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A Comprehensive Examination of the Various Stains and Images on the Shroud of Turin

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The chemistry of the various stains and images on the Shroud of Turin is presented. The chemical conclusions were drawn from all the data and observations, both physical and chemical, collected by direct investigation of the Shroud in 1978. The conclusions are that the body image is made up of yellowed surface fibrils of the linen that are at more advanced stages of degradation than the non-image linen. The chromophore is a conjugated carbonyl. No evidence was found in the body image of any added substances that could have contributed to the yellow color of the fibrils that form the image. The blood images on the cloth are made of blood. The data, taken together, do not support the hypothesis that the images on the Shroud are due to an artist.

A TEAM OF SCIENTISTS AND TECHNICIANS known as the Shroud of Turin Research Project (STURP) took part in direct physical testing on the Shroud of Turin in October 1978. The object of their efforts was a piece of ancient linen measuring approximately 4.3 m × 1.1 m presently kept in the Chapel of the Holy Shroud in the north Italian city of Turin. The cloth's value stems from the presence of the frontal and dorsal image

of a man purported to be that of the dead Jesus of Nazareth. A major goal of the testing was to gather data that could be used to determine the chemical composition of these images. Some background information as it was known before the 1978 testing can be found in Reference 1.

During the 1978 test program, members of STURP performed photographic imaging; visible, UV, and IR spectroscopy; IR thermography; x-ray fluorescence analysis; and x-radiographic imaging. They also collected microscopic samples of the various kinds of images and marks on the Shroud for chemical testing (2). Details of these tests with results can be found elsewhere (3–10). Results of chemical testing can be found in References 11 and 12.

The previously cited references do not deal with a comprehensive picture of the chemistry of the marks and images on the Shroud, nor do they propose a satisfactory explanation for how the body image got on the cloth. However, Pellicori and Evans (7) have proposed direct contact as a candidate with full recognition of its drawbacks. A series of three articles by McCrone (13–15) are not so cautious; these conclude that the Shroud is simply a clever painting. Although some of McCrone's visual observations are consistent with those reported by others, we find his conclusion to be inconsistent with the chemical picture presented here. Further, it will be clear to the reader that one of the few causes of the body image that can be ruled out is a painting. It is, however, not our intention in this chapter to directly address the question of image formation but rather to bring together the results of all the previous work in an attempt to arrive at a definitive description of the chemistry of the images and marks on the Shroud. The reader is directed to Reference 16, where various hypotheses for image formation are examined.

In order to consider in detail each kind of image/mark on the Shroud, it is essential to describe these images and stains, thereby establishing unambiguous meanings and reference points. Figure 1 shows a photograph of the Shroud with pointers indicating the various types of stains and images. First note the frontal and dorsal image of what appears to be a nude adult male, labeled A. Superimposed on these "body" images are what appear to be wounds in "blood," labeled B. In this chapter, images in category A will be referred to as body-only images, that is, these are only body images and not body images that are "contaminated" by the superimposed blood images. The "blood" images will then be referred to as simply as blood images.

Because other stains/images on the cloth (which are of known origin) are important for comparison, we will also refer to some of these, as we will to extraneous pieces of cloth that are presently attached to the Shroud in one way or another. The most obvious marks are those resulting from a fire in A.D. 1532. These can be classified as burns (labeled C), marks actually composed in part of charred linen, and scorches (labeled D),
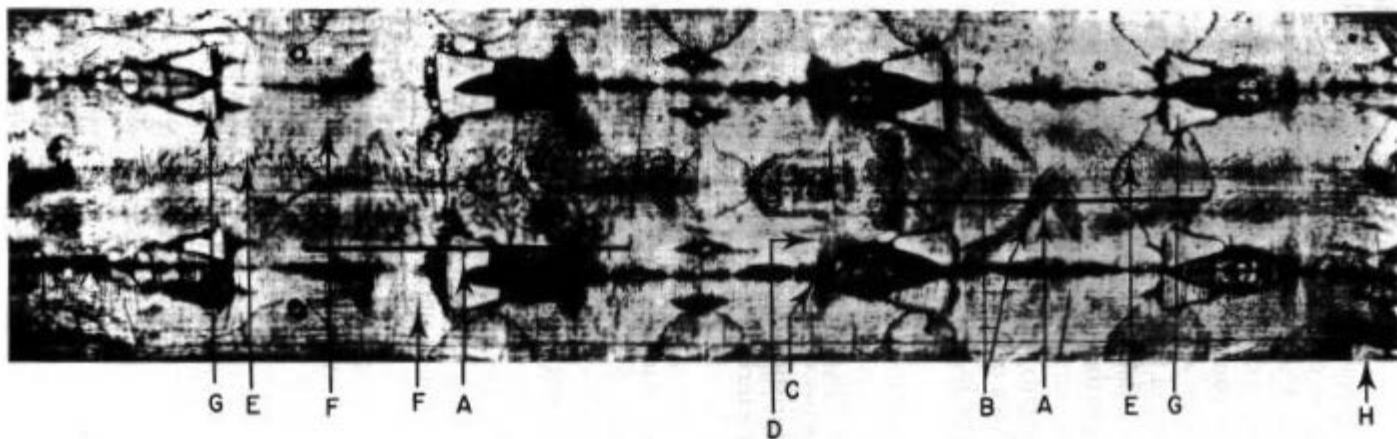
Figure 1. Photograph of the Shroud showing examples of the various types of marks and images. Key: A, body-only image; B, blood image; C, burn mark; D, scorch mark; E, water-stain mark; F, clear area; G, patches; and H, Holland cloth. (Reproduced with permission. Copyright 1978, Vernon Miller.)

where the linen is noticeably discolored but not actually reduced to char. These scorches vary in optical density from barely noticeable when compared to the background to optical densities that approach those of the charred or "burn" areas. Also important are the water-stain marks (labeled E) that were produced at the time of the 1532 fire, when water was poured on the silver container in which the Shroud was kept. The clear areas (i.e., non-image areas) also have some bearing on the identification of the chemistry of the other marks on the Shroud and as such are identified in Figure 1 (labeled F). For the sake of completeness we will also make reference to the patches (labeled G) and the Holland cloth backing cloth, which was attached to the Shroud in 1534 in an attempt to restore structural integrity lost in the 1532 fire. Because the Holland cloth is attached to the back of the Shroud it only appears where portions of the Shroud are missing in Figure 1 (labeled H).

Body-Only Images

The first type image we will discuss is the body-only type (labeled A in Figure 1). First the macroscopic characteristics will be discussed, then the microscopic characteristics, and finally the chemical characteristics.

  Macroscopic Characteristics. COMPOSITION. As can be noted in Figure 1, that portion of the Shroud showing visible front and back images of a man is composed of a continuous range of optical densities from background density to its darkest density in areas like that of the tip of the nose. It is important, for comparison purposes, to note that the shading density of the body-only images falls in the same density range as the scorches, D, and not the burns, C. On close examination, the surface fibrils of the threads composing the weave of the cloth here are yellow. With both aided and unaided eye, we find that the densities above background making up the body-only image are composed of groups of these yellow fibrils residing only on the uppermost portions of the threads (7). These groups of fibrils are not cemented to one another as was demonstrated by probing with a dissecting needle. Thus, no pigment "binder" appears to be present. Further, with few exceptions, we find that the yellow coloration of the fibrils is interrupted as the thread goes beneath a crossing thread in the weave pattern. Those few exceptions where the yellowing appears to pass under the crossing thread seem due to mechanical stretching of the cloth, because these are usually accompanied by a region of uncolored fibrils at the opposite end of the exposed thread where it comes up from beneath a crossing thread. The yellowed fibrils are not yellowed continuously over their entire length. We observed a fibril that was yellow only on the part that was on the uppermost portion of the thread but lost its coloring as it left the upper portion of

the thread in its normal course of following the twist to the lower portion of the thread. In examining the cause of the differing integrated densities of the body-only image as seen by the eye, we found that the darker portions of the image were not due to a variation of the degree of the yellowing of the fibrils, but rather to the presence of more yellowed fibrils per unit area (7). Thus, the extent of yellowing of a given fibril was the same, to within 10% (of full scale) of any other yellowed fibril on the basis of microdensitometric measurements of the color photomicrographs. The shading of the body-only image, then, is much like that of a halftone. In this regard, it should be noted that there are ubiquitous examples of yellowed fibrils lying adjacent to unyellowed fibrils. Thus, body-only image to the unaided eye (also, to the aided eye to 50 ×) appears as a striping of uniformly yellowed fibrils on the uppermost portions of the uppermost threads of the cloth and exhibits no cementing between fibrils.

