

Fig. 1. Edge contrast enhanced negative and positive images of the Shroud of Turin.

## CHEMICAL AND PHYSICAL ASPECTS OF THE SINDONIC IMAGES

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### **Introduction**

The image-bearing cloth now known as the Shroud of Turin became an object of dispute following its display in the late 1300s at Lirey by the Charny family, as they presented it as the authentic burial cloth of Jesus (Figure 1). However, it became scientifically polemical following the 1898 Exposition in Turin, when for the first time it was photographed by Secondo Pia. Scientific interest was aroused by the fact that the plate bearing the photographic negative of the body showed details more clearly and gave a more natural appearance than the visually observed image on the cloth.<sup>1,2,3</sup> As the Shroud's historical antecedents predated the invention of photography, this observation stimulated scientific inquiry hypothesis, and controversy.

### **Science and the Shroud**

Validation of scientific conclusions differs from the criteria used in historical investigations in that the hypotheses must be testable by a reproducible experiment. For example, determining the chemical structures comprising the images on the cloth can test whether or not it is a painting. Science cannot establish the authenticity of the Shroud as Christ's burial cloth, as no acceptable laboratory experiment exists for testing the identity of the human image seen on the cloth, but evidence that it is a painting could disauthenticate it. Furthermore, initial test results supporting a hypothesis do not necessarily prove it. An alternative hypothesis equally well supported by the observations is always possible, e.g., the presence of interferences can lead to false positive or negative conclusions. The test may not be sensitive enough to draw a proper conclusion or it may be so sensitive that it will give misleading conclusions. There is also the problem of errors, both random (affecting precision, i.e., reproducibility) and systematic (affecting accuracy), particularly for quantitative measurements. One must carry out enough measurements to establish precision and enough control experiments to distinguish which of all reasonable possible explanations best fits all of the data and not simply select or delete data that favors what might seem to be an obvious conclusion. Scientific truth becomes a matter of relative probabilities to which one approximates by continued application of the scientific method.

### **Vignon and Barbet**

The pioneering scientific investigations carried out by Paul Vignon<sup>4,5</sup> and Pierre Barbet<sup>6</sup> well illustrate the principles presented above. Their hypotheses and experiments presaged all the subsequent scientific studies which have continued to illuminate and elaborate on their conclusions.

Trained as a biologist, Vignon was also an amateur painter and therefore began his study by considering the physical evidence that the Shroud was a painting, as claimed in the historic d'Arcis memorandum. He first noted that there was no evidence of flaking of any parts of the image as would be expected if a cloth bearing an applied pigment had been rolled and folded as had been the Shroud. Therefore he tested this idea by oil painting replicas of the image and observing that such mechanical actions did produce obvious flaking. Next he observed that the images showed no evidences of outlining, but appeared to continuously fade into the cloth. Then coating his own face with red chalk he attempted to reproduce the characteristics of the image as a contact transfer. As this was also unsuccessful, he concluded that the image was somehow projected onto the cloth. On the basis of these experiments and further artistic criteria, he rejected the notion that the Shroud was a painting.

He also established the consistency of all the blood marks with those expected for a man who had been beaten and then crucified. For example, the blood marks on the arms demonstrated that they were in an elevated and extended position at the time the wounds were bleeding — as blood does not flow contrary to gravity as the observed image would appear to indicate. Most importantly, he noted that the blood images were forensically consistent with those of clotted blood and not a freshly flowing wound in that they appear thickened on the edges. As blood forms a scab it contracts, thickening the edge of the scab and exuding serum onto the surface and edges of the contracting clot. This phenomenon is simply termed clot retraction.

Vignon initiated the field of iconography by comparing specific characteristic image and blood marks and other features common to the Shroud and to numerous iconographic examples to demonstrate a history of this image prior to the 14th century and traceable even to the 6th century. Finally, he proposed and tested a process for formation of the image based on the diffusion of ammoniacal vapors formed from the perspiration of a man suffering a traumatic death that would convert colorless plant pigments postulated on the cloth to a colored form. However, this vaporographic theory has been shown in later experiments to be untenable, e.g., the exposure of image bearing fibers to acid vapors does not reverse the color.

As an experienced battle surgeon, well acquainted with the appearance of blood wounds on cloth, Barbet continued the forensic studies initiated by Vignon. He further confirmed that all the various blood marks seen in the images were consistent with the historic descriptions of Christ's crucifixion and unlike the body images they got on the cloth by actual contact transfer with a wounded human body. He noted that the major blood wounds even showed to the eye what appeared to be serum contraction rings, thus supporting Vignon's observation that these were transfers of clot exudates. He further investigated some of the physiology and mechanics of the crucifixion process. For example, by carrying out experiments on corpses and severed arms with attached weights, he demonstrated that nails driven through the palms as shown in most artistic renditions of a crucifixion will not support the weight of a suspended human body. Rather such nails must be driven through the wrists as is clearly seen on the

Shroud where a correct image is shown, unlike that in early artistic depictions. The studies of several physicians, although differing in some details, since then have confirmed and further elaborated on these conclusions.<sup>3,7, 8, 9</sup> In particular, studies show that these images are blood marks transferred to the cloth by direct contact with a wounded human body bearing the marks historically ascribed to those of Christ's crucifixion. In addition, the conditions and timing of the clotting process have been experimentally investigated, demonstrating that only clotted blood will give the type of clear unsmearred blood images seen on the cloth<sup>10</sup> and therefore that these wound marks are really images of clot exudates and not whole blood.

