exhausted. When that point is reach the resin must either be replaced, regenerated, or stirred until so that different resins come into contact with the surface. The tile is sprayed each time too, guaranteeing the resin a wet surface to react with.

Before, during, and after the experiment photographs were taken of the tile with a Canon PowerShot S5 IS. At the end of the experiment, the treated area from each sample was examined with reflected light under the Leica MZ16 stereomicroscope at 7.1x and 115x magnification with quartz-halogen illumination using a Leica KL2500 LCD, 3200K, and additional Volpi Intralux 5000-1 dual gooseneck fiber optics to examine the surfaces after treatment. The samples were also examined under fiber optic raking light alone, to better examine topographical changes (such as pitting and disaggregation). If the samples display different degrees of deterioration, it can be assumed that the unique component in their treatment (in this case the ion exchange resin) is contributing to this change. Photomicrographs were taken with a Nikon DSFi1 digital camera and NIS Elements computer software (see table 5.8). Overall images were taken at 7.1x magnification.

The purpose of these examinations is to determine whether or not the resins have any effect on limewash, whether the type of resin has an effect (i.e. different resins exchange differently), to determine an approximate number of applications required to remove limewash layers, and to determine whether or not the resins have more effect than a tradition cellulose poultice (the control).

Appendix B contains additional product and supplier information. Appendix C contains the Material Safety Data Sheets for the ion exchange resins used.

5.4.3 RESULTS

When the resin formulations were applied to the limewashed terracotta substrate, sample 1 contained C-211 H. As expected the formulation was a reddish-pink, indicating an acidic mixture with a pH around 4.0. When removed every hour, the resin retained its pink color, indicating little or no change in pH, even after the final treatment. Sample 2 contained C-211 Na, whose pale green coloring suggested a pH between 7.0 and 8.0. The mixture appeared slightly whiter at the end of each hour, which could be due to a loss of moisture or an exchange of calcium ions. Sample 3, containing CNP 80, went on as a paler pink than sample 1, perhaps indicating that the formula is slightly less acidic. Nonetheless, the removed resin contains a definite white layer on the side that was in contact with the limewash. This is the strongest evidence that calcium ions were exchanged, as the particles only appear on the side of contact, they are a different color from the resin, and it does not appear on the other formulas. Sample 4 contained TP 207, whose formulate went on purple, suggesting a pH

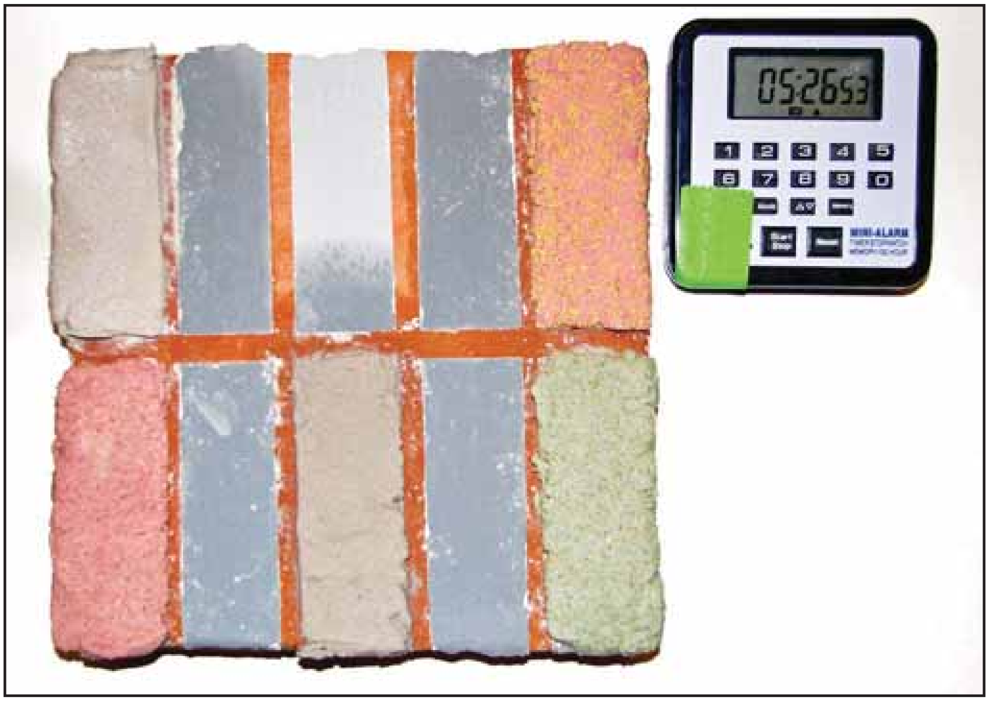

Figure 5.7: Tile covered with fresh resin formulations. Counterclockwise from bottom: C-211 H, control, C-211 Na, CNP 80, TP 207 (Source: C. Smith, 2009).

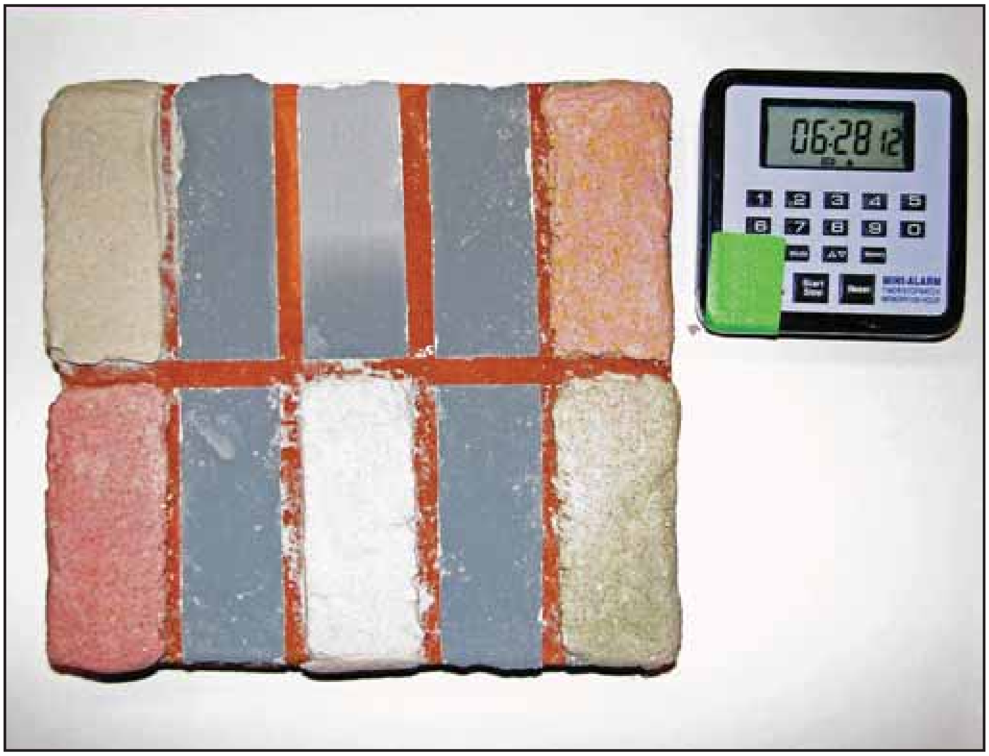

Figure 5.8: Used resins exposed after one hour (Source: C. Smith, 2009).

between 9.5 and 10.0. As it dried it became whiter, no other phenomena were observed. Finally the control, sample 5, appears grey-purple, suggesting a pH between 9.0 and 10.0. When this dried, it turned an off-shade of white.

Each hour the tile was examined by sight, and each time no changes were observed. The surface retained its original appearance. By the end of the experiment, three of the five areas tested looked as if their might be some microscopic changes in texture. After viewing the areas under a stereomicroscope at 7.1x and 115x magnification (see Appendix A, Table 5.8), the following observations were made: (1) sample 1 looked extremely grainy, with possible signs of pitting, (2) sample 2 exhibited colorful staining that coincides with a loss of material, (3) sample 3 appeared extremely grainy, with possible signs of pitting, (4) sample 4 contained a few grains but was largely unchanged, (5) sample 5's results resembled those of sample 4. (See table 5.8).

5.4.4 DISCUSSION

Put in the context of the first experiment, the results for formulas 1, 3, and 5 are not surprising. Formulas 1 and 3 contain resins in the hydrogen-form, making them slightly acidic and stronger than the other resins. Both caused the limewash surface to deteriorate, but formula 3, which contained CNP 80, also carried visible quantities of ions away in the removed mixture. This fits with the results of the first experiment, which determined that resin 3 had the greatest effect on limewash. The results for the control, formula 5, are also not surprising. Without the presence of an ion exchange resin, no significant deterioration was caused in the first experiment. The results appear to be confirmed in the second test, even with the inclusion of additives.

Formulas 2 and 4, on the other hand, performed differently in tests one and two. This could be due to operator error and imperfections caused during sample preparation, or it could be related to the formula additives. It could be that the additives allowed the C-211

Na in formula 2 to retain more water for longer periods of time, facilitating the ion exchange process. Meanwhile formula 4, containing TP 207, was inhibited or interfered with by one or more additives in the mixture.

None of the formulas produced enough deterioration to make limewash cleaning by ion exchange resin a practical option. In their current formulas, the resins might be useful in treating very fine lime haze and in areas where a very gradual, controlled cleaning is required. Further testing is necessary to determine which additives and mixture ratios best maximize the ion exchange process.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 SUMMARY

The field of ion exchange technology promises to continue to bring new technologies and new opportunities for less destructive cleaning and testing methods. Applications on a wider scale for architectural conservation need to further explore the ion exchange process, where it takes place and how to make it more efficient. Wall painting and plaster conservators should first look at the work of their colleagues in the fields of stone and metal conservation, as these are the pioneers of heritage-related ion exchange. They have developed methods for quantifying ion removal, improving rheological properties, and have generally developed a frame of reference that could prove invaluable to researchers contemplating such a treatment program.

The field is young but promising, the high degree of control afforded by the limited reactive surface, the ability to create "tailor-made" resins, the possibilities for charging and recharging resins, among other things, make the technology attractive. However, a lack of literature detailing results and processes, and an almost complete lack of literature reviewing previous treatments, proves that there is still much work to be done.

6.2 BENEFITS

There are many reasons why ion exchange cleaning should be explored:

1. No material is lost from the reaction itself – the resin is insoluble in water and what is used can be regenerated and reused. This may be a cost-saver in the long term.
2. The resins are relatively non-hazardous and can be easily handled and transported by conservators.
3. The exchange reaction only occurs at the interface between the ion exchange resin and the substrate, thus it should not penetrate into the material being treated.

4. The dwell time, rheological additives, and limited reactivity depth all give conservators a large degree of control over the cleaning process.
5. When applied to limewash, acidic resins should be somewhat neutralized.
6. The resins can double as consolidators and desulfators, reducing the need to introduce extraneous chemicals and treatments to a material.
7. When properly chosen, the resin can replace detrimental ions with innocuous ones.

6.3 DISADVANTAGES

On the other hand, there are a number of issues that accompany ion exchange cleaning:

1. The resins only act on the surface they are in contact with, so in situations where highly concentrated substances are being treated it may take multiple treatments to penetrate far enough.
2. The ion exchange reaction is slow, treatments require dwell time, during which they need to remain moist, and repeated applications.
3. The ion exchange resins can be quickly rendered ineffective.
4. The resins may be too acidic or alkaline for sensitive historic finishes.
5. The exchangeable counterion needs to be chosen carefully to prevent the creation of undesirable byproducts, such as insoluble carbonate layers or strong sulfuric acid.
6. The resins may be too costly, time-consuming, and require pre-conditioning to be effective.

6.4 RECOMMENDATIONS FOR FUTURE RESEARCH

In the future, research should incorporate those international studies that were not translated or located for this thesis. Laboratory testing should be done at a larger-scale to conclusively determine what effect ion exchange resins have on limewash. In these new trials, changes in temperature, RH, and resin type should be included as variables. When choosing a resin, the researcher should be aware of the matrix type and size, the counterion charge, the resin strength, and the pH. The ion exchange resin testing in this study demonstrates the need to, at least when treating calcium carbonate, investigate resins with higher porosities and less reticulation. Researchers should also experiment with preconditioning the resins to neutralize the pH and increase the exchange capacity before applying the treatment to a substrate. Formulate additives should be re-examined to determine if they interfere in any way with the exchange of calcium ions, perhaps being included in the exchange reaction themselves.

Successful laboratory tests will have to be conducted before exporting any applications to Iglesia San José. Laboratory testing should include samples with a plaster substrate, and microscopy or SEM should be utilized to examine changes in the limewash layer, the design layer, and the plaster substrate. Care should be taken to ensure that the resin is not degrading the substrate. The pH of the wall should be monitored, and test areas checked over a period of time to ensure that not products are introduced into the wall, that there is no discoloration. Other methods of verifying chemical efficacy and/or potential harm should be explored, especially those that are relatively easy to use to monitor treatments.

When field testing gets underway, cost- and time-analyses should be included in the treatment regimen. Conservators can calculate the amount of surface area cleaned by one person. Test areas of a standardized size should be chosen, a standard goal should be established (such as the removal of one lime layer), and the amount of resin it takes to obtain the desired result should be noted. These calculations, in addition to confirmations of ease of use and ion exchange capacity, should enable conservators to estimate the cost- and time-effectiveness.

Direct comparisons should be made to other mechanical and chemical cleaning methods. From small-scale testing, time and cost estimates should be extrapolated and compared to other cleaning methods for areas of a similar size. Tests should be applied to a variety of limewash layers, in different thicknesses and different conditions resembling those found on the Rosario murals.

When conducting these experiments, evaluation criteria similar to the one utilized in this report should be established. Effectiveness should be measured against these principles, including:

- ✓ No resin or deleterious byproduct should be left behind on the substrate.
- ✓ The time and mode of application should allow the operator to conduct an efficient and complete removal of limewash.
- ✓ The application should be under the full control of the operator.
- ✓ The resin should not harm the decorative finishes or the substrate.

