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Special Report

PHYSICS AND CHEMISTRY OF THE SHROUD OF TURIN
A Summary of the 1978 Investigation[a]

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SUMMARY

This report reviews and correlates results obtained from tests conducted on the Shroud of Turin during the October 1978 investigation. Several image formation hypotheses are addressed. Although no single theory adequately accounts for all of the observations, it is concluded that the image is the result of some cellulose oxidation—dehydration reaction rather than an applied pigment. The application or transfer mechanism of the image onto the cloth is still not known. Because many proposed mechanisms of image formation strongly depend upon historical considerations, a determination of the age of the Shroud by radiocarbon dating is necessary for further hypothesis testing. Available data from the "blood" areas are considered and the results show these to be blood stains.

The Shroud of Turin, believed by many to be the burial cloth of Jesus, has generated considerable controversy, but unlike some other controversial subjects (e.g. flying saucers and ghosts), the Shroud exists as a material object. It can be observed directly and objectively. The results of studies can be analyzed by scientific methods.

The 1898 photographs by Secondo Pia stirred initial scientific interest in the Shroud. These and subsequent studies prior to 1978 are described in both popular [1—4] and technical accounts [5, 6]. The most recent observations were initiated during a five-day examination in October 1978 by the Shroud of Turin Research Project [7], two members associated with the International Center of Sindonology (Shroud studies) in Turin, and three other investigators. The description and results of the tests conducted at that time have appeared in separate publications [8—14]. The purpose here is to present as comprehensively as possible our current understanding and interpretation of available data.

Two views of the 4.3 × 1.1-m linen cloth are shown in Figs. 1 and 2. The most significant aspect of the Shroud is the visible frontal and dorsal image on the fabric surface. The greater part of this discussion is, therefore, given

[a]Further information available from: The Shroud of Turin Research Project, P.O. Box 7, Amston, CT 06231, U.S.A.

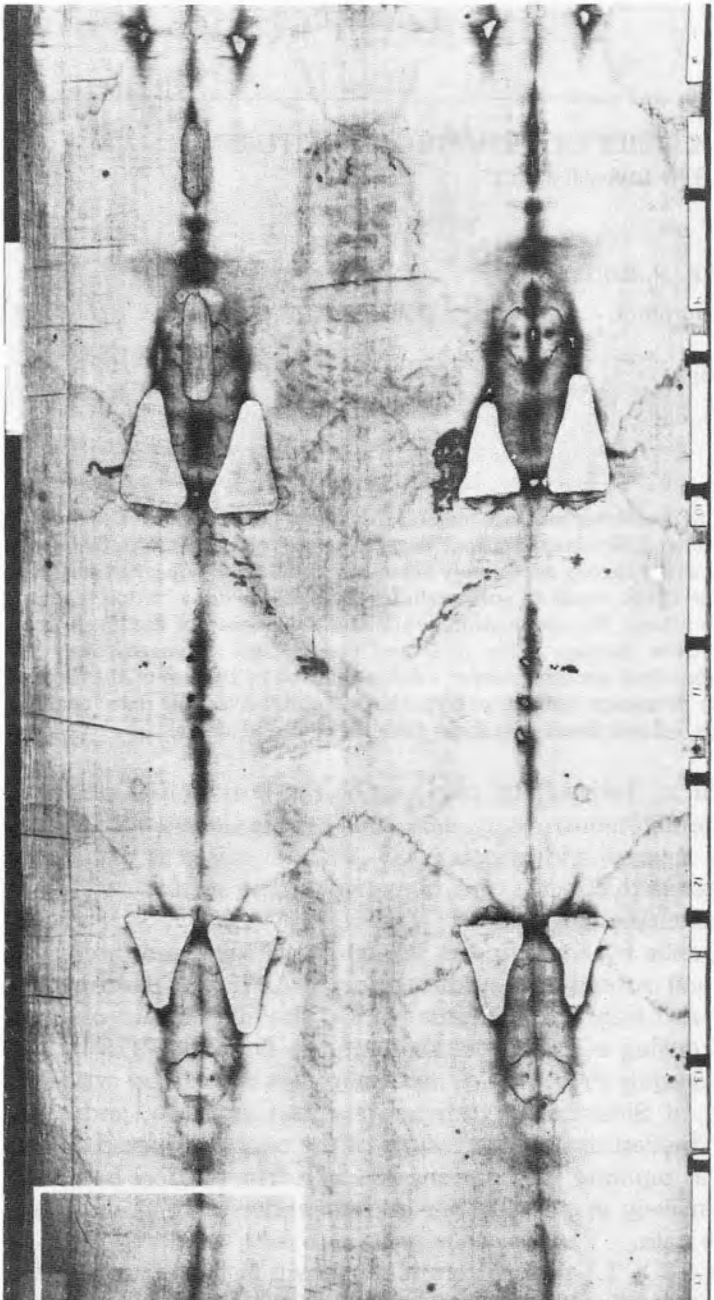

Fig. 1. Photograph of the Shroud area containing the full frontal image. A radiograph of the region indicated at the bottom of the figure is presented in Fig. 7.

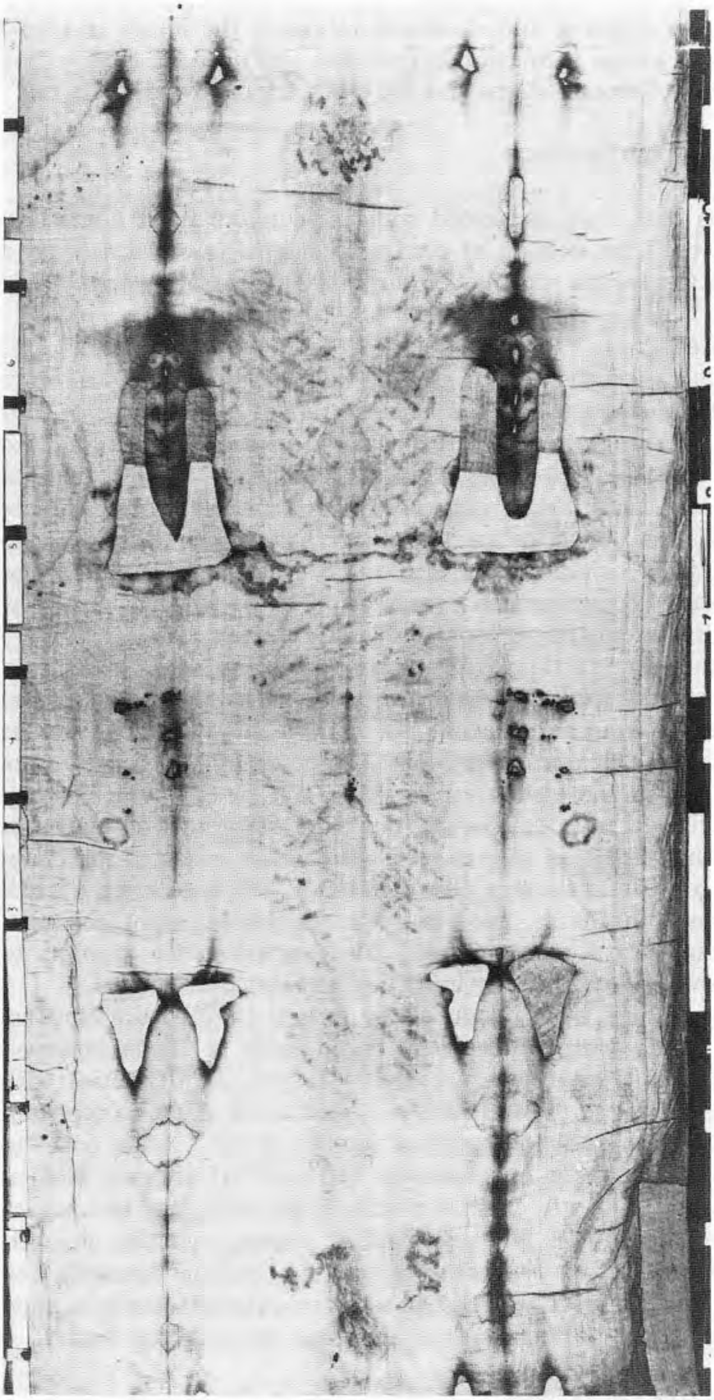

Fig. 2. Photograph of the Shroud area containing the full dorsal image.

to observations of the physical and chemical nature of the image and how these relate to various image formation hypotheses (see note 1). Finally, the data obtained from the "blood" stains and the cloth are reviewed.

GENERAL IMAGE CHARACTERISTICS

Two observations that have generated some discussion merit comment. The first has to do with the subject of contrast perception of faint images; the second concerns the results of some earlier image-processing work.

Faint image properties

Much has been made of the fact that the image on the Shroud is more readily perceived at a distance than it is at close range. At distances of four to five meters, all of the image features illustrated in Figs. 1 and 2 can be easily recognized; whereas, up close, it is difficult even to differentiate image from non-image areas. Some have considered specular versus diffuse reflection to explain this image property; others have taken this effect as evidence for the mystic origin of the Shroud. Neither argument need be invoked. D. H. Janney recognized this observation to be wholly consistent with the process of human visual perception of faint images.

Physiologically, the effect is described in terms of lateral neural inhibition [15]. The human eye enhances edge contrasts. A bright region imaged on one part of the retina inhibits adjacent parts from adapting to a darker region. The image on the Shroud is very faint (reflected optical densities are typically less than 0.1 in the visible range [12]) and generally lacks sharp boundaries. When viewed at close range, the total difference in darkness between image and non-image is spread across the entire width of the visual field. At distances of several meters, the difference is spread over a small region, and the lateral inhibition process enhances the apparent contrast. Such effects are familiar to radiographers, for example, who attempt to examine small features microscopically in diffuse or faint film images.

If the Shroud image had been produced by an artist and if the contrast values at the time of its composition were comparable to those observed today, the faint image qualities suggest severe technical difficulties with execution. For example, if the Shroud had been painted, it might be expected that the artist would have stood first within a meter of the cloth in order to control the medium effectively and then at distances of at least 4—5 m to observe the progress of the work. Similar difficulties with other techniques can also be envisaged. Although the potential of human ingenuity in overcoming such technical difficulties must never be underestimated, any hypothesis that the Shroud is the work of an artist must satisfactorily explain how the problems posed by the faintness of the image were circumvented.

Density shading and color properties

The density shading properties of the image have been a subject of scientific interest for over 80 years. During this time, the apparent negative image characteristics, revealed in the 1898 Pia photographs, have received the most attention. However, as early as 1902, Vignon [16] imagined the cloth draped over the human figure and noted that the image densities appeared to vary inversely with the anticipated cloth—body separations. To our knowledge, this observation was not examined in any great detail until much later.