### **Following the Pioneers**

In addition to the body and blood images there are also burned areas, scorch marks and waterstains on the cloth incurred at the time of the historically recorded 1532 fire, consistent with a pattern of forty-eight folds. There is also another set of non-historically recorded burn marks present showing a folded-in-four pattern, as well as various wrinkles and fold marks. These, along with the non-image areas of the background cloth serving as a reference, have been the subject of much scientific investigation in further pursuing the pioneering studies on the nature of the body and blood images. Much of this work has been summarized in professional review papers<sup>11,12,13</sup> following the intensive Shroud of Turin Research Project (STURP) study in 1978, as well as in the monographs already cited. A variety of investigative techniques has been employed by numerous experienced investigators. In general, these studies have more firmly supported the conclusions drawn by Vignon and Barbet.

### **Image Investigations**

Several types of photographic studies have been conducted and in different regions of the electromagnetic spectrum. The images have then been further subjected to several forms of analysis by different types of computer algorithms. These studies have then been compared to the microchemical and spectroscopic investigations to test the consistency of the conclusions drawn.

Using appropriate light sources and filters, a series of ultraviolet fluorescent photographic images were made of the Shroud and compared to color reflectance photographic images taken of the same areas.<sup>14</sup> The blood marks, waterstains, scorches, and body images all appear as red brown to brown yellow images of approximately the same intensity range of variation in the color reflectance photographs. However, these images all appear quite differently in the ultraviolet emission and absorption photographs. The background cloth shows a light greenish yellow emission not typical of other known old linen cloths and perhaps suggesting the presence of some type of thin coating of a fluorophore on the original linen. The scorches show the typical reddish orange fluorescence associated with scorched cellulosic fabrics. The body images absorb somewhat more strongly than in reflectance, but show no emission characteristics. Therefore the body images were not produced by a scorching type process, but their mechanism of production did chemically modify and quench the background

cloth fluorophore. Like the body images, the waterstains also appear somewhat darker and show no emission, but they now show more color variation than in reflectance, as might be expected for an image of a diffusive process. The blood marks are all now highly absorbing, as would be expected if hemoglobin were present, as the porphyrin structure in this chromophore is a very strong near-ultraviolet absorber. Also the border of every blood mark shows the typical yellowish fluorescence of the serum exudate ring around scabs as expected for clot retraction transfer marks, thus confirming the medical forensic analysis and the observations of Barbet (cf., Figure 2). Further, all the scourge marks now show a pattern of scratches on the narrow ends, not visible in reflectance, that would be expected for wounds produced by a typical Roman scourge. Therefore an artist painting the blood marks would not only require a 20<sup>th</sup> century knowledge of the physiology of clot retraction, but would have to produce images of serum rings and scratches that are only obviously evident under ultraviolet excitation.

A series of color microphotographs of the different types of image areas were made at magnifications ranging from 3.6X to 36X.<sup>15</sup> Two of these microphotographs taken at 18X are shown in Figure 3. The top photograph is a close-up view of a portion of the blood mark found in the small of the back; the bottom photograph is a close-up view of a portion of the right eye. Utilizing the microscope employed in making these image area microphotographs, a visual mechanical examination of these same image areas was conducted with the aid of a probing needle.<sup>11, 12</sup>

The blood area photograph in Figure 2 shows all the characteristics that would be expected for a clot retraction transfer to a fabric. As confirmed by the probing needle, the fibers are cemented together by the applied chromophore and show capillarity in that they penetrate to the back of the cloth. They can also be seen under the crossing threads of the weave. There is evidence of abrasion of the chromophore from the more exposed surfaces as would be expected if this were an applied material with mechanical characteristics different from its cloth substrate. There is a variation in the color of the adherent particles from orange yellow to deep red as would be expected for clotted blood, as the formation of a clot leads to some separation and aggregation of the blood and serum components. However, this type

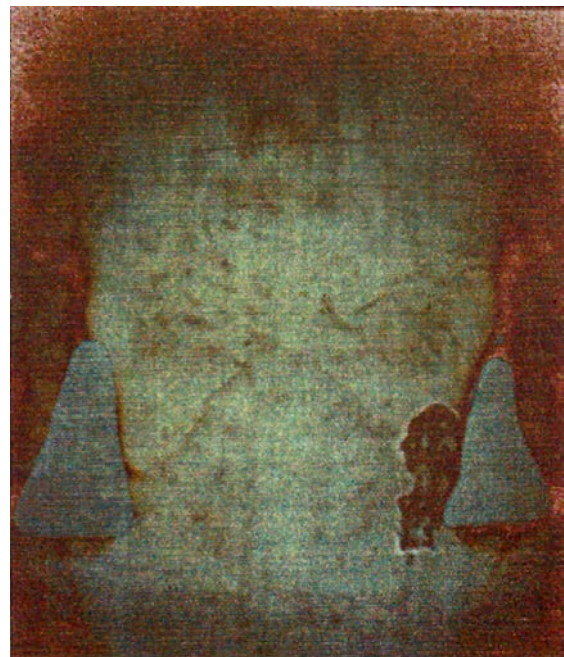


Fig. 2. Ultraviolet photograph of the upper part of the frontal body image. Note the serum contraction ring easily seen about the lance wound.