6.5 CONCLUSION

Numerous heritage sites the world over are dealing with issues akin to those found at Iglesia San José. Meanwhile, conservators continue to strive for less destructive, less invasive, and more sustainable treatments. The ion exchange method is as yet a comparatively untested technique for cleaning painted and plastered surfaces. Nevertheless its versatile nature would suggest that, much like the murals it cleans, is has great promise concealed within its bounds.

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APPENDIX A

PHOTOMICROGRAPHS

TABLE 5.1: R.1 C-211 H

Formula Tested: 7 g C-211 H, 2 mL water, 1 mL Universal pH Indicator System

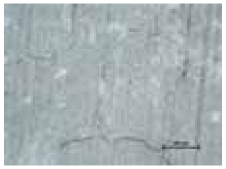
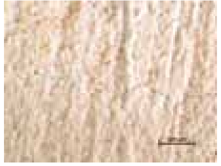
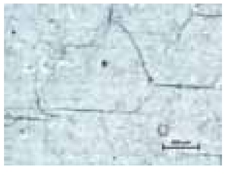
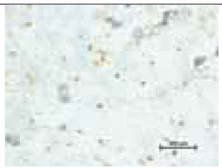
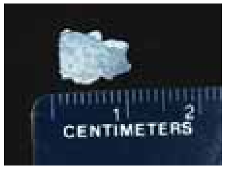
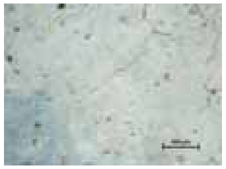
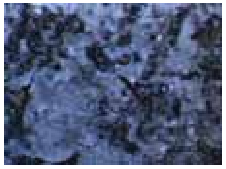
CUMULATIVE DWELL TIME (HR)	RESIN 7.1 X	SIDE 1 OVERALL 12.5 X	SIDE 1 115 X	SIDE 1 RAKING 115 X	SIDE 2 OVERALL 12.5 X	SIDE 2 115 X	SIDE 2 RAKING 115 X
0				**N/A**			**N/A**
0.5				**N/A**			**N/A**
1.5							
13.5							
37.5							

TABLE 5.2: R.2 C-211 NA
Formula Tested: 7 g C-211 Na, 2 mL water, 1 mL Universal pH Indicator System

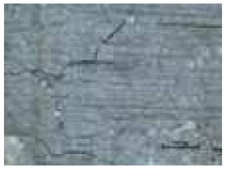
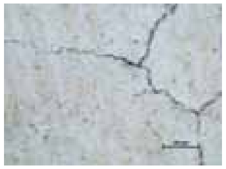
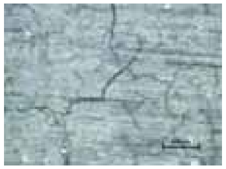
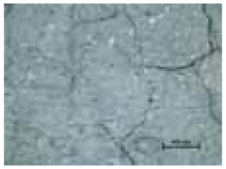
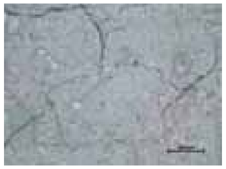
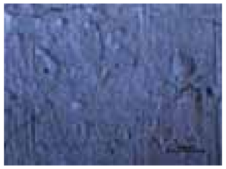
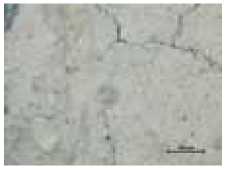
CUMULATIVE DWELL TIME (HR)	RESIN 7.1 X	SIDE 1 OVERALL 12.5 X	SIDE 1 115 X	SIDE 1 RAKING 115 X	SIDE 2 OVERALL 12.5 X	SIDE 2 115 X	SIDE 2 RAKING 115 X
0				**N/A**			**N/A**
0.5				**N/A**			**N/A**
1.5							
13.5							
37.5							

TABLE 5.3: R.3 CNP-80

Formula Tested: 7 g CNP-80, 4 mL water, 1 mL Universal pH Indicator System

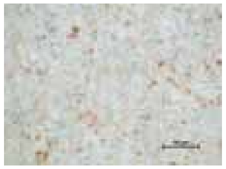
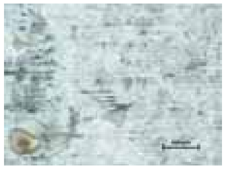
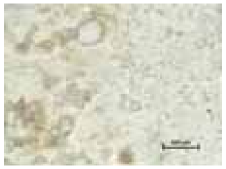
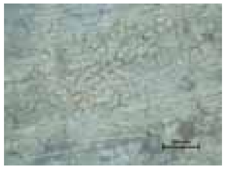
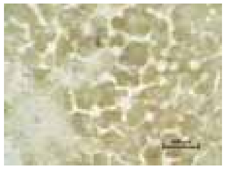
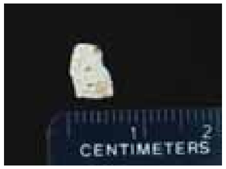
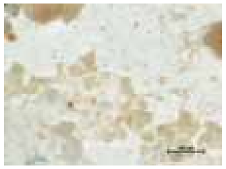
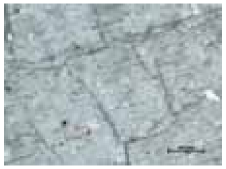
CUMULATIVE DWELL TIME (HR)	RESIN 7.1 x	SIDE 1 OVERALL 12.5 x	SIDE 1 115 x	SIDE 1 RAKING 115 x	SIDE 2 OVERALL 12.5 x	SIDE 2 115 x	SIDE 2 RAKING 115 x
0				**N/A**			**N/A**
0.5				**N/A**			**N/A**
1.5							
13.5							
37.5							

TABLE 5.4: R.4 TP-207
Formula Tested: 7 g TP-207, 2 mL water, 1 mL Universal pH Indicator System

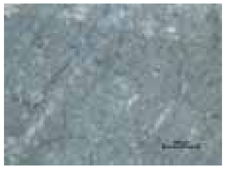
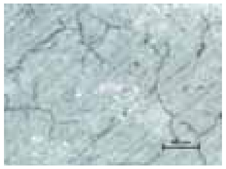
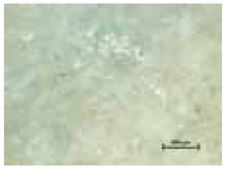
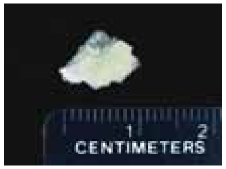
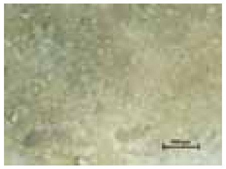
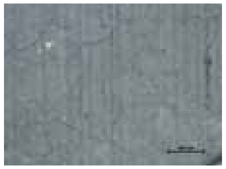
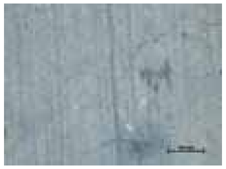
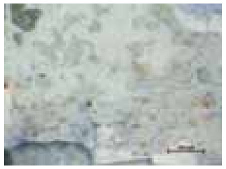
CUMULATIVE DWELL TIME (HR)	RESIN 7.1 x	SIDE 1 OVERALL 12.5 x	SIDE 1 115 x	SIDE 1 RAKING 115 x	SIDE 2 OVERALL 12.5 x	SIDE 2 115 x	SIDE 2 RAKING 115 x
0				**N/A**			**N/A**
0.5				**N/A**			**N/A**
1.5							
13.5							
37.5							

TABLE 5.5: C.5 CONTROL
Formula Tested: 2 mL water, 1 mL Universal pH Indicator System

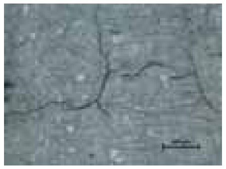
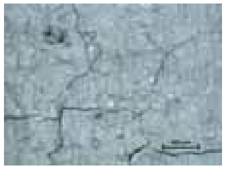
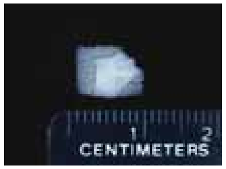
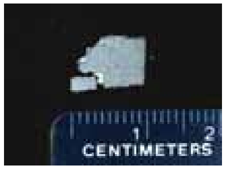
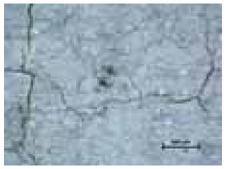
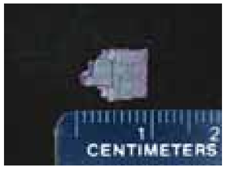
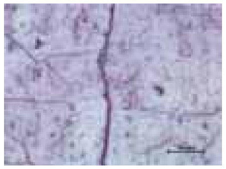
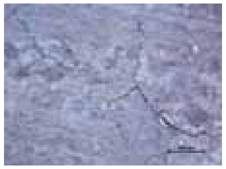
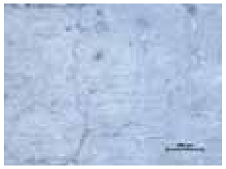
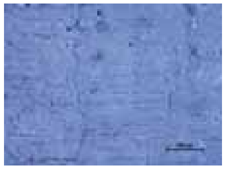
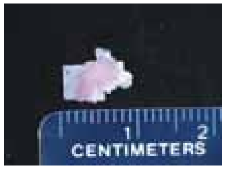
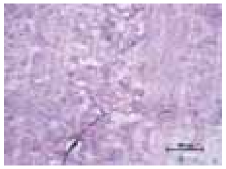
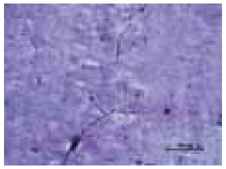
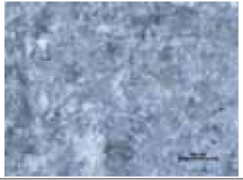
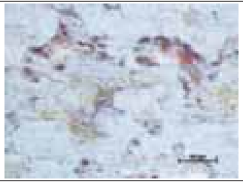
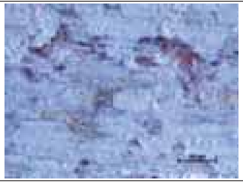
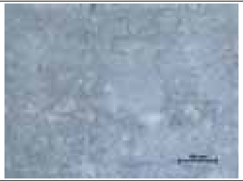
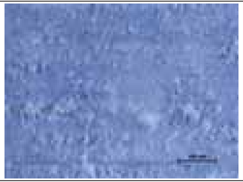
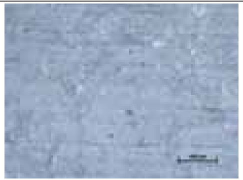
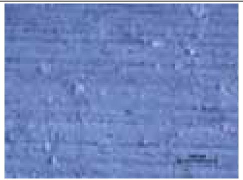
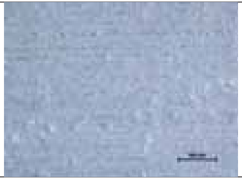
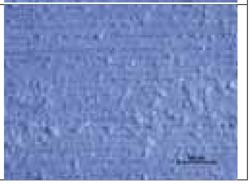
CUMULATIVE DWELL TIME (HR)	RESIN 7.1 x	SIDE 1 OVERALL 12.5 x	SIDE 1 115 x	SIDE 1 RAKING 115 x	SIDE 2 OVERALL 12.5 x	SIDE 2 115 x	SIDE 2 RAKING 115 x
0				**N/A**			**N/A**
0.5				**N/A**			**N/A**
1.5							
13.5	**N/A**						
37.5							

TABLE 5.8: FORMULA EFFICACY COMPARISON AFTER SIX HOURS
Formula Tested: 14 g Resin, 2 g Arbocel BWW40, 5 g Vitacel L 601 FCC, 3 g Attapulgite, 33 mL water, 2 mL Universal pH Indicator System

FORMULA	RESIN AFTER ONE HOUR 7.1 x	OVERALL 7.1 x	OVERALL RAKING 7.1 x	DETAIL 115 x	DETAIL RAKING 115 x
1 – C-211 H					
2 – C-211 Na					
3 – CNP 80					
4 – TP 207					
5 - Control					

APPENDIX B

MATERIAL AND SUPPLIERS

Englehard Minerals and Chemicals Corp.
Attapulgite E 1890
Menlo Park
Edison, NJ 08817

Fisher Science Education
Deionized Water
4500 Turnberry Drive
Hanover, Il 60133
Tel: 1-800-955-1177

Fisher Scientific
Universal pH Indicator Solution
One Reagent Lane
Fair Lawn, NJ 07410
Tel: 201-796-7100
Fax: 201-796-7102
www.fishersci.com

Graymont Dolime (OH) Inc.
Dolomitic Hydrate Type S Lime
21880 West State
Route 163
Genoa, Ohio 43430-0158
Tel: 450-449-2262
www.graymont.com

Home Depot
Graymont Lime, Shur-Line 7" Pad Painter
21880 West 1651 S Columbus Blvd
Philadelphia, PA 19148
Tel: 215-218-0600

J.J. Rettenmaier USA LP
Arbocel® BWW 40, Vitacel® L601 FCC
16369 US 131 Highway
Schoolcraft, Michigan 49087
Tel: 269-679-2340
Fax: 269-679-2364
Toll Free: 877-895-4099

LANXESS Corporation
Sybron Chemicals, Inc.
Lewatit® Ion Exchange Resins
Phil Fatula
Market Manager
Chemical Processing Market Segment
200 Birmingham Road
Birmingham, NJ 08011
Tel: 800-678-0020
Fax: +1-609-894-8641
Email: IonExchange@SybronChemicals.com

PAVÉ Tile & Stone, Inc.
Handmade Terra Cotta Tile, 6" x 6"
10 West Street West
Hatfield, MA 01088
Tel: 413-247-7677
Fax: 413-247-8383
http://www.pavetile.com/

