Old Warriors Get New Armor

Scientists and archeologists are working to preserve the coatings on China's 2,200-year-old Terracotta Army.

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Hidden underground for more than 2 millennia, the coatings on a famous collection of ancient Chinese artifacts unearthed just 30 years ago are being preserved in a decidedly modern fashion.

A popular attraction for tourists and archeologists alike, the burial complex of Emperor Qin Shihuang near Xi'an, China, features thousands of terracotta statues formed in the likeness of warriors. China's first emperor, Qin Shihuang, ruled from 221 to 210 B.C. According to Catharina Blänsdorf, a conservator with the Bavarian Cultural Relics Office (Munich, Germany), "Qin Shihuangdi" means "First Heavenly Emperor of Qin." The name was adopted by Ying Zheng, who became king of the state of Qin in 246 B.C. at age 13. From 238 to 221 B.C., he conquered the other kingdoms that eventually would be part of his empire.

This photo shows a group of warriors in the Terracotta Army at the burial complex of China's first emperor. Photo © copyright Professor A.C. Scott, Geology Department, Royal Holloway University of London. Used with permission.

Now that approximately one-third of Qin Shihuang's "Terracotta Army" is no longer buried, and despite the fact that unearthed statues are now protected inside a large hall, the original lacquer and mineral-based paint on the statues are susceptible to flaking. Since 1988, a team of Chinese and German conservators and scientists have been trying to stabilize this "polychromy" or "paint layer." Having successfully used a new treatment on some of the statues, the investigators are confident that the paint and lacquer will continue to stand the test of time.

A terracotta fragment treated with HEMA. Photo courtesy of Heinz Langhals, Department of Organic and Macromolecular Chemistry, Ludwig-Maximilians University of Munich.

An Archeological Treasure

Blänsdorf says that the Terracotta Army and the surrounding burial complex honor the accomplishments of one of China's most famous emperors. "It is one of the largest burial complexes of Chinese emperors," says Blänsdorf, adding that most of the burial complexes of other emperors remain unexcavated. "The Terracotta Army belongs to the burial complex of the first Chinese emperor, who is very important for Chinese History because he united the China empire and laid the foundation of the state existing until today." Work on another important Chinese landmark—the Great Wall—began during the Qin Dynasty, which ended 4 years after the first emperor's death in 210 B.C.

The Terracotta Army was discovered in 1974 by farmers digging for water near the town of Lintong, which is approximately 45 km east of Xi'an. The entire burial complex was adorned with valuables by Qin Shihuang's subjects to assist him in the afterlife. Blänsdorf says that the elaborate system of pits containing "precious burial objects" set the standard for how successive emperors would be interred. "Later on, the 'normal furnishing' of an emperor's tomb included a terracotta army and everything that belonged to the emperor's court," she says, noting that the Terracotta Army at Lintong is the earliest one of its kind with so many figures.