SPATIAL DISTRIBUTION. The spatial distribution of the optical densities that make up the body-only image appear to correlate with a well-defined mapping function (17). Considerable work has been done on the frontal image of the man on the Shroud. These studies show that a relationship exists between the shading density of the image and expected cloth–body distances obtained by enfolding volunteer human subjects in a full scale model of the Shroud. Two points should be noted: first, this characteristic of the image is not obtained by considering it to arise from a reflectance of an albedo image of its "source;" and secondly, it accounts for the "reversed" nature of the tonal scale as perceived by the eye, that is, its so-called negativity (*see* Figure 2).

Extensive study of the back image has not yet been undertaken; however, there appear to be striking similarities between the frontal and dorsal body-only images. We find, for example, that the maximum optical densities of the dorsal image are nearly the same as those for the frontal image. Further, qualitatively, the optical density of the dorsal image falls off from peak density to that of the background over anatomical distances (e.g., in the region of the calf) suggesting a similar correlation to cloth–body distance as exists for the frontal image. However, other portions of the dorsal image might be interpreted as characteristic of a contact mechanism (17). A more definitive statement must await further study.

There are areas on the body-only image that are relatively lower in optical density than other areas in relation to the background. Most noticeably these areas appear as stripes running longitudinally on the Shroud and are due to the different lots of thread used in the manufacture of the cloth. The most notable example of this phenomenon is seen bordering the face. Two of these stripes, measuring approximately 2.5 cm each, run along the sides of the face (*see* Figure 2) and have often

Figure 2. Pictures of the face on the Shroud. The right-hand picture is photographically reversed; arrows on the left-hand picture indicate the 2.5-cm stripes along the face. (Reproduced with permission. Copyright 1978. Vernon Miller.)

been referred to as due to a "chin bandage" in popular writings on the Shroud (*1*). This interpretation is mistaken, as these are part of the same lighter bands that can be seen to run the length of the Shroud.

COLOR.   In white light, the color of the body-only image is yellow [c.f. spectra (*4,6*)]. It is interesting that the image has been described prior to the 1978 testing as a monotonic sepia color; however, the perceptual judgement of color is extremely sensitive to lighting and the distance from the cloth to the observer. Under low color temperature lighting, it is possible that the color could be mistaken for sepia because the yellow is due to a broad absorption of the blues (shorter wavelengths in the visible spectra) (*4,6,7*). It should be noted that the color of the body-only image is distinctly different from that of the blood images (c.f. later section). The color of the body-only image (as viewed in the visible) when irradiated by UV light (390–420 nm) is neutral gray or black (*10*).

THERMOGRAPHY.   Accetta and Baumgart viewed the image in the IR both at 3–5 μm and at 8–14 μm (*5*). In the 3–5 μm range no discernible image was evidenced. In the 8–14 μm range a clearly discernible emission image was visible. They could find no apparent differences in spatial distribution between the IR and visible image (*5*) (unlike the case for most paintings).

Microscopic Characteristics.   At 50× magnification, the body-only image is composed of yellow fibrils (c.f. above) on the uppermost portions of the uppermost threads (*7*). At higher magnifications, up to 1000×, two types of "red" particles identified as either iron oxide or "blood" are occasionally present on some of the yellow fibrils (*12,13*); however, it is clear that these particles do not account for the yellow color of the fibrils or the image itself for several reasons. x-Ray fluorescence analysis of the Shroud shows that there is no correspondence of the body-only image density to the concentration of high-Z elements (particularly note, Fe) within the resolution of the analysis (*3*). The spectral characteristics of body-only image are different from those of iron oxide (*4,6*). Further, one would expect that an image of comparable optical density to that of the visual body-only image on the Shroud, if made from iron oxide pigments, would have appeared on the x-radiographs. The water-stain margins, which do contain iron oxide (*12*), are present on the x-rays; the body images do not appear on the x-rays (*9*) (c.f. below).

In a more definitive sense, examinations of samples taken on sticky tape (*12,13*) have shown that the color of the yellow fibrils does not arise from any inorganic pigments (*12*). Both oxidative and reductive reversal of color back to "new"-linen white readily demonstrates that the color of the fibrils cannot be due to the presence of iron oxides. Thus the body-only image is due solely to the distribution of the yellow fibrils.

We turn, then, to the cause of the body-only image fibrils' being yellow. We have already mentioned that the yellow fibrils are not ce-

mented to one another as would be expected in the presence of a pigment binder. At magnifications of up to 1000×, these fibrils do not appear to have any coating. This is most clearly demonstrated by observations made at the joint locations of the linen fibrils. These joints exhibit no meniscus, but are clearly and sharply defined with no evidence of a coating. Further, under phase contrast microscopy, these fibrils not only appear uncoated, but show "corroded" surfaces as would be expected for an oxidatively degraded cellulosic material (12). Although protein-covered fibrils can be readily demonstrated in blood image areas (c.f. later section), the body-only image fibrils test negative for protein to the nanogram level (12). Several tests were used, including the amido black test (14), the more sensitive fluorescamine test, and protease digestion (12). That this conclusion is contrary to previously reported results (13–15), seems to arise from a failure of those investigators to discriminate between body-only image and blood image fibrils. They have apparently concluded by visual inspection only that the yellow-appearing fibrils from these two disparate types of locations are identical. Chemical observations do not agree with this assumption. Blood image fibrils do test positive for protein. Further, the "yellow-coated" fibrils found in the blood-image areas are yellowed by a distinctly different cause, that is, serum proteins (12). A further possible contribution to the misidentification of protein on fibrils from the body-only image areas (14) is due to the use of only the amido black test as a confirmatory test for protein. Amido black is not a metachromatic stain, that is, it does not show a color change on its staining interaction with protein. Amido black, being a basic dye, also stains oxidized cellulose in the same fashion, as is readily demonstrated by its staining rayon (i.e., regenerated cellulose that is completely protein free) (12). Therefore, positive amido black tests without proper controls do not demonstrate the presence of protein as claimed in Reference 14.

Schwalbe and Rogers note that in removing the tape samples, the tape pulled up more easily from the body-image areas than from the non-image areas. The linen fibrils seen on the body-image tapes are shorter and more fractured than are those from non-image areas (16). Both of these observations suggest that the body-image fibrils are more chemically degraded than are those from the non-image areas.

Explanation for the Yellow Color of the Fibrils. It seems clear that the cause of the body-only image is the yellow fibrils and that the yellow color is not due to inorganic pigments. We turn, then, to considering other possible causes of the yellow color of the fibrils.

One possible explanation might be an organic stain or dye. The body-only image exhibits broad nonspecific absorption in the shorter visible wavelengths (4,6), unlike many naturally occurring dyes (16). Further, many natural dyes are soluble in water and would have migrated at the time the water marks were made (c.f. below). As Schwalbe and

Rogers point out, the body-only images were unaffected by such water (16). Further, most organic dyes are affected by temperature, and the Shroud body-only images exhibit no color change in areas where scorch marks from the 1532 fire intersect body-only images (16). Many organic chromophores are fluorescent in the visible when excited by UV light, and the body-only images are nonfluorescing (10).