of color variation would not be anticipated for an artist's uniformly ground and mixed pigments in some type of protein binder for application to the cloth substrate. All these visual characteristics are also clearly seen in the 3.6X microphotograph, as well as the fact that the diffusive borders are not as sharp as would be expected if these transfers were of fresh blood and not a clot exudate.

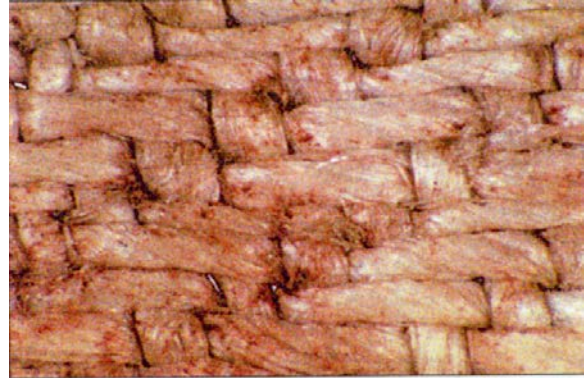


Fig. 3. 18X microphotographs of image areas on the Shroud of Turin. Top: Blood mark on the small of the back. Bottom: A portion of the right eye.

In contrast to the blood area image, the body image photograph in Figure 2 does not show any evidence of abrasion or cementation. Furthermore, the examination with the probing needle confirms that there is no cementation, that the body image fibers are more brittle than those of the non-body image fibers, and that there is no evidence of capillarity.<sup>11, 12</sup> Thus there is no evidence for



an artist's pigment binder. The body image coloration does not appear under the crossing threads of the weave or penetrate the cloth, but only goes one fiber deep into the thread. The body image literally lies only on the very top exposed fibers of the weft threads, leaving the unexposed fibers of the threads of the weave unchanged. Furthermore, all the modified portions of the fibers show a uniform straw yellow coloration, as confirmed by a densitometric study of the photo image, yielding a less than 2% variation in the absorbance of the individual colored body image fibers.

This uniformity of color of the body image fibers again argues against the body image being a painting. To provide shading and detail in a painting, an artist varies the concentration of an applied pigment thus creating a variation in color, i.e., a pigment concentration gradient. However, the body image seen on the Shroud is provided by variation in the number of uniformly colored fibers per unit area, i.e., it is an areal density image.<sup>12</sup>

Thus a painter would have to monitor the number of fibers he paints per unit area of his painting while visualizing in his mind's eye the macroscopic image he is trying to create. Note that a single fiber is about half the thickness of an average human hair, putting rather severe restrictions on the size of the artist's brush and the time required to produce the finished painting. While this observation of the uniformity of colored fibers argues against a painting, it might possibly be construed as evidence for a dry powder contact transfer process. However, there is no evidence seen for the presence of the powder particulates required and the

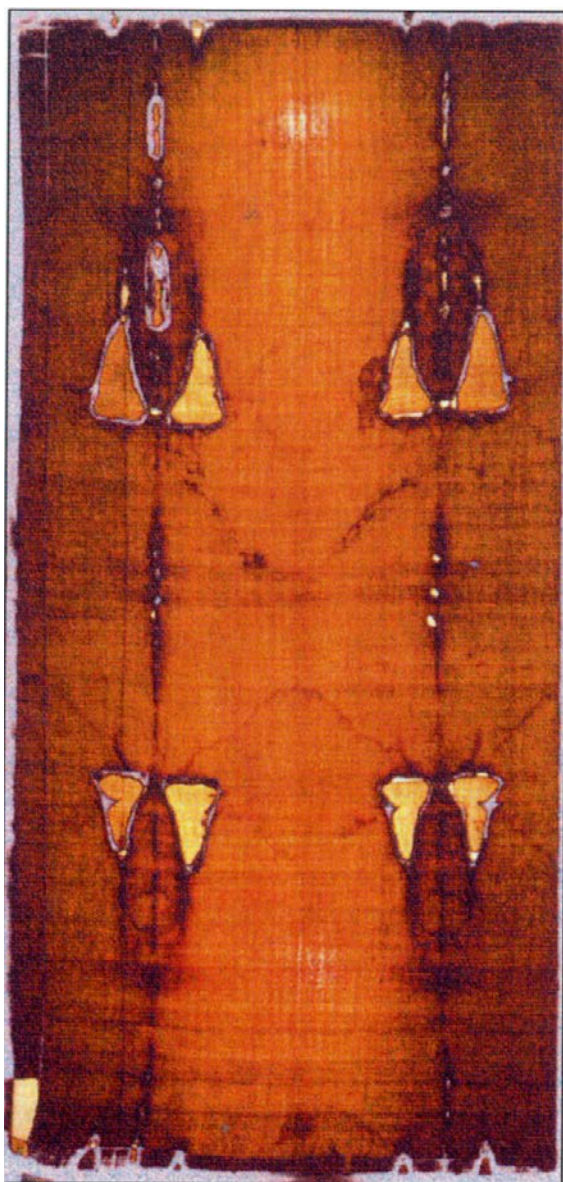


Fig. 4. Left: Transmission photograph of the frontal view of the Shroud of Turin. Right: X-radiograph of a waterstain on the Shroud of Turin.