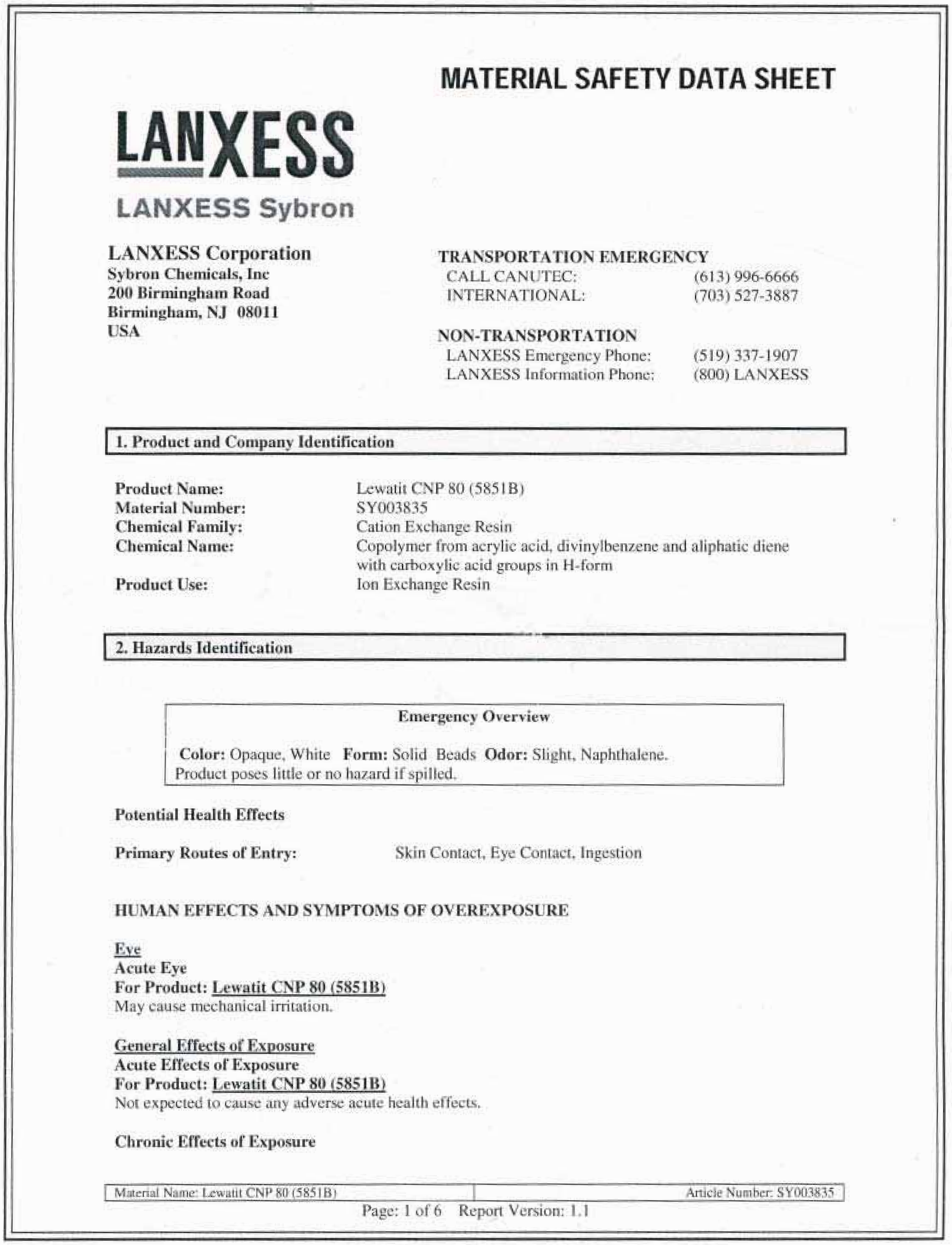
Polyken® Covalence Adhesives
Berry Plastics – Tapes & Coatings Division
Franklin, KY 42134
www.berryplastics.com

APPENDIX B - MATERIAL AND SUPPLIERS

Siemens Water Technologies Corp.
USF™ Brand Ion Exchange Resins
Greg Bachman
Director of Operations
181 Thorn Hill Road
Warrendale, PA 15086
Tel: 815-877-3046
Customer Service: (800) 466-7873
Tech. Support: (800) 875-7873 ext. 5000
http://www.siemens.com/water

APPENDIX C

MATERIAL SAFETY DATA SHEETS



MATERIAL SAFETY DATA SHEET

LANXESS

LANXESS Sybron

LANXESS Corporation
Sybron Chemicals, Inc
200 Birmingham Road
Birmingham, NJ 08011
USA

TRANSPORTATION EMERGENCY

CALL CANUTEC:	(613) 996-6666
INTERNATIONAL:	(703) 527-3887

NON-TRANSPORTATION

LANXESS Emergency Phone:	(519) 337-1907
LANXESS Information Phone:	(800) LANXESS

1. Product and Company Identification

Product Name:	Lewatit CNP 80 (5851B)
Material Number:	SY003835
Chemical Family:	Cation Exchange Resin
Chemical Name:	Copolymer from acrylic acid, divinylbenzene and aliphatic diene with carboxylic acid groups in H-form
Product Use:	Ion Exchange Resin

2. Hazards Identification

Emergency Overview

Color: Opaque, White **Form:** Solid Beads **Odor:** Slight, Naphthalene.
Product poses little or no hazard if spilled.

Potential Health Effects

Primary Routes of Entry: Skin Contact, Eye Contact, Ingestion

HUMAN EFFECTS AND SYMPTOMS OF OVEREXPOSURE

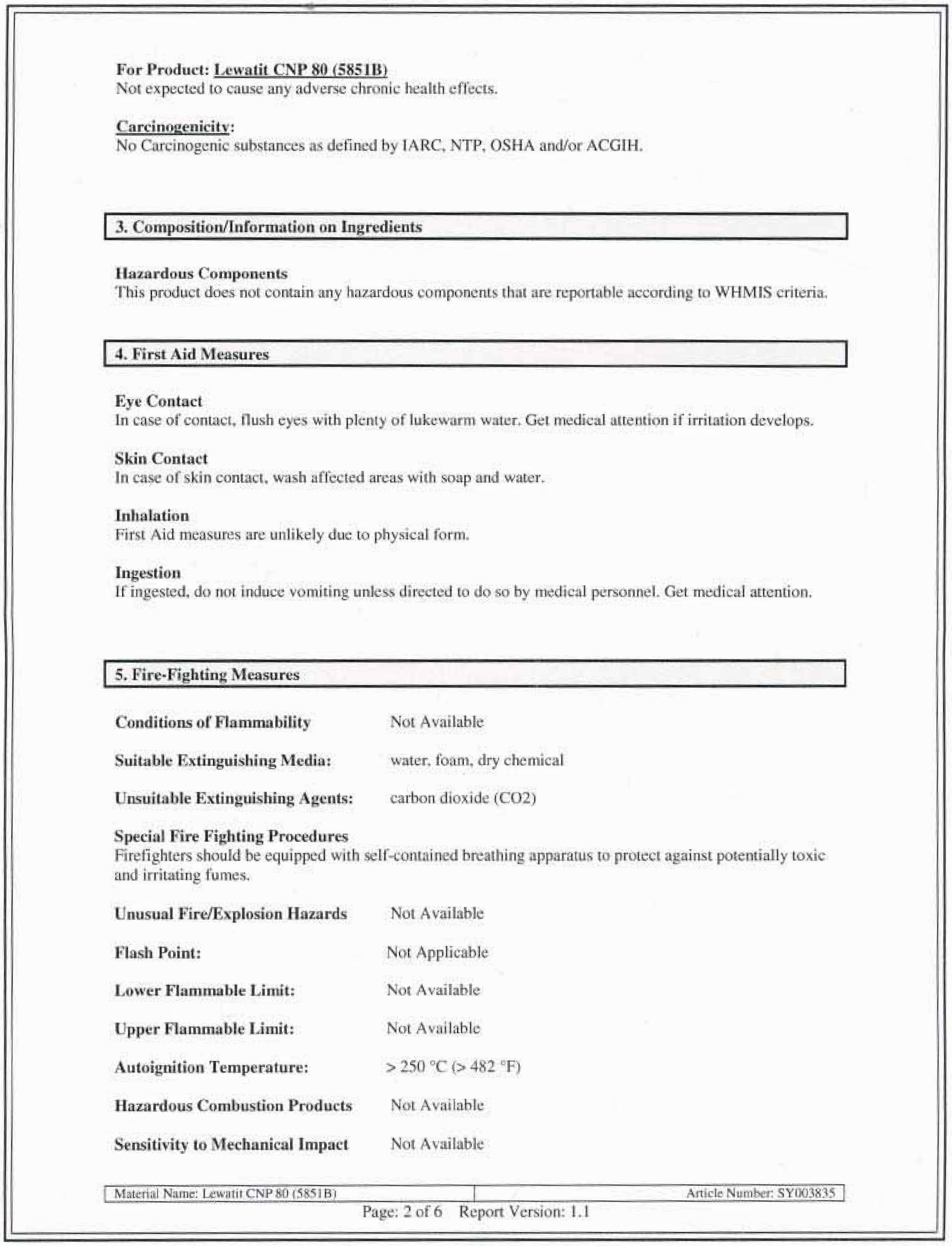
Eye
Acute Eye
For Product: Lewatit CNP 80 (5851B)
May cause mechanical irritation.

General Effects of Exposure
Acute Effects of Exposure
For Product: Lewatit CNP 80 (5851B)
Not expected to cause any adverse acute health effects.

Chronic Effects of Exposure

Material Name: Lewatit CNP 80 (5851B) Article Number: SY003835

Page: 1 of 6 Report Version: 1.1



For Product: Lewatit CNP 80 (5851B)
Not expected to cause any adverse chronic health effects.

Carcinogenicity:
No Carcinogenic substances as defined by IARC, NTP, OSHA and/or ACGIH.

3. Composition/Information on Ingredients

Hazardous Components
This product does not contain any hazardous components that are reportable according to WHMIS criteria.

4. First Aid Measures

Eye Contact
In case of contact, flush eyes with plenty of lukewarm water. Get medical attention if irritation develops.

Skin Contact
In case of skin contact, wash affected areas with soap and water.

Inhalation
First Aid measures are unlikely due to physical form.

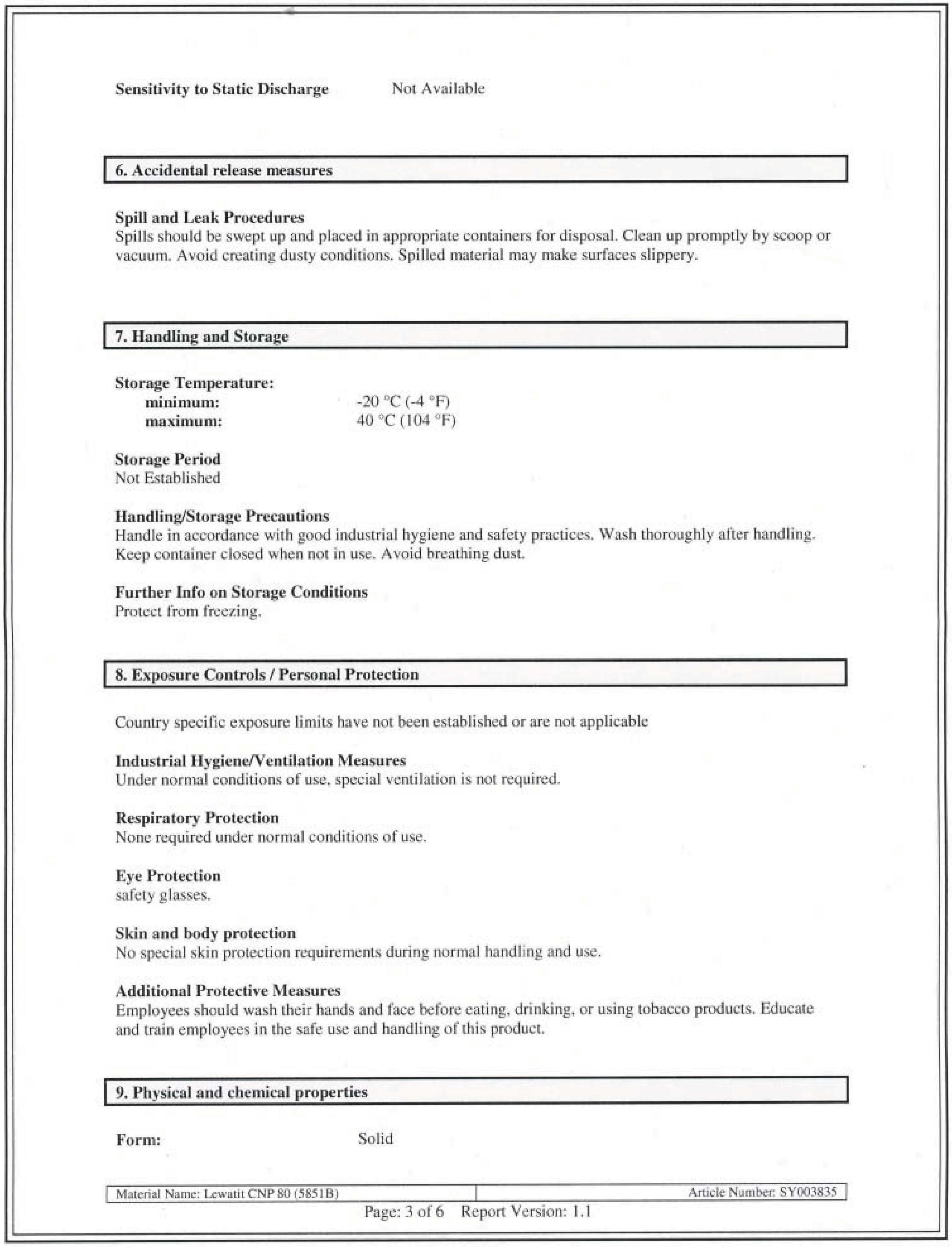
Ingestion
If ingested, do not induce vomiting unless directed to do so by medical personnel. Get medical attention.

5. Fire-Fighting Measures

Conditions of Flammability	Not Available
Suitable Extinguishing Media:	water, foam, dry chemical
Unsuitable Extinguishing Agents:	carbon dioxide (CO2)

Special Fire Fighting Procedures
Firefighters should be equipped with self-contained breathing apparatus to protect against potentially toxic and irritating fumes.

