FACES FROM YESTERDAY: Daguerreotypes of unknown subjects from the Eastman House's study collection. University and Eastman House researchers are working together to find out how to preserve daguerreotypes in the face of mysterious deterioration.

A Vanishing Past?

Can science save the daguerreotype, the first successful medium of photography?

By Kathleen McGarvey

BRANDON VICK

As the microscopes of the Integrated Nanosystems Center in Wilmot Hall hum and thrum with power, a tiny piece of the 19th century—sharply etched, infinitely fragile—undergoes their inspection.

"There!" says photo conservator Ralph Wiegandt, pointing excitedly to an image on his screen that looks like a giant insect conjured from a science fiction movie. "You're looking at 33,000 times magnification."

The object of his scrutiny is Robert Cornelius's 1841 daguerreotype of chemist Martin Hans Boyè. Cradled within the electron microscope, the daguerreotype begins to give up the secrets of its surface. To the naked eye, it is flecked with small spots. Under the electron microscope's exacting gaze, it is another world.

"I'm a daguerreian rover," Wiegandt says, only half facetiously, "and I'm now negotiating myself around the terrain of a daguerreotype."

His adventures there are no lark. Daguerreotypes are the first photographic images, formed by a process Louis-Jacques-Mandé Daguerre invented in 1839. The predominant mode of photography in the United States from that year until the Civil War, daguerreotypes are unique, nonreproducible images of almost confounding clarity—and they may be deteriorating before our eyes. No one knows exactly why, or how to save them.

So Wiegandt—senior project conservator at the George Eastman House International Museum of Photography and Film—together with Nicholas Bigelow, the Lee A. Dubridge Professor of Physics, are racing for answers. Using 21st-century technology, they're trying to learn more about the science of daguerreotypes, the nanotechnology created by 19th-century inventors that makes them possible, and the activities of nanoparticles that may be their undoing.

The Eastman House, just four miles from the River Campus, holds one of the world's largest collections of daguerreotypes, with about 5,000 images. In 2005, the Eastman House organized a major daguerreotype exhibition, *Young America,* a comprehensive retrospective of the works of Boston daguerreotype firm Albert Sands Southworth and Josiah Johnson Hawes. One of the first photographic studios in the United States, it operated for 20 years beginning in 1843 and counted figures such as Ralph Waldo Emerson, Harriet Beecher Stowe, and Daniel Webster among its clients.

The greatest proportion of the 160 daguerreotypes on display came from the Eastman House, the Metropolitan Museum of Art, and the Museum of Fine Arts, Boston. In a review, art critic Holland Cotter of the *New York Times* described daguerreotypes as "diamond-cut empiricism bathed in apparitional light" and called the exhibition "precious in the very best sense: literally beyond price, and almost, but not quite, beyond praise."

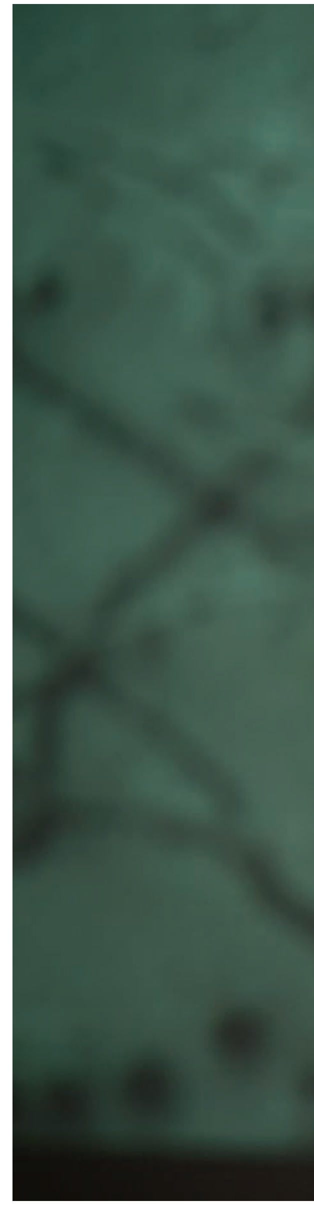
Just one month after the exhibit opened at the International Center of Photography in New York City, curators discovered degradation in the condition of some of the daguerreotypes: a disfiguring bloom or white haze on the surface of the images. It was decay, sudden and unmistakable, that no one could explain. Thirty daguerreotypes showed damage; for five of them, it was critical degradation.

"To an art curator, this is traumatizing," says Bigelow. "The notion that you had just sent these irreplaceable objects on tour and something happened, that overnight you could ruin them—what's going on?"