color of these body image fibers' cannot be removed by rubbing or brushing with a probe. In particular it should be noted that this straw yellow color of the body image fibers does not match the color of any of the known forms of ferric iron oxides.<sup>16</sup>

The burn, scorch, and waterstain marks all penetrate the cloth and careful low power microscopic examination of their areas of intersection with body image areas provides further confirmation of Vignon's arguments against the body images being a painting.<sup>12</sup> Though the scorches can clearly be seen to have conducted heat into the body image areas, there is no evidence of any color change along the heat gradient as would be expected if the body image chromophore was an organic pigment or stain or if it was a yellow hydrated form of a ferrous iron oxide. Similarly, while the waterstain margins give the appearance of chromatographic diffusion of material to the edges, the body images within the waterstains show no change in color, arguing against the presence of any water

soluble pigments, stains, or applied powdered materials as the chromophore. It is also of interest to note that the microphotographs of the waterstains have a "rusty" appearance.

Further evidence for the body images being only one fiber deep is demonstrated by the transmission photograph shown in Figure 4. This photograph was produced by placing the light source behind the suspended Shroud and recording the image of the radiation transmitted through the cloth. In the usual reflectance photographs of the Shroud the light source is placed in front of the cloth and the recorded image is then that of the radiation reflected from the surface of the cloth. In reflectance photographs the images of the waterstains, scorches, blood, and body images are all approximately of about the same intensity. In the transmission photograph the waterstains, scorches, and blood marks are all still clearly evidenced, confirming that they do penetrate the cloth. However, the body images have almost completely disappeared. In the reflectance mode the colored body image fibers produce 100% of the reflected radiation recorded, but in the transmitted mode they only contribute about 1% of the radiation recorded, thus demonstrating their superficial one-fiber-deep nature.

X-ray radiographs of the Shroud were taken employing a medical type diagnostic instrument.<sup>17</sup> An example of one of these radiographs is shown in Figure 4, depicting one of the waterstains. The waterstain margins, burned areas, and the details of the weave of the cloth were all that were evidenced in this study. The body images and blood marks are not seen. Under the conditions employed, one expects strong absorption characteristics for the element calcium, the evidence for which is confirmed chemically and spectroscopically to be in the linen fibers. This explains why the cloth weave is seen clearly and also explains why the waterstain margins show up strongly, as one would anticipate chromatographic concentration of this element in the margins under the conditions of the 1532 fire. Although the element iron does not absorb strongly under these conditions, since the blood stains penetrate the cloth and are therefore concentrated, one would expect to see these marks (especially if they also contained the element mercury as has been proposed) if one attributes the blood marks to be painted images composed of iron oxide and mercuric sulfide pigments in a protein binder. However, as the mineral content of a blood exudate is comparatively low, the absence of these marks in this examination is consistent with the forensic conclusions. Clearly the blood marks are not painted images.<sup>12</sup>

Infrared thermographs of the Shroud were also taken.<sup>18</sup> This technique has been applied in the examination of paintings to detect evidence of any underlying paint structures or evidence of an outline of the composition. Neither of these types of evidence was seen, again in agreement with the conclusion that the body images are not paintings. However, the body images, blood marks, and burned areas can be distinguished from one another and from the background cloth, indicating differences in chemical composition between these different areas as shown by the differences in the infrared spectral characteristics.

Several computer studies employing various types of algorithms have been carried out on the photographic images of the Shroud.<sup>19, 20</sup> For example, the black and white images were scanned into a computer with the intensities at each pixel



point being assigned a gray scale value. The program then removed the pixels at each ascending gray scale value a level at a time. At each level the pixels were observed to disappear at random with no evidence of a directional pattern. This shows that there is no evidence for a brush mark pattern as would be expected for a painting.

The body images were also examined with a VP-8 image analyzer. This instrument treats the intensity of the image at each pixel point as if it were a projection from a surface. The algorithm employs an inverse distance function analyzer such that darker pixels are translated into points closer to the receiving surface and pixels of lighter intensity are translated into points farther away. The shape of this distance projection surface is then displayed on a video screen. When the Shroud image is analyzed with this instrument an excellent correlation of the image intensity to the 3-dimensional shape of a human body is revealed, i.e., true 3-D information is encoded into the Shroud's body images. Further, refinements of this analysis show that the distances encoded are not from the body surface to taut cloth stretched over the body, but to a cloth surface draped over the body. The information transfer process was shown to be collimated, as is consistent with the absence of any image between the frontal and dorsal body images (i.e., the top of the head is not seen). Therefore the process producing the body images must involve some type of radiational mechanism transferring energy from a human body shape to a draped cloth covering this body shape and with the amount of energy transferred in a collimated process to produce an image being inversely proportional to the distance between the two surfaces. Since the image is seen at points where there is no contact between these two surfaces, this process cannot be one involving a contact transfer. Note, this supports previous conclusions that the body images and the blood marks have gotten onto this cloth by distinctly different mechanisms. Common sense suggests that no medieval artisan would be able to visualize how to do all this at a time in history almost a century before the recognition of perspective and its incorporation into painted images.