Unusual Fire/Explosion Hazards	Not Available
Flash Point:	Not Applicable
Lower Flammable Limit:	Not Available
Upper Flammable Limit:	Not Available
Autoignition Temperature:	> 250 °C (> 482 °F)
Hazardous Combustion Products	Not Available
Sensitivity to Mechanical Impact	Not Available



Sensitivity to Static Discharge Not Available

6. Accidental release measures

Spill and Leak Procedures
Spills should be swept up and placed in appropriate containers for disposal. Clean up promptly by scoop or vacuum. Avoid creating dusty conditions. Spilled material may make surfaces slippery.

7. Handling and Storage

Storage Temperature:
minimum: -20 °C (-4 °F)
maximum: 40 °C (104 °F)

Storage Period
Not Established

Handling/Storage Precautions
Handle in accordance with good industrial hygiene and safety practices. Wash thoroughly after handling. Keep container closed when not in use. Avoid breathing dust.

Further Info on Storage Conditions
Protect from freezing.

8. Exposure Controls / Personal Protection

Country specific exposure limits have not been established or are not applicable

Industrial Hygiene/Ventilation Measures
Under normal conditions of use, special ventilation is not required.

Respiratory Protection
None required under normal conditions of use.

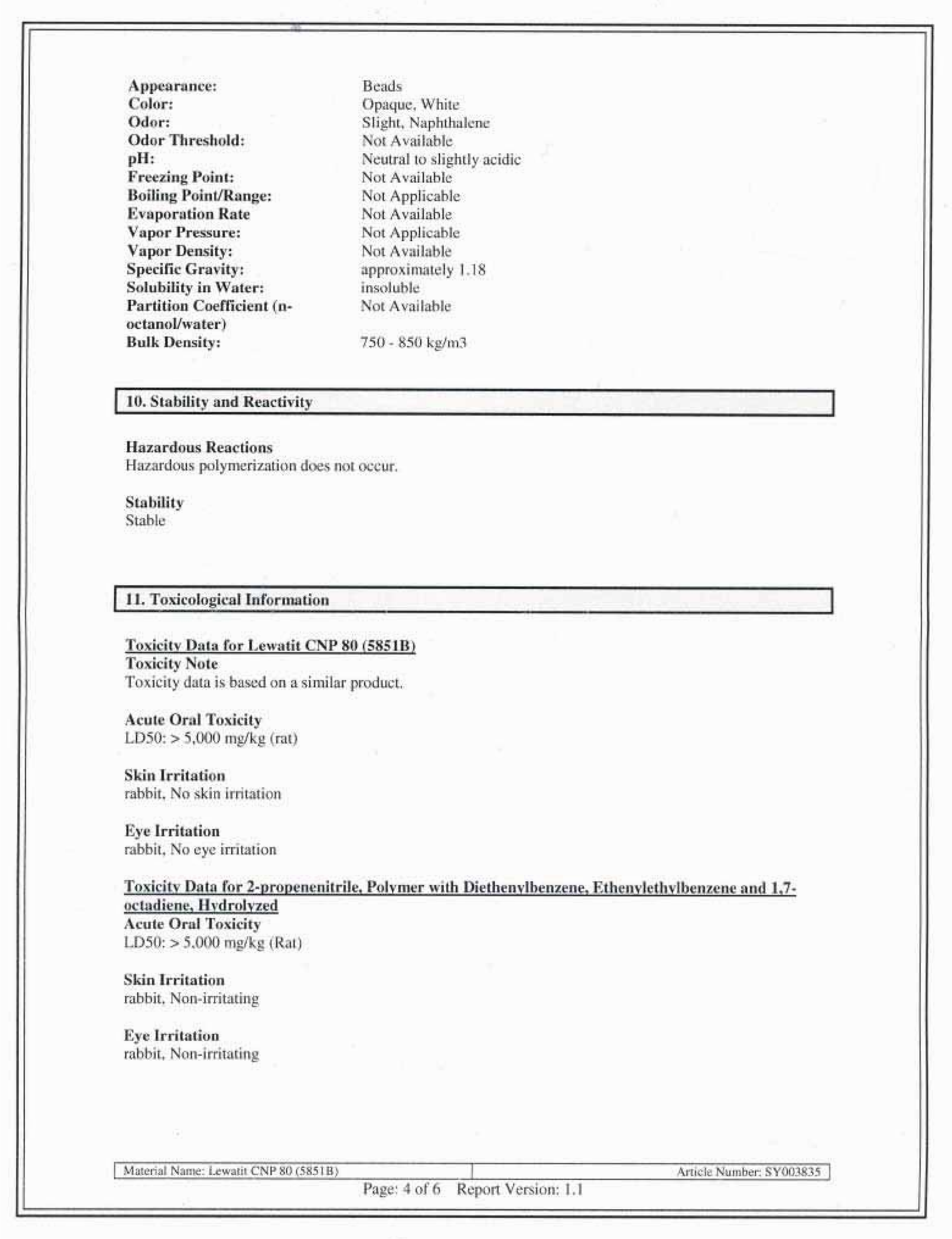
Eye Protection
safety glasses.

Skin and body protection
No special skin protection requirements during normal handling and use.

Additional Protective Measures
Employees should wash their hands and face before eating, drinking, or using tobacco products. Educate and train employees in the safe use and handling of this product.

9. Physical and chemical properties

Form: Solid



Appearance:	Beads
Color:	Opaque, White
Odor:	Slight, Naphthalene
Odor Threshold:	Not Available
pH:	Neutral to slightly acidic
Freezing Point:	Not Available
Boiling Point/Range:	Not Applicable
Evaporation Rate	Not Available
Vapor Pressure:	Not Applicable
Vapor Density:	Not Available
Specific Gravity:	approximately 1.18
Solubility in Water:	insoluble
Partition Coefficient (n-octanol/water)	Not Available
Bulk Density:	750 - 850 kg/m3

10. Stability and Reactivity

Hazardous Reactions
Hazardous polymerization does not occur.

Stability
Stable

11. Toxicological Information

Toxicity Data for Lewatit CNP 80 (5851B)
Toxicity Note
Toxicity data is based on a similar product.

Acute Oral Toxicity
LD50: > 5,000 mg/kg (rat)

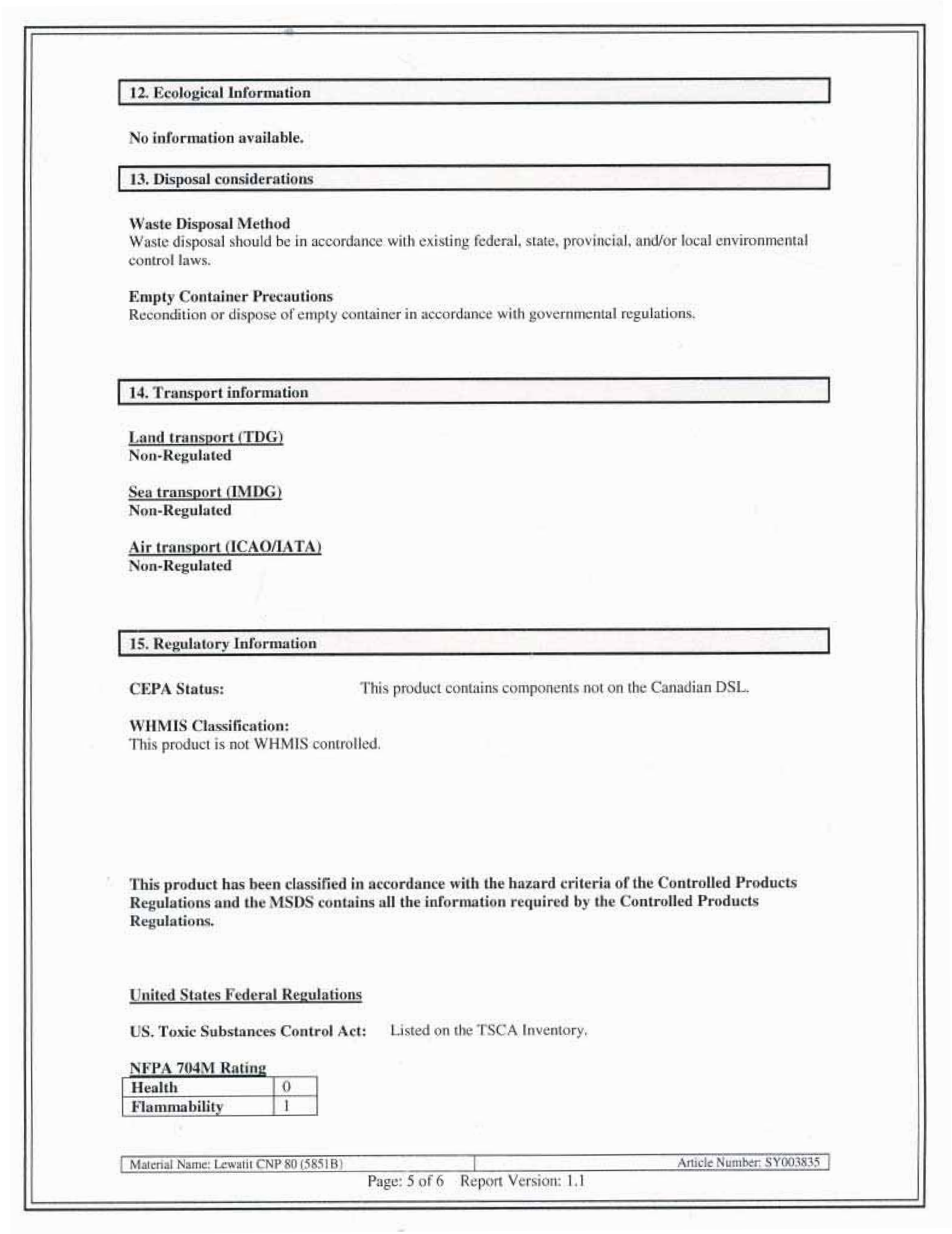
Skin Irritation
rabbit, No skin irritation

Eye Irritation
rabbit, No eye irritation

Toxicity Data for 2-propenenitrile, Polymer with Diethenylbenzene, Ethenylethylbenzene and 1,7-octadiene, Hydrolyzed
Acute Oral Toxicity
LD50: > 5,000 mg/kg (Rat)

Skin Irritation
rabbit, Non-irritating

Eye Irritation
rabbit, Non-irritating



12. Ecological Information

No information available.

13. Disposal considerations

Waste Disposal Method
Waste disposal should be in accordance with existing federal, state, provincial, and/or local environmental control laws.

Empty Container Precautions
Recondition or dispose of empty container in accordance with governmental regulations.

14. Transport information

Land transport (TDG)
Non-Regulated

Sea transport (IMDG)
Non-Regulated

Air transport (ICAO/IATA)
Non-Regulated

15. Regulatory Information

CEPA Status: This product contains components not on the Canadian DSL.

WHMIS Classification:
This product is not WHMIS controlled.

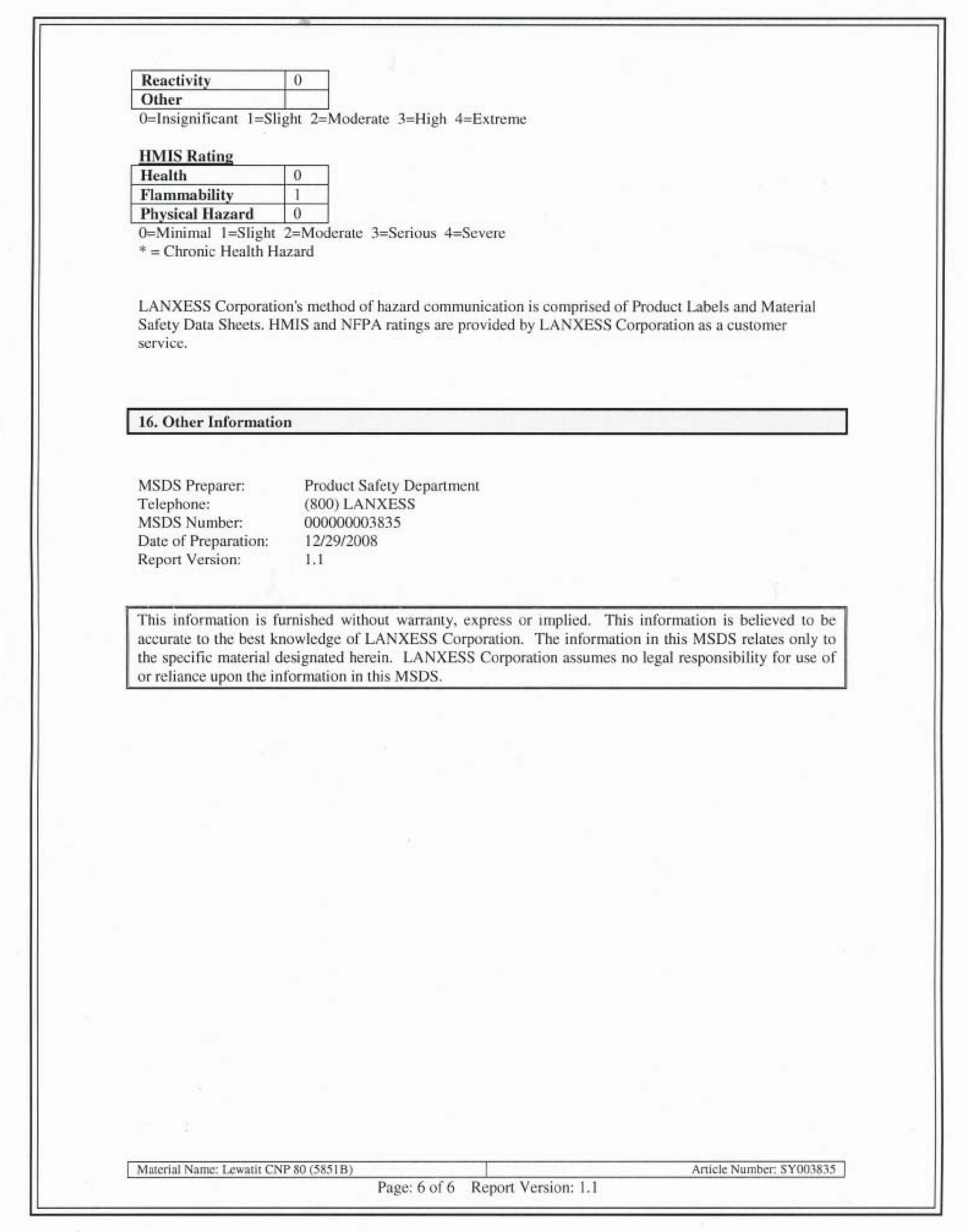
This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations and the MSDS contains all the information required by the Controlled Products Regulations.