All the foregoing suggests that the yellow color is not due to a stain or dye; however, to test further the possibility of the presence of a stain or dye, the microsamples were subjected to a battery of tests (12): the color is not extractable in various organic solvents covering the entire range of solubility classes; the color does not change on treatment with strong acids and(or) bases; the color was not bleached by weak oxidants (even under UV irradiation), nor by weak reductants; and a wide range of specific metallic elements and chromophoric organic groups were not evidenced by specific chemical tests. This battery of tests showed that the only ubiquitous microdetectable metal species present were calcium and iron, and their presence was shown to be consistent with their having been deposited in the cloth as coordinate covalently bound species during the original retting process in the manufacture of the linen (c.f. below). These observations agree with the findings of Morris et al. (3). It should be noted here that the iron oxide particles occasionally seen on and also in the medulla of fibrils could have been formed during this same retting process or even possibly at the time of the water staining during the 1532 fire by a process similar to the production of "mineral khaki" (12).

We can also rule out the possibility that the yellow color arises from diffraction and/or dichroic phenomena; there is no evident angular dependence for the apparent color, as is required by such mechanisms.

Selective scattering by the cellulose structure is also ruled out because the surface structures in both the body-only image areas and the background areas are essentially the same. Scattering from both areas is due to the fibrils, but the body-only image areas have enhanced density of "yellow" color over background areas that are pale straw color to the eye. The slightly rougher fibril appearance in the body-only image areas is at a scale size orders of magnitude greater than the wavelengths in question, and therefore does not contribute selectively to the color.

Finally, microchemical tests (12), mass spectroscopy (16), and laser-microprobe Raman spectroscopy (16) all fail to show the presence of any added materials on the yellow body-only image fibrils to within their limits of detection. We conclude that no material has been added to these yellowed fibrils to produce the color (12,16).

What then is the cause of the fibrils' yellow color? The nature of the absorption curve (4) demonstrates that the yellow color is similar to the light scorches. Miller and Pellicori point out the similarity is not complete, because the body-only image does not show the same UV-

stimulated, orange-red fluorescence as the scorch-image areas (D) (10) (c.f. discussion on high vs. ambient temperature decomposition below). The case for the yellow color being due to chemistry similar to that of a light scorch or ambient temperature process goes further, however. The physical properties of the cloth in the areas of the body-only image (the microscopically corroded appearance, the lack of migration of the image with water, the lower tensile strength of the colored fibrils, and the lack of color change in the presence of elevated temperatures) are all consistent with this sort of chemistry (16).

These suggestions have been given corroborative support from the microchemistry results (12) (c.f. above). Organic functional groups that are characteristic of dehydratively oxidized, degraded cellulose have been found. Further, such groups have also been found in the "ghost" patterns on the sticky tape after the fibrils have been removed. The absence of products expected from a high-temperature cellulose degradation, however, suggests that the process that formed the final chemistry took place at lower temperatures (less than 200 °C), because no pyrolytic compounds were found (6,12). The fluorescence of the scorch image areas, however, demonstrates the presence of high-temperature pyrolytic products in these areas (10). The cause, then, of the yellowing is chemically altered cellulose consisting of structures formed by dehydration, oxidation, and conjugation products of the linen itself. Heller and Adler have postulated that the most probable chromophores are conjugated carbonyls (12). Possible chemical schemes for forming such structures are shown in Figure 3 and in the box on the page that follows it.

This conclusion is supported by laboratory simulations using controlled accelerated aging processes that produce the same spectral reflectance curves as the body-only image areas and the background areas on the Shroud (6). The changes in cellulose known to be the result of aging are the same dehydrative and oxidative processes described above (18,19). Such chromophores result in a broad UV absorption decreasing monotonically toward longer wavelenths. Further, the conjugation of such chromophores in varying chain lengths results in the observed broad gradual nature of the absorption (4,12).

It is important to note that this chemistry is similar to the chemistry that causes the yellowing of linen with age. The fact that we can see the body image tells us that the body image is due to a more advanced decomposition process than the normal aging rate of the background linen itself. For this reason, we will from this point on refer to the chemistry of the body-only image as advanced decomposition. Later in this chapter we will briefly address possible causes for catalyzing the decomposition process. It will suffice to close this section with the simple statement that the body-only image is due to a yellowing of the uppermost fibrils of the linen threads of the cloth, the darkness of the image being
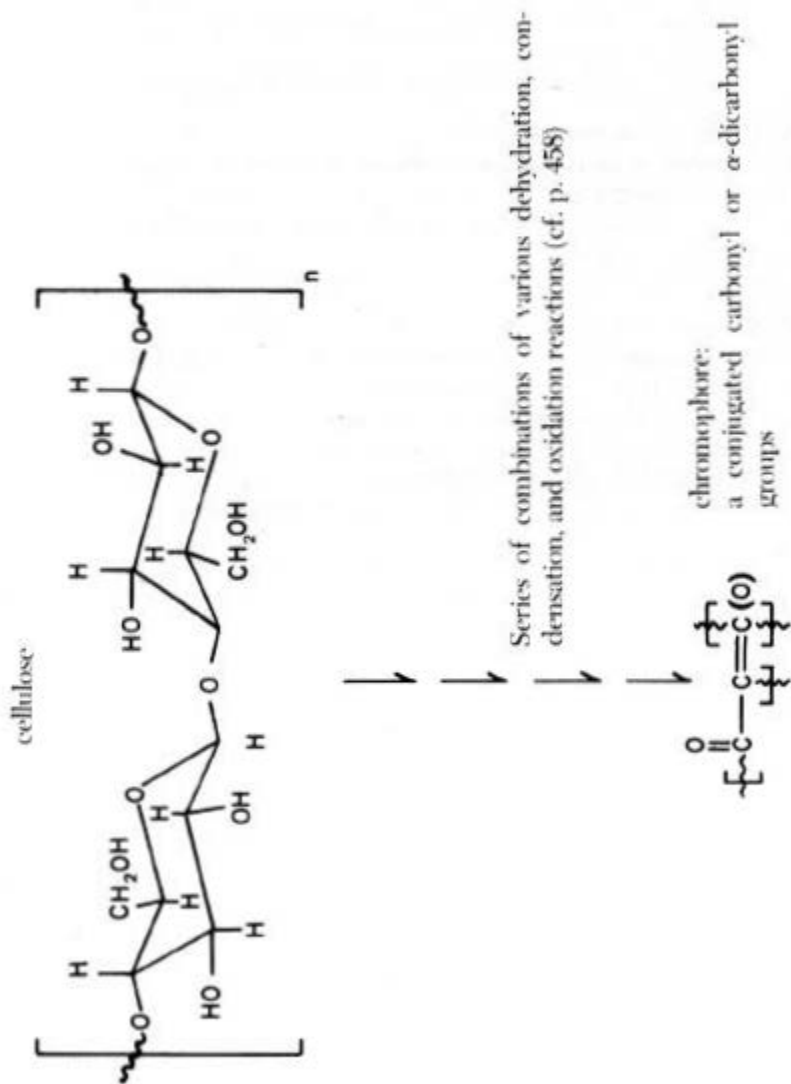
cellulose

Series of combinations of various dehydration, condensation, and oxidation reactions (cf. p. 458)

chromophore:
a conjugated carbonyl or α-dicarbonyl groups

Figure 3. *Generation of chromophoric groups from cellulose structure of the linen of the Shroud.*

Cellulose Reactions Pertinent to the Formation of the Chromophore* of the Shroud Body-Only Image

A. *Condensation Reactions (internal and cross-linking)*
  1. acetal + water $\rightleftharpoons$ hemiacetal
  2. hemiacetal $\rightleftharpoons$ linear saccharide (free carbonyl group)
  3. aldol condensation (intra and inter)
  4. esterification (intra and inter)
  5. double bond addition (e.g., ionization-produced radical polymerization)
  6. radical polymerization (e.g., ionizing conditions)

B. *Dehydration Reactions*
  1. alcohol dehydration $\rightarrow$ alkene + water (e.g., pyrolytic conditions)
  2. α,β-diol dehydration $\rightleftharpoons$ enol + water (e.g., anhydroglucose formation)
  3. aldol dehydration $\rightarrow$ α,β-unsaturated carbonyl* + water

C. *Oxidation Reactions*
  1. primary alcohol + [O] $\rightarrow$ aldehyde (e.g., 6-OH groups)
  2. aldehyde + [O] $\rightarrow$ carboxylic acid
  3. secondary alcohol + [O] $\rightarrow$ ketone
  4. ketone + [O] $\rightarrow$ 2-carboxylic acids
  5. alkene + [O] $\rightarrow$ 2-carbonyls
  6. enol + [O] $\rightarrow$ aldehyde + carboxylic acid (e.g., dehydrative)
  7. α,β-diol + [O] $\rightarrow$ 2-carboxylic acids (ionizing conditions)
  8. α,β-unsaturated carbonyl $\rightarrow$ carbonyl + α-dicarbonyl*

*Conjugated carbonyl.

due to a greater number of these fibrils, and the yellowing of these fibrils being due to dehydration, oxidation, and conjugation of the cellulose of the fibril itself (advanced decomposition).