Although no one has as yet discovered a mechanism that accurately reproduces the VP-8 characteristic of the body images, VP-8 can be utilized to test any proposed image formation mechanism. Numerous artistic techniques have been so tested and all have failed to meet this strict VP-8 criterion.<sup>20</sup> These include albedo (simple reflection) images from a bust of a bearded man, phosphorescent emission images from this same bust, artistic sketches and paintings of various types (including copying from a photo of the Shroud face), chemical contact images, thermal imaging, diffusion images, electrostatic imaging, bas reliefs, dry powder contact images, scorching contact with an engraving, and various hybrid mechanisms. While these tests do not preclude the possibility that some form of artistic rendition has been employed to produce the Shroud, they severely restrict any proposed methods to what has not already been shown to be inadequate. One must also explain how this proposed process has been properly incorporated with the blood marks.

This last point is illustrated by another interesting study utilizing a full size photograph of the Shroud face and blood marks.<sup>21</sup> The blood marks were traced onto a piece of cloth and carefully cut out. The mask was then applied to the face

of a bearded man whose facial features were dimensionally in good agreement with those on the cloth and the blood marks were then applied to the man's face by filling in the cut-outs. When the mask was removed a long-standing apparent anomaly was resolved. The blood marks that appear to be on the hair without matting it together are seen to be actually on the cheeks where bloodflows from the wounds in the temples would be expected to be found. The apparent discrepancy arises from the fact that the blood marks have been transferred to the cloth by direct contact with clot exudates from wounds, while the man's facial features have been projected onto the cloth by a non-contact mechanism of a radiational type. Therefore they are not in stereoregister. This same evidence of non-stereoregister can also be seen by careful examination of some of the scourge marks on the edges of the legs as seen in the 3-D computer image studies. This simple visual experiment confirms the conclusions from both the forensic and computer analysis investigations.

A polarized image overlay technique has been utilized to facilitate and better quantify the comparisons of images in iconographic studies.<sup>22</sup> This technique requires the use of two projectors with one mounted above the other. The two images one wishes to compare are projected onto one another and by means of zoom lenses brought to the same magnification and into an overlapping register. Plane polarizing sheets are then mounted in the front of each projector, but in a crossed configuration to one another's planes of polarization. By rotating a third polarizing sheet while viewing the superimposed images through it, one can readily visualize the degree of congruence of the two images. Using this technique, various types of iconographic and mandylion images as well as coins were compared to the facial image on the Shroud. Comparisons of this type have also been applied to the relationships between the blood marks on the head images of the Shroud and the blood marks on the Cloth of Oviedo. This latter relic is reputed to be the Sudarion or the napkin applied to the face of Christ immediately upon his removal from the Cross and can be historically traced to the 7<sup>th</sup> century.<sup>9,23</sup>

### **Chemical Investigations**

The chemical testing of the Shroud has been conducted on material removed from it by various sampling techniques, mainly "sticky tape" sampling.<sup>11,12,24</sup> At the time of the STURP investigation, samples were removed from designated and documented locations by means of a special tape holder providing a controlled pressure and supplied with a Mylar tape coated with an inert adhesive. Microchemical testing was then carried out on specimens removed from these tapes at off-site chemical laboratories. However, this type of sampling provides some difficulties in deciding which specimens collected are really typical of the designated location.

There is the problem that the mechanical folding and rolling of the cloth will displace abraded material (cf., the discussion of the microphotographs of the blood image areas) and brittle fibers (cf., the discussion of the microphotographs of the body image areas) from an original site to an inappropriate location, e.g., some occasional abraded blood particles are found in non-blood image locations.

There is also the problem of obvious contaminants, e.g., on every tape are found red silk fibers from the protective covering cloth in which the Shroud was rolled up before the present conservation measures were taken. Occasional airborne materials that have fallen on the cloth can also be seen, e.g., dust, industrial soot, insect parts, tiny fragments of siliceous materials, modern synthetic fibers, etc. A somewhat more serious type of contaminant is the occasional appearance of materials that can be clearly identified as artist's pigments such as rose madder or cinnabar, etc. Historical studies have established that over four dozen painted copies of the Shroud have been produced and that almost all these finished copies were sanctified by pressing the painted copy to the original thus unwittingly providing some contact transfer of materials between the two cloths.<sup>25</sup> Therefore, unless such materials can be shown to be present in predominating amounts, they cannot be construed as evidence that the Shroud image itself is a painting, but only that the cloth has been contaminated by the painted copies that were laid on it to be sanctified.<sup>13,24</sup> It should also be noted that none of these known artistic copies show any of the forensic or image characteristics that typify the Shroud of Turin.