United States Federal Regulations

US. Toxic Substances Control Act: Listed on the TSCA Inventory.

NFPA 704M Rating

Health	0
Flammability	1



Reactivity	0
Other	

0=Insignificant 1=Slight 2=Moderate 3=High 4=Extreme

HMIS Rating

Health	0
Flammability	1
Physical Hazard	0

0=Minimal 1=Slight 2=Moderate 3=Serious 4=Severe
* = Chronic Health Hazard

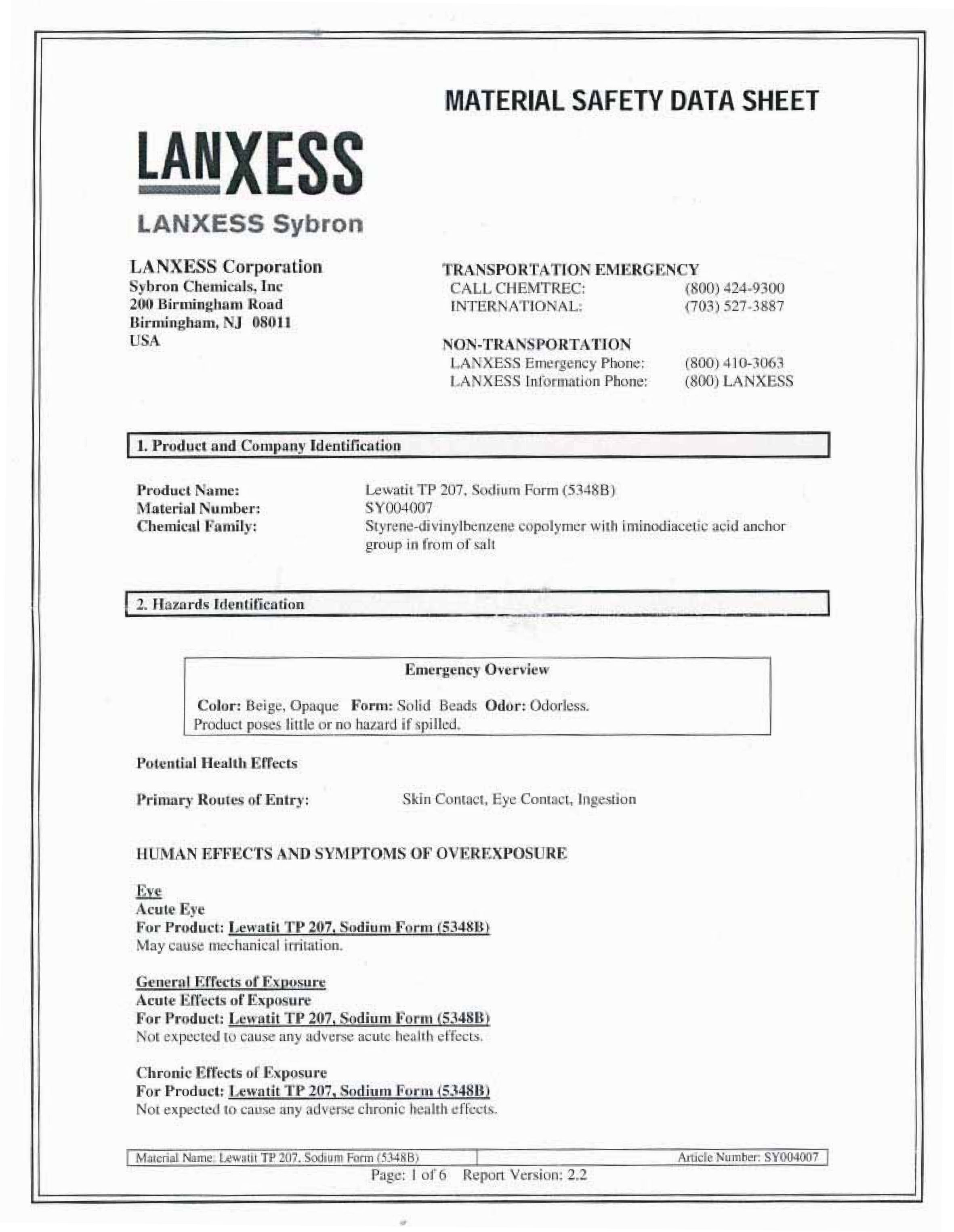
LANXESS Corporation's method of hazard communication is comprised of Product Labels and Material Safety Data Sheets. HMIS and NFPA ratings are provided by LANXESS Corporation as a customer service.

16. Other Information

MSDS Preparer:	Product Safety Department
Telephone:	(800) LANXESS
MSDS Number:	000000003835
Date of Preparation:	12/29/2008
Report Version:	1.1

This information is furnished without warranty, express or implied. This information is believed to be accurate to the best knowledge of LANXESS Corporation. The information in this MSDS relates only to the specific material designated herein. LANXESS Corporation assumes no legal responsibility for use of or reliance upon the information in this MSDS.

APPENDIX C - MATERIAL SAFETY DATA SHEETS



MATERIAL SAFETY DATA SHEET

LANXESS

LANXESS Sybron

LANXESS Corporation
Sybron Chemicals, Inc
200 Birmingham Road
Birmingham, NJ 08011
USA

TRANSPORTATION EMERGENCY

CALL CHEMTREC:	(800) 424-9300
INTERNATIONAL:	(703) 527-3887

NON-TRANSPORTATION

LANXESS Emergency Phone:	(800) 410-3063
LANXESS Information Phone:	(800) LANXESS

1. Product and Company Identification

Product Name:	Lewatit TP 207, Sodium Form (5348B)
Material Number:	SY004007
Chemical Family:	Styrene-divinylbenzene copolymer with iminodiacetic acid anchor group in from of salt

2. Hazards Identification

Emergency Overview

Color: Beige, Opaque **Form:** Solid Beads **Odor:** Odorless.
Product poses little or no hazard if spilled.

Potential Health Effects

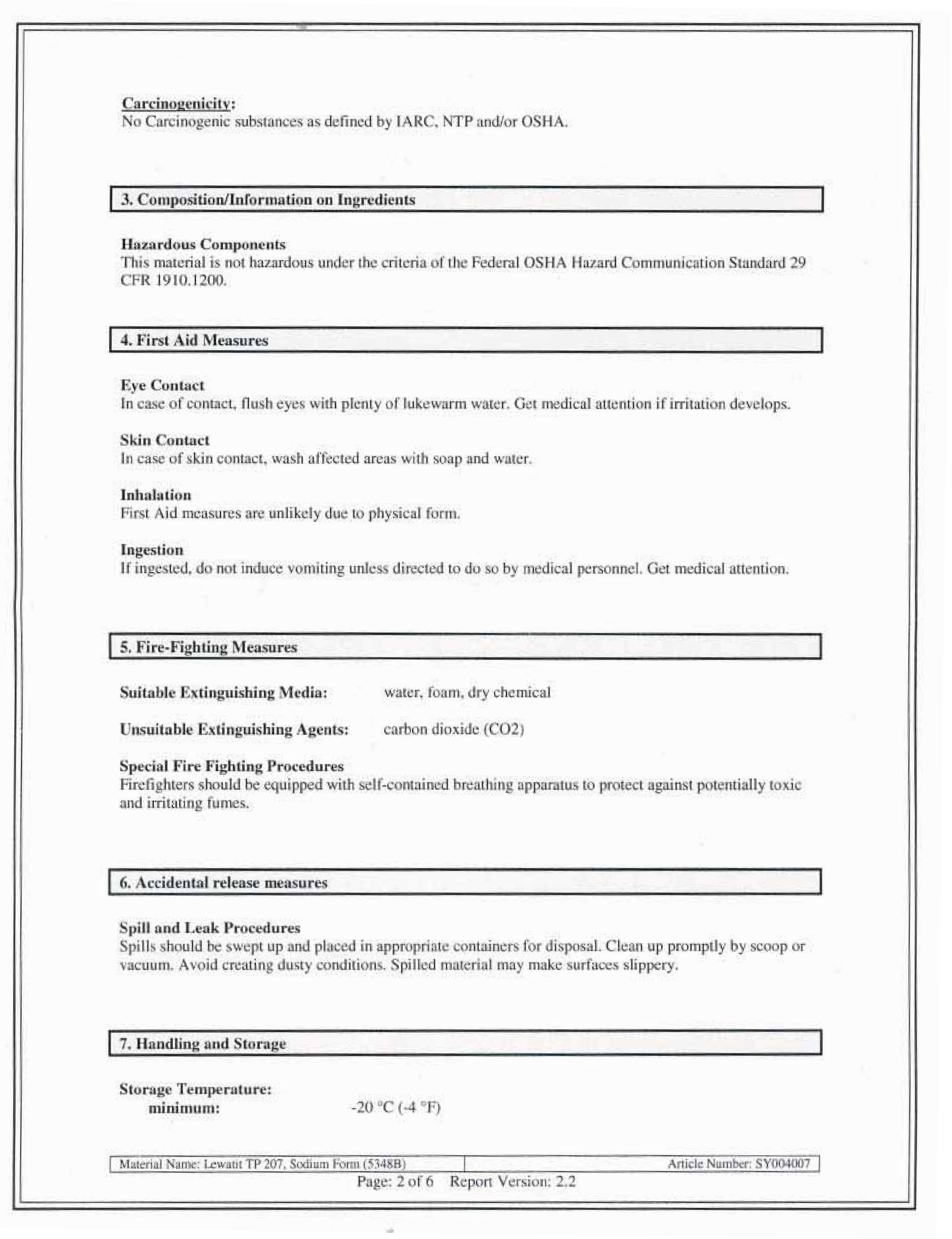
Primary Routes of Entry: Skin Contact, Eye Contact, Ingestion

HUMAN EFFECTS AND SYMPTOMS OF OVEREXPOSURE

Eye
Acute Eye
For Product: Lewatit TP 207, Sodium Form (5348B)
May cause mechanical irritation.

General Effects of Exposure
Acute Effects of Exposure
For Product: Lewatit TP 207, Sodium Form (5348B)
Not expected to cause any adverse acute health effects.

Chronic Effects of Exposure
For Product: Lewatit TP 207, Sodium Form (5348B)
Not expected to cause any adverse chronic health effects.



Carcinogenicity:
No Carcinogenic substances as defined by IARC, NTP and/or OSHA.

3. Composition/Information on Ingredients

Hazardous Components
This material is not hazardous under the criteria of the Federal OSHA Hazard Communication Standard 29 CFR 1910.1200.

4. First Aid Measures

Eye Contact
In case of contact, flush eyes with plenty of lukewarm water. Get medical attention if irritation develops.

Skin Contact
In case of skin contact, wash affected areas with soap and water.

Inhalation
First Aid measures are unlikely due to physical form.

Ingestion
If ingested, do not induce vomiting unless directed to do so by medical personnel. Get medical attention.

5. Fire-Fighting Measures

Suitable Extinguishing Media:	water, foam, dry chemical
Unsuitable Extinguishing Agents:	carbon dioxide (CO2)

Special Fire Fighting Procedures
Firefighters should be equipped with self-contained breathing apparatus to protect against potentially toxic and irritating fumes.

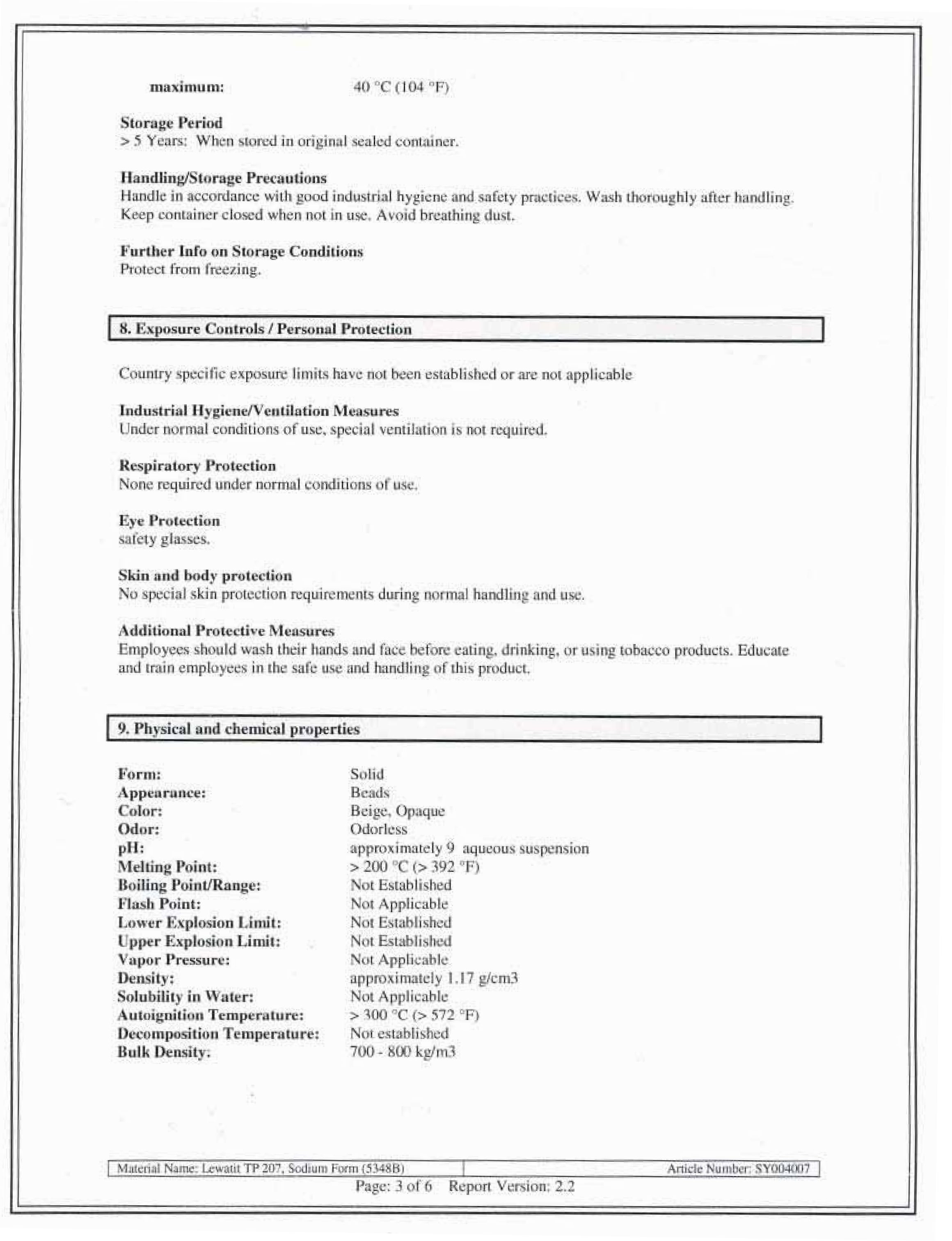
6. Accidental release measures

Spill and Leak Procedures
Spills should be swept up and placed in appropriate containers for disposal. Clean up promptly by scoop or vacuum. Avoid creating dusty conditions. Spilled material may make surfaces slippery.