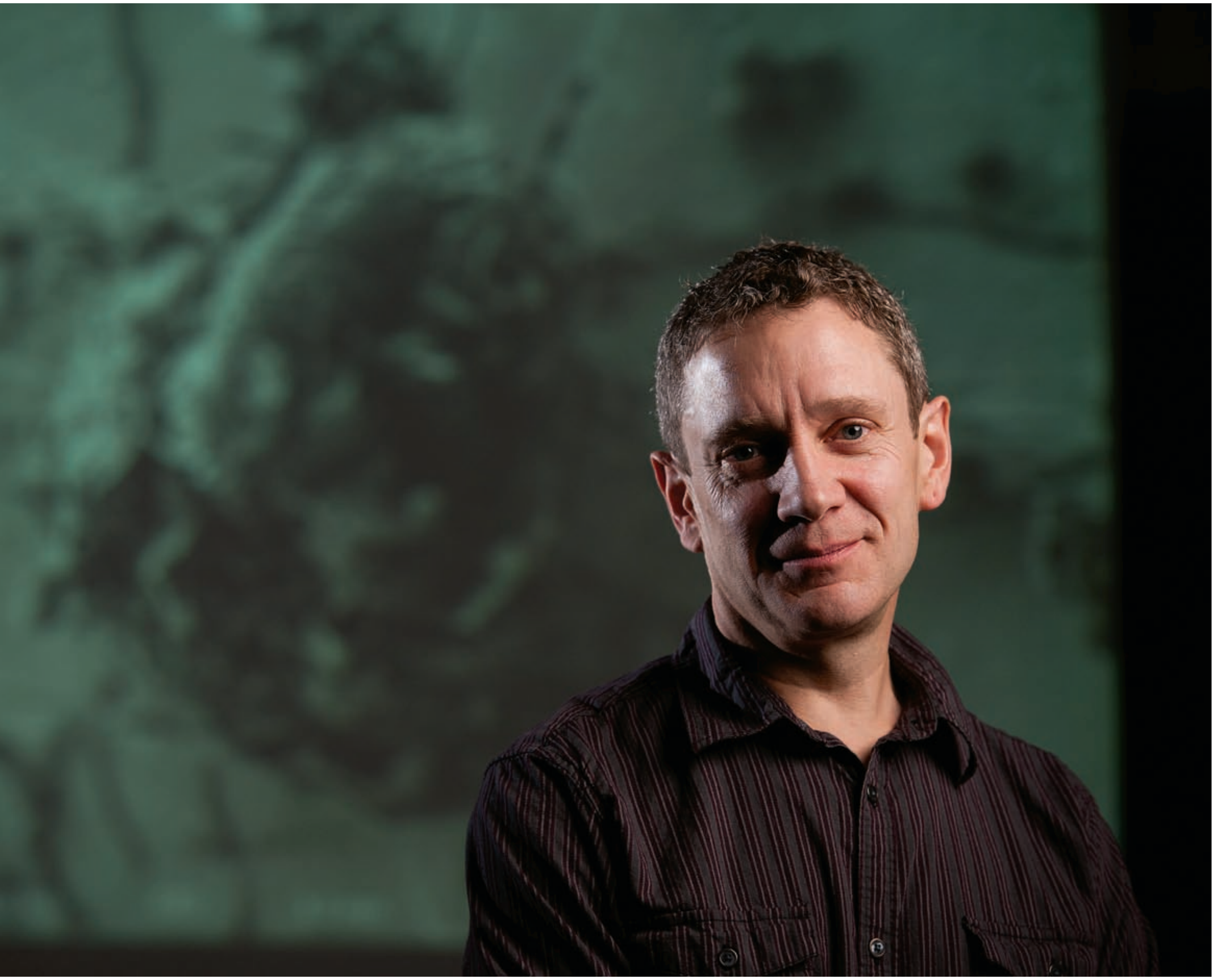
"We always thought it was okay to shine light on a daguerreotype, unlike paper," because it was essentially a silver surface—"like a silver teapot," says Malcolm Daniel, senior curator of the Metropolitan Museum's Department of Photographs. But for this exhibition, the lighting was "absolutely meticulous," as was the documentation of the daguerreotypes' condition. Lighting didn't cause the "dramatic" degradation, says Daniel, but "light-sensitive photochemistry was there, waiting to be triggered."

