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# **Shrouded in Mystery**

**by Joseph C. Tausta**

It was curiosity that made biophysicist John Heller drive from western Connecticut to a small village in the east-central part of the state on Labor Day weekend, 1978. He attended a meeting of scientists who were planning how to conduct a scientific study of a controversial religious object—the Shroud of Turin. Many people held that this piece of linen was the burial cloth of Jesus. Heller, however, had already formed a mental hypothesis: the Shroud of Turin is a fraud. Heller couldn't resist the scientific challenge of trying to prove his hypothesis. When he got to Amston, Conn., Heller found scientists from some of the most prestigious universities and research centers in the United States who shared his curiosity. The group would become known as STURP, the Shroud of Turin Research Project, Inc. Heller started reading about the history of the shroud.

Until the early 20th century, the shroud was simply one of many Christian relics of questionable origin, such as the “crown of thorns” and the “true cross.” Church authorities have never agreed on the authenticity of these artifacts, but the relics have long been objects of popular veneration. Medieval Europe had perhaps 30 obviously painted shrouds, but only this 4.3-by-1.1 m hand-woven linen cloth evoked such intense and sustained interest.

The image on the shroud consists of a faint, straw-colored representation of an adult male of average build who apparently had been crucified. There are reddish spots that appear to be blood. The image includes both front and back views, as if the cloth had covered the entire body by being folded over at the head.

Reliable records of the shroud date to about 1350. Heller's own investigation turned up only one earlier and believable account, from

the year 1157, in the writings of an Icelandic pilgrim and abbot. This document refers to a “shroud with the blood and body of Jesus on it.”

In 1898, during one of the rare expositions of the shroud in Turin, a photographer named Secundo Pia made some astounding photographs of the shroud that attracted worldwide attention. He discovered that the *negatives* of his photographs were far more realistic than the original image on the shroud. The original image on the shroud was a “negative”—areas that would normally be light appeared dark, and dark areas appeared light. However, the photographic negative reversed these tones, making them look more like a normal “positive” photograph of a man. Furthermore, the features of the face on the shroud showed a striking resemblance to artistic renditions of Jesus since the sixth century. With details of the image made clearer, scientists and archaeologists took a serious interest in the shroud.

### **Accurate wounds**

Physiologists did most of the early work on the shroud. Robert Bucklin, a forensic doctor for Los Angeles County, concluded that the shroud details were uncannily similar to the expected pathology of a crucified man. The details were complete enough for Bucklin to identify the cause of death as asphyxiation. Bucklin’s work is in general agreement with earlier studies by Pierre Barbet, a French physician who published his work on the shroud in 1950. Barbet, a battlefield surgeon during World War I, was very familiar with wounds and the appearance of blood on bandages. He claimed that most paintings did not accurately depict wounds or blood on cloth dressings, but the shroud was accurate in all details.

In the mid-1970s, John Jackson, a physicist at the Air Force Weapons Laboratory in Albuquerque, N.M., made another remarkable photographic discovery. He processed a photograph of the shroud with a VP-8 analyzer, a computerized image analyzer that converts light intensity data into a three-dimensional television image. Satellite data from space are routinely fed to the VP-8, and the analysis results in the spectacular, computer-generated pictures of planetary topography. When pictures of the shroud were analyzed by the VP-8, a realistic, “three-dimensional” image of a face appeared on the screen. In Heller’s words, it was “a three-dimensional image as stunningly different from the photograph as a statue is from a painting.” When ordinary photos are analyzed by the VP-8, they produce only distorted images. However, the shroud image not only showed the two-dimensional shape of a face but, somehow, also contained information about the

depth of facial features. Excitement generated by this discovery led Jackson to become a major organizer of STURP.

### **Speculation about image**

In 1532 a fire burned the church of Sainte Chapelle in Chambéry, France, where the shroud was stored. The silver casket holding the shroud was barely rescued from the flames. This event attracted the attention of Ray N. Rogers, a thermochemist at Los Alamos, N.M., whose hobby is chemical archaeology. Rogers devised three hypotheses for the formation of the image: it was a painting; it was produced naturally by chemicals or volatile products from a body, or by fluids produced by a combination of processes involving organic reactions or materials; or it was caused by rapid heating.