Beginning in 1974, Jackson and coworkers [17] took a more analytic approach to the problem. In their experiments, a human volunteer was draped with a full-scale model of the Shroud, and cloth—body distances were measured along the profile from side-view photographs. The results were then compared with microdensitometer readings along a corresponding line from the 1931 Enrie photographs of the Shroud. Jackson et al. found that a relatively simple functional form could adequately relate the two sets of data and then used this function to map film densities from the entire two-dimensional photograph into a three-dimensional surface with a modified VP-8 image analyzer system [18]. The result of the exercise was that the three-dimensional relief generated in this simple way strongly resembled that of a human figure with surprisingly little distortion. They further illustrated with the same video technique that comparable results were not ordinarily obtained from paintings, drawings, or normal photographs. In almost all cases, obvious and gross distortions were apparent although satisfactory relief surfaces were ultimately generated from photographs of phosphorescent objects taken through light-attenuating media.

The results of this study led Jackson et al. [17] to conclude that there is "three-dimensional information" encoded in the image. (This is not to imply that the image itself has any three-dimensional or layered structure; only reflected optical densities and an empirical mapping function were used to generate the reliefs.) Jackson et al. could offer no explanation for how this "information" arrived on the cloth; the results of this experiment have not yet suggested any particular image formation mechanism. Yet the significance of their findings has been the subject of considerable discussion. Jackson and Jumper view the implications of their work more in terms of where this density shading information originated and how the information was transmitted, ultimately to the cloth surface. To them, the three-dimensional effect from the frontal image implies that either a statue or an actual human body was used, at least at some stage, to produce the image. They argue that the comparatively flat appearance of the dorsal image is consistent with this interpretation, although for this part of the image, it is much more difficult to obtain quantitative evidence to support their hypothesis. Jackson similarly observes certain image distortions that, in his opinion, might have resulted from the cloth drape over a human body, although certain special assumptions still seem necessary to account for the absence of the "imprint" from the top of the head.

In this report, discussion is limited to the question of how the image was actually transferred to the cloth. Considerations of the image resolution and the density shading characteristics bear on this discussion only insofar as they examine various physical processes and their potentials for generating or preserving these characteristics. In this context, the VP-8 results do not prove that a three-dimensional object was used directly in the image formation process. That is, it may still be appropriate to consider image transfer mechanisms from flat models (paintings, etchings, or shallow bas reliefs, for example) which themselves may contain the information that gave rise to the contour shading properties of the image. For this discussion, the most significant result of the VP-8 study is the apparent global consistency of the three-dimensional reconstruction. To us, this implies the existence of a simple function that maps Shroud image densities to cloth—body distances in a global sense. This is potentially important because it would establish a condition that must be satisfied by any seriously considered image transfer mechanism.

LaRue [19] has expressed caution concerning the use of the Enrie photographs for further three-dimensional studies. The 1969 photographs of Judica Cordiglia [20] show that Enrie's use of orthochromatic emulsions introduced tonal distortions especially for the reds that might critically affect results. These difficulties have now been overcome. The work by Judica Cordiglia and the more recent high-resolution photographs by Miller were taken and developed under controlled and recorded conditions. The latter include panchromatic and multispectral narrow-band mosaics at 5.6:1 and 22:1 reductions of the entire cloth surface. For the multispectral photography, Miller used a liquid filter to isolate the 335—375-nm ultraviolet band and a subtractive set of filters: B (370—500 nm), G (500—575 nm), and R (585—750 nm) for the visible range.

Preliminary VP-8 analyses of these latest photographs have shown results that are quite similar to those obtained from the original studies; the frontal images yield rather impressive three-dimensional relief figures whereas the dorsal images remain comparatively flat in appearance. The effect, therefore, does not seem to arise from some peculiarity of the Enrie photographs but appears to be a genuine property of the image. Jackson and Jumper are presently continuing work with the 1978 photographs to establish more accurate limits for the mapping function. Considerable uncertainty exists in the analytic form of their original function because it was chosen somewhat arbitrarily to represent the relatively imprecise correlation of data over a limited region. Further refinements are constrained somewhat by the resolution of the image, but most severely by the assumed cloth drape and the expected uncertainties in the detailed appearance of the reconstructed three-dimensional model [21]. Nevertheless, it is useful to define the mapping function as accurately as possible for comparison with predictions from image-transfer models and empirical results.

Preliminary studies of other aspects of the image analysis problem have also been reported [22—25]; yet an abundance of work remains to be done in this area. For example, film density differences or ratios among the multispectral photographs at all locations could provide further information about spatially-dependent color variations. Thus far, only limited image analysis work has been done with the 1978 photographs.

HYPOTHESES ON BODY-IMAGE FORMATION

The image on the Shroud is most intriguing because it is not immediately obvious how it was produced. The primary goal of the 1978 investigation was to apply a series of nondestructive tests to determine the physical and chemical characteristics of the image more exactly. Various hypotheses about the image formation can now be tested with these data. Unfortunately, the years of controversy have generated a large number of arguments about how the image may have been formed. Each of these hypotheses cannot be tested individually, but the discussion in this section has been organized, according to Fig. 3, to consider rather broad categories.

In most cases, the available data are insufficient to allow individual hypotheses or entire categories to be discarded, but these deficiencies serve to direct efforts in continuing research. It is emphasized that this article is a status report, and specific problems are mentioned as they arise. Interest from specialists in areas (art history and techniques, textiles, etc.) outside our range of technical expertise is encouraged.

Hypothesis: The image is an artifact

When first introduced to the subject of the Shroud, many suspect that the image was produced by human skill and ingenuity. Indeed the hypothesis

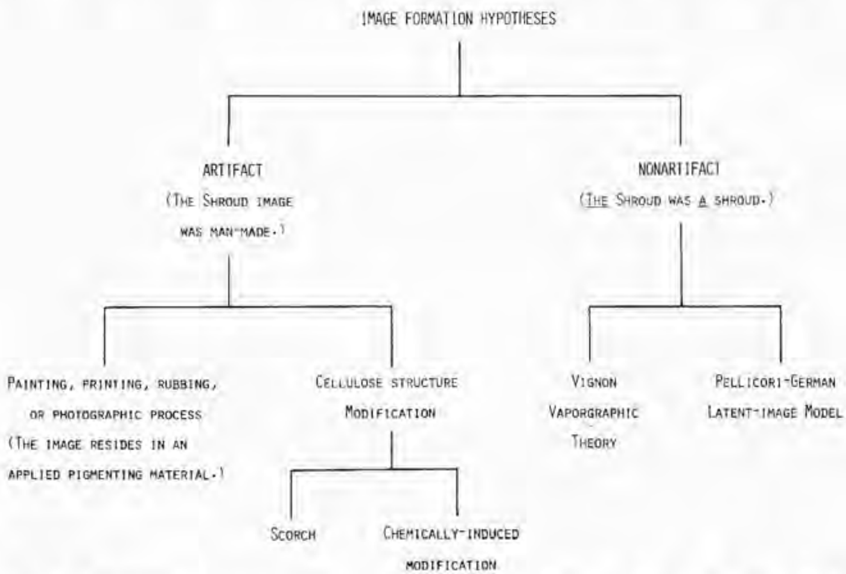

Fig. 3. Schematic representation of the logical structure of the section dealing with hypotheses on image formation.

that the image is a medieval artifact is at least 600 years old. A letter [26] written in 1389 by Pierre d'Arcis, Bishop of Troyes, refers to an investigation by his predecessor that allegedly exposed the artist who had painted it. The controversy was revitalized in this century when Chevalier [27] based his own opinion on this historical evidence.

Unfortunately, the materials and painting method were not specified in the bishop's statement, leaving us with an open-ended problem. We are left to consider all possible materials and methods that could have been used to produce an image on cloth through human skill or cunning. This situation results in the fact that elimination of all known methods does not prove that a clever artist or hoaxer did not use a method currently unknown. However, the elimination of historically known (and unknown but technologically feasible) methods would make image production by willful human action appear less probable. If the Shroud image is an artifact, few presuppositions about the time and place of its origin can be held. It could have been produced in Europe during the 14th century or somewhere else before that time; even remote possibilities cannot be discounted [28, 29] (see note 2). In any case, it is reasonable to suppose that if an artist produced the image, it would have been necessary to have either added a colored material to the cloth or changed the composition of the cloth to produce a color. Different observations are required to test these two corollaries.

Corollary: The image is an applied pigment

If the image were produced by painting (using the normal dictionary definition), block printing [29], transfer-rubbing over a bas relief [30, 31], spray painting, or some unreported photographic-like process [32], a foreign material would have been added to the cloth. The foreign material would cause changes in relative density, chemical composition, spectral reflectance characteristics, mechanical properties, and/or microstructure.

Within the limitations imposed by time, expense, and damage to the Shroud, tests and observations that have been made include (1) direct microscopic observations and photomicrographs [8], (2) x-ray fluorescence spectrometry [9] to observe discontinuities in elemental composition, (3) low-energy x-radiography [10] to observe areal density discontinuities, (4) infrared, visible, and ultraviolet reflectance spectra [11–13], (5) photoelectric [12] and photographic [14] fluorescence, (6) direct macroscopic visual observations and photographic images in different, known wavelength regions, and (7) thermal emission images [11] in different wavelength regions. Visible transmission, side-lit, and glancing-angle photographs of the Shroud were also taken. Riggi examined vacuumed material from the cloth and its repository by electron microscopy and microprobe. Finally, surface-transfer samples were taken on specially prepared, pure hydrocarbon adhesive tape for later microscopic and chemical examination and various microchemical and instrumental techniques.

Microscopy

The most important observations for testing the painting hypothesis are those made by direct microscopy. The Shroud threads (nominally 0.15 mm in diameter [10]) are composed of linen fibers of 10—15 μm diameter. What the eye sees as the image is caused by a discontinuous translucent-yellow discoloration of these fibers. In pure image areas, the colored fibers appear only on the topmost segments of the threads [33], and coloration extends only 2 or 3 fibers deep into the thread structure.

The image has a half-tone quality; its density or darkness is determined by the number of colored fibers per unit area. The hue of discolored fibers is the same on light and dark density areas. The front and rear images of the body show the same distribution of fiber coloration and maximum image densities [33]. Color does not penetrate the cloth in any image area [33] (see note 3) nor is there any evidence for cementation between fibers or capillary flow of liquids. Fibers from the image area have a "frosty" appearance; that is, their surfaces show a more diffuse light reflectance than do the non-image fibers. No pigment particles can be resolved at 50× magnification in image areas. The image does not look like a painting by direct microscopic examination.