One thing that the group's microscopic explorations have revealed is that the silver daguerreotype plate is a biologically active surface, a remarkable finding because silver is naturally antimicrobial. But on virtually every daguerreotype the team has examined, small colonies of fungi are growing—and damaging the surface. "They're not just living out there—they're engaging with" the daguerreotype, Bigelow says, bringing the daguerreotype's metals into the fungi's biological system and then, perhaps, extruding them to the surface, as metallic nodules and other forms.

It's quite an astonishing discovery, "almost like finding life on Mars," says Brian McIntyre, a senior engineer at the Institute of Optics who is collaborating with Bigelow and Wiegandt. Daguerreotypes that have been stored improperly often have visible accumulations of filament-like material on their surfaces. The growths'



NEW TERRITORY: Physicist Nicholas Bigelow is bringing his expertise to bear on the field of photo preservation through research on daguerreotypes as 19th-century instances of applied nanotechnology.



appearance suggested fungi to early observers, but later analysis indicated that the filaments were purely chemical. The scans Wiegandt and McIntyre have made, however, show growths "clearly biological in nature," Bigelow says. That was confirmed by a study published last year in which a group of Harvard microbiologists and photo conservators confirmed the filaments were fungal by identifying their DNA.

"There's a miraculous piece of all this—forget about the daguerreotype for a minute: what on earth is going on in the physics that underlies this, and the chemical process that forms this?" says Bigelow.

Through the technology available at the Integrated Nanosystems Center—known more familiarly as URnano, with Bigelow as its director and McIntyre, its director of operations—the team is pursuing answers to those questions. They're using a focused ion beam to extract samples, revealing activity below the surface—"like a biopsy," says Bigelow, and performed only on samples that are not of museum quality. A scanning electron microscope scatters electrons off the surface of the daguerreotypes, providing magnification of 150,000 times and analyzing the elemental composition of any given spot on the image. A transmission electron microscope offers magnification of 250,000 to 300,000 times, and installation in the spring of a new device for X-ray photoemission spectroscopy will offer yet another avenue of investigation.

"Even 10 years ago, what we're doing would have been very different," says McIntyre.

The project has received $450,000 in support from the National Science Foundation, through its SCIART award program that funds projects bringing together science and art. The team's work has also benefitted from an alliance announced in 2010 between the University and the Eastman House. "I always think of art and science as great collaborators," says Thomas DiPiero, dean for humanities and interdisciplinary studies. "This time we're working with a partner institution, and the science is in service to our cultural heritage."

What initially drew Bigelow—chair of the physics department, also a professor of optics, and an expert in quantum optics and quantum physics—to the project was something extraordinary

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about daguerreotypes. The daguerreotype isn't only the first form of photography; it may also be one of the first forms of controlled nanotechnology. Daguerreotypists used nanotechnology to create pictures, and now, more than a century and a half later, scientists and conservators are turning to nanotechnology in a bid to save them.

Most people think of nanotechnology as nanochips or tiny electronic circuits, the processor in their computer tablet or phone, the whiz-bang of modern microelectronics. "But it's a much broader field," says Bigelow. Nanoscience is the study and control of materials, biological or chemical, that are between one and 100 nanometers in size. A nanometer is just a billionth of a meter; this sheet of paper is about 100,000 nanometers thick.

One part of nanoscience involves building things on the nanometer scale; another is constructing tools with which to see at that scale and understand how nanoparticles work. Matter behaves differently at the nanoscale than it does when in "bulk."

To create a daguerreotype, photographers treated a silver-plated copper sheet with halogens—reactive elements such as iodine or bromine—in vapor form. Bonding to the silver, the vapor created a light-sensitive surface of silver halide.

Light reflected off the object or person to be pictured in the daguerreotype and created an image on the silver plate. The bromide or silver iodide converted to silver where the light reflected; the images were dark where the silver halide remained. Wiegandt compares the effect to "condensation on a mirror after you take a shower: with no light above, if you then wipe the glass, the wiped area will look black."

Daguerre discovered that he could develop a latent image by exposing it to mercury fumes. Doing so created silver-mercury crystals in tiny, snowlike grains, forming an exquisite direct positive photograph. A wash of sodium thiosulfate fixed the image by removing the unreacted halogen, leaving on the plate a pure silver surface and the silver-mercury crystals—a "mirror with a memory" and a "triumph of human ingenuity," as Oliver Wendell Holmes wrote in the *Atlantic Monthly* in 1859.

In 2011, a research group at the University of Louisville, aiming to create a solution that would yield nanoparticles, stumbled upon precisely the formulation of gold chloride and sodium thiosulfate, heated slightly, that 19th-century French physicist Hippolyte Fizeau developed to make daguerreotypic images physically stronger and visually more lively.