7. Handling and Storage

Storage Temperature:

minimum:	-20 °C (-4 °F)



maximum: 40 °C (104 °F)

Storage Period
> 5 Years: When stored in original sealed container.

Handling/Storage Precautions
Handle in accordance with good industrial hygiene and safety practices. Wash thoroughly after handling. Keep container closed when not in use. Avoid breathing dust.

Further Info on Storage Conditions
Protect from freezing.

8. Exposure Controls / Personal Protection

Country specific exposure limits have not been established or are not applicable

Industrial Hygiene/Ventilation Measures
Under normal conditions of use, special ventilation is not required.

Respiratory Protection
None required under normal conditions of use.

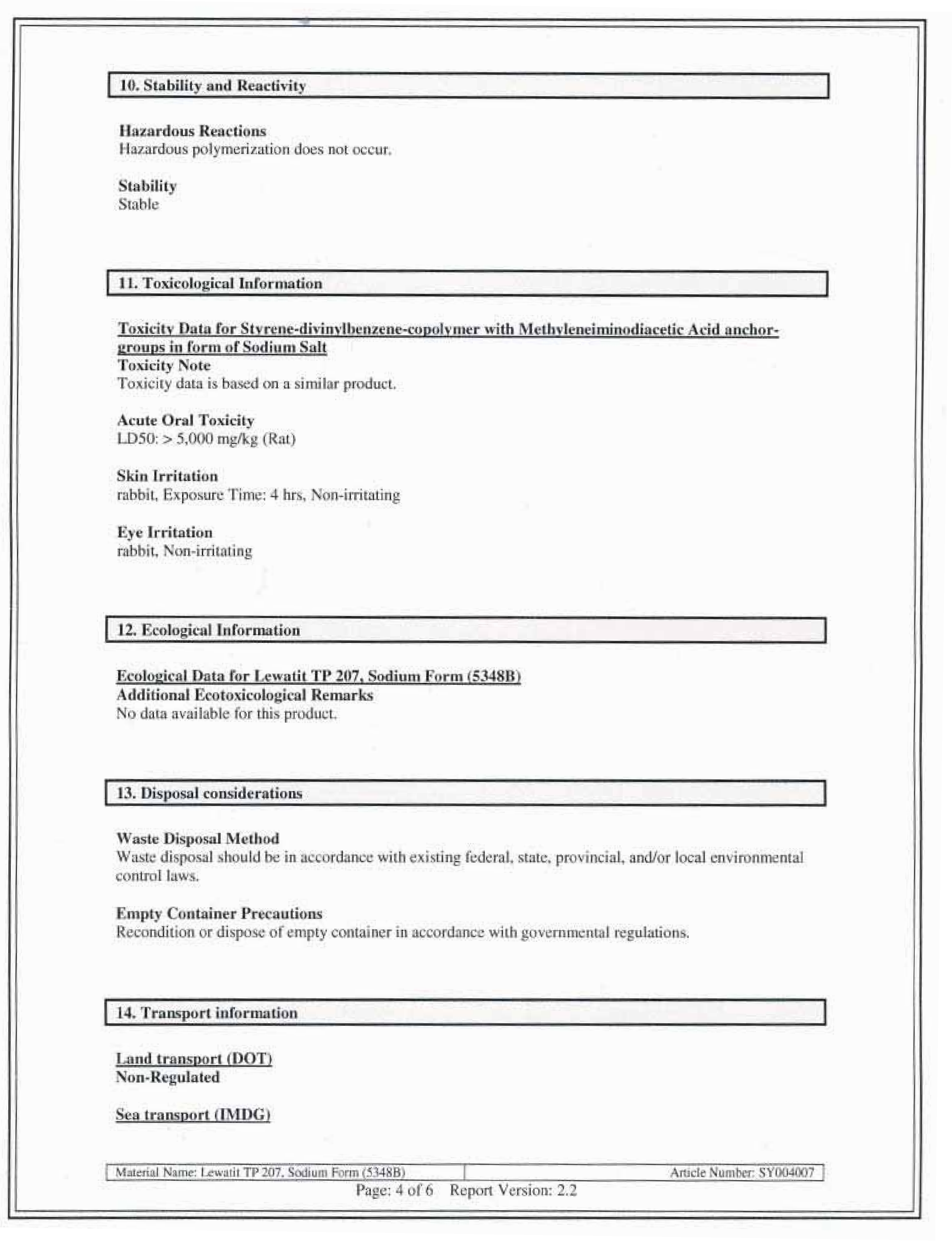
Eye Protection
safety glasses.

Skin and body protection
No special skin protection requirements during normal handling and use.

Additional Protective Measures
Employees should wash their hands and face before eating, drinking, or using tobacco products. Educate and train employees in the safe use and handling of this product.

9. Physical and chemical properties

Form:	Solid
Appearance:	Beads
Color:	Beige, Opaque
Odor:	Odorless
pH:	approximately 9 aqueous suspension
Melting Point:	> 200 °C (> 392 °F)
Boiling Point/Range:	Not Established
Flash Point:	Not Applicable
Lower Explosion Limit:	Not Established
Upper Explosion Limit:	Not Established
Vapor Pressure:	Not Applicable
Density:	approximately 1.17 g/cm3
Solubility in Water:	Not Applicable
Autoignition Temperature:	> 300 °C (> 572 °F)
Decomposition Temperature:	Not established
Bulk Density:	700 - 800 kg/m3



10. Stability and Reactivity

Hazardous Reactions
Hazardous polymerization does not occur.

Stability
Stable

11. Toxicological Information

Toxicity Data for Styrene-divinylbenzene-copolymer with Methyleneiminodiacetic Acid anchor-groups in form of Sodium Salt
Toxicity Note
Toxicity data is based on a similar product.

Acute Oral Toxicity
LD50: > 5,000 mg/kg (Rat)

Skin Irritation
rabbit, Exposure Time: 4 hrs, Non-irritating

Eye Irritation
rabbit, Non-irritating

12. Ecological Information

Ecological Data for Lewatit TP 207, Sodium Form (5348B)
Additional Ecotoxicological Remarks
No data available for this product.

13. Disposal considerations

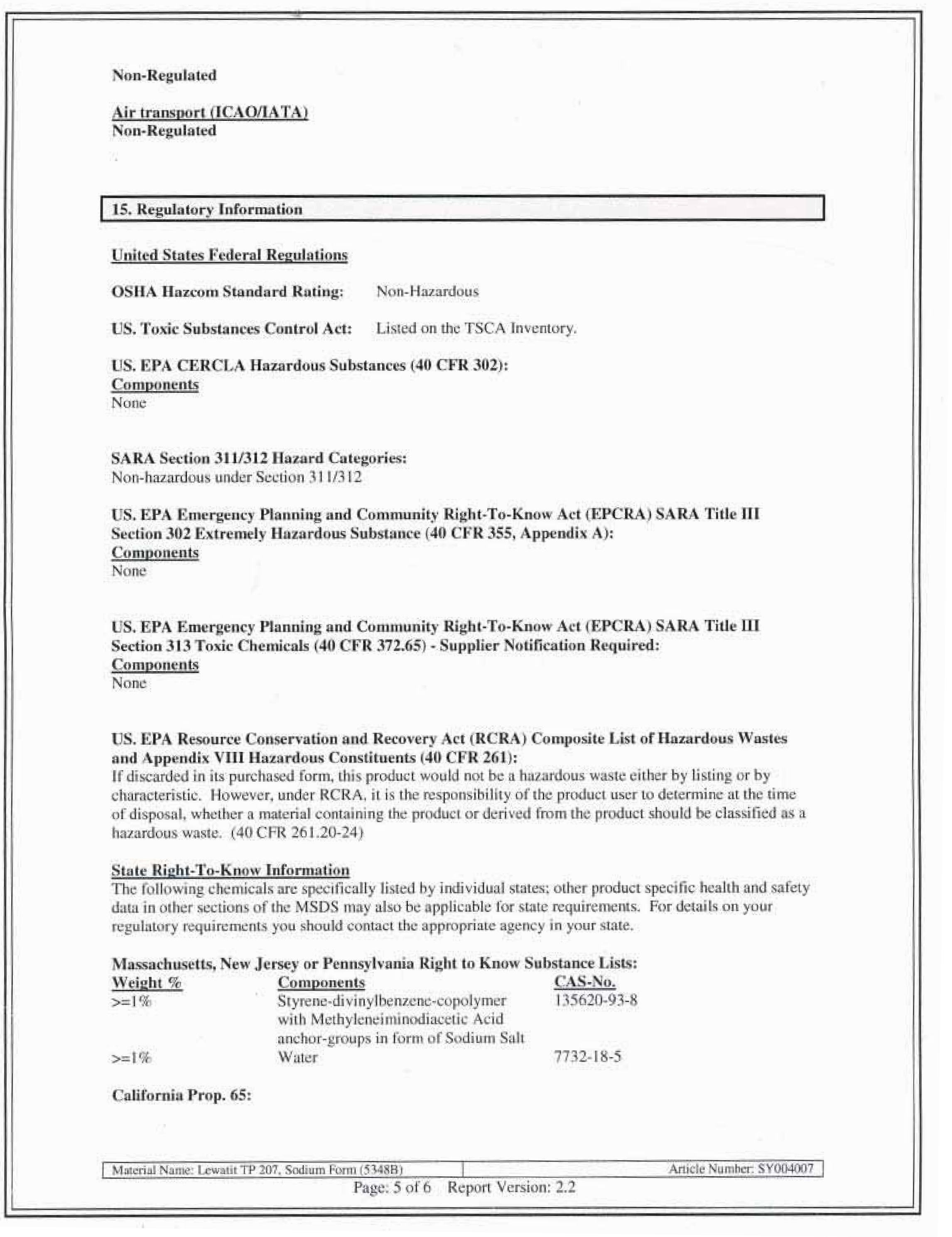
Waste Disposal Method
Waste disposal should be in accordance with existing federal, state, provincial, and/or local environmental control laws.

Empty Container Precautions
Recondition or dispose of empty container in accordance with governmental regulations.

14. Transport information

Land transport (DOT)
Non-Regulated

Sea transport (IMDG)



Non-Regulated

Air transport (ICAO/IATA)
Non-Regulated

15. Regulatory Information

United States Federal Regulations

OSHA Hazcom Standard Rating: Non-Hazardous

US. Toxic Substances Control Act: Listed on the TSCA Inventory.

US. EPA CERCLA Hazardous Substances (40 CFR 302):
Components
None

SARA Section 311/312 Hazard Categories:
Non-hazardous under Section 311/312

US. EPA Emergency Planning and Community Right-To-Know Act (EPCRA) SARA Title III Section 302 Extremely Hazardous Substance (40 CFR 355, Appendix A):
Components
None

US. EPA Emergency Planning and Community Right-To-Know Act (EPCRA) SARA Title III Section 313 Toxic Chemicals (40 CFR 372.65) - Supplier Notification Required:
Components
None