An arbitrary minimum threshold of 15 specimens of a particular type of visually identifiable characteristics (mainly color and surface appearance under phase contrast microscopy) was set to constitute a class of fibers or particles assignable to a specific location on the cloth to be subjected to chemical testing. When removed from the tape the specimens can be further classified by their fluorescence characteristics (both the adhesive and the tape are fluorescent and therefore interfere if specimens are not first removed from the tape) and also for their polarization characteristics (the Mylar tape is form birefringent and again interferes unless the specimen is removed from the tape). Carrying out this prescription excluded all the various types of contaminants discussed above and yielded 11 classes of sample objects for testing.<sup>24</sup> Usually at least 5 of each of these types of objects were tested and were always compared against appropriate controls prepared from laboratory chemical samples, modern linen, a sample of 17th century Spanish linen, heated linens, protein coated linens, blood coated linens, etc.<sup>24</sup>

Twenty two different types of microchemical spot tests for 17 different common metallic elements that could be conjectured to be involved in the formation of images on the Shroud were checked against chemical controls and also checked for possible interferences and then applied to the sample objects and other appropriate linen controls as well. All the types of Shroud fibers gave positive tests for only two elements, calcium and iron. However, these elements do not derive from the presence of iron oxides or calcium carbonates in the fibers, as positive tests are obtained without the need for prior acidic digestion and therefore these elements can be considered as being coordinately covalently bound to the linen's cellulosic structure. Other samples of old linens show the same type of results and therefore the presence of these elements can be ascribed to chemistry arising during the manufacture of linen from flax, e.g., the retting process carried out in naturally occurring hard waters. Since these tests are ubiquitous and uniform for both body image and non-body image fibers, it demonstrates that the body image chromophore cannot be ascribed to the presence of a metallic pigment.

One class of the test objects can be clearly identified as ferric iron oxide particles. They are reddish, birefringent, pleochroic, give a positive spot test for iron only if predigested with hydrochloric acid, etc. They are found predominantly only in the scorched blood areas and in the waterstain margins. As the combustion of blood is known to produce ferric oxide, its presence in the scorched blood area is expected. A chromatographically induced reaction under the conditions of extinguishing the 1532 fire that produced the waterstains has been proposed and tested by control experiments with the -Spanish linen. It produced iron oxide particles of the same appearance and properties as those found in the water-stain margins and therefore suffices to explain their presence at these locations. It should be noted that the waterstain fibers test negatively for the presence of protein as a possible paint particle pigment binder and that particles of this iron oxide type are not found in the body image area samples.

Another class of particles ranging in color from red to orange tests as blood derived residues. They test positively for the presence of protein, hemin, bilirubin, and albumin; give positive hemochromagen and cyanmethemoglobin responses; after chemical generation display the characteristic fluorescence of porphyrins; etc. They are found predominantly in the blood areas, although some are also seen in displaced locations, as would be expected from the abraded appearance of the blood marks as seen in the microphotographs. In traumatic shock as would be experienced under flogging and crucifixion, red blood cells lyse and the released hemoglobin is both bound up in haptoglobin-hemoglobin aggregates (a brownish denatured methemoglobin color) and also degraded by enzymatic action in the liver to convert the heme portion to bilirubin which is also then bound up in protein complexes, mainly with albumin (a yellowish orange color). When such blood is shed and then clots, the exudate will contain these protein bound complexes with an expected range in a non-uniform color from red to orange, but any intact cells will remain in the clot. A simulation of such a traumatic blood exudate prepared from laboratory chemicals as a control matches the appearance and properties of this class of test objects. However, a simulated artistic paint pigment mixture of iron oxide and mercuric sulfide in a gelatin protein binder does not make such a match. Thus the chemical testing not only supports the forensic conclusion that the blood marks are derived from contact of the cloth with clotted wound exudates, but that the shed blood was from someone who suffered a traumatic death as depicted in the body images.

Confirmation of these blood mark conclusions has been further provided by immunochemical testing by two independent investigators.<sup>3,12</sup> One of the investigators obtained positive tests with antibodies for the blood type and human globulin, both oligosaccharide type antigens; while the other investigator obtained positive tests with antibodies for human whole serum and human albumin, a polypeptide type antigen. This pattern of tests ensures against false positive results, as for example from bacterial cell wall debris, and allows one to identify the blood as human with a high degree of certainty even though chimpanzee antibody employed as one of several controls also gave the expected positive cross serological reaction. It should be noted that at the time of the Charny display, no one had the medical knowledge of the details of blood clotting, nor access to a supply of traumatic clotted blood exudates from humans

or non-human primates to have considered painting the blood mark images in the forensically correct manner in which we see them displayed on the Shroud of Turin.