Blood Images

The next major type of image is the blood image labeled B on Figure 1. Again we will consider this image type by examining the macroscopic, microscopic, and chemical descriptions.

Macroscopic Characteristics. COMPOSITION. The blood images appear as three major types: areas that might be termed wounds, on the wrists, for example; areas of blood flow, along the small of the back, for example; and "scourge" marks that are ubiquitous over the torso and legs. All of these types bear certain similarities and differences. On close examination one sees that blood flows have gone onto the cloth as viscous liquids penetrating the cloth through to the back, and diffusively seeping

along threads near the edges of the stains demonstrating some limited capillary flow. Menisci are clearly visible at the edges of the stains. Heavily colored portions of the stains have not diffused very far, which suggests high viscosity. The color of the darker portions of the blood images is quite red. The color is not uniform, however, and the color ranges from a brown through red to orange. In general, the color has a crimson appearance as would be expected for old blood stains composed of a solid-phase mixture of methemoglobin (brown) and its degradation products [e.g., bilidienes, such as rubins (orange)], both of which have been demonstrated to be present in these blood images (6,11,12). In some areas there is evidence of some apparently colorless fluid bordering or diffusing farther out than the darker fluid (one could thus conclude that this fluid would be thinner than the darker fluid, c.f. below). All blood stains appeared to have had the upper portions of the dried stain removed as if abraded by mechanical wear; the most intact stain is seen in the interstices of the weave of the cloth. Repeated folding of the cloth has apparently translocated some of this abraded material to other locations. Therefore, the material comprising the stains is absent on the crowns of the threads and is most abundant between threads and penetrating between the fibrils of the thread (c.f. figures in Refs. 7 and 20). In those parts of the stain where the darker material has been removed, one can see "yellow" fibrils that appear to be coated and cemented together. These coated yellow fibrils are also a deeper yellow color than those in the body-only areas (6), and are not confined to the first layer of fibrils as are those in the body-only areas. Fibrils in the blood areas are clearly cemented together, even in areas where there appears to be a thinner fluid progressing beyond the edges of the darker portion of the stain. The appearance of the cemented fibrils has been described as appearing matted together in some areas (16). In those areas where the water stains have intersected the blood areas, there is a clear indication that the presence of the blood images has impeded the progress of the diffusion of the water through the cloth. Before moving to the specific types of blood stains, it should be emphasized that the blood images are distinctly different in appearance from the body-only images (c.f., previous section). Finally, at $50 \times$ the cementing of fibrils, coating of the fibrils, capillarity, and variation of color are more clearly seen (6,7).

WOUNDS.   These images appear to be located at distinct and clearly identifiable parts of the anatomy of the man on the Shroud, which would suggest they are wounds. While there is no mistaking the location of the major wounds, there are some examples of blood images that do not coincide with any particular anatomical detail, for example the apparent trace of blood off the right elbow as seen in the frontal image. There are also other examples of the blood image being off-register with respect to the anatomical detail upon which it is clearly associated, for example,

on the right foot as seen on the dorsal image of the man on the Shroud. Bucklin has made an extensive investigation of the correlation of these locations to specific types of injuries (21). It is interesting to point out that many of these wound images appear to have a border encircling the darkly colored area where body image is absent, a halo of sorts that can clearly be seen as such in the UV photography (10). These are the areas where the flow pattern suggests a thinner fluid was present in the cloth as we have noted above (10). This absence of body image on the wound image margins suggests that the blood images were present on the cloth before the body image was "placed," "appeared," or perhaps "developed." This suggestion is consistent with the chemistry of the body-only image, because this thinner fluid could have coated these margin fibrils sealing them and preventing the advanced decomposition reaction. This conclusion is supported by microscopic examination of the fibrils from the blood areas after removing the serum coating by protease digestion. Fibrils, so treated, more closely resemble those from the off-image clear areas than those from the body-only image areas when viewed by phase contrast microscopy (12).

BLOOD FLOW.   In these areas, the fluid seems to have flowed along contours of the cloth such as folds. The clearest area of this happening is in the region corresponding to the area of the small of the back above the buttocks.

SCOURGE MARKS.   These appear to be somewhat different from the other two types of blood images. Under UV fluorescence, they appear to be darker than the image and, also, to be much more sharply defined than they appear in visible light (10), as would be expected on the basis of the known spectral characteristics of iron porphyrin compounds (11). The geometric similarity of groups of these dumbbell-shaped marks is also quite striking (21). Fine "scratches" from the distal ends of these dumbbell-shaped marks appear in the UV-stimulated fluorescence photographs (10).

Microscopic Characteristics.   At magnifications of 250× to 1000×, the fibrils in the blood areas are clearly coated. Joints of the linen fibril are filled with some substance. Samples of ca. 300-year-old Spanish linen were treated with partially clotted blood and allowed to sit for 18 months (11,12). Microscopic samples of this treated linen made with sticky tape in the same manner as the Shroud samples appeared to be very similar to the Shroud samples. Amorphous globs colored orange to orange-red to yellow to yellow-red were observed in the Shroud samples and appeared similar to those from samples taken from such treated linen. In other words, microscopically the Shroud samples taken from the blood areas looked like blood as seen on a simulacrum (12).

Also present on the Shroud samples was a significantly high number of nonbirefringent red particles identified as blood and decomposed blood

materials (*12*) and not as protein "cemented" iron oxide (*13–15*). These particles were ubiquitous in the blood areas. This finding is in distinct contrast to the limited quantity of nonbirefringent and birefringent red particles present in body-only and off-body clear areas on the Shroud. The relative quantities of all such red particles in these off-blood areas were several orders of magnitude less than those in the blood areas. These blood image particles are clearly associated with blood materials and are present only incidentally in other regions of the cloth where they are occasionally observed due to translocation (c.f. background section). Some of the blood-image red particles near scorch intersections have darkened and test as charred blood (*12*).

A mechanical description of the blood image areas can be divided into that for the fibril coatings and that for the globs, particulates, and "shards" (*12*). The nonbirefringent, red-coated fibrils test positively for the presence of heme materials and proteins (*12*). The yellow-coated fibrils test positively for protein with fluorescamine and also positively for serum albumin with bromcresol green indicating that they are blood serum coated (*12*). Suggestions (*14*) that this protein coating is a "collagen-type" animal glue used in medieval times as a paint binder are inconsistent with positive selective tests for serum albumin. The identification of the albumin (*12*) has now been immunochemically confirmed. Further, the suggestion that the body-only image was formed by such "yellowed" collagen is also unjustified as no protein can be detected by the fluorescamine and protease tests on such fibrils. Also, Miller and Pellicori found that both laboratory-prepared animal-glue collagen as well as glue used as a binder in a bible (ca. A.D. 1400) fluoresced brightly in the visible range when excited by UV radiation (365 nm); both the Shroud blood images and body-only images were nonfluorescing under the same conditions (*10*).

The globs, shards, and particulates range in size and color. They can be variously shown to contain proteins, hemes (*11*) and(or) bile pigments, small black carbon particles, and only relatively small amounts of iron (*12*). Iron can only be identified in these materials after oxidative degradation. This finding is consistent with the globs, shards, and particulates being derived from the blood itself in various stages of decomposition, even including "charred" blood near scorch areas. Birefringent red particles identified as iron oxide are occasionally seen only in these scorch blood areas. Such birefringent red iron oxide particles are only prevalent in the water stain margins (c.f., below).