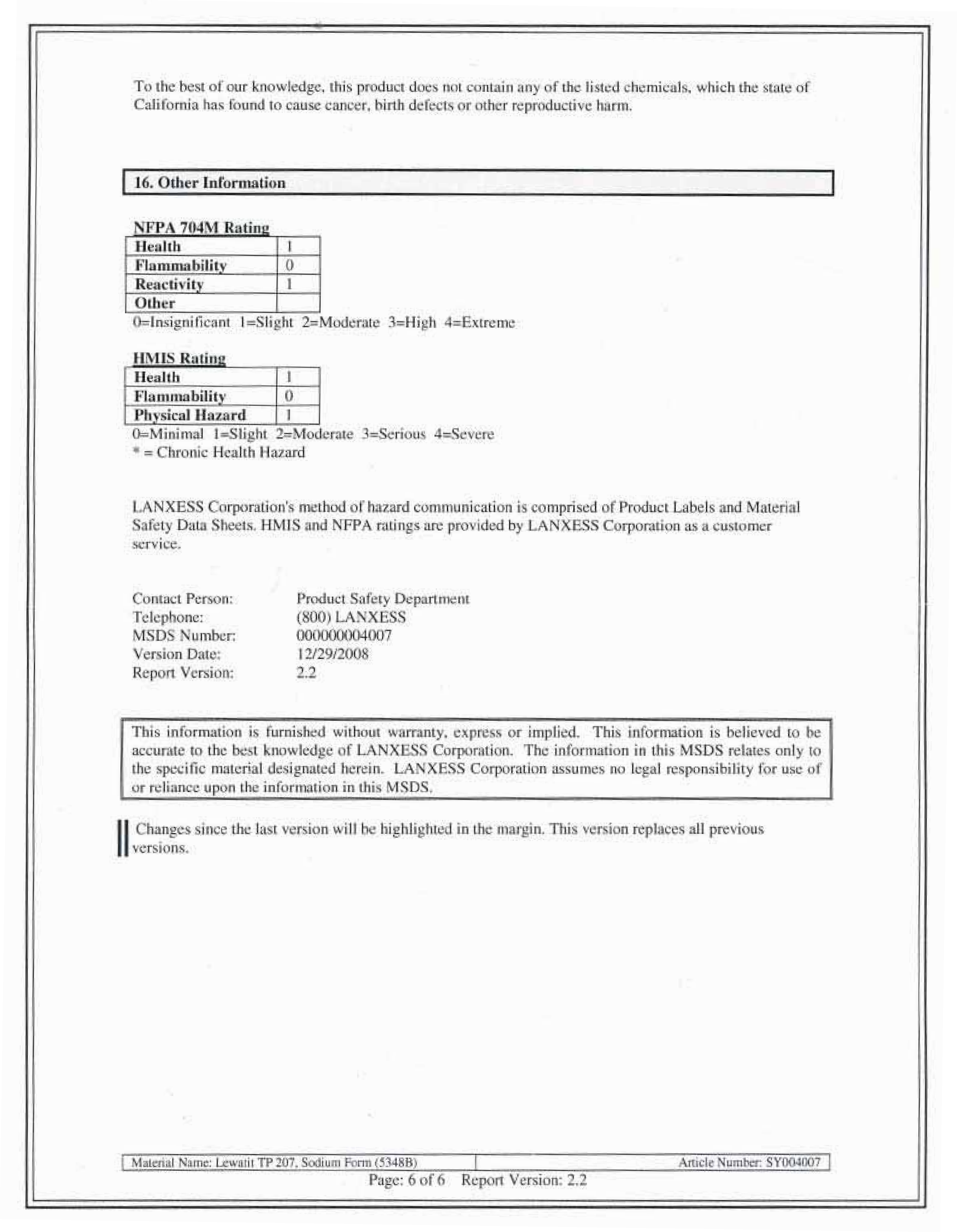
US. EPA Resource Conservation and Recovery Act (RCRA) Composite List of Hazardous Wastes and Appendix VIII Hazardous Constituents (40 CFR 261):
If discarded in its purchased form, this product would not be a hazardous waste either by listing or by characteristic. However, under RCRA, it is the responsibility of the product user to determine at the time of disposal, whether a material containing the product or derived from the product should be classified as a hazardous waste. (40 CFR 261.20-24)

State Right-To-Know Information
The following chemicals are specifically listed by individual states; other product specific health and safety data in other sections of the MSDS may also be applicable for state requirements. For details on your regulatory requirements you should contact the appropriate agency in your state.

Massachusetts, New Jersey or Pennsylvania Right to Know Substance Lists:

Weight %	Components	CAS-No.
>=1%	Styrene-divinylbenzene-copolymer with Methyleneiminodiacetic Acid anchor-groups in form of Sodium Salt	135620-93-8
>=1%	Water	7732-18-5

California Prop. 65:



To the best of our knowledge, this product does not contain any of the listed chemicals, which the state of California has found to cause cancer, birth defects or other reproductive harm.

16. Other Information

NFPA 704M Rating

Health	1
Flammability	0
Reactivity	1
Other	

0=Insignificant 1=Slight 2=Moderate 3=High 4=Extreme

HMIS Rating

Health	1
Flammability	0
Physical Hazard	1

0=Minimal 1=Slight 2=Moderate 3=Serious 4=Severe
* = Chronic Health Hazard

LANXESS Corporation's method of hazard communication is comprised of Product Labels and Material Safety Data Sheets. HMIS and NFPA ratings are provided by LANXESS Corporation as a customer service.

Contact Person: Product Safety Department
Telephone: (800) LANXESS
MSDS Number: 000000004007
Version Date: 12/29/2008
Report Version: 2.2

This information is furnished without warranty, express or implied. This information is believed to be accurate to the best knowledge of LANXESS Corporation. The information in this MSDS relates only to the specific material designated herein. LANXESS Corporation assumes no legal responsibility for use of or reliance upon the information in this MSDS.

Changes since the last version will be highlighted in the margin. This version replaces all previous versions.

SIEMENS **Water Technologies**

Material Safety Data Sheet

SECTION 1 – CHEMICAL PRODUCT AND COMPANY INFORMATION

Product Name: C-211 Ion Exchange Resin
Part Number: multiple **Chemical Family**: ion exchange resin

Manufacturer's Name: Siemens Water Technologies Corp.
Address: 181 Thorn Hill Road, Warrendale, PA 15086
Product/Technical Information Phone Number: (815) 877-3041
Medical/Handling Emergency Phone Number: Call CHEMTREC at (800) 424-9300
24 hours a day
Transportation Emergency Phone Number: Call CHEMTREC at (800) 424-9300
24 hours a day
Issue Date: May 15, 2000
Revision Date/Revision Number: September 19, 2003/Rev 2

SECTION 2 – COMPOSITION INFORMATION

Chemical Name	**Percent by Weight**	**CAS#**
Sulfonated copolymer of styrene and divinylbenzene in sodium form	40 - 70 %	69011-22-9
Water	30 - 60 %	7732-18-5

SECTION 3 – HAZARDS IDENTIFICATION

Appearance & Odor: Spherical beads/Odorless to slight amine odor

Emergency Overview:

- May cause eye irritation.
- May cause toxic fumes/vapors if burned.
- May react violently when exposed to oxidizing agents such as Nitric Acid (HNO_3).

Fire & Explosion Hazards: This material will not burn until moisture is removed, then resin starts to burn in flame at 230°C. Under fire conditions some components of this product may decompose. The smoke may contain unidentified toxic and/or irritating compounds. Nitric acid and other strong oxidizing agents can cause explosive-type reactions when mixed with ion exchange resins. Proper design of equipment to prevent build up of pressure is necessary if use of an oxidizing agent such as nitric acid is contemplated.

Primary Route(s) of Exposure: skin and eye contact

Inhalation – Acute Effects: Vapors are unlikely due to physical properties.

Skin Contact – Acute Effects: Prolonged or repeated exposure is not likely to cause significant skin irritation. May cause more severe response if skin is scratched or cut. Skin absorption is unlikely due to physical properties.

Eye Contact – Acute Effects: May cause severe eye irritation. May cause moderate corneal injury. Effects are likely to heal.

Ingestion – Acute Effects: Single dose oral toxicity is considered to be low. No hazards anticipated from swallowing small amounts incidental to normal handling operation.

SECTION 4 – FIRST AID MEASURES

Inhalation First Aid: Remove affected person from area to fresh air and provide oxygen if breathing is difficult. Give artificial respiration ONLY if breathing has stopped and give CPR ONLY if there is no breathing and no pulse. Obtain medical attention. No adverse effects anticipated by this route of exposure.

Skin Contact First Aid: Immediately remove clothing from affected area and wash skin vigorously with flowing water. Clothing should be washed before reuse. DO NOT instruct person to neutralize affected skin area.

Eye Contact First Aid: Immediately irrigate eyes with flowing water continuously for 15 minutes while holding eyes open. Contacts should be removed before or during flushing. Obtain medical attention. DO NOT instruct person to neutralize.

Ingestion First Aid: No adverse effects anticipated by this route of exposure incidental to proper industrial handling. If ingestion does occur, if victim is alert and not convulsing rinse mouth with water and give plenty of water to drink. If spontaneous vomiting occurs, have affected person lean forward with head down to avoid breathing in of vomitus. Rinse mouth again and give more water to drink. Obtain medical attention.

Medical Conditions Aggravated: There are no known conditions aggravated by exposure.

Note to Physician: No specific antidote. Supportive care. Treatment based on judgment of the physician in response to reactions of the patient.

SECTION 5 – FIRE FIGHTING MEASURES

Flash Point/Method: Not applicable

Auto Ignition Temperature: Above 500°C (900°F)

Upper/Lower Explosion Limits: Not applicable

Extinguishing Media: Water, carbon dioxide, dry chemical

Fire Fighting Procedures: Keep people away. Isolate fire area and deny unnecessary entry. Cool surrounding area with water to localize fire zone. Soak thoroughly with water to cool and prevent reignition.

Fire-Fighting Equipment: NIOSH approved positive-pressure self-contained breathing apparatus (SCBA) and protective fire fighting clothing (includes fire fighting helmet, coat, pants, boots and gloves). If protective equipment is not available or not used, fight fire from a protected location or a safe distance.

Fire & Explosion Hazards: This material will not burn until moisture is removed, then resin starts to burn in flame at 230°C. Under fire conditions some components of this product may decompose. The smoke may contain unidentified toxic and/or irritating compounds. Nitric acid and other strong oxidizing agents can cause explosive-type reactions when mixed with ion exchange resins. Proper design of equipment to prevent build up of pressure is necessary if use of an oxidizing agent such as nitric acid is contemplated.

Hazardous Products of Decomposition and/or Combustion: May include but not limited to hydrocarbons, sulfur oxides, organic sulfonates, carbon monoxide, carbon dioxide and benzene compounds.

NFPA Ratings:

HEALTH- 1 FLAMMABILITY- 1 REACTIVITY- 1 OTHER- none

SECTION 6 – ACCIDENTAL RELEASE MEASURES

Spill/Leak Procedures: Isolate spill area to prevent falls as material can be a slipping hazard. Avoid contact with eyes and skin. Material is heavier than water and has limited water solubility. It will collect on the lowest surface.

Cleanup: Clean up floor area. Sweep up.

Regulatory Requirements: Follow all applicable Federal, State, Local, or Provincial regulations.

Disposal: DO NOT DUMP INTO ANY SEWERS, ON THE GROUND, OR INTO ANY BODY OF WATER. All disposal methods must be in compliance with all Federal, State, Local and Provincial laws and regulations. Regulations may vary in different locations. Waste characterizations and compliance with applicable laws are the responsibility solely of the waste generator.

SECTION 7 – HANDLING AND STORAGE

Handling: Practice reasonable care and caution. Metal equipment should be compatible with feed, regenerant, resin form and effluent of that process.

Storage: Keep containers tightly closed when not in use. Store between 2°- 38°C (35° - 100°F).

General Comments: Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

SECTION 8 –PERSONAL PROTECTION/ EXPOSURE CONTROL

Respiratory Protection: No respiratory protection should be needed.

Skin Protection: Wear gloves impervious to this material to prevent skin contact.

Eye Protection: Wear protective eyeglasses or chemical safety goggles. Contact lenses are not eye protective devices. Appropriate eye protection must be worn instead of, or in conjunction with contact lenses.

Ventilation Protection: Good general ventilation should be sufficient.

Other Protection: Never eat, drink, or smoke in work areas. Practice good personal hygiene after using this material, especially before eating, drinking, smoking, using the toilet, or applying cosmetics.

Safety showers, with quick opening valves which stay open, and eye wash fountains, or other means of washing the eyes with a gentle flow of cool to tepid tap water, should be readily available in all areas where this material is handled or stored. Water should be supplied through insulated and heat-traced lines to prevent freeze-ups in cold weather.

Exposure Limits:
Exposure limits have not been developed.

SECTION 9 – PHYSICAL AND CHEMICAL PROPERTIES

Appearance & Odor: Spherical beads/Odorless to slight amine odor

Vapor Pressure: not applicable

Vapor Density (Air=1): not applicable

Boiling Point: not applicable

Melting Point: not determined

Specific Gravity: not determined

Solubility in Water: Insoluble

Volatile Percentage: not determined

pH: not determined

Flash Point/Method: not applicable

Auto Ignition Temperature: Above 500°C (900°F)

Upper/Lower Explosion Limits: not applicable

SECTION 10 – STABILITY AND REACTIVITY

Stability: Stable under normal handling and storage conditions.

Incompatibilities: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions and could result in slightly degraded resin up to an explosive reaction. Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

Polymerization: Hazardous polymerization cannot occur.

Decomposition: Hazardous decomposition products depend upon temperature, air supply, and the presence of other materials. Hazardous decomposition products may include and are not limited to: aromatic compounds, hydrocarbons, organic sulfonates, sulfur oxides.

Conditions to Avoid: Resin can decompose at temperatures greater than 90°C (194°F). Do not pack column with dry ion exchange resins. Dry beads expand when wet. This expansion can cause a glass column to shatter.

SECTION 11 – TOXICOLOGICAL INFORMATION

Inhalation – Acute: Vapors are unlikely due to physical properties.

Inhalation – Chronic: There are no known chronic inhalation effects.

Skin Contact – Acute: Prolonged or repeated exposure is not likely to cause significant skin irritation. May cause more severe response if skin is scratched or cut. Skin absorption is unlikely due to physical properties.

Skin Contact – Chronic: There are no known chronic dermal effects.

Eye Contact – Acute: May cause severe eye irritation. May cause moderate corneal injury. Effects are likely to heal.

Ingestion – Acute: Single dose oral toxicity is considered to be low. No hazards anticipated from swallowing small amounts incidental to normal handling operation.

Ingestion – Chronic: There are no known chronic ingestion effects.

Carcinogenicity/Mutagenicity: There are no known carcinogenic/mutagenic effects.

Reproductive Effects: There are no known reproductive effects.

Neurotoxicity: There are no known neurotoxic effects.

Other Effects: There are no other known toxic effects.

Target Organs: This product will affect the eyes.

SECTION 12 – ECOLOGICAL INFORMATION

The environmental fate and ecological toxicity are not known.

SECTION 13 – DISPOSAL CONSIDERATIONS

Spill/Leak Procedures: Isolate spill area to prevent falls as material can be a slipping hazard. Avoid contact with eyes and skin. Material is heavier than water and has limited water solubility. It will collect on the lowest surface.

Cleanup: Clean up floor area. Sweep up.

Regulatory Requirements: Follow all applicable Federal, State, Local, or Provincial regulations.