Based on the extent of the scorches on the shroud and the melting point of the silver alloy that dripped from the casket onto the cloth during the 16th-century fire, Rogers estimated that the shroud had been exposed to a temperature between 200 °C and 900 °C. At these temperatures, Rogers said, any known organic paint pigment or binder of inorganic pigment would have been altered in hue and would show different colors on different parts of the shroud. The image of the man on the shroud, however, is uniform in color. Whatever produced the image was not sensitive to the temperatures in the casket during the fire and, therefore, must not be an organic pigment. Rogers also noted that the image appears only on the surface and doesn't penetrate the linen. Capillary action usually carries paint in between the fibers of a fabric. Later work on the shroud confirmed the lack of capillarity, except in the spots thought to have been made by blood.

### **The expedition**

When the owners of the shroud agreed to allow nondestructive testing during the 1978 exposition, STURP organized an expedition of scientists who traveled to Italy to conduct the tests.

Doctors who studied the blood spots were convinced that the spots were placed precisely as expected if a person were executed by crucifixion. The blood spots indicated wounds in the wrists, the side, and in one foot. (Apparently the legs had been crossed; the image shows only one foot and one foot wound). The head area had blood spots indicating many small wounds. There were many other blood spots, presumably from being beaten with a scourge, a whip designed to rip flesh.

Because STURP had a limited budget, Heller could not travel to Italy for the exhibition of the shroud, so he stayed behind in Connecticut and waited for samples. As he waited, other scientists in Italy collected

samples of suspected blood and pigments, using tape developed especially for this purpose by 3M Corporation. The researchers carefully applied the adhesive tape to various parts of the shroud, both on and off the image, and mapped the position of each tape.

When the tape samples arrived in the United States, they were first examined by Walter McCrone, a prominent microscopist and particle-identification specialist with his own research center in Chicago. McCrone quickly asserted that the image on the shroud was a painting and that the shroud was, therefore, a hoax. By microscopy, he had identified crystals of iron(III) oxide and mercury(II) sulfide, which were widely used as pigments in red paint. This caused a stir among the STURP scientists because their tests by X-ray, infrared, ultraviolet, and fluorescence spectra, along with other physical tests, seemed to rule out painting. The slight amounts of iron(III) oxide and mercury(II) sulfide that their instruments had detected were spread evenly over the fabric and were not concentrated in the image areas. McCrone discounted the physical data, and further claimed that the "vehicle" for the pigment was a protein material much like gelatin. Since McCrone had considerable experience in microscopy applied to art, his conclusions had to be considered seriously, even though they disagreed radically with STURP's tests.

When the sample tapes finally arrived in Heller's laboratory, he enlisted the help of Alan Adler, a chemist at Western Connecticut State University. They began experiments to identify the alleged blood spots and to determine the chemical composition of the image proper.

## **Human blood?**

Adler and Heller began by carefully separating tiny linen fibers and other residues from the tapes. The samples were so small that the scientists worked with a microscope. They then tested the blood residues with visible light microspectrophotometry, which showed light absorptions characteristic of an iron porphyrin, a component of hemoglobin. As a confirmatory test, a powerful reducing agent, 97% hydrazine,  $N_2H_4$ , was added to the suspected blood. This reagent reduced any iron that might have been present from +3 (ferric) to +2 (ferrous) and also solubilized the organic constituents of the suspected blood particles. The iron(III) oxide in paint pigments is not soluble in hydrazine, but the suspected blood particles were soluble. To displace the iron atoms present in the hemoglobin of blood, the samples were treated with 97% formic acid. Under ultraviolet light, the samples now showed the red fluorescence that is characteristic of iron-free porphyrin. This was regarded as a confirmation that the spots were probably blood

and not paint. The iron in these spots was the iron that occurs normally in hemoglobin.

In Italy, the STURP team had taken ultraviolet photographs of the shroud, and these revealed fluorescent rings surrounding the blood spots. This is characteristic of blood, because the colorless serum spreads through fabric farther than the clotting blood cells. To test whether the fluorescence resulted from the protein in blood serum, fibrils from the suspected serum regions were chemically analyzed. Included were fluorescamine, enzymatic, and bromocresol green tests. All were positive, indicating the presence of blood serum proteins.

Pieces of hardened material that had broken away from linen fibrils also were examined because they resembled dried blood under the microscope. Potassium cyanide and ammonium hydroxide made these pieces turn the color of cyanomethemoglobin—another positive blood test. Some of these samples appeared to be greenish brown in color. This coloring led the researchers to test for bile pigments, which are metabolic products of hemoglobin. A chemical assay gave the characteristic blue azobilirubin color for bile pigments.

No chemical test thus far had been negative for blood. Heller later reported that “Any one of these (chemical tests) is proof of the presence of blood, and each is acceptable in a court of law. Taken together they are irrefutable.” The “blood spots” were indeed blood, but were they human blood?