In 1973, Frei [34] used sticky tape to remove samples of surface debris for subsequent pollen studies. The same technique was also used in 1978 by Rogers and Dinegar who took and documented a total of 32 samples from the Shroud image, "blood" stain, scorch, water stain, and background areas. The tape samples, each about 5 cm^2 in area, were applied with a specially designed roller and then carefully pulled from the cloth surface. Rogers noted immediately that the sticky tape surfaces retained a wide diversity of materials but that the amounts of material varied from sample to sample and in some cases appeared to depend upon the thread lot associated with the sampled area. He also observed that the image-area tapes "lifted" more easily than non-image tapes suggesting that the topmost fibers in the image area were somehow weakened.

Later, McCrone and Skirius [35], McCrone [36], and Heller and Adler [37] examined the tapes by light microscopy. Heller and Adler documented and classified the observed materials into two general categories. The first included "occasional" materials such as insect parts, pollen (see note 4), wax, wool, red silk, and modern synthetic fibers. The second category included the more consistently occurring materials: linen fibrils (or fiber fragments) and several types of red and less frequent black particles.

McCrone and Skirius [35], who first examined the samples, found two types of linen fibrils present, some clear and others uniformly colored yellow to faint yellow. Their study showed that significantly greater ratios of yellow to clear fibrils were present on the tapes from the image area than on those from the non-image areas. The yellow fibrils are considered to be the most important direct observations of the Shroud and subsequent photomicroscopic examinations indicate that they represent the dominant and probably sole visible image element.

In addition, McCrone and Skirius reported that eighteen of the tapes showed significant amounts of submicrometer-sized red particles which they identified as Fe_2O_3 of varying degrees of hydration. According to their report, most of the particles appeared to be "well dispersed" and, of these, the majority were intimately associated with the linen fibril surfaces. Smaller quantities of the particles were seen to be clustered and perhaps bound into larger (20—30 μm diameter) aggregates especially in the "blood" area samples. In a further examination, the tapes were separated into two groups depending on the microscopically observed presence or absence of red particles but without prior knowledge of the sample location on the Shroud. The results showed that none of the control samples (those with no image) contained red particles whereas all the samples from the "blood" area and two-thirds of the samples from the body-image area showed significant amounts of the material. They concluded that a direct correlation exists between Fe_2O_3 particle concentrations and the image areas and postulated that this material may have been used to enhance the image contrast. The well-dispersed particle distribution suggested to them that the "red pigment" may have been applied as a very dilute particle—liquid suspension. In particular, they state that the fiber discoloration may have resulted from a paint medium that had yellowed with age.

The postulated identification of fiber discoloration with a pigment vehicle offers an hypothesis that can be tested. There are several media that could have been used by a medieval painter. Thompson [38] lists glair (egg white), size (animal collagen or gelatin and fish glue), and plant gums (arabic, tragacanth) as several commonly used pigment vehicles in the 14th century. These vehicles were taken separately or in combinations depending on the particular application. Honey, sugar, egg yolk, and even ear wax were occasionally added to obtain certain desired effects. Drying oils such as linseed, hempseed, walnut, and possibly poppyseed were known and used in painting although the extent of their application has been debated. Gettens and Stout [39] suggest casein, starch, and waxes as further but less likely possibilities. Although, once again, the possibility remains that some other vehicle was employed, there is no evidence to support the contention that any of the above media produced the yellow fiber discoloration.

One general problem has to do with the observed fibril structure. Linen fibers consist of plant cells joined end-to-end. Microscopically they have a bamboo-like appearance; the joints are seen as well-defined circumferential structures. Our observations of both clear and colored fibrils from a pure-image area showed no obvious evidence for a coating of paint medium. The growth joints are clear and sharp with no evident meniscus marks. (Phase microscopic examinations [37] of fibrils from a pure-image area also showed well-defined surface erosion features which, we believe, give rise to the general "frosty" appearance of the image fibers in the photomicrographs.) It could be supposed that a sufficiently non-viscous or diluted tempera vehicle was used; however, it is then difficult to explain the absence of either discoloration or liquid capillary flow into the deeper portions of the threads without, at the same time, postulating some unusual mechanism of application.

Even if this possibility is accepted, there is another problem that has to do with the chemical nature of the discoloration. Heller and Adler [37] applied a series of microchemical tests to the various types of fibrils. Among these were several protein tests including the biuret/Lowry, coomassie blue, bromothymol blue, amido black, bromocresol green and fluorescamine tests and various controls including several types of protease digestions. With these, they found that positive protein tests could only be obtained from fibrils associated with the "blood" areas. McCrone [36] similarly obtained positive results in the amido-black test for samples 3-CB (right side wound) and 1-AB (back of right foot), both nominal "blood" areas.

The results are interesting for several reasons. First, they indicate that minute quantities of aged protein materials can be detected by microchemical techniques. (Heller and Adler have confirmed that the fluorescamine test is sensitive to protein under these conditions at the 1—10 nanogram level.) Although the presence of protein in the "blood" may suggest that a pigment vehicle was used there, the result is most interesting in connection with certain independent evidence for the presence of blood in these stains [40]. In this case, positive protein tests would actually be expected. In contrast, negative tests on yellow fibrils from pure-image areas would effectively eliminate all protein-based vehicles including glair, egg yolk, size, and casein.

McCrone's opposite conclusion [36] is not well supported because his positive amido-black tests were observed in "blood" areas only and cannot be taken as evidence for the presence of a protein-based tempera vehicle for the image areas generally. In our view, McCrone's inference has two problems: first, no protein has been observed by any method in pure-image areas as distinguished from "blood" areas; second, a more selective test must be employed, because amido black stains cellulose easily, making false positive results probable.

Heller and Adler [37] conducted further tests on the fibrils to detect inorganic compounds. These results were consistently positive for iron and calcium but negative for manganese, cobalt, nickel, aluminum, arsenic, tin, lead, magnesium, and silver. Although these tests were not sufficiently sensitive to detect siccative (oil drying) compounds, they show that the yellow fibril discoloration does not result from any likely (non-ferrous) inorganic or lake pigmentation (see note 5).

Additional tests for organic dyes and stains gave similar results. Heller and Adler could not extract the yellow color with strong acids, strong bases, or a variety of organic solvents including ethanol, methanol, carbon tetrachloride, benzene, pyridine, ethyl acetate, and acetone. Moreover, the color could not be bleached by strong oxidants (e.g., hydrogen peroxide) or by treatment with standard addition reagents such as iodine in the Hanus, and Wijs methods. However, they found that strong reductants, diimide and hydrazine (though at a slower rate), could bleach the color of image fibrils. Tests for the presence of nitro groups, phenol groups, steroids, and lignin were negative, but the fibrils did show positive tests for aldehyde and carboxyl groups. Semi-quantitative tests indicated the greatest aldehyde and carboxyl concentrations for scorch-area fibrils, with lesser relative quantities for image and least for non-image fibrils.

Shroud samples from the tapes and excised threads [41] were examined by both laser-microprobe Raman spectroscopy and mass spectrometry. Results from the Shroud samples were compared with those obtained from modern samples of linen prepared by primitive techniques. No quantitatively significant Raman spectra could be obtained from any of the samples. The only unequivocal spectrum that could be obtained was that of the Mylar backing of the tape. There was no evidence for Saponaria or any other coating on the excised threads or image fibrils.

Mass spectrometry was run by pyrolysis of the samples within the source unit of the instrument. Mass spectrometry should provide the most sensitive and general method for the detection of foreign organic materials. (The system was sufficiently sensitive to detect traces of polyethylene that had been transferred to an excised thread by contact with its wrapping material, for example.) Although these data have not yet been fully evaluated, some conclusions have been drawn. There is a significant difference between the Shroud and the modern-primitive samples. The latter were found to contain lignin. This result was not entirely unexpected, because independent microscopic examinations of the modern-primitive samples had revealed lignin with the phloroglucinol/hydrochloric acid test, although the same test showed none on the Shroud samples. The mass spectrometric measurements detected no foreign materials on the image fibrils. Neither did mass spectrometry show any significant difference between the pyrolysis products observed from control areas and image areas at the level of data analysis that is now available.

The results of these studies lead toward some interesting conclusions. If any of the expected dyes, stains, pigments, or painting media had been present in the image, there should have been some indication from the microscopic, chemical laser microprobe, or mass spectrometric examinations. Subjects of earlier speculation, which involve the presence of burial spices (aloes, myrrh), oils (skin secretions), or saponins [3], likewise receive no support. By contrast, the chemistry of the fibrils does indicate a difference in the degree of oxidation and dehydration of the cellulose structure between image and non-image fibrils. The microscopic and chemical data, therefore, suggest the image to be the result of some cellulose degradation effect rather than an applied pigment. However, before this conclusion is accepted, the hypothesis must be subjected to the remaining evidence. More discussion of "painting hypotheses" will follow in later sections.

First, the presence of iron oxide and its suspected correlation with image areas requires some comment. Thus far, only the possibility that it represents an artist's attempt to enhance the image has been mentioned, but there have been other suggestions. Riggi, fcr example, postulated that the Shroud may have been contaminated with some remnant of a jeweler's rouge polishing agent by inadvertent contact with one or more of the protective glass plates used in earlier exhibits.

As another possibility, Heller and Adler [37] observed that the appearance of the particles, and especially their occasional occurrence within the fibril medulla, are identical to those produced by an iron salt, alkaline precipitation, and dehydration reaction which were formerly used in khaki manufacture. They state that such reactions are known to occur naturally during the linen retting process. Detection of iron and calcium bound by ion exchange on both the image and non-image fibrils supports this hypothesis. The observed Fe_2O_3 particles could have been produced during the original retting or, also, at the "dousing" of the 1532 fire, by a chromatographic concentration mechanism similar to the khaki-type process. Heller and Adler observed Fe_2O_3-coated fibrils most frequently in the samples from the margins of the water stains and consider the latter process to be the major source of this type of artifact. Although the ultraviolet and x-radiographic data, described at greater length in later sections, tentatively support this conclusion, future x-ray fluorescence examination of the water-stain margins should provide more conclusive evidence.

In addition to Fe_2O_3, Heller and Adler [37] found "blood sherds" and "blood flakes" on many of the samples. The "blood flakes" are nearly indistinguishable from the comparably-sized Fe_2O_3 particles by the usual optical techniques. However, the two materials may be differentiated by the solubility of the "blood flakes" in hydrazine and the acid solution properties of Fe_2O_3. (The "blood sherds", which they found to be detached fiber-coatings of blood, are similarly distinguished from the identically appearing scorched fibrils by the "sherd" solubility in hydrazine.)