In closing this section we can state that the blood image areas appear to be composed of blood. Whether the blood is of human origin we cannot definitively say. However, we have recently confirmed the Italian immunochemical tests (*22*) suggesting that it is, in fact, human blood on the basis of positive tests involving human antiglobulin. Our tests em-

ployed human antialbumin and anti-whole sera. However, the problem
of cross-serological interactions of other primate bloods prevents an ab-
solute identification of the blood as human at this time. There seems
ample evidence to explain all the red particles on the Shroud as origi-
nating from either the blood itself, the retting process, or, possibly, the
water of the 1532 fire incident (c.f. above); we reject the hypothesis (13–
15) requiring that an artist had to have touched up an earlier image. We,
therefore, strengthen our statement on the blood to say that all of what
we see in the blood area is derivable from blood itself or its products
(12).

Burns and Scorches

We turn now to the burns and scorches identified in Figure 1 as C and
D, respectively.

   Macroscopic Characteristics.   In white light, the scorches and burns
vary from a light brown shading into a darker brown and finally into
black. As indicated previously, the light scorch marks resemble the body-
only image in the visible spectrum (4), but not under fluorescence (10).

   At 50× magnification, the color gradations appear to range from a
few yellowed fibrils to a complete black char. Under UV light (335–375
nm), an orange fluorescence is seen in the darkest areas (10). This ob-
servation is compatible with combustion of linen in a limited oxygen
environment and at elevated temperatures rather than an ambient tem-
perature oxidation process, which does not produce an orange fluores-
cence (10). In this regard, the more intensely burned areas showed the
expected differences in spectral characteristics from those of the body-
only image areas (4–6,10).

   Microscopic Characteristics.   At 500× to 1000× magnification with
transmitted or reflected lighting, the fibrils range from yellow to brown
to black. There are translocations of charred and scorched fibrils to other
areas of the Shroud. This observation confirms the folding-contact mech-
anism mentioned earlier as that which translocated occasional blood par-
ticles to other locations.

   The chemistry of the lightly scorched fibrils is very similar to the
chemistry and appearance of the body-only image fibrils (12). This sim-
ilarity is also evident in the IR spectra (5). In the more heavily scorched
and charred areas, both chemistry and surface appearance begin to di-
verge from that of the body-only image areas (5,12). Indeed, it appears
that a graded series of these fibrils can be made. If a series is made of
off-image fibrils, body-only image fibrils, light scorch, to char, the num-
ber of aldehyde groups and carboxyls increases along with the corroded
appearance, evidencing an increasing state of dehydrative oxidation. It
should also be noted that the difference in the UV spectra and fluores-
cence characteristics between scorch and body-only image noted earlier

can be explained by the presence of pyrolytic products that form at higher temperatures. This explanation indicates an upper limit to the temperature of reaction during the formation of the body-only image.

Water Marks

The water marks are labeled E in Figure 1.

Macroscopic Characteristics.   The water marks are interesting as they are the only marks (other than added material like the patches) that show up distinctly in the x-radiographs (9). Clearly, the density of heavy elements in the water-mark boundaries is sufficiently great to be apparent on these x-radiographs. These images conform closely to the water marks seen by the unaided eye in white light. These roughly diamond-shaped water marks derive from the extinguishing of the 1532 fire (when the molten silver of the Shroud's container burned through the folded layers of the Shroud, scorching it).

At 50× magnification there is little that is remarkable other than the observation that neither the body-only images nor blood images migrated, although loose debris from them can be seen in the boundaries of the water marks. However, the blood did pose a barrier to the migration of the water, as would be expected of aged clotted blood. This can be best seen at the side wound blood flow. However, the body-only image did not impede nor facilitate the migration of the water through the cloth.

Microscopic Characteristics.   At 500× to 1000× magnification it can be easily seen that virtually everything "movable" on the Shroud migrated to the boundaries of the water marks: blood coated fibrils, blood particulates, blood shards, off-image fibrils, body image fibrils, charred and burned fibrils, pollen, insect parts. Most interesting is the presence of birefringent red particles, which, although observed occasionally in other locations such as blood/scorch, are only prevalent in this area.

Chemistry.   Since, as mentioned above, virtually everything movable on the Shroud can be found in this area, the chemistry of this debris need not be discussed here (having been discussed earlier) with one exception: the birefringent red particles. These red particles were found to be ferric oxide (Fe_2O_3) (12). Further, no manganese, nickel, or cobalt could be detected in these particles, confirming their origin from a "khaki-like" chromatographic process (c.f. above), rather than from an "ore-derived" pigment (12,14).

Clear Off-Image Area

The clear off-image, labeled F in Figure 1, served as a basic control for virtually all the observations on the Shroud.

Macroscopic Characteristics. Under white light, the linen is seen to be slightly yellow-tan with age. The material feels remarkably supple, considering it is at least six centuries old. The threads are seen in the x-radiographs to be inhomogeneous and the weave is somewhat uneven, as would be expected of a hand-spun, hand-loomed linen (9). As was indicated in the body-only image section, inhomogeneous lots of thread have resulted in the apparent effect of stripes appearing to run laterally and longitudinally the length of the cloth. The stripes are undoubtedly due to the fact that different lots of thread will show different degrees of degradation. We know that the body-only image is due to advanced degradation of the cellulose. Hence, it is perfectly consistent that the body-only image also reflects these same differentials. There are no extensive patches of mildew, although there are large numbers of mildew spores present. Earlier speculation that the lack of mildew is due to *Saponaria* is not borne out by chemical tests (12). Under UV light (335–375 nm), the off-image fluoresces a greenish-yellow (10). x-Ray fluorescence and microchemical tests both showed the presence of calcium and iron, which is consistent with that expected due to the normal retting process (c.f. below).

The weave of the cloth is seen to be a 3-to-1 herringbone twill (7) [supposedly typical of near-Eastern cloths of antiquity (23)]. The fibrils on the surface show mechanical wear indicative of many flexions and aging degradation.

Microscopic Characteristics. At $500 \times$ to $1000 \times$ magnification, the fibrils have the typical morphology of linen, but their surfaces are only lightly corroded (oxidized) although clearly less than body-only image fibrils as seen by phase microscopy. There are, also, fewer broken and crushed fibrils than in the body-only image areas, showing less degradation in further support of the arguments presented in the body-only image chemistry. Scanning electron micrographic images show pollen, spores, insect parts, and mites (24). Normal microscopic observations also reveal the presence of red silk, pink nylon, green polyester, and microdebris of the ages.

It is important to note that there are also charred linen fibrils, body-only image fibrils, blood particulates, globs, and shards occasionally present on these off-image areas. To our mind, this observation is best explained by the translocation mechanism referred to earlier. This explanation was proposed by Jackson et al. (17) who attribute numerous foldings of the cloth as the most dominant mechanism. There appear to be at least four distinct fold patterns that are identifiable in the permanent-fold patterns that are on the Shroud. Jackson performed an experiment in which he deposited ferric oxide in locations corresponding to the blood images on the Shroud on a clean piece of cloth of the dimensions of the Shroud. After just four foldings he took sticky tape

samples on his laboratory cloth in the same manner as samples made on the Shroud and found that the ferric oxide had migrated to every location where blood debris has been occasionally found on the Shroud. Because, as stated earlier, there is clear evidence that material is missing from the blood-image areas, the translocation model explains how the occasional blood particles, and other particles as well, could have been relocated to all parts of the cloth including the off-image areas. This translocation mechanism coupled with the water-caused migration at the time of the 1532 fire explains why various "atypical occasional" objects are found in various locations on the Shroud.