Adler turned to an immunological test. He obtained some antibody to human albumin that had been modified to make it fluorescent and applied it to albumin from cow, pig, and the shroud material. Only the shroud albumin gave a positive test. It was human or, at least, primate blood.

Had a medieval artist put the finishing touches on a fraudulent painting with human blood? Art experts were consulted. Their opinion was that the use of blood would be unlikely since blood changes color and the artists of the period were concerned with finding unchanging pigments. Still, use of blood as paint could not be ruled out. Under the microscope, fibrils from the body image looked partly corroded and had a yellow-amber color—like a lightly roasted marshmallow. The dehydration and oxidation of a carbohydrate can produce this color, and since linen is a carbohydrate polymer, Heller and Adler tried to get rid of the color by reduction. First they tried the reducing agent ascorbic acid with no success. Next a stronger reducing agent, diimide, was applied and the color disappeared. Concluding that the color was caused by dehydration and oxidation, they placed some normal fibrils in sulfuric acid, a good dehydrating reagent and one in which oxidation

can occur. In time, the exact color of the image fibrils was reproduced and could be reversed with diimide. The image seemed to have been made by some sort of dehydration-oxidation process.

Heller and Adler noted that the fibrils under the blood spots were not yellow-amber after enzymatic removal of the blood. This indicated that the blood had been applied to the shroud before the image-forming process took place. If the shroud was the work of an artist, he must have painted the blood spots first and then applied the image around them, though it is unlikely that anyone would look under the blood spots to check this detail.

### **Replicating the image**

It was no problem to generate the yellow color of the fibrils of the cloth in the laboratory. Heat, body chemicals, and X-rays all give the characteristic color, but no one could explain how it might have been produced by a medieval artist or a natural process. Professor Giles Carter of Eastern Michigan University suggested that low-energy X-rays caused the dehydration. Adler responded that the science was accurate, but that “anyone who was that radioactive would probably be dead long before he was crucified.” The STURP scientists tested and found flaws in all hypotheses of image transfer. Getting the proper color on a sample of linen was easy. Producing an image as detailed and undistorted as that on the shroud remained an unsolved problem.

After all the work by the STURP team, the shroud image remained as before—a mystery. The STURP scientists concluded that the only hypothesis that could be ruled out was that the image is a clever painting.

### **Ancient fabric?**

After STURP had concluded its investigation, an improved technique for measuring the age of cloth (and other materials) was perfected. Carbon-14 dating recently completed by using a tandem accelerator mass spectrometer (TAMS) indicated that the linen fabric is about 660 years old (see “Carbon-14 Dating,” page 12). Even if the shroud were found to be 2000 years old, its authenticity still could not be proved scientifically because the image could have been the work of an artist working shortly after the death of Jesus, or it could have been produced centuries later on a very old cloth.

Even though the cloth is medieval, the mystery of the image process remains. At this time, no known image-transfer mechanism satisfactorily explains all the details of the image. Science still faces the challenge of explaining how, apparently without the use of paint, a

historically accurate, three-dimensional, negative image of a brutally tortured man was transferred to the linen cloth.

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## CAPTION

The left image is a normal, positive photograph of the shroud; the right image is a negative photograph. Arrows identify examples of the various types of marks and images. A is the body image of unknown origin; B, blood image; C, burn mark; D, scorch mark; E, water-stain mark.

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## BIOGRAPHY

**Joseph C. Tausta** teaches chemistry at State University College of New York, Oneonta, N.Y.

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## REFERENCES

- Culliton, B. "The Mystery of the Shroud of Turin," *Science* **1978**, *201*, 235-39.
- Heller, J. H. *Report on the Shroud of Turin*; Houghton Mifflin: Boston, 1983.
- Heller, J.H.; Adler, A.D.; "Blood on the Shroud of Turin," *Applied Optics*, February 21, 1983, p. 35
- Jumper, E.J. et. al. "A Comprehensive Examination of the Various Stains and Images on the Shroud of Turin," In *Archaeological Chemistry—III*; Lambert, J.B., Ed.; Advances in Chemistry 205; American Chemical Society: Washington, D.C., 1984, pp. 447-476.
- Raloff, J. "Controversy Builds as Shroud Tests Near," *Science News*, April 16, 1988, p. 245.
- Turro, N.J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, Calif., 1978.
- Zurer, P. "Archeological Chemists Grapple with Shroud of Turin," *Chemical & Engineering News*, February 21, 1983, pp. 34-35.