McCrone and Skirius [35] reported large concentrations of Fe_2O_3 particles for the "blood" areas, but Heller and Adler found most of these red particles to be "blood flakes" and not Fe_2O_3. It is, therefore, possible that the "Fe_2O_3" particle correlation with image areas reported by McCrone and Skirius is in fact a "blood flake" correlation obtained by translocation in the cloth folding. Jackson has experimentally tested the translocation hypothesis. From the sizes and positions of the burned holes, he has reconstructed the folded configuration of the Shroud at the time of the 1532 fire. Using these results, he then demonstrated that if the "blood" stain regions are assumed to contain substantial amounts of submicrometer-sized particulate material, a correlation almost identical to McCrone's is obtained by simple contact transfer in folding and unfolding the cloth several times.

The chemical composition of the true Fe_2O_3 particles may ultimately identify their origin. Heller and Adler [37] noted that iron found in hematite, ochers, and earth pigments is invariably contaminated with manganese, nickel, cobalt, or aluminum. They conducted a series of spot tests on the various particles. After acid digestion, all but one of the red particles gave positive tests for iron although no traces for manganese, cobalt, nickel, aluminum, arsenic, copper, lead, or magnesium were detected above the estimated detection level of 1% (by weight). These results suggested to them that the iron oxide was of either hydrologic or biologic origin. The one exceptional red particle, which was found on the non-sticky side of one tape and tested positively for mercury and negatively for iron, was identified as mercury(II) sulfide. The black particles were generally found to contain iron although occasionally some of these near the scorch areas contained silver and not iron. Heller and Adler suggested that the silver may represent molten debris from the casket, that was deposited onto the cloth in the 1532 fire. The black (iron-containing) particles might similarly be postulated as Fe_3O_4 that formed either from Fe_2O_3 or the "blood" during the fire.

McCrone and Skirius [35] also reported seeing a few particles of orpiment, ultramarine, azurite, wood charcoal, madder rose, and larger quantities of vermillion. Although these observations have not been confirmed independently, Heller and Adler note that the occasional occurrence of such materials may not be unexpected because the Shroud is known to have been reproduced by artists and was, therefore, probably exposed to pigment-contaminating environments. Most recently, McCrone [42] detected the presence of minute amounts of mercury(II) sulfide in several material agglomerates tested from a single tape taken from the area of the side wound. The observation may warrant more precise x-ray fluorescence measurements there in the future; however, the data of Morris et al. [9] suggest that mercury is present nowhere in amounts greater than about 10 $\mu g\ cm^{-2}$.

X-ray fluorescence

Prior to the 1978 investigation, there was little information about the Shroud image beyond that provided by rather qualitative descriptions of its color and superficial distribution. In view of the vague historical references to a painted image, operations in the Shroud of Turin Research Project were planned to test this hypothesis thoroughly. In the 14th century, there were several pigments that might have been used to produce an image (see note 5). The most important nondestructive test applied to detect inorganic pigments specifically was x-ray fluorescence. With this technique, a painting produced from an iron, arsenic, lead, or other heavy-metal compound would be expected to reveal its presence as a discontinuous element distribution between image and background areas.

Morris et al. [9] reported results of the x-ray fluorescence studies. Their system excitation source consisted of an x-ray tube and tin secondary emitter that produced a nearly monochromatic beam of 25.5-keV $Sn{-}K_\alpha$ x-rays incident to the sampled area. A nominal 160-eV Si(Li) detector and energy-dispersive instrumentation were used to detect and process fluorescent x-rays in the range 1.5—22.0 keV. This system allowed detection of elements with atomic number greater than 16 with varying degrees of efficiency.

(The technique cannot be applied directly to detect low-atomic-number organic dyes or tempera vehicles.)

Generally, the x-ray fluorescence results showed no evidence for a painted image. Within the detection and precision limits of the data, there were no detectable differences in the heavy-element concentrations between image and non-image areas. Unfortunately, because of time constraints and the desire to examine as many different areas as possible, the precision levels of the measurements were rather limited. For example, Morris et al. estimated a detection limit to changes in iron concentrations of 5 $\mu g\ cm^{-2}$; longer counting times could have improved overall data precision. Despite these and other difficulties, the x-ray fluorescence results were sufficient to establish weight concentration limits for most elements of potential interest; however, in the absence of microscopic evidence for the presence of inorganic pigments (with the exception of Fe_2O_3 discussed below), there seemed little need to relate these numbers to corresponding pigment concentration levels.

Morris et al. reported relatively uniform concentrations of calcium and strontium in all of their spectra (see note 6). The large quantities of calcium ($200 \pm 50\ \mu g\ cm^{-2}$) and traces of strontium ($2.5 \pm 1.0\ \mu g\ cm^{-2}$) were tentatively interpreted as dust accumulations, probably natural calcium carbonate, on the Shroud. Riggi similarly observed substantial quantities of calcium compounds in the samples that he vacuumed from the back-side of the cloth. Although Riggi's observation tends to support Morris' interpretation, subsequent microscopic examination of the tapes showed little or no calcium compound debris from the Shroud image surface. Heller and Adler [37] have since postulated that the calcium and strontium were absorbed into the linen during the retting process (in which case the elements would be detectable with x-rays but not with the tape surface samples). They draw support for this hypothesis from both an experimental demonstration of the ion-exchange process and the observed presence of iron and calcium in several other antique linen samples.

In addition to calcium and strontium, small concentrations of iron were also detected in the non-"blood" areas. Quantities of about 30 $\mu g\ cm^{-2}$ were reported for the (non-image/water stain) foot scan and 10 $\mu g\ cm^{-2}$ for the (image) face scan regions. These results are generally consistent with microscopic observations, made during the period of direct examination, of particulate material throughout the Shroud. Pellicori and Evans [8] noted significantly higher concentrations of particulates in the nose and foot regions of the image. In these areas, x-ray fluorescence indicated statistically significant excesses of iron above background levels.

The data of Morris et al. [9] have provided some information to supplement the results of the tape study discussed above. McCrone and Skirius [35] postulated in their work that iron oxide contributes to the coloration of the image, but they gave no quantitative estimates either for the number densities of particles adhering to the fibrils or for macroscopic areal weight concentrations of the material. Morris et al. measured changes of 0.01 in neutral reflected optical density for 1 $\mu g\ cm^{-2}$ changes in iron concentrations of (anhydrous) Fe_2O_3 at low densities. A minimum visually-detectable quantity of this material is, therefore, about 2 μg Fe cm^{-2}, which is a result that has been confirmed by Pellicori [13]. If an artist deliberately used a hematite pigment to produce a visual effect on the image, then he must have applied at least this amount.

This hypothesis can be followed further. If an Fe_2O_3-enhancement implies an intentional darkening of faintly dark image areas, then one would expect to see some direct correlation of iron concentration with image density. Morris et al. [9] presented results of their x-ray fluorescence scan of the facial region indicated by the enclosed area in Fig. 4. The measurements were taken over roughly 1-cm^2 areas at 1-cm intervals along a scan line from the tip of the nose out to the "blood" trickle in the hair. It can be observed from the figure that the image density varies visibly along this scan, yet, except for the end points, the x-ray fluorescence showed no statistically significant variations in element density along the scan. Although the areal-concentration data for iron qualitatively suggest a correlation, these variations are smaller than the $\pm 2.5\ \mu g$ Fe cm^{-2} precision limits of the measurements.

This data precision is, therefore, insufficient to test the hypothesis of image enhancement with Fe_2O_3 definitively, but the results do place rather narrow limits, 2—5 $\mu g\ cm^{-2}$, on whatever areal weight concentrations such an hypothesis might imply for hematite. (Hematite or anhydrous Fe_2O_3 would represent a "worst case" because the hydrous forms are less potent coloring agents. Thus, for an equivalent darkening, hydrated Fe_2O_3 would require greater relative iron concentrations than the hydrous compound and would, therefore, be more readily detected with the x-ray fluorescence.) A more precise x-ray fluorescence study could be made in some future attempt to improve on the present results. However, variations in a large but visually undetectable background quantity of iron may preclude any more definite conclusions than those drawn here.

Low-energy radiography

Mottern et al. [10] radiographed the entire Shroud with a Baltograph 5-50 x-ray unit operated at 15 (peak) kV and 10 mA for 10 min. The tungsten tube had a focal spot 1.5-mm square and inherent filtration of 1.0-mm beryllium. Mottern used Class I films (Kodak Types DR and M) with a source to object/film distance of 1 m.

Ordinarily, x-radiographic techniques are well suited for observations of paintings produced with heavy-metal pigments laid on at appreciable thickness, but the Shroud image is certainly not in that category. No density discontinuities that correspond to visible body image could be observed anywhere, although the weave structures and cloth density variations are easily visible in all of the radiographs. The water-stain margins are also seen as high-density structures, but in the absence of x-ray fluorescence data, the