"These guys had discovered how to do nanotechnology—in the 1800s. It was probably one of the first examples of people discovering a nanotechnology and really harnessing it," Bigelow says. "I think all evidence has it that people were thinking like a chemist would think. 'Nano' was just not in the vocabulary."

Nineteenth-century inventors couldn't see the nanoparticles they'd created in the solution or in the finished daguerreotypes—it wasn't possible to do so until the 1990s, when nanoscientists began to use microscopes capable of observing nanoscale objects. The nanoparticles that form the image of a daguerreotype would need to number between 100 and 1,000, if stacked side by side, to equal the width of a human hair. Those nanoparticles make daguerreotype images extraordinarily precise, so sharp that a good example can be enlarged 20 to 30 times—something most photography today can't achieve, Wiegandt says.

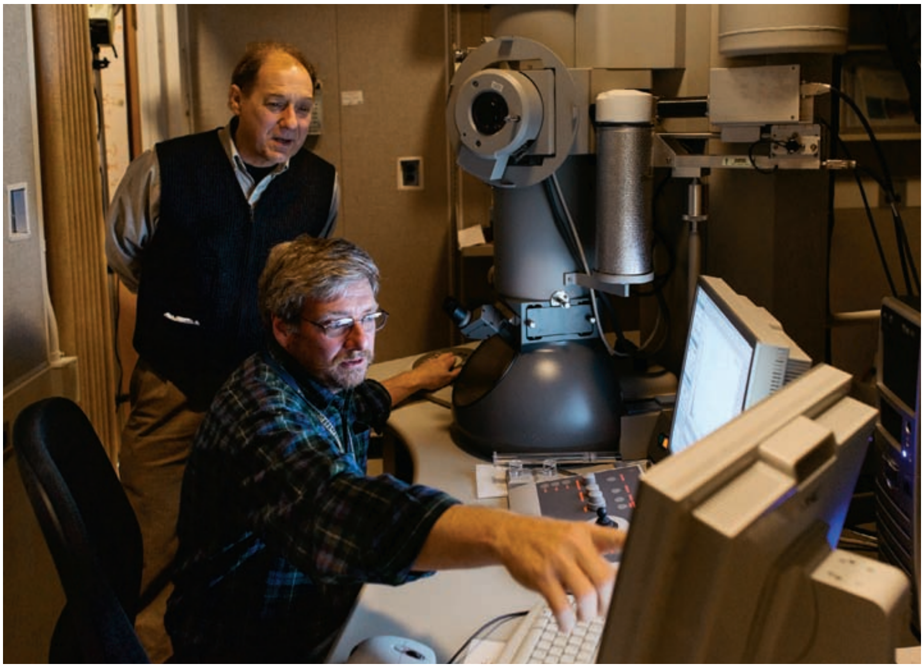
"We often say photography was born fully mature," says Daniel.

Daguerreotypes "degrade through a number of mechanisms—the daguerreotype, its container, things happening on the surface," says McIntyre. Exposed to sea air, as those produced by Boston-based Southworth and Hawes would have been, daguerreotypes can experience corrosion similar to the rust a car would acquire in a coastal setting. Other factors in their environment could have equally damaging effects. "The daguerreotype, probably as much as any single object I can think of, is actually an environmental sensor, so it will record, with extremely high sensitivity, events that have occurred to it," says Wiegandt.

"There isn't any one thing. There are many modes of degradation that we observe," Bigelow says. "Some of them are interrelated, and some might be quite distinct."

Thirty years ago, a graduate student at Penn State began the first comprehensive, modern study of the science of daguerreotypes. Using an electron microscope, she scanned daguerreotypes and found that much was happening beneath their surface. On the basis of her scans, she and other experts proposed cleaning methods and restorative techniques that they believed were safe but that Wiegandt says new research has shown to have "altered the surface structure" of the daguerreotypes. It was premature advice, he says.

New technologies for microscopy and nanofabrication now



IN PURSUIT: Working at the transmission electron microscope at URnano, Ralph Wiegandt (standing) and Brian McIntyre examine the degradation process of daguerreotypes in search of solutions.

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permit much closer examination, and at URnano, Wiegandt and McIntyre are able to see, at strengths of hundreds of thousands of times magnification, what investigators in the 1980s saw only at 1,000 to 5,000 times enlargement. “What really counts, at some level, are these nanoparticles and what’s going on with them,” Bigelow says.