A series of 22 microchemical spot tests for 16 different organic structures or functional groups postulated as possible stains or dyes that could account for the body images was also carried out, again by comparison with appropriate controls. The only positive results were seen for the presence of aldehydes and cellulosic carboxyl functional groups. These results argue against the body images being the result of painting with some type of applied stain or dye, but suggest instead that the image was produced by some type of chemical process yielding a dehydrative oxidation of the cellulosic structure of the linen itself. Note, this is consistent with the corroded surface appearance of the body image fibers as observed under phase contrast microscopy and with their brittleness. Thus the chromophore accounting for the body image fiber color would be a mixture of conjugated carbonyl structures generated within the cellulose polymer itself. This type of chemistry accounts for the natural yellowing of linen as it ages and therefore the body image chemistry can be thought of as some type of selective differential accelerated aging process. It should be noted that as yet no one has experimentally demonstrated a chemical mechanism that would yield this type of chromophore and at the same time be consistent with the observed physics of the image studies.

A series of microchemical tests for the detection of the presence of proteins was also carried out on appropriate test objects. Control studies revealed that many of the basic dyes usually employed for these purposes, e.g., amido black, bromthymol blue, etc., also stain oxidized cellulosic structures whose presence therefore constitutes an interference. Similarly, it was found that the presence of covalently bound iron interferes with the usual ninhydrin tests. However, the use of fluorescamine tested against controls not only proved to be specific, but was sensitive under the test conditions to the picogram level. The blood particles and the serum coated fibers from the margins of the blood marks all gave positive responses. All the other test objects gave negative results, including specifically the body image fibers, which therefore are not coated with an artistically applied protein pigment binder. Proteases were also employed to confirm these results and yielded the same conclusions. While treatment of the body image fibers with proteases yielded no changes even after several hours of treatment, in less than 20 minutes it removed the coating of the serum coated fibers to reveal a smooth and uncorroded surface. This interesting observation suggests that the blood marks were on the cloth before the image producing process took place and protected the blood mark areas from this process. This further confirms that there were two separate processes involved in generating the images seen on the Shroud of Turin. Any proposed image forming mechanism must account correctly for both sets of images.

The body image fibers were also tested with 21 different solvents and test reagents to see if the color could be extracted or modified. Although the solvents employed covered the entire solubility scale, none of them could remove the yellow color. Only very strong oxidants or reductants could bleach the yellow color.

These results are consistent with the conclusion that the chromophore is a conjugated carbonyl integral to the cellulosic polymer itself. In the course of these tests it was discovered that treatment of modern linen fibers with concentrated sulfuric acid produces a simulacrum for body image fibers with many of the same observed chemical and physical properties. Since concentrated sulfuric acid is both a strong dehydrating and oxidizing agent this is not really surprising, but it further supports the identification of the chromophore.

Thus the chemical investigations are in complete agreement with the forensic and image studies concluding that the blood marks derive from the contact of the cloth with a real wounded human body and that the body images are not composed of applied pigments, stains, or dyes, but have been produced by a process different from that of the blood marks. Note that if one ignores the results of other investigators, does not consider alternative hypotheses and proper control tests, but simply microscopically observes protein coated fibers, iron oxide particles, and the presence of other artistic pigments, one can incorrectly conclude that the Shroud is a painting.

### **Spectroscopic Investigations**

An X-ray fluorescence investigation<sup>26</sup> was carried out on the Shroud to complement the X-radiographic study.<sup>17</sup> The calcium content was shown to be more or less uniformly distributed over the whole cloth, supporting the chemical conclusion that it derives from the manufacture of the linen. Similarly, the iron distribution was uniformly distributed over the whole cloth with a few notable exceptions, again supporting the chemical conclusion that the iron content is in a covalent form and like the calcium derives from the manufacture. As one crosses a waterstain boundary one finds the background value on the outside of the stain to be a slight elevation above the background value in the margin, and a slightly depressed value on the inside of the stain. This is consistent with the chemical model proposed to explain the presence of iron oxide in the waterstain margins. The blood marks show an element distribution consistent with a blood clot exudate, including an iron value elevated over the background value, but with no evidence for the presence of mercury. This observation supports blood mark identification as blood derived and is in agreement with the chemical and X-radiographic conclusions, but it does not support the proposal that the blood marks are painted mineral pigment mixtures of iron oxide and mercuric sulfide. If one follows the iron content from the tip of the nose across the cheek and into the background cloth, it again shows a uniform value along this path, although the image intensity varies by about an order of magnitude over this same path. Therefore to attribute the image intensity variation to any form of iron, let alone iron oxide, would constitute a violation of the Beer-Lambert law. Again this study supports the contention that the blood images are blood derived and that the body images are not a painting.

Ultraviolet and visible reflectance studies and some fluorescence spectroscopy were carried out on the Shroud.<sup>27,28</sup> In general these results complemented the observations seen in the fluorescence photographic study.<sup>14</sup> The visible reflectance spectra and red-blue-green characteristics of the body images were a

closer match to the lightly scorched areas (an oxidized form of cellulose) than to controls of linen with an iron oxide coating, while the near UV spectra showed a broad band assignable to those observed for conjugated carbonyl absorption.