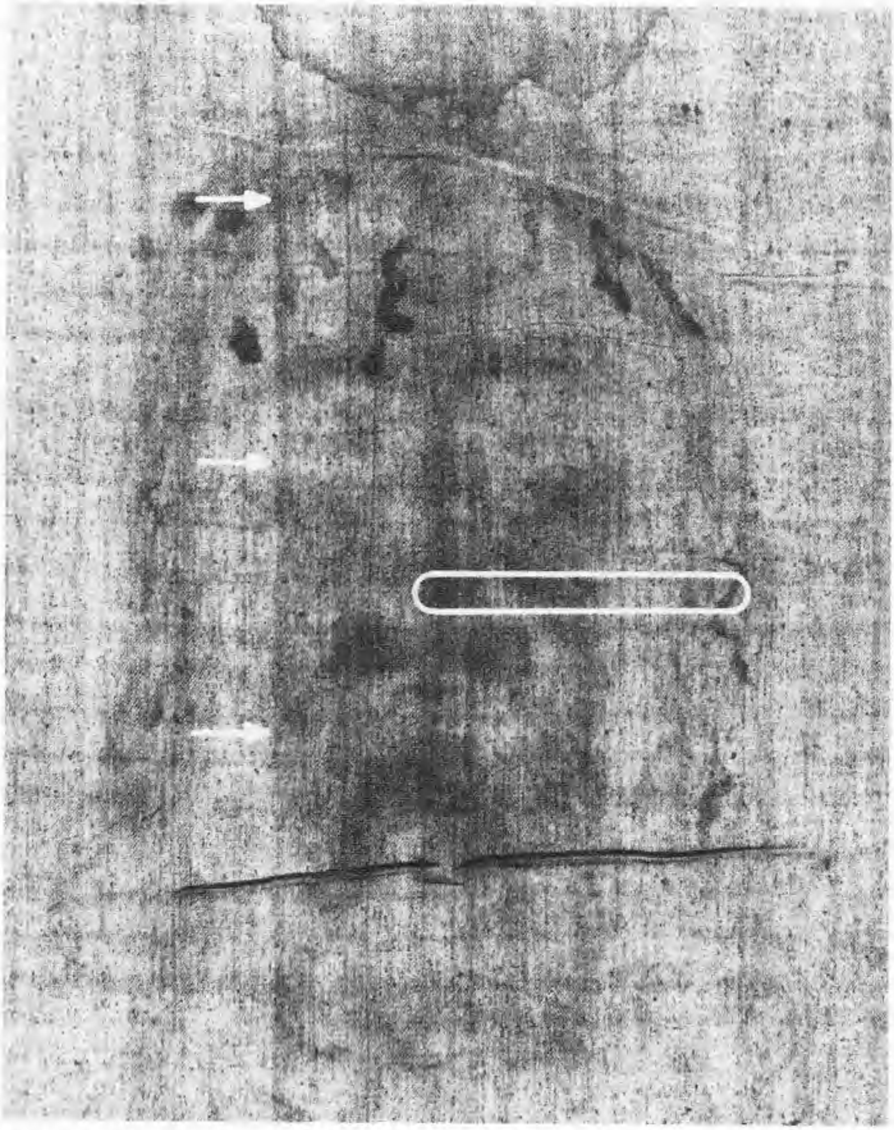

Fig. 4. Slightly contrast-enhanced photograph of the frontal-image face region. The enclosed region in the figure roughly indicates the area examined by x-ray fluorescence. The arrows point out the position of an abrupt change in the image density at the side of the face.

elemental composition of these deposits remains unknown. Mottern et al. [10] estimated the radiographic sensitivities to be about 5% for changes in areal cloth density. They used effective-energy considerations to estimate radiographic sensitivities to Fe_2O_3 and other high-Z pigments and found that these were roughly an order of magnitude less than the sensitivities reported for the x-ray fluorescence studies.

Photoelectric spectrophotometry

Accetta and Baumgart [11] measured infrared spectral reflectives on the Shroud image, scorch, and background areas. Their source consisted of a black-body emitter operated at ca. 1250 K (11.5 μm) with a 500-Hz chopper (for background and self-emission component rejection) and $f/1$ NaCl lenses to focus the incident beam onto a target spot with a nominal diameter of 2 cm. The HgCdTe detector and circular variable filter system scanned the 3—5 μm and 8—14 μm ranges with a spectral resolution, $\lambda/(\Delta\lambda)$, of 60. Their procedure consisted of alternately measuring the sample and reference standard (flat-black enamel on 240-grit sandpaper) in identical geometries.

Accetta and Baumgart [11] noted that their single-beam configuration was quite susceptible to instabilities. They found, for example, that relatively large fluctuations in atmospheric absorption and system noise precluded absolute reflectance measurements. The inherent low reflectance (5—10%) of the cloth also added to the uncertainty. Although their experiment showed an impressive similarity between the spectral features of the Shroud image and scorches, the results were judged to be inconclusive. In subsequent laboratory studies, similar spectral properties of linen, cotton, and scorches of varying visual intensity suggested to them that surface effects most likely dominate chemical or composition differences. Limited instrumental sensitivities have, thus far, largely precluded definitive infrared results for the Shroud.

Gilbert and Gilbert [12] measured u.v.—visible reflectance and fluorescence spectra from body image, scorch, "blood" stain, and background (clear) cloth areas on the Shroud. Their instrument was a specially constructed dual-monochromator system that allowed continuous scans to be made over the wavelength range 250—750 nm with an effective instrumental bandwidth of 5 nm. For the reflectance measurements, they used a 150-W xenon source lamp to irradiate an area of 6 × 3 mm and a magnesium oxide reference surface to convert their data to absolute reflectances. By comparing the results of several scans at single locations, they established that their individual measurements were reproducible to about ±3%.

The Gilberts measured the absolute reflectance of five background (clear) areas. These curves generally increased monotonically from about 0.08 at 250 nm to about 0.50 at 750 nm and are qualitatively consistent with the expected reflectance behavior of old linen material. Cellulose aging is evidenced by yellowing and loss of strength [43]. Chemically, the aged cellulose chain contains carboxyl and carbonyl groups, free radicals, and double bonds of varying degrees of conjugation [44]. These groups absorb light increasingly toward shorter wavelengths to produce the observed discoloration. The individual spectra in the background series were offset by as much as 7% from their mean curve. These differences are probably not excessive in view of the weave structure interference and the diffusely mottled visual appearance of the cloth background. It is assumed that the mottling results either from unevenly deposited pyrolysis products from the 1532 fire or from varying extents of cellulose degradation in these areas.

Reflectance measurements of the body image were made in eight different locations. The Gilberts referenced these data to the same mean clear-area spectrum and presented the results of four typical reflectance scans in their report. Generally, the relative reflectance of the image increases with increasing wavelength although there are noticeable differences among the individual measurements. For example, the Gilberts observed rather large and nominally constant offsets among the spectra; some of these appear to be as large as 40% to 50%. These offsets probably result from the different image densities in the different sampled areas and their magnitudes do not seem unreasonable.

Besides these, there are obvious non-uniformities in the detailed functional behavior of the individual scans, variations that are occasionally beyond the limits established for the maximum probable variance of the measurements. These variations are believed to represent actual signal variations rather than instrumental noise, but they cannot be immediately attributed to corresponding changes in the image density. The Gilberts suggested that they most likely arise from non-uniformities in the local background reflectances. This unavoidable difficulty prevents each of the measurements from being interpreted individually; however, we have compared possible fine-structure variations and have found none common to the spectra in this series.

Figure 5 illustrates that none of the spectral characteristics expected from normal dyes, stains, and pigments are observed. Included in the plot are the results obtained from a scan of (anhydrous) Fe_2O_3. The steep slope in the data over the approximate range 550–600 nm exemplifies a rather characteristic

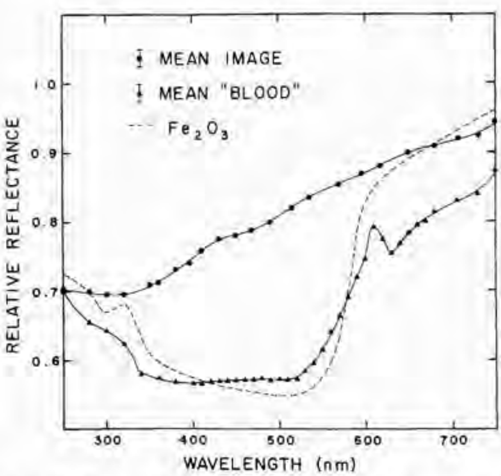

Fig. 5. Plots of the mean relative reflectance (referenced to the same mean "clear"-area spectrum) of five body-image and four "blood"-stain areas [12]. The Gilberts' scans were continuous. The points indicated in the plots do not represent individual measurements but values obtained from manually averaging the individual relative reflectance spectra. Error bars in the legend represent estimated maximum probable variances for the respective curves. Also included are results obtained from a scan of (anhydrous) Fe_2O_3.

behavior of pigments, stains, and dyes. Pellicori [13] suggested that the absence of a corresponding discontinuity in the image-area data places an upper limit of roughly 5 μg Fe cm^{-2} for hematite there, and that this material does not contribute significantly to the coloration of the image.

Pellicori [13] reported results of similar Shroud measurements on six samples of each type of stain and clear background. In his system, a 500-W tungsten source illuminated a 1-cm^2 sample area. This sample area is about 4.4 times that of the Gilbert measurements and presumably allowed Pellicori to integrate more effectively over local inhomogeneities such as the cloth weave. Pellicori reported an approximate $\pm 1\%$ repeatability for the measurements and a spectral resolution of 17 nm (FWHM). Whereas the Gilberts' scans were continuous, Pellicori's signals were read out digitally at 20-nm intervals in the wavelength range 440—700 nm. The results of the two independent reflectometry systems in Turin reportedly agreed within 5% on an absolute scale [13].

The photographic results are qualitatively consistent with the spectral reflectance data obtained. The multispectral narrow-band photographs of Miller show decreasing image contrast from the near ultraviolet to the red-visible. The Gilberts' plot of the average image density as a function of wavelength showed a broad maximum of about 0.15 near 300 nm and a general monotonic decrease to about 0.02 at 750 nm.

Photoelectric and photographic fluorescence

For their optical fluorescence measurements, the Gilberts used a 200-W mercury arc lamp with the source monochromator set at 365 nm. They also placed a u.v.-transmitting/visible-absorbing filter in the source beam to eliminate visible radiation incident to the target. The detector monochromator was then scanned continuously from 390 to 700 nm. In this configuration, the instrument had an effective bandwidth of 8 nm. The Gilberts' results showed that background cloth areas fluoresce in a broad band with a maximum near 435 nm. Pure cellulose fluoresces weakly, if at all. For comparison, they showed that a reference sample of Whatman 42 (ashless filter paper) produced a peak fluorescence at 435 nm which was only 0.28 times that from the clearest tested area on the Shroud.

The image itself did not fluoresce measurably. (Although the data suggested low-level fluorescence signals in the 600—700 nm region, the observation can be accepted only tentatively because the signals were of approximately the same magnitude as the stated maximum probable data variance.) The Gilberts observed that the image reduced the fluorescence of the underlying background and shifted the maximum slightly to longer wavelengths. They also found that this fluorescence reduction and maximum shift is produced by the scorches and to some extent by the mottling in the background areas.

The fluorescence reduction is probably a combined result of several factors. A decrease in the areal density of fluorescent material would contribute, as would an attenuation of both incident excitation and emitted fluorescent radiation through the scorches and image. The Gilberts' data show that, within a given series of sampled areas (scorches, image, or background), as the reflectance is reduced, the fluorescence is also reduced. This observation is consistent with any of the proposed mechanisms, but the shift of the background fluorescence peak to longer wavelengths suggests that an attenuation of the emitted background fluorescent radiation is a contributing factor.

Miller and Pellicori [14] photographed the visible light emitted from the Shroud as it fluoresced under ultraviolet (335—375 nm) radiation. The u.v.-source lamps were filtered to eliminate any visible light, and the camera was filtered to eliminate any ultraviolet contribution to the image on the film. Their photographs illustrate the effect observed in the spectrophotometric data; the image appears to attenuate the fluorescence of the underlying cloth.