Chemistry. The fibrils all give a strong positive calcium reaction and a positive reaction for iron (even at test reagent conditions, pH 4.5, and even where Fe_2O_3 particles are not visible), indicating that ion exchanged (chelated) bound iron is present. It is of interest to note that only when the ferric oxide particles are present on a fibril does the iron test become "stronger" than the calcium test (12). Our estimate is that at least 90% of the iron present on the Shroud is of the ion exchange bound type. In the manufacture of linen from flax at that time, the linen was subjected to a process called retting. Retting involved submerging the linen an extended time in natural bodies of water while it underwent a fermentative process. During retting the linen can act as an ion exchange resin and selectively take up iron and calcium. Subsequently, some of this iron could become converted to ferric oxide in the water-stain margins by a process similar to the production of "mineral khaki." Of possible interest is the finding that we have similar positive tests for calcium and iron in the 300-year-old Spanish linen, some Coptic funerary linen (ca. A.D. 350), and some Pharaonic funerary linen (ca. 1500 B.C.).

Iron oxide particles found on the Shroud are chemically pure to the level of $99+\%$, as would be expected if they were formed by a "khaki-like" process from the iron taken up by the original retting. The only other source of iron on the Shroud is from blood, which is also pure as of biological origin. In contrast, earth pigments (13–15) such as Venetian red or ocher from medieval or older European, North African, or Middle Eastern sources are always contaminated with elements such as manganese, nickel, or cobalt above the level of 1% (unless pure hematite crystals were employed by the artist, which, although possible, is highly unlikely). Examination of medieval Venetian red and ocher demonstrates that these contaminants are omnipresent above the 1% level. Indeed, electron microprobe of late medieval ferric oxide-derived paints or even modern ones shows such contaminants. In contrast, electron microprobe analysis of Shroud samples shows uncontaminated iron—with no detectable manganese, nickel, or cobalt.

Microchemical analysis of large numbers of ferric oxide particles from the waterstain margins also shows contaminating impurity elements

not to be present. It is of interest to note that the method of making "khaki" depends upon steeping linen in a soluble iron salt, adding base, and dehydrating it. An experiment was carried out producing such "khaki" linen fibrils containing iron oxide on the linen and occasionally, also, inside the lumen of the linen fibril. Photomicrographs of these fibrils on sticky tape were indistinguishable from the red birefringent particle-coated Shroud fibrils from the water-stain margins (12).

One further observation should be made. There are occasional tiny black irregular specks (and one larger one) that are only found in scorch areas. These specks give a positive silver reaction and are undoubtedly due to the molten silver splatter at the time of the 1532 fire (12). No lead was detectable, but a possible positive copper contaminant was seen in the large silver particle.

Patches and Holland Cloth

For the sake of completeness, we mention the patches, labeled G on Figure 1, and also the Holland cloth. As these are of known origin (sewn on in 1534 to repair damage caused in the 1532 fire), they are of little interest to the investigation of the Shroud and will not be pursued to any depth here; however, two interesting points should be mentioned. First, debris of all sorts found on the Shroud were also found on these areas (including blood debris) and even on the back of the Holland backing cloth. This finding underscores the extent of the translocation action.

Secondly, a series of transmission photographs were made where the Shroud was illuminated from behind while the photographs were taken from the front. Although these were made primarily to be used in correlating the x-radiographs, they revealed an interesting fact. From reflectance photographs we know that the patches appear to be approximately the same optical density as the Shroud, suggesting that they may have aged approximately as much as the Shroud; however, in transmission the patches are much lighter than the Shroud. No doubt some of the difference can be accounted for by the thickness differences in the cloths used for the patches and the Shroud, but this will not adequately explain the difference in the transmission coloration. This is an indirect indication that the Shroud is a great deal older than the patches and implies that the Shroud probably has a history prior to the known A.D. 1350 date. Some corroborating evidence of the disparate ages of the Shroud and the Holland cloth backing can be found in a location where a triangular piece of the Shroud was removed in 1973. Here the surface of the Holland cloth appears "whiter" than the Shroud, although the portion of the backing cloth exposed prior to 1973 looks the same color as the Shroud. Although this observation indicates that the Shroud is quite old, we urge caution in interpreting it and strongly encourage judgment be withheld until such time as a carbon-14 dating is performed.

Conclusions

We have attempted to assemble from various studies all the known facts that bear on the chemistry of the images on the Shroud. This chapter reveals the self-consistency of the chemical conclusions with all the physical observations made since 1978. In these concluding statements we will attempt to highlight our major conclusions.

First, let us turn to the blood images. These are clearly made of blood, likely human; however, we cannot state absolutely that the blood is of human origin. It is in these blood areas that we [and others (22)] find proteins present of the types associated with blood serum. Finally, there is nothing unaccounted for in the blood areas that would lead one to suspect that anything but blood formed the blood images (12). We therefore do not agree that there has been an attempt to artistically enhance a "preexisting" blood image (13–15); nor do we feel that these are "painted" blood images.

The body-only image posed a more difficult problem of identification, because the final coloring of the image is only a more advanced stage of the natural aging-type decomposition present over the entire cloth. Iron (entirely of the chelated type) is present incidentally, but only at levels that match (and sometimes are even less than) those of off-image areas. There is no evidence of the ubiquitous presence of any stains, dyes, or pigments in these body-only image areas. Although occasional particles, possibly identifiable as artist's pigments, have been reported in Shroud studies (13–15), they are not seen in consistent or adequate enough amounts to account for any of the images—blood or body-only images. The Shroud is known to have been reproduced by several artists since the 14th century and therefore to have been exposed to pigment "debris." This is sufficient explanation for such incidental appearances. However, the observed concentrations of these materials are not sufficient, by many orders of magnitude, to account for what is observed visually. All observations confirm that the body-only image is visible because the topmost fibrils of the linen are yellowed to a greater extent than the non-image linen. This yellowing is due to the natural process of dehydration, oxidation, and conjugation typical of low-temperature cellulose decomposition; the chromophore is some form of conjugated carbonyl groups.

The large amounts of iron present on the cloth (along with Ca) are consistent with the retting process in common use in the preparation of linen throughout the ages. We estimate that 90% of the iron exists in the cellulosic chelated state. Only a small amount of the iron found exists as ferric oxide, and this is found in the largest amounts in the fronts or margins of the water stains. These findings lead us to believe that the iron oxide was water transported (i.e., "chromatographed") at the time of the 1532 fire, and then deposited in the manner of a method for making

"mineral khaki." Smaller amounts of ferric oxide found in the scorch–blood-image area can be attributed to charred blood, and it can be readily demonstrated that ferric oxide can be formed by heating whole blood. The purity of the iron oxide, wherever located, in itself tends to rule out any connection with naturally occurring earth pigments, thereby supporting our suggestions as to its origins. Iron is also present in the blood areas in heme forms that one expects to find in blood. In short, the iron forms present on the Shroud are as expected and natural, rather than "painted" onto it.

Epilog

Although this chapter was not meant to address the specific question of how the images got on the Shroud, it does seem appropriate to conclude with a brief discussion of those things that seem obvious. To begin this discussion let us take one last look at the most widely publicized explanation for the Shroud images, the painting hypothesis. This hypothesis, detailed in References 13, 14, and 15, proposes that both the body images and blood images are composed of the same substance, a gelatin-based paint whose pigment consists of iron oxides and mercuric sulfide (iron earths and vermilion). It is obvious that the chemistry presented in this chapter is inconsistent with this explanation; however, the hypothesis can be tested without resorting to the detailed chemistry reported here. Figures 4–7 show the same area of the Shroud from four different perspectives. The first, Figure 4, shows a normal reflectance photograph of the side-wound area on the Shroud. The arrows point out water stains and a heavy blood flow. Figure 5 shows the same area in a transmission photograph (i.e., lit from behind). Figure 6 is an x-ray image of the same area. Finally, Figure 7 is the same area in UV fluorescence. Recall that our analysis shows that the water marks are rich in calcium and iron and, in particular, rich in very pure ferric oxide; in other words, these water stains are not untypical of common iron- and calcium-rich hard water stains. In addition, the visual appearance of these water stains is enhanced by organic debris from the fire. The x-ray image of Figure 6 is an absorption image. This x-ray image is a direct consequence of areal density (i.e., the density in grams per cubic centimeter integrated along the path length of the x-radiation so that the units become grams per square centimeter, that is to say the mass density between the x-ray source and the x-ray plate). The heavier the atomic weight, the more absorption and the lighter the x-ray image. In the first two images, it is clear that the blood stain is both darker and denser than the water stains. If the blood image were the result of iron oxides and mercuric sulfide, it would show up far more distinctly on the x-ray than the water stains, but quite the opposite is true. As reported in Reference 9, none of the blood marks