This is in agreement with the body image chromophore being a dehydrated oxidized form of cellulose and not an artist's applied iron oxide paint. The reflectance spectra of the blood marks from the whole cloth and also a near UV-visible microspectrophotometric study of blood particles from the sticky tapes<sup>29</sup> are consistent with the spectra expected for a traumatic blood clot exudate. In a more recent study<sup>13</sup> transmission UV-visible spectra of a simulacrum of a traumatic clot exudate prepared from laboratory chemicals matches these observed Shroud spectra, but the spectra of a simulacrum of a mineral pigment blood composed of iron oxide, mercuric sulfide, and gelatin is a complete mismatch. This confirms the previous chemical and forensic conclusions. It is of interest to note that the position of the near UV peak for albumin bound bilirubin is indicative of the type of species from which the blood originates and in these observed spectra is consistent with a primate origin,<sup>24</sup> again supporting the identification of a human source for the blood marks.

An infrared reflectance examination of the Shroud accompanied the thermographic study.<sup>18</sup> Although the spectra taken were of low resolution, the peak ratios of the carbonyl region to that of the hydroxyl region showed clear evidence of an increasing state of oxidation in going from the background cloth to body image to scorch to the burned areas. The typical amide absorptions associated with proteins could be evidenced in the blood mark spectra, but not in those of the body images. These results were confirmed and extended in a more recent high resolution microspectrophotometric-Fourier Transform Infrared investigation of fibers and particles extracted from the STURP sticky tape samples.<sup>13</sup> Each type of fiber now showed a distinctive absorption pattern. A conjugated carbonyl absorption pattern was clearly seen in the body image samples, but no evidence for protein amide bands which, however, were clearly seen in the serum coated fibers and blood particles. Utilizing the spectral analysis capabilities of the computer program accompanying this instrument, which allows one to add or subtract standard spectra of a known molecule to the observed sample spectrum, it was demonstrated that the observed spectrum of the blood particles contained both methemoglobin and protein bound bilirubin. Infrared spectra of the traumatic blood clot simulacrum matched that of the observed blood particle samples, but the mineral pigment blood simulacrum did not. These spectroscopic results are again in accordance with the above forensic and chemical conclusions and do not support the contention that the blood marks and body images on the Shroud of Turin are simply paintings.

### **Dating Investigations**

The Shroud of Turin has had a known history from the late 1300s. While its possible prior history is a matter of conjecture, a reasonable theory tracing its existence back to the time of the crucifixion has been proposed and is well supported by a great deal of varied historic, artistic (iconographic), and other circumstantial evidence, including a pollen analysis of tape samples from the Shroud, to establish a provenance matching this proposed history.<sup>1</sup> Needless to

say, this argument for the Holy Shroud's authenticity has been a matter of polemic.

To resolve this polemic, a radiocarbon dating examination was authorized and carried out in 1988.<sup>30</sup> As this examination assigned a 14<sup>th</sup> century date to the Shroud, it only exacerbated the polemics. Unfortunately, the protocol recommended by a convened panel of experts for the taking of proper cloth samples for the radiocarbon analysis was not followed. Only a single sample was taken and that was from a most unsuitable location, i.e., from the edge of a bounded waterstained scorch area where evident repairs had been made. Therefore while this dating study can claim good precision for its reported date, it cannot assign any accuracy to the Shroud's historical date as it is not clearly established that the location sampled is typical of the rest of the cloth. In order to check this point, fibers from the radiocarbon sample were included in the microspectrophotometric-FTIR study cited above<sup>13</sup> for comparison with other Shroud fiber types. The radiocarbon samples show a distinctly different spectrum and therefore it can be inferred that their composition is not typical of the rest of the cloth. Why this is so is not entirely clear, but it does establish the fact that the accuracy of the radiocarbon date can be questioned on the basis of direct experimental evidence. Many theories and explanations have been advanced to attempt to resolve the dating inconsistencies but the matter can really only be resolved by further experimental investigation of cloth samples from the Shroud itself.

### **Conservation Issues**

Nothing lasts forever and this includes the Shroud of Turin. There is already evidence of degradative processes taking place, as for example in the observed abrasion of the blood marks. Exposure to industrial air pollution poses a real threat. The 1997 fire in the Cathedral emphasizes some of the storage and display problems. The conservation and preservation issues and their possible resolution have been analyzed and reported in some detail.<sup>31</sup> As the need for action is paramount and pressing, a Conservation Commission has been appointed by Cardinal Saldarini and a program to actively carry out their recommendations has been initiated. This program deserves the active support of everyone who has viewed the Holy Shroud and been awed by the mystery of its existence.

### **Summary**

The blood marks on the Shroud of Turin result from a transfer to the cloth effected by its direct contact with the exudates of clotted blood from the wounds of a man who suffered a traumatic death in accord with that historically described for the death of Christ. The body images on the cloth result from some as yet unknown radiational type non-contact process that followed the impression of the blood marks to produce a selective dehydrative oxidation of the cellulose structure to that of the observed chromophore. The body images do not result from the application of any pigments, stains, dyes, dry powders, or hot surfaces to the cloth. The accuracy of the reported radiocarbon date is questionable and strong evidence places the cloth's apparent age to at least as early as the 7<sup>th</sup> century. The conservation and preservation of this object is of the utmost importance.



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