These u.v.-fluorescence results may serve as an independent test for the hypothesis that a paint vehicle based on animal collagen was used on the cloth. However, preliminary results on modern collagen indicated that both Knox gelatin (which, incidentally, is used in photographic emulsions!) and gelatin extracted from a laboratory rat's tail fluoresced noticeably in the visible under ultraviolet illumination. The test samples evidently contained significant quantities of aromatic amino acids or other fluorescent compounds. If a collagen-binder hypothesis were valid, it must be assumed that the vehicle either contained no fluorescent compounds or that their fluorescent properties disappeared uniformly with time or in the heat of the 1532 fire.

Heller pointed out that a yellow animal collagen should contain aromatic amino acids and, therefore, should fluoresce. Miller has examined a 13—14th century Bible and found that both the page binding material and the manuscript illuminations fluoresced visibly under ultraviolet radiation. An interesting study might be to examine the fluorescent properties of known 14th-century animal-tempera paintings.

Photographic and direct macroscopic visual observations

Direct observation of the Shroud shows that it was subjected to very steep thermal gradients at the time of the 1532 fire, and a number of locations can be identified where scorches intersect image areas. Those parts of the image that intersect scorches were observed to have identical color tone and density as the image areas at the farthest (as folded) distance from scorches. This can be taken to indicate that neither the color nor density of the image changed as a result of either heating or reactive pyrolysis products from the scorching cloth. Organic dyes and stains, inorganic pigments, and painting media can be tested against this observation.

Pure silver melts at 960°C, but because of suspected alloy contaminants, the silver casket in which the Shroud was stored in 1532 would probably have melted at 820—850°C. (Pure cellulose begins to produce gaseous products at an appreciable rate at about 310°C [44].) Few organic dyes or stains could survive the scorching conditions, and most of the inorganic pigments available during the 14th century would have suffered some change. Hydrated iron oxides, the ochers and siennas for instance, change color on heating to become their "burnt" equivalents, and even Fe_2O_3 tends to be reduced to black Fe_3O_4. Sulfide pigments (orpiment, realgar, etc.) would be converted to salts, many of which would be water-soluble and all of which would be a different color. If the image had been painted with a proteinaceous, plant-gum-, or starch-based vehicle, the medium would have scorched more rapidly than the cellulose of the linen. No evidence for a scorched medium can be seen.

The water used to extinguish the fire in 1532 migrated through the cloth in both scorched and unscorched image areas. No evidence has been found that any part of the image was water-soluble either before or after scorching. Any hydrophobic medium (oils, waxes, etc.) that migrated through the cloth would retard water migration. It can be seen that water migration through the cloth was not inhibited by the presence of the image, although it was retarded by several "blood" stains including that at the side wound, for example.

There is no apparent evidence of brush marks that might suggest a painting. Neither is there any general non-uniform image fading or variation of color with position. Infrared thermographic images [11] likewise showed no evident anomalies in the investigated areas (face, back of head, hands, foot, and side wound areas). However, any good photograph of the Shroud does show that the relative density of the image changes abruptly across a single thread in many places. These density changes correlate with thread overlaps where they can be observed in weft locations. That is, the image density changes at a location where the material used to weave the cloth changes.

An abrupt change in the image density can be seen in Fig. 4 at a single warp thread at the side of the face. The effect at this location has been mistakenly taken as evidence for a chin band [45, 46]. Such a change in density would not occur if the material had been brushed or sprayed, but it might be observed from a block print or rubbing where thread-lot thickness or surface discontinuities affected the amount of material transferred in the process. In this particular region, the radiographs show no discontinuity in the cloth areal density; it can, therefore, be concluded that adjacent warp-thread-lots differed either in their surface or chemical characteristics.

Corollary: The image results from chemical changes of the cloth

We have reviewed the experimental results of the Shroud of Turin Research Project and have found no evidence to suggest that the Shroud image consists of a colored foreign material on the cloth. The only alternative seems to be that the chemical composition of the cellulose fabric was somehow altered to produce the effect. In the following discussion, the processes that may have accomplished this are grouped into two categories. The first of these involves simply scorching or burning the material either by direct contact or radiant energy transfer. The second category includes mechanisms in which the cloth is treated locally by some applied reagent. In this case, a dehydrating agent, such as an acid, may produce the image directly, or a catalyst may sensitize the cloth to produce a latent image which is then developed either by a direct application of heat, radiant energy, or by aging.

Scorch hypotheses

In 1966, Ashe [47] suggested that the image was a surface scorch and produced experimental images on cloth by using a heated brass ornament. This hypothesis has become particularly interesting because the Shroud image appears to have many of the physical and chemical properties of a light scorch. With properly controlled heat and timing, superficial scorches can be produced on cloth without affecting the gross mechanical properties of the fabric. Generally, scorches do not fade with time and are stable to further heating up to temperatures and times that will produce an equivalent scorch in the base material. Scorches do not move as water percolates through them nor do they impede water flow. The chemical components of scorches are not soluble in acetic acid, organic or redox solvents. The fibers in lightly scorched areas are translucent and closely resemble the observed image-area fibril color.

Unfortunately, the term "cellulose scorching" does not describe a unique or simple set of chemical reactions. Conditions of time and temperature determine whether or not a visible scorch is produced and the chemical nature of the color. The mechanisms of scorching processes are extremely complex [44], and the phenomena cannot be described here in any great detail. However, it can be stated that dehydration is the main reaction at moderate temperatures (less than 280°C). Dehydration produces unsaturation and conjugated double bonds with different degrees of conjugation which absorb light at specific wavelengths. If the wavelengths absorbed are in the visible region of the spectrum, the transmitted or reflected light appears colored. Higher temperatures can produce color in shorter times, but the colored products may be much different at different temperatures. Free radicals, multiple carbonyl groups, and free carbon can be involved in the observed color as well as conjugated double bonds.

The strongest supporting evidence for the scorch hypothesis is found from the spectrophotometric work of Gilbert and Gilbert [12]. Their report includes relative spectral reflectance curves for both image areas and scorches of different densities. Whereas the deepest scorches were found to absorb strongly and broadly near 375 nm, the lighter ones exhibited a more nearly monotonic behavior which is qualitatively consistent with the expected absorption behavior of dehydrated cellulose. Figure 6 compares the mean reflected density from three light scorches with that of five image areas;

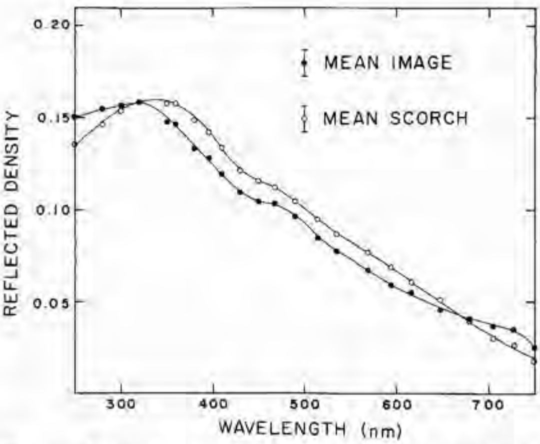

Fig. 6. Plots of mean reflected densities from the image and from scorch [12]. These results were obtained by averaging continuous relative reflectance spectra from five body-image and three light-scorch areas. The points in the plot do not represent individual measurements but the values obtained from averaging these data. Error bars in the legend represent estimated maximum probable variances for the curves.

the two curves agree within experimental error. The Gilberts also reported that image and the light scorch-areas reduce the background fluorescence in a similar way.

Despite this correlation, there has been some disagreement about the visual similarity of the image and scorches on the Shroud. In Pellicori's opinion, the resemblance is only superficial. He perceives the scorches on the Shroud to be visually redder than the body image [8], and notes their different characteristics in the u.v.-fluorescence photographs [14]. (The Gilberts' spectra likewise suggest that the scorches fluoresce more strongly than the image in the 600—700-nm region, but again, these were both very weak responses and no quantitative evaluations can be made.)

If the Shroud image is a scorch, the slight differences between it and the known scorches from the fire may be attributed to different ambient conditions during the two processes. It is known that in 1532, the Shroud was burned while it was inside a metal box [1] and may be supposed that the oxygen in this environment was rapidly consumed. As the temperature increased in the scorching zones, several fluorescent or reactive pyrolysis products would have been produced, including furfural, formaldehyde, formic acid, and levulinic acid, for example. Miller and Pellicori [14] demonstrated experimentally that pure cellulose heated in an oxygen-depleted environment produced pyrolysis products that fluoresced faintly red in the same manner as those Shroud areas damaged in the 1532 fire. In those areas of previous fire damage, which Wilson [1] has speculated to be hot-poker holes (see note 7), no fluorescence is observed. These results suggest that the earlier burns and perhaps also the Shroud image, if it is a scorch, occurred in the presence of oxygen.

Pellicori has raised some questions about the latter hypothesis. Miller and Pellicori [14] produced light sources on modern linen in an atmospheric environment with a hot soldering iron. They found that scorches produced at various temperatures on both dampened and dry cloth all fluoresced yellow—green under ultraviolet radiation. Further experiments showed that the fluorescent compounds were quite water-soluble, although even after repeated rinsing, the scorched areas retained their fluorescent properties. In addition, they demonstrated the stability of the fluorescent compounds by baking the samples at 145°C for six hours. Pellicori recalls that the Shroud image itself does not fluoresce measurably. In view of the results of these scorch studies, he feels that it is unlikely that the image was produced by scorching, for otherwise there should have been some characteristic fluorescent behavior observed.

These results draw the "air" scorch hypothesis into serious question; however, it was chosen to leave the matter as an open question for now. Before the non-fluorescent property of the image is taken as conclusive evidence against scorch hypotheses generally, the conditions and reactions that are involved in the formation of these compounds must be better understood. Future studies should include many of Miller and Pellicori's original experiments on actual Shroud threads.

There has been some speculation that a short burst of high-intensity radiation might produce effects on cloth that resemble the Shroud image [3]. Direct photolysis of cellulose occurs at wavelengths shorter than about 340 nm [44]. At longer wavelengths, energy absorption can allow similar reactions to proceed indirectly. However, our own experiments with intense flash lamps, and ultraviolet, visible, and infrared lasers have not successfully reproduced the color density and distribution observed on the Shroud. Although very short flashes are required to obtain a superficial discoloration, these radiant energy sources produced different relative amounts of products and, therefore, different colors. These studies also showed that high radiant-energy flux tends to cause surface explosions and damage that was not observed on the Shroud image. The results suggest that so-called "flash-of-light" hypotheses are difficult to support.