Disposal: DO NOT DUMP INTO ANY SEWERS, ON THE GROUND, OR INTO ANY BODY OF WATER. All disposal methods must be in compliance with all Federal, State Local and Provincial laws and regulations. Regulations may vary in different locations. Waste characterizations and compliance with applicable laws are the responsibility solely of the waste generator.

SIEMENS Water Technologies

Material Safety Data Sheet

SECTION 14 – TRANSPORTATION INFORMATION

DOT Shipping Description: This product is not regulated by DOT when shipped domestically by land.

Canadian TDG Information: For TDG regulatory information, if required, consult transportation regulations, or product shipping papers.

SECTION 15 – REGULATORY INFORMATION

US Regulations:
SARA HAZARD CATEGORY: This product has been reviewed according to the EPA "Hazard Categories" promulgated under Sections 311 and 312 of the Superfund Amendment and Reauthorization Act of 1986 (SARA Title III) and is considered, under applicable definitions, to meet the following categories:

An immediate health hazard

TSCA Considerations: Every different salt or ionic form of an ion exchange resin is a separate chemical. If you use an ion exchange resin for ion exchange purposes and then remove the by-product resin from its vessel or container prior to recovery of the original or another form of the resin or of another chemical, the by-product resin must be listed on the TSCA Inventory (Unless an exemption is applicable). It is the responsibility of the customer to ensure that such isolated, recycled by-product resins are in compliance with TSCA. Failure to comply could result in substantial civil or criminal penalties being assessed by the EPA.

State Regulations: Consult individual state agency for further information.

Canadian Regulations:
WHMIS INFORMATION: The Canadian Workplace Hazardous Materials Information System (WHMIS) Classification for this product is:

D2B - eye or skin irritant
Refer elsewhere in the MSDS for specific warnings and safe handling information.

CPR Statement: This product has been classified in accordance with the hazard criteria of the Canadian Controlled Products Regulations (CPR) and the MSDS contains all the information required by the CPR.

SECTION 16 – OTHER INFORMATION

Disclaimer: The information contained herein is based on data considered accurate. However, no warranty is expressed or implied regarding the accuracy of these data or the results to be obtained from the user thereof. It is the buyer’s responsibility to ensure that its activities comply with federal, state, provincial and local laws.

APPENDIX C - MATERIAL SAFETY DATA SHEETS

SIEMENS Water Technologies

Material Safety Data Sheet

SECTION 1 – CHEMICAL PRODUCT AND COMPANY INFORMATION

Product Name: C-211 H Ion Exchange Resin
Part Number: multiple **Chemical Family**: cation exchange polymer

Manufacturer's Name: Siemens Water Technologies Corp.
Address: 181 Thorn Hill Road, Warrendale, PA 15086
Product/Technical Information Phone Number: (815) 877-3041
Medical/Handling Emergency Phone Number: Call CHEMTREC at (800) 424-9300
24 hours a day
Transportation Emergency Phone Number: Call CHEMTREC at (800) 424-9300
24 hours a day
Issue Date: April 1, 2000

SECTION 2 – COMPOSITION INFORMATION

Chemical Name	Percent by Weight	CAS#
Sulfonated copolymer of styrene and divinylbenzene in hydrogen form	40 - 70 %	069011-20-7
Water	30 - 60 %	007732-18-5

SECTION 3 – HAZARDS IDENTIFICATION

Appearance & Odor: Spherical beads/Odorless to slight amine odor

Emergency Overview:

- May cause eye and skin irritation.
- May cause toxic fumes/vapors if burned.
- May react violently when exposed to oxidizing agents such as Nitric Acid (HNO_3).

Fire & Explosion Hazards: This material will not burn until moisture is removed, then resin starts to burn in flame at 230°C. Under fire conditions some components of this product may decompose. The smoke may contain unidentified toxic and/or irritating compounds. Nitric acid and other strong oxidizing agents can cause explosive-type reactions when mixed with ion exchange resins. Proper design of equipment to prevent build up of pressure is necessary if use of an oxidizing agent such as nitric acid is contemplated.

Primary Route(s) of Exposure: skin and eye contact.

Inhalation – Acute Effects: Vapors are unlikely due to physical properties.

Skin Contact – Acute Effects: Skin contact may cause mild irritation and redness.

Eye Contact – Acute Effects: May cause severe eye irritation and redness. May cause moderate corneal injury. Effects are likely to heal.

Ingestion – Acute Effects: Single dose oral toxicity is considered to be low. No hazards anticipated from swallowing small amounts incidental to normal handling operation. Swallowing large amounts may cause irritation to the gastrointestinal tract.

SECTION 4 – FIRST AID MEASURES

Inhalation First Aid: Remove affected person from area to fresh air and provide oxygen if breathing is difficult. Give artificial respiration ONLY if breathing has stopped and give CPR ONLY if there is no breathing and no pulse. Obtain medical attention. No adverse effects anticipated by this route of exposure.

Skin Contact First Aid: Immediately remove clothing from affected area and wash skin vigorously with flowing water. Clothing should be washed before reuse. Seek medical attention if irritation occurs. DO NOT instruct person to neutralize affected skin area.

Eye Contact First Aid: Immediately irrigate eyes with flowing water continuously for 15 minutes while holding eyes open. Contacts should be removed before or during flushing. Obtain medical attention. DO NOT instruct person to neutralize.

Ingestion First Aid: No adverse effects anticipated by this route of exposure incidental to proper industrial handling. If ingestion does occur, if victim is alert and not convulsing rinse mouth with water and give plenty of water to drink. If spontaneous vomiting occurs, have affected person lean forward with head down to avoid breathing in of vomitus. Rinse mouth again and give more water to drink. Obtain medical attention.

Medical Conditions Aggravated: There are no known conditions aggravated by exposure.

Note to Physician: No specific antidote. Supportive care. Treatment based on judgment of the physician in response to reactions of the patient.

SECTION 5 – FIRE FIGHTING MEASURES

Flash Point/Method: not applicable

Auto Ignition Temperature: Above 500°C (900°F)

Upper/Lower Explosion Limits: not applicable

Extinguishing Media: Water, carbon dioxide, dry chemical

Fire Fighting Procedures: Keep people away. Isolate fire area and deny unnecessary entry. Cool surrounding area with water to localize fire zone. Soak thoroughly with water to cool and prevent reignition.

Fire-Fighting Equipment: NIOSH approved positive-pressure self-contained breathing apparatus (SCBA) and protective fire fighting clothing (includes fire fighting helmet, coat, pants, boots and gloves). If protective equipment is not available or not used, fight fire from a protected location or a safe distance.

Fire & Explosion Hazards: This material will not burn until moisture is removed, then resin starts to burn in flame at 230°C. Under fire conditions some components of this product may decompose. The smoke may contain unidentified toxic and/or irritating compounds. Nitric acid and other strong oxidizing agents can cause explosive-type reactions when mixed with ion exchange resins. Proper design of equipment to prevent build up of pressure is necessary if use of an oxidizing agent such as nitric acid is contemplated.

Hazardous Products of Decomposition and/or Combustion: May include but not limited to hydrocarbons, sulfur oxides, organic sulfonates, carbon monoxide, carbon dioxide and benzene compounds.

NFPA Ratings:
HEALTH- 1 FLAMMABILITY- 1 REACTIVITY- 1 OTHER- none

SECTION 6 – ACCIDENTAL RELEASE MEASURES

Spill/Leak Procedures: Isolate spill area to prevent falls as material can be a slipping hazard. Avoid contact with eyes and skin. Material is heavier than water and has limited water solubility. It will collect on the lowest surface.

Cleanup: Clean up floor area. Sweep up. Avoid generation of dust.

Regulatory Requirements: Follow all applicable Federal, State, Local, or Provincial regulations.

Disposal: DO NOT DUMP INTO ANY SEWERS, ON THE GROUND, OR INTO ANY BODY OF WATER. All disposal methods must be in compliance with all Federal, State, Local and Provincial laws and regulations. Regulations may vary in different locations. Waste characterizations and compliance with applicable laws are the responsibility solely of the waste generator.

SECTION 7 – HANDLING AND STORAGE

Handling: Practice reasonable care and caution. Metal equipment should be compatible with feed, regenerant, resin form and effluent of that process.

Storage: Keep containers tightly closed when not in use. Store between 2°- 38°C (35° - 100°F).

General Comments: Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

SECTION 8 –PERSONAL PROTECTION/ EXPOSURE CONTROL

Respiratory Protection: No respiratory protection should be needed.

Skin Protection: Wear gloves impervious to this material to prevent skin contact.

Eye Protection: Wear protective eyeglasses or chemical safety goggles. Contact lenses are not eye protective devices. Appropriate eye protection must be worn instead of, or in conjunction with contact lenses.

Ventilation Protection: Good general ventilation should be sufficient.

Other Protection: Never eat, drink, or smoke in work areas. Practice good personal hygiene after using this material, especially before eating, drinking, smoking, using the toilet, or applying cosmetics.

Safety showers, with quick opening valves which stay open, and eye wash fountains, or other means of washing the eyes with a gentle flow of cool to tepid tap water, should be readily available in all areas where this material is handled or stored. Water should be supplied through insulated and heat-traced lines to prevent freeze-ups in cold weather.

Exposure Limits:
Exposure limits have not been developed.

SECTION 9 – PHYSICAL AND CHEMICAL PROPERTIES

Appearance & Odor: Spherical beads/Odorless to slight amine odor

Vapor Pressure: N/A*	**Vapor Density (Air=1):** N/A
Boiling Point: N/A	**Melting Point**: N/A
Specific Gravity: N/D**	**Solubility in Water**: Insoluble
Volatile Percentage: N/A	**pH**: N/A
Flash Point/method: N/A	**Auto Ignition Temperature**: Above 500°C (900°F)
Upper/Lower Explosion Limits: N/A	**Other:** N/D

*N/A=Not applicable
**N/D=Not determined

SECTION 10 – STABILITY AND REACTIVITY

Stability: Stable under normal handling and storage conditions.

Incompatibilities: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions and could result in slightly degraded resin up to an explosive reaction. Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

Polymerization: Hazardous polymerization cannot occur.

Decomposition: Hazardous decomposition products depend upon temperature, air supply, and the presence of other materials. Hazardous decomposition products may include and are not limited to: aromatic compounds, hydrocarbons, organic sulfonates, sulfur oxides.

Conditions to Avoid: Resin can decompose at temperatures greater than 90°C (194°F). Do not pack column with dry ion exchange resins. Dry beads expand when wet. This expansion can cause a glass column to shatter.

SECTION 11 – TOXICOLOGICAL INFORMATION

Inhalation – Acute: Vapors are unlikely due to physical properties.

Inhalation – Chronic: There are no known chronic inhalation effects.

Skin Contact – Acute: Skin contact may cause mild irritation and redness.

Skin Contact – Chronic: There are no known chronic dermal effects.

Eye Contact – Acute: May cause severe eye irritation and redness. May cause moderate corneal injury. Effects are likely to heal.

Ingestion – Acute: Single dose oral toxicity is considered to be low. No hazards anticipated from swallowing small amounts incidental to normal handling operation. Swallowing large amounts may cause irritation to the gastrointestinal tract. Swallowing extremely large amounts may produce gastrointestinal disturbances.

Ingestion – Chronic: There are no known chronic ingestion effects.

Carcinogenicity/Mutagenicity: There are no known carcinogenic/mutagenic effects.

Reproductive Effects: There are no known reproductive effects.

Neurotoxicity: There are no known neurotoxic effects.

Other Effects: There are no other known toxic effects.

Target Organs: Target organs include the eyes and skin.

SECTION 12 – ECOLOGICAL INFORMATION

The environmental fate and ecological toxicity are not known.

SECTION 13 – DISPOSAL CONSIDERATIONS

Spill/Leak Procedures: Isolate spill area to prevent falls as material can be a slipping hazard. Avoid contact with eyes and skin. Material is heavier than water and has limited water solubility. It will collect on the lowest surface.

Cleanup: Clean up floor area. Sweep up. Avoid generation of dust.

Regulatory Requirements: Follow all applicable Federal, State, Local, or Provincial regulations.

Disposal: DO NOT DUMP INTO ANY SEWERS, ON THE GROUND, OR INTO ANY BODY OF WATER. All disposal methods must be in compliance with all Federal, State Local and Provincial laws and regulations. Regulations may vary in different locations. Waste characterizations and compliance with applicable laws are the responsibility solely of the waste generator.

SECTION 14 – TRANSPORTATION INFORMATION

DOT Shipping Description: This product is not regulated by DOT when shipped domestically by land.

Canadian TDG Information: For TDG regulatory information, if required, consult transportation regulations, or product shipping papers.

SECTION 15 – REGULATORY INFORMATION

US Regulations:
SARA HAZARD CATEGORY: This product has been reviewed according to the EPA "Hazard Categories" promulgated under Sections 311 and 312 of the Superfund Amendment and Reauthorization Act of 1986 (SARA Title III) and is considered, under applicable definitions, to meet the following categories:

An immediate health hazard

TSCA Considerations: Every different salt or ionic form of an ion exchange resin is a separate chemical. If you use an ion exchange resin for ion exchange purposes and then remove the by-product resin from its vessel or container prior to recovery of the original or another form of the resin or of another chemical, the by-product resin must be listed on the TSCA Inventory (Unless an exemption is applicable). It is the responsibility of the customer to ensure that such isolated, recycled by-product resins are in compliance with TSCA. Failure to comply could result in substantial civil or criminal penalties being assessed by the EPA.

State Regulations: Consult individual state agency for further information.

Canadian Regulations:
WHMIS INFORMATION: The Canadian Workplace Hazardous Materials Information System (WHMIS) Classification for this product is:

D2B - eye or skin irritant
Refer elsewhere in the MSDS for specific warnings and safe handling information.

CPR Statement: This product has been classified in accordance with the hazard criteria of the Canadian Controlled Products Regulations (CPR) and the MSDS contains all the information required by the CPR.

SECTION 16 – OTHER INFORMATION

Disclaimer: The information contained herein is based on data considered accurate. However, no warranty is expressed or implied regarding the accuracy of these data or the results to be obtained from the user thereof. It is the buyer's responsibility to ensure that its activities comply with federal, state, provincial and local laws.

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