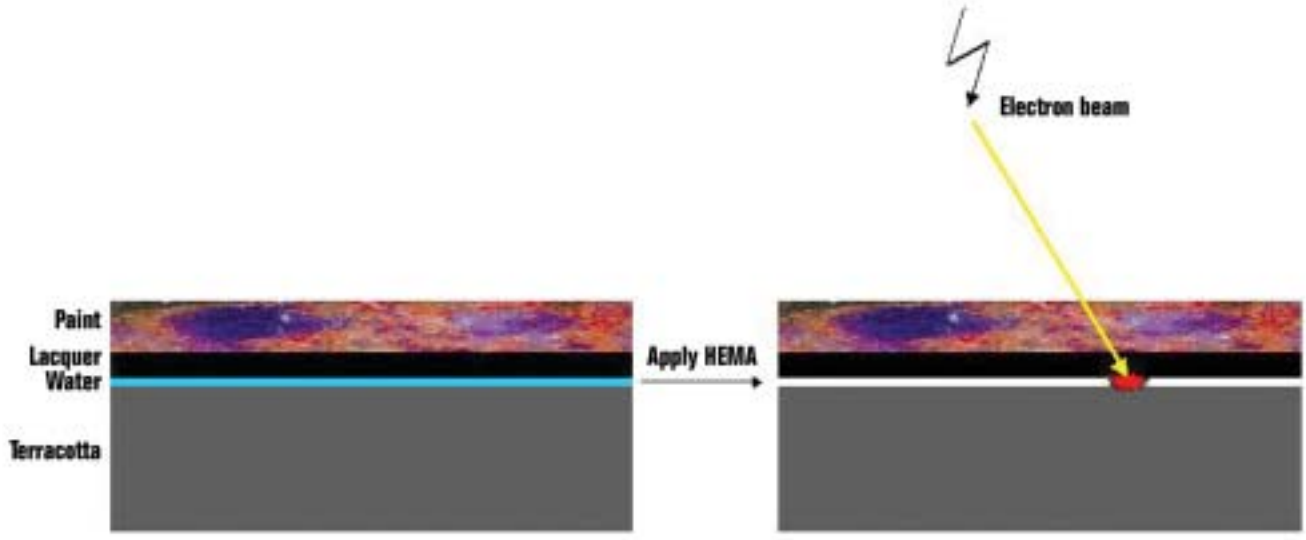
Blänsdorf notes that each of the more than 100 pits depicts a specific part of the emperor's court. The terracotta soldiers are in one pit. Other pits include depictions such as horses, bronze birds, chariots, weapons, judges, and civil servants. The only known human remains are those of the emperor's children and the conscripts who worked on the burial complex. The emperor's actual tomb, surrounded by the network of pits, rests inside a 70-m-high mound that has not yet been excavated. "In the future, with more and more pits unearthed, the focus probably will shift from the terracotta to the mausoleum itself," Blänsdorf predicts. "Slowly we see the army as only a small part of the whole complex that contained everything the emperor had in his life or could need in a life after death."

Premium Polychromy

Not only were the items in the pits considered status symbols, but the manner in which they were painted was considered high art. "The statues have been painted after firing," says Blänsdorf, explaining that this "cold painting" method did not use glaze. "The priming layer consists of East Asian lacquer [called "qi" in Chinese], a natural product that is obtained by injuring the bark of the lacquer tree [*Toxicodendron verniciflua*] and collecting the sap. It turns black during the hardening process. It is—and always has been—very precious, so priming the terracotta statues with qi lacquer is a luxury."

Noting that the priming is applied in two thin lacquer layers, Blänsdorf says that thick layers of natural and artificial mineral pigments are applied on top of the lacquer. "The aqueous binding media could not be determined but could have

The shiny areas in this close-up of a terracotta fragment may appear wet, but they are actually solid HEMA that has polymerized at the surface. Photo courtesy of Heinz Langhals, Department of Organic and Macromolecular Chemistry, Ludwig-Maximilians University of Munich.



HEMA/Electron Beam Hardening

This diagram illustrates the HEMA/electron beam solidifying process. After HEMA is applied to terracotta coated with paint and lacquer, an electron beam is applied. The electron beam penetrates the paint and lacquer, causing the original water to evaporate and allowing the HEMA to cure and establish a bond between the polychromy and terracotta. Diagram courtesy of Heinz Langhals, Department of Organic and Macromolecular Chemistry, Ludwig-Maximilians University of Munich.

been something like gum or animal glue," she says. The various pigments present in the top layers include bone white, lead white, hematite, cinnabar, malachite, azurite, black ink, kaolin, red and yellow ochre, minium, and yellow lead.

A New Combination

"HEMA [HydroxyEthylMethAcrylate]/electron beam solidifying has been specifically adapted for the Terracotta Army," says Heinz Langhals, Professor of Organic and Macromolecular Chemistry at Ludwig-Maximilians University of Munich (Munich, Germany). Langhals' technique involves treating the lacquer layer with HEMA, which is a water-soluble monomer that is said to penetrate the lacquer, paint, and terracotta. "It penetrates objects like water does, but it evaporates as long as it is not polymerized—and therefore it is only polymerized in the lacquer layer and the interface toward the terracotta," explains Blänsdorf. The polychromy being treated subsequently is barraged by electron beams emanating from a particle accelerator, which dramatically increases the speed—and hence the energy—of electrons. The electron beams reportedly cause the HEMA to cure, establishing a bond between the terracotta and the polychromy. Langhals emphasizes that a distinct protective layer does not form in this case. "Such a layer would loosen from the terracotta," he explains.