At this time, the most likely scorch hypothesis is that the Shroud image is a light "air" scorch produced at temperatures lower than those sufficient to carbonize the material. While some data support this hypothesis, they do not prove its validity nor do they suggest what scorching technique may have been used. Any complete hypothesis must also account consistently for the observed density shading characteristics of the image.

Following Ashe [47] and in direct response to the article by Culliton [4], there has been increased speculation about the so-called "hot-statue" hypotheses [48, 49]. Generally these arguments are based on the known 14th-century existence of full-sized statues in either stone or metal. They postulate that one of these statues was heated and then pressed or tented with the cloth. Hot-statue hypotheses have the image scorched by radiant energy and the contour information recorded on the cloth as different scorch densities in different locations depending upon the respective distances from the cloth to the heated statue surface.

Jackson has done both theoretical [50] and experimental work to address three-dimensional hot-statue hypotheses. He found that a simple isotropic radiation source could not yield the observed Shroud-image shading and resolution (see note 8) although it could be obtained if emission (or cloth absorption) anisotropies were assumed or if significant attenuation were present in the intervening medium. However, in these cases the resulting directionality of the radiation normal to the surface of the hot statue would introduce an unacceptable distortion of the image on the cloth. Moreover, at cloth-contact points one would expect to see "hot spots" or well-defined regions of enhanced image density that result from thermal conduction. No evidence for "hot spots" in the Shroud image has been found.

Because Jackson's studies have shown that three-dimensional hot-statue hypotheses are rather unlikely, we suggest that perhaps an etched or scribed flat-plate may have been used. In this case, either the differing directional or radiant intensity characteristics of metallic and insulator materials [51] might be used to produce the observed image. So far, no experimental work has been done to test this hypothesis, but there would be potential problems, particularly with controlling the temperature distribution within a 1×2-m metal plate. At present, we are aware of no scorching technique that satisfactorily accounts for the observed image density characteristics.

Hypotheses on chemically-induced cellulose degradation

It has been shown that light surface-scorches have many important Shroud-image characteristics, but stains produced by the action of certain locally applied reagents can have similar properties. Concentrated sulfuric acid, for example, dehydrates cellulose to produce a convincing yellow discoloration; however, attempts to create an image with acid were rather disappointing. In particular, it proved quite difficult to control the depth penetration and densities of the stains. Also, unless the acid is properly neutralized, the continuing reaction can cause disastrous effects. Mainly because of these problems, an "acid-painting" hypothesis seems rather unlikely, although the possibility cannot be strictly ruled out.

Pellicori has developed a slightly different technique that has shown more promising results. A previous section briefly mentioned the effects of cellulose aging. Pellicori [13] described laboratory simulations of these changes in which he used a baking technique that is similar to that employed in paper and textile research. The results obtained after baking for about 7.5 h at about 150°C qualitatively reproduced the spectral reflectance and fluorescence characteristics of the Shroud background areas. In addition to this, he applied thin, invisible coatings of skin secretions (perspiration plus oils), myrrh, and olive oil to different areas of his linen samples. After baking in air at 140°C for 3.5 h, these treated areas attained a yellow density in excess of the observed background discoloration. (The reaction is apparently limited because continued baking of the samples did not darken them further.) Similar discoloration was produced at 125°C, but longer times were required. Although the materials used to catalyze the stains showed either no fluorescence or very faint emission (olive oil: neutral to reddish), the spectrophotometric character of the treated areas (and of myrrh, in particular) after baking closely matched that of the Shroud image.

Pellicori observed that the specific foreign material responsible for locally advancing the degradation of the cellulose is not of prime importance. It need only satisfy the requirement of greater optical absorption for blue light than red in the case of photosensitization [43], or of some property like a reduction of the cellulose crystallinity or the improved thermal impedance matching for the surface reaction involved. Although no traces of sensitizing materials were observed on the Shroud, these may have been lost in time by chemical transformation, evaporation, or washing.

The results of experiments with chemically-induced cellulose degradation have, so far, provided the closest approximation to the observed image characteristics; however, the approach has some difficulties. The problem of controlling depth penetration of the applied materials has already been mentioned. (The Shroud image coloration extends no deeper than a few fiber thicknesses and generally does not follow the dips of the threads.) Depth penetration can depend not only on the fluid properties of the foreign materials but also on the surface and absorption characteristics of the linen fibers. Simulated image stains, to date, have been fairly successful, but more work is necessary. It may be suggested that future studies account for other possibly significant factors. For example, the moisture absorptivity of the fibers, the foreign material composition, and the ambient atmosphere are but a few potentially influential parameters. Pretreatment of the linen may also be significant. Druzik suggested that if the large calcium concentrations [9] had been present in the cloth before the image was formed, it might be expected that it would have buffered certain types of reactions and, thereby, assisted in confining the discoloration to the tops of the thread crowns.

Another problem is that a detailed mechanism for the application of the image has not yet been formulated, although it appears, in the present context, that some direct-contact material transfer must be involved. Vapor diffusion of the sensitizing materials from a three-dimensional model seems unlikely, because the image appears only on the thread crowns and not in the lower weave structure. Moreover, a material distributed by diffusion would be essentially isotropic ($1/r^2$ density) and susceptible to convective fluctuations, and, therefore, would not preserve the shading and resolution according to Jackson's arguments [50].

If the image were the result of cellulose degradation processes, the possibility cannot be discounted that the Shroud was artificially imprinted with a cloth-sensitizing material and the image subsequently developed, perhaps by baking as Pellicori has described. Although the spatial gradation of image density, which has been correlated with vertical cloth-body separation, does not result in an obvious manner from simple contact models, there may be some possibilities.

Smith [52] suggested that a latent image transfer may have occurred as the cloth contacted an existing flat painting, perhaps during storage. In this case, loose pigment particles may have been transferred to the cloth surface, or slightly volatile organic components from a painting medium may have diffused there. In a damp environment, water-soluble materials might have been adsorbed onto the surface fibers. Smith argued that foreign materials could locally modify the darkening of the fabric with age even if their presence could not be detected visually. To support this hypothesis, he noted that such transfer effects can be seen in many old books that contain color illustrations. So far, there has been no experimental work done to test the feasibility of Smith's general model.

As another possibility, Nickell [30, 31] described several contact transfer mechanisms that might produce the observed contour density effects. His latest technique [31] involves molding a wetted cloth to conform to the surface contours of a "suitable" bas relief model. The cloth is permitted to dry, and powdered pigment is applied with a cotton or cloth dauber. Although microscopic examination of the Shroud shows that the image does not consist of powdered pigments, any of a number of cellulose-sensitizing materials could have been used instead. One may postulate that the image was developed as the deformed cloth material was ironed flat, baked, or exposed to the sun for some period of time.

There seems to be no historical evidence to suggest that any such technique was used before the 19th century. Thus Nickell's method, "using only 14th century technology", may at best represent a unique and subsequently forgotten innovation. Some have questioned the possibility of preserving the global precision of the Shroud image with this technique. (Jackson has analyzed some of Nickell's images with the VP-8 system, but the results have been quite disappointing.) Nevertheless, these and further ideas are to be encouraged. It must be stressed, however, that hypotheses can only be meaningfully evaluated from detailed quantitative comparisons of test results to actual Shroud data.

Conclusions

The only existing evidence that the Shroud of Turin is an artifact is the letter written by Pierre d'Arcis in 1389 that simply states it as a fact. Although this historical reference is not subject to verification, it deserves serious consideration. Humber [2] wrote that in medieval Europe there were at least forty-three "True Shrouds", some with and some without figures. Shroud-image forgeries, and most likely very good ones, existed. Eastlake [53] noted that tempera and watercolor paintings on linen were common in

England and Germany in the 14th century. Unfortunately, we have not examined any of these and have no basis for comparison with the Shroud image. Our conclusions are based mainly on direct observations and the results of other follow-up studies.

There has been no evidence found to suggest that the visible image results from a colored foreign material on the cloth. In this regard, the data are quite internally consistent. Microscopic studies have revealed the image to be highly superficial; the image resides in the topmost fibers of the woven material as a translucent yellow discoloration. No pigment particles can be resolved by direct Shroud observation at 50× magnification, nor can unambiguously identified pigment particles be found on the tape samples at 1000×. Microchemical studies of yellow fibrils taken from tape samples of the pure-image area have shown no indication for the presence of dyes, stains, inorganic pigments, or protein-, starch-, or wax-based painting media. X-ray fluorescence shows no detectable difference in elemental composition between image and non-image areas. Spectrophotometric reflectance reveals none of the characteristic spectral features of pigments or dyes. Ultraviolet fluorescence shows no indication of aromatic dyes or aromatic amino acids that might be expected from animal-collagen pigment binders. Direct visual observations of image areas that intersect scorch and water stains reveal nothing that might suggest the presence of organic dyes or water-, protein-, or starch-based painting media.

The possible correlation of submicrometer-sized Fe_2O_3 particles with image areas has been discussed. One interpretation of this observation has been that it represents an artist's attempt to enhance a pre-existing image. However, the observation of red particles from the tape samples has provided only limited, qualitative information. The results of independent tests have not supported the image-enhancement hypothesis. Spectrophotometric reflectance and x-ray fluorescence data have established rather severe limits for whatever iron-oxide areal concentrations that such an interpretation might imply. Indeed there is some doubt that the original identification of this material is valid. The red particles are most likely "blood flakes" distributed by cloth folding from the "blood" areas. In view of the small amounts of this material present and the alternative hypotheses that have been proposed to explain its appearance and distribution, this evidence is judged to be irrelevant to the image-formation problem.

The reflectance and fluorescence characteristics, as well as the apparent chemical nature and microscopic appearance of the image, suggest more strongly that it is an effect of cellulose structure modification. Within the context of the present category of hypotheses, it has not been definitely determined whether the image was scorched at moderate temperatures or treated chemically and subsequently developed. If scorched, there was probably no structurally three-dimensional model used. If treated chemically, a direct-contact transfer was probably employed. In either case, there remains the unanswered question of how the apparent global precision and resolution of the image was maintained. Certainly more work is necessary; further research might also include investigations of sequential processes which have so far received little attention.

Hypothesis: The image is not an artifact

This class of hypotheses includes natural processes not involving direct, willful human intervention. These hypotheses are based exclusively on the assumption that the Shroud was actually a burial shroud and that the image was formed or initiated by some unaided natural mechanism. (With the possible exception of Smith's contact model, which involves an existing painting [52], no other "natural" processes have been examined that might have produced such a detailed and anatomically correct image on cloth without the presence of a human body.) This discussion will, therefore, be limited to the physical evidence as it pertains to the question of whether the Shroud was a shroud without considerations given to the time or place of origin.