The group’s work may help pave the way for technological applications far beyond the preservation of the daguerreotype. “Self-assembling nanotechnology” is an area of fervid research, especially in the area of biomedical applications—and self-assembly of nanoparticles is what Bigelow, Wiegandt, and McIntyre are finding in the active surface of the daguerreotype. Even the holes, pores, and cavities that they’ve found formed beneath some of the particles hold clues to nanoscience’s potential. It’s a “network of holes through which moisture, or anything in the atmosphere, if it gets in there can actually undermine the image and allow it to decay from within,” Bigelow explains. Dire for the daguerreotype, similar hollow particles could be a boon to medicine as medical nanocapsules.

As up to 170-year-old examples of nanotechnology, daguerreotypes, already cultural treasures, may also be invaluable for what they can demonstrate about how nanoscale materials age. “We don’t know what’s going to happen to these nanoparticles we’re making now—but you know, we’ve got almost 200 years of damage on these daguerreotypes. We can recreate conditions and see what’s happening,” McIntyre says. “It’s got a million applications.”

But for now, the group cares, foremost and fiercely, about the fate of the daguerreotypes. In February, Bigelow and Wiegandt traveled to New Zealand to speak to conservators at a conference sponsored by the American Institute for Conservation of Historic and Artistic Works and the International Council of Museums. Their aim was one of urgent persuasion: “to alert the community of photograph conservators to the reactivity of the daguerreotype’s highly nanostructured surface composed of silver and gold and their unique nano properties; and to propose new preservation strategies that can halt the virtually undetectable nano-level deterioration before it advances to micro and macro stages,” they wrote.

At the Eastman House, under Wiegandt’s guidance, those preservation strategies include cases that seal the daguerreotypes in an argon atmosphere, which will hold them in a suspended state. The argon displaces the air from the daguerreotypes’ environment, taking moisture out of the system and stopping most of the chemical activity. “It’s literally the only action I think we can take,” he says.

The tools to restore the damaged daguerreotypes have yet to be invented, Wiegandt says, and he doesn’t want to act in haste. For now, he, Bigelow, and McIntyre are engaged purely in exploration and analysis. “Nobody really robustly understands what’s happening, either to create the image or what’s happening as the image degrades. Understanding the fundamental chemistry and physics of the daguerreotype process is seminal to understanding how to preserve them,” says McIntyre.

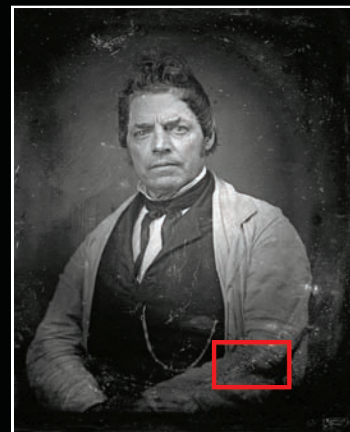
“We see infinitely more surface structure and what’s going on” than earlier analysts could, Wiegandt says. “It’s essential that we revisit assumptions that have been made by previous analyses to understand the material object better, and take care of it better.”

As befits a man who has devoted his career to one of the more extraordinary creations of the 19th century, his prudence is informed by a belief in the power of technology.

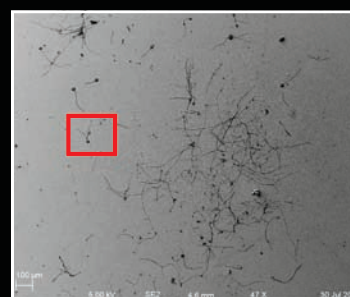
“I have enough faith in science that I don’t want to preempt what might be done in 50 years.” R

Under the Microscope

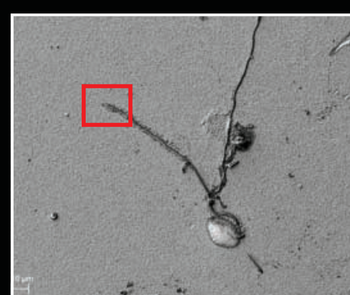
Researchers have found biometallic interaction on the surface of every daguerreotype they’ve examined with a scanning electron microscope.



Biometallic interaction on this daguerreotype of an unknown sitter is highlighted in the red box.



MAGNIFIED
47×
One of the many regions of filamentary biogrowths on the plate.



MAGNIFIED
479×
A detail of the filamentary biogrowth highlighted in the image above.

MAGNIFIED
4,720×
A close-up of the left biofiber branch shown above and the phenomena of particle-crystalline aggregations and interruption of the plate surface.

COURTESY OF RALPH WIEGANDT/EASTMAN HOUSE