Langhals points out that his preservation method is unprecedented because it links two previously unrelated technologies: polymeric HEMA and electron beam-induced polymerization. "The combination is new," he says. Polymeric HEMA, which Langhals describes as a "very stable substance," has been used to isolate ceramic water pipes and other building applications requiring isolation—particularly in cases involving contact with soil and water. "The long-term stability, even under severe microbial attack, is of special importance for such applications," he explains. The electrical and electronics industry has used electron beam-induced polymerization to prepare insulating materials such as heat-shrinkable tubes and foils.

Out in the Open

Blänsdorf admits that the Terracotta Army's exposure to climatic conditions, thousands of visitors each year, dust, and other factors can make preservation of the statues particularly cumbersome. "It is a big challenge to preserve and exhibit such a huge excavation in situ," she says, adding that such a situation is rare in the conservation of ancient artifacts. "Normally, the objects are taken out and are presented in a museum and the site is covered again or destroyed."

According to Blänsdorf, it is generally true that ancient objects are better preserved in dry, sandy environments rather than moist, muddy ones. "But objects can also be very well preserved in humid or wet environments—for example, on the bottom of the ocean," she adds. "The mate-

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- **the capability to function properly despite the site conditions**
- **low-cost simplicity.**

rial of the object is important. In the given environment in Lintong, inorganic materials such as stone, metal, and pigments are more stable than the organic materials such as wood, fabric, leather, and binding media. This lacquer on the terracotta objects is an organic material."

A problem at the Lintong site that Blänsdorf and other conservators are trying to manage is the dramatic change in humidity to which an artifact is exposed once it is unearthed. "What produces the damages are the changes of the environment," she says. "If you put objects from dry to wet or wet to dry environment, they 'suffer' from physical and chemical changes taking place. In our case, we have an organic material—the lacquer—that has spent 2,200 years in a wet environment [loess soil that 'stores' a great deal of groundwater]. Water has penetrated into the material, water-soluble components have been 'washed out,' and the whole structure is swollen. After excavation, the water evaporates, the material loses volume, shrinks, and falls apart."

Emphasizing that the terracotta itself is in very good condition, Blänsdorf points out that the rapid escape of moisture from the soil threatens the lacquer layers as well as other materials in the pits. "Without conservation, the paint is completely lost [approximately] 1 week after excavation," she says, adding that the biggest problem for the preservation of sensitive materials is the rapid drying out of the soil. "The loess soil cracks and crumbles, and sensitive organic materials [such] as the polychromy and remnants of wood, leather, textiles, etc. suffer and decay," says Blänsdorf. "With better and more careful methods and treatment of the objects during excavation, much more can be preserved. This is developing in a promising way."

Blänsdorf notes that the HEMA/electron beam technique is being developed to integrate three design characteristics: large-scale usability, the capability to function properly despite the site conditions, and low-cost simplicity.

Conservators in Lintong examine a statue of a kneeling archer for cracks. Photo courtesy of Catharina Blänsdorf, Bavarian Cultural Relics Office, Munich, Germany.

Not Just for Warriors

The researchers contend that video holography has shown that the HEMA/electron beam method can visualize changes of dimensions—such as deformations and the formation of cracks on a microscopic scale and detect "movements" caused by changes in humidity. Langhals explains that holography, a nondestructive testing method that uses laser light to examine the surface of a material, has measured the three-dimensional changes, or movements, of the lacquer layer—evidence that curing occurs.

Pointing out that he is optimizing his invention for use at the burial site (it is not up to full scale at this time), Langhals contends that the HEMA/electron beam technique could be useful in other archeological restoration projects.

"I see a market for HEMA and electron beam polymerization in the consolidation of damaged surfaces of terracotta, ceramic materials, stone, wood, and so on because monomeric HEMA can penetrate the surface of such things and can be solidified by electron beam polymerization," he says. "The penetration of electrons is high enough that surfaces and lower layers [but not the substrate] can be solidified. The polymeric HEMA allows water steam to penetrate. Thus, there are no problems with changes of humidity. Therefore, the method is especially suitable for the conservation of artwork." *MP*