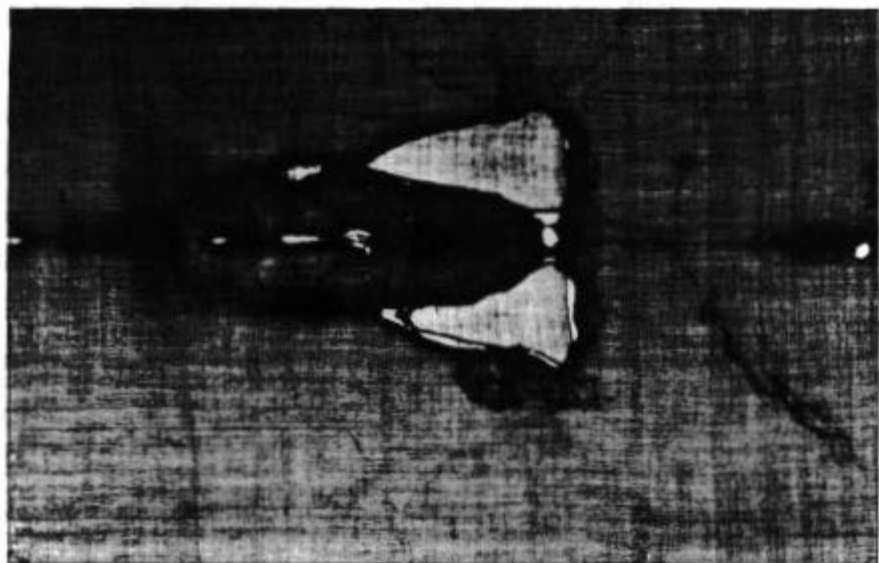Figure 4. *Reflectance photograph of side-wound area. Key: A, water stains; B, blood flow.*

Figure 5. *Transmission photograph of side-wound area.*

showed up on the x-rays, while all the water marks were clearly visible. Further, the extensively darker appearance of the blood mark compared to the water stains in Figure 7 can be explained by the nature of porphyrin (heme) compounds, which are highly absorbing in the UV region. The point is that one need not look far to find inconsistencies in the painting hypothesis.

This kind of exercise is typical of many such exercises that can be performed; they tell us what the Shroud is not, but not what it is. In fact, Reference 16 is devoted to these kinds of exercises. Because we have not been able to propose a mechanism that explains all the characteristics of the Shroud, a viable hypothesis remains undiscovered. This is not to say that our findings have not led to some implications about the origin of the images.

First, the blood images present no mystery; all evidence suggests that the blood went on as one would expect for a cloth in contact with wounds or the normal secretions of such wounds. We therefore suggest that the blood images are the natural consequences of the linen being in contact with wounds.

If the blood images were made by contact with wounds, it follows that the cloth was used to enfold a body. We have independent evidence that the cloth was used in this way. The mapping function, which maps body-only image density to expected cloth-body distance and the two-dimensional placement of the image on the cloth, offers a consistent argument that the Shroud enfolded a human-body shape. If we couple this argument with the testimony of the forensic pathologists, we can say more: not only was it a human form, but further, it was a human body.

Because the yellow fibrils comprising the body-only image are confined to the uppermost portions of the threads of the cloth, mechanisms that would evidence migration by capillary action can be excluded. Our attempts to reproduce this surface quality of the image have been most successful with various catalyzed-decomposition contact mechanisms. Laboratory simulations (8) have produced very convincing results both in chemistry and appearance (see Figure 8).

The Shroud's mapping relationship, however, poses the strongest objection to a contact mechanism. Contact mechanisms have not been able to produce a convincing cloth-body distance relationship. In fact, taken alone, this mapping function seems to suggest some kind of a "projection" mechanism, because there seems to be image present even where it does not appear to have been possible that the cloth was in contact with the body. We are left to identify what kind of "projection" mechanism, and this we have been unable to do. Simple molecular diffusion and "radiation" models, for example, fail to account for the apparent resolution of the image as we understand it.

Whatever the body-image production mechanism, it appears that it was prevented from acting by the presence of the blood/serum. This
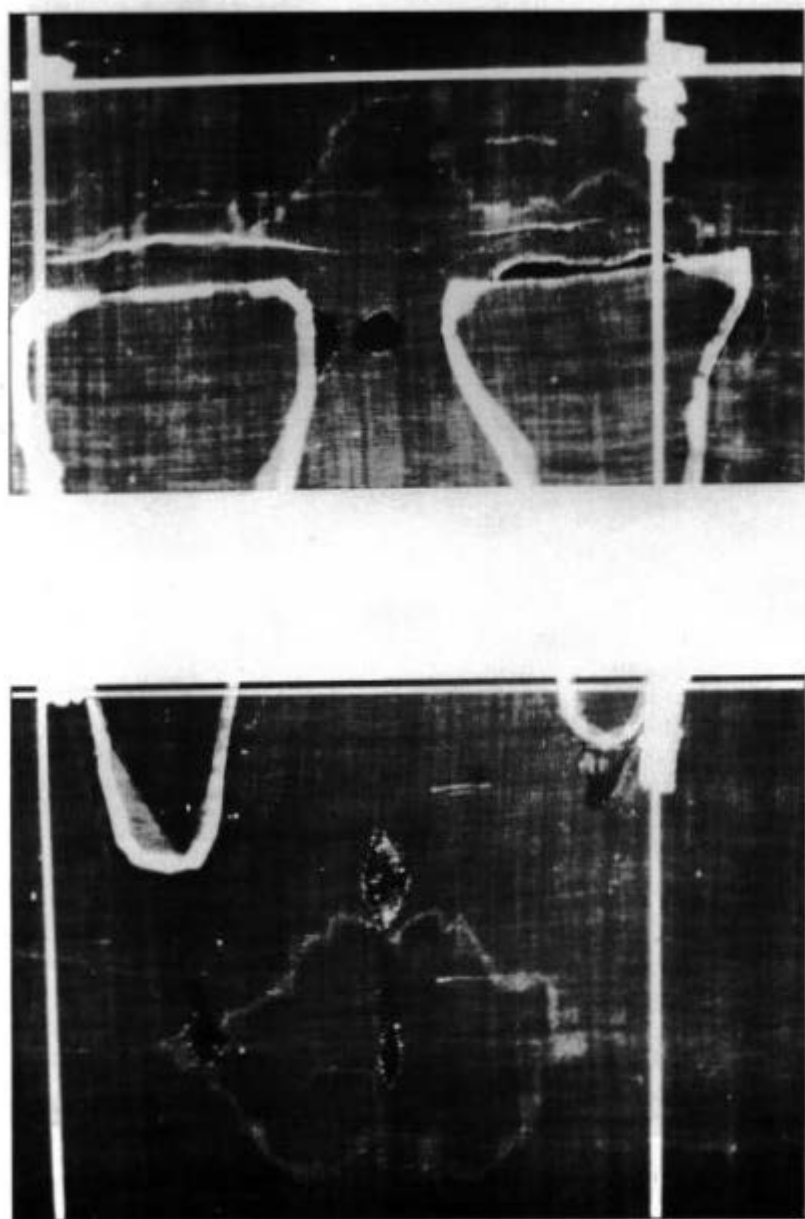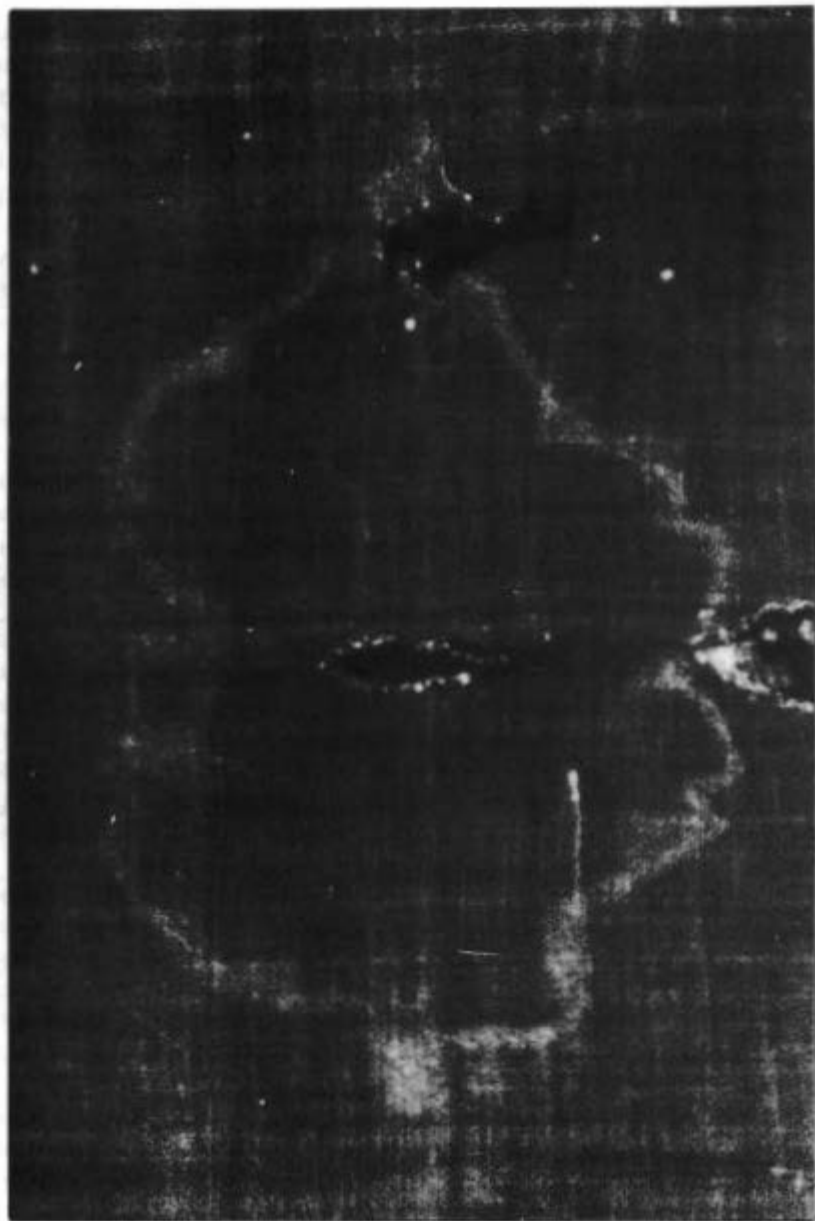
Figure 6A. x-Ray of side-wound area.

Figure 6B .   Detail of left water stain .

Figure 6C.   Detail of right water stain.

Figure 7. UV fluorescence photograph of side-wound area.

observation is suggested by both the presence of the "halo" around the heavy blood areas and the less degraded nature of the linen fibrils in the blood and serum areas.

We really do not have a satisfactory, simple explanation for how the body image got on the cloth. We think this fact is underscored by the fact that to our knowledge no other image on any cloth—grave cloth or art form—like the body image on the Shroud is known to exist today. If another example were to exist, our task of identifying the origin of the body image would be much simplified.

In the end, the question of the authenticity of the Shroud as the burial cloth of Jesus of Nazareth remains open-ended. We should all keep in mind that science is really not in a position to ever prove categorically that the Shroud is authentic (i.e., Jesus' burial cloth). We have, however, examined the probability that the Shroud was artistically produced and find it improbable. The question is left so that those who wish to believe it authentic are not hindered with scientific objection to doing so. However, without proof of authenticity, those who choose to believe the Shroud is not authentic are also free to do so without scientific objection, provided they do not assert a production mechanism that is excluded by the information now available.

The case for carbon-14 dating of the Shroud now seems to be more critical than ever. If we had discovered categorical proof that the Shroud was the work of a clever forger, there would be no need to pursue the question further. Lacking such evidence, the Shroud should be put to this further test. With the advent of accelerator carbon dating methods, little enough sample need be sacrificed to put the Shroud to this test
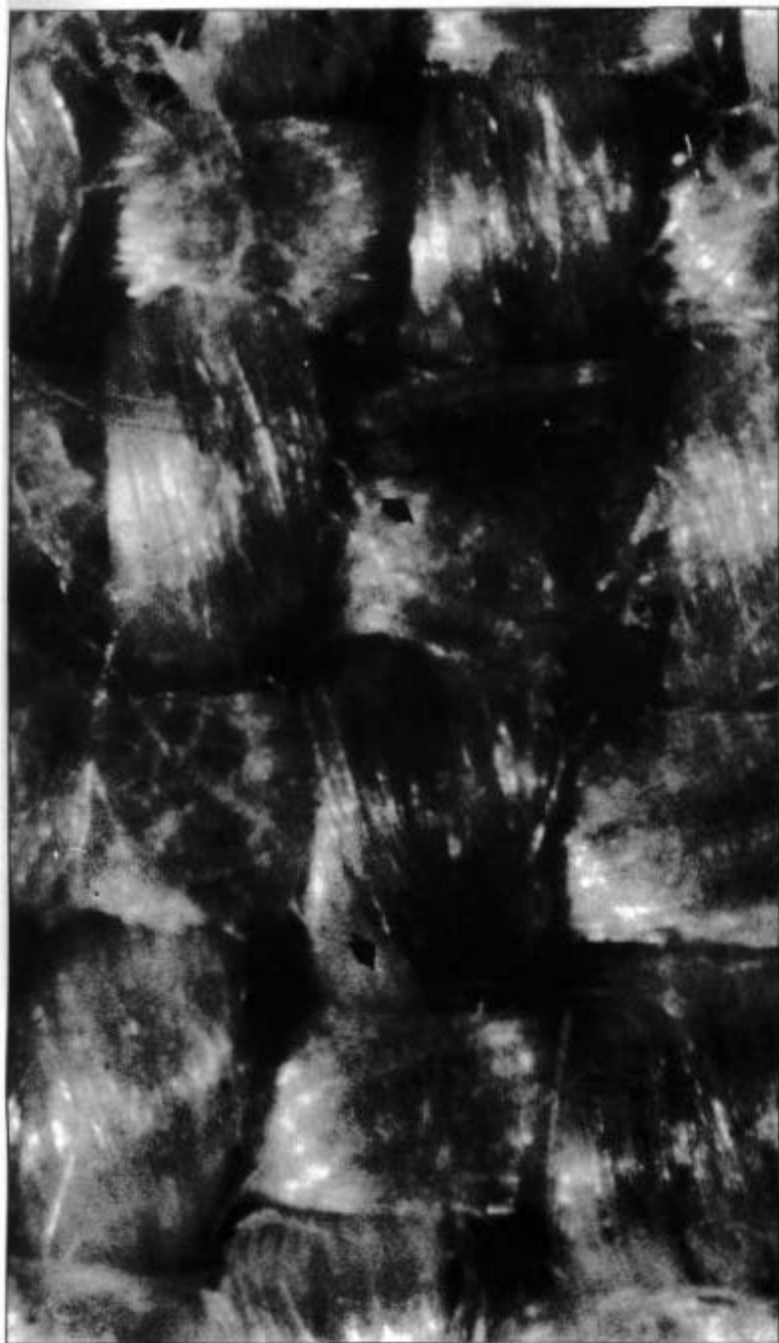
Figure 8. Photomicrograph of laboratory simulation by Pellicori (~40×). Arrows indicate placement of image on thread which matches Shroud body-only image.

(which if "negative," i.e., not first century, can prove lack of authenticity, but cannot prove authenticity).

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