Vignon vaporgraphic theory

Vignon [16, 54] documented the first scientifically based hypothesis to account for the apparent negative image characteristics, revealed in the Pia photographs, in terms of physical and chemical processes. He knew that a body in pain perspires and that the perspiration contains urea. Under certain conditions, fermentation may convert the urea into carbon dioxide and ammonia. Vignon assumed that the burial cloth was soaked in aloetine, an embalming formula consisting of aloes and olive oil, and that the ammonia diffused from the corpse to the cloth where it reacted with the aloetine to produce the observed brown stains. He reasoned that those cloth areas nearest the body would stain darker because of their shorter diffusion path length, and a negative body image would result.

The resolution limitations involved with the diffusion transfer mechanism have already been discussed. Vignon's theory presents additional problems. A necessary condition for the hypothesized chemical reaction to proceed is that the cloth be damp. Vignon himself realized that a damp cloth would cling to the body in various locations and cause image saturation and distortions; these effects are not observed on the Shroud image [55]. A more compelling argument is that ammonia or, at contact points, low-molecular-weight fatty acids from the body and essential oils from spices should permeate the fabric. The image, as noted above, is characteristically superficial and cannot be seen on the reverse side of the cloth as Vignon had thought. Yet another problem is that the amount of ammonia needed to produce a satisfactorily intense image is greater than might be expected from the natural reactions described above [31].

Judica Cordiglia, Romanese, and Scotti have experimented with related techniques [56], but these have all generally involved the same materials and chemical reactions as in Vignon's model. Sebaceous secretions from a body should be about 65% fatty-acid esters of glycerol, sterols, and wax alcohols with about 30% unsaponifiable materials [57]. The chemical properties of these natural products eliminate them from consideration. Few are thermally stable; many are surface-active on water. Formaldehyde, as would have been produced during the 1532 fire, denatures proteins, reacts with amines, couples with phenolic compounds, reacts with alcohols and sterols, and acts as a potent reducing agent. Steam and acids hydrolyze esters, and many fractions would volatilize [58]. If unstable natural-product systems were responsible for the image, they should have decomposed, changed color, or volatilized at different rates depending on their distances from high-temperature zones during the fire. No such changes have been observed using available photographs or by direct observation of the Shroud. In addition, no foreign materials have been detected spectrophotometrically, chemically, or microscopically in the image areas on the cloth.

Latent-image hypothesis

Certain details of Pellicori's latent-image process have already been described under the artifact category of hypotheses. His work involved sensitizing materials that might be found on an interred human corpse; it is therefore appropriate that his arguments be reconsidered within the context of natural mechanisms. Pellicori's hypothesis is that the burial cloth was sensitized by adsorbed materials transferred from the corpse by direct contact and that the latent image developed in time by a gradual process of locally-catalyzed cellulose degradation [8]. He demonstrated that linen stains, having many of the chemical and physical properties observed for the Shroud image, can be produced by treating the cloth with thin coatings of perspiration, olive oil, myrrh, or aloes and then baking.

There has been some discussion about the baking technique and its postulated equivalence to aging on an accelerated time scale. At moderate temperatures, the dominant cellulose degrading reactions are oxidation and dehydration. However, at the elevated temperatures (125–150°C) used in the baking experiments, it might be expected that greater relative concentrations of more complex pyrolytic products would be observed, because their respective activation energies form a nearly continuous distribution in the energy-equivalent temperature range below 230°C. Pellicori argues that these effects contribute negligibly to his results. Many of these additional products would be colored or fluorescent, but neither fluorescence nor spectrophotometric data from his simulations show any appreciable concentrations of these more complex structures. The equivalence of baking to accelerated aging has been fairly well established, but there are still some questions about the detailed effects resulting from differential reaction kinetics between amorphous and crystalline cellulose phases. Work in this area is continuing.

It was noted above that Pellicori's latent image process has provided the closest approximation to the color and chemical properties of the image.

However, the process, by itself, provides no description for the well-characterized density distributions of the image. Some additional physical mechanism that may have generated (or preserved) the observing shading must be postulated. Earlier, there were some possible ways suggested by which an artist may have accomplished this; here image-transfer mechanisms that may have operated by "accident" rather than by human design must be considered.

If the Shroud were a burial shroud and if the image were recorded by a latent-image type process, the transfer of sensitizing material must have taken place either by direct contact or vapor diffusion from the corpse. Pellicori believes that direct contact is the more likely of the two and cites some positive evidence to suggest that a cloth—body contact did occur. Miller and Pellicori [14] pointed out that, in visible reflected light, the so-called scourge marks have the appearance of diffuse "blood"-red dumbell shapes, but in fluorescence they show more sharply defined structure. (In several areas, including the right dorsal calf image in particular, the scourges are resolved into fine scratches. Three, and in some cases four, parallel scratches can be distinguished.) The scourge marks appear to have been directly imprinted onto the linen because their high-resolution fluorescence characteristics would not otherwise have been preserved. Total cloth—body contact is suggested by the fact that scourge marks with these characteristics are to be found over nearly the entire image area.

The one major deficiency seems to be just how a contact mechanism could have operated to produce the peculiar density gradations. German proposed a model to account for this by postulating the Shroud as originally somewhat stiff either from pressing or possibly starching. When it was laid over the body, it initially contacted only the high points of the profile. During the course of some time, water vapor either from the body tissues or from the damp atmosphere of a tomb, was slowly absorbed into the cloth causing it gradually to lose its stiffness and droop, much like a starched shirt on a damp day. Eventually, the cloth touched all of the body where image is observed.

German suggested that acceptable contour-shading qualities might be generated if the recording mechanism were to permit the image density to vary in proportion to the time of cloth—body contact. According to this argument, longer periods of cloth contact with higher portions of the profile would yield a darker image and the global mapping function, suggested by the earlier work of Jackson et al. [17], would be readily explained. Although Pellicori's latent-image process has not yet specifically allowed for an explicit time-dependence for material transfer, satisfactory density gradations might ultimately be generated with this composite mechanism.

In the meantime, several difficulties with the German model must be resolved. Although this contact transfer may avoid the resolution limitations inherent to Vignon's theory [16], it provides no constraints against diffusion of the sensitizing material into the damp cloth. Moreover, as Jumper noted, particularly for the facial region, there are no absences (drop outs) in density. (The face is an ideal area to test such a theory, because it is expected to contain the highest contour gradients.) This would imply that the cloth must have become flexible enough to contact every point on the face. Evidently, for the mechanism to have worked, the face contours would either have been much shallower than those typically assumed, or the cloth would have had to have been much more flexible than the Shroud appeared to be.

Another point is that the face shows no evidence of image saturation [55]; that is, with the possible exception of the eyes, the three-dimensional reconstructions show no plateaus [17]. This constraint would require the time-dependence of the German model to be extremely sensitive. The overall superficial nature of the image and the fact that densities at presumed contact points along the profile ridgeline region [17] are not all identical suggest rather severe limits for the assumed distribution of the sensitizing material over the body. Further special assumptions would seem necessary to account for the appearance of the hair.

This entire category of hypotheses is predicated on the assumption that the Shroud was a burial shroud and that the image was formed by some unaided natural mechanism. If the image had been caused by the catalytic action of materials present on the corpse, direct contact of the body with the cloth seems to be the only likely material transfer mechanism. A general problem now becomes apparent. It would seem to follow that the dorsal image area was influenced by the weight of the body whereas the frontal image was imprinted only by the lesser weight of the covering cloth. Recall, however, that the densities at presumed contact points on both frontal and dorsal images do not differ significantly. These characteristics along with the superficial nature of the image would suggest that the contact transfer mechanism is pressure-independent. This apparent contradiction challenges not only the Pellicori—German model but most other hypotheses in this category.

Conclusions

The evidence seems to be quite conclusive for ruling out the Vignon vaporgraphic theory as an image formation hypothesis. Vignon's theory [16] suffers two major problems. First, it has the image residing in chemically transformed (darkened) foreign materials on the cloth, but none of the physical or chemical properties expected for any of the suggested materials has been observed. The second problem is the inadequacy of diffusion transfer to explain the superficial nature of the image or to preserve the observed resolution.

Recent work has attempted to avoid these two difficulties. Pellicori's latent-image recipe [8, 13] adequately accounts for many of the observed image characteristics; it has the image residing in the chemically-transformed cellulose material in the cloth itself. Although Pellicori similarly postulates the addition of foreign materials, these are assumed to have acted only as catalysts and need no longer be present on the cloth at all. The idea appears promising, but the question remains how the image transfer occurred.

German's time-dependent, direct-contact model would seem to avoid several obvious deficiencies of Vignon's diffusion mechanism. However, it too has met with considerable objections; to produce the qualities observed on the Shroud image, too many special conditions seem necessary. At this time, the image has not been explained completely by the latent image hypothesis chiefly because a satisfactory image-transfer mechanism has not yet been formulated.

"BLOOD"-STAIN COMPOSITION

The discussion thus far has mainly concerned the physical and chemical properties of the body image areas and the question of how the image was formed. Generally, the "blood"-stain observations have little relevance to this problem. The chemical composition of the "blood" provides only circumstantial evidence bearing on the question of the origin of the Shroud. A forger could have used blood to produce the stains, or a genuine shroud, containing an image only, could have been touched up with red paint by someone who was impressed but dissatisfied with the overall effect. Nevertheless, the "blood"-stain composition poses an interesting problem in itself, and the observations may ultimately give some clues to help us understand how the image was formed. For example, one important question that might be answered is whether the "blood" or the image was applied first.

Wilson [1] and Humber [2] have provided qualitative descriptions of the "blood" areas on the Shroud. Frache et al. [59] and Filogamo and Zina [60] documented in more detail the results of their earlier studies on materials removed from a few of these stains. One of the goals of the 1978 investigation was to characterize the "blood" areas further. All of the tests that were performed on the body image, scorches, and background cloth were also applied to the "blood".

Microscopy and photomicrography

Even superficially, the "blood" and image areas appear to be quite different in their color, texture, and composition [33]. At 50× magnification the "blood" looks as if it were applied as a viscous fluid which then flowed around the threads [41, 59] and soaked through to the opposite side of the cloth where it is also visible. The meniscus characteristics of viscous fluids can be seen throughout the "blood" areas. Thread fibers are matted and cemented together. The stains appear brownish-red in reflected white light and crimson in transmission.

The earlier microscopic investigations of Frache et al. [59] revealed the "blood" threads to have slanting or diagonal bands of "granulation" that ranged in color from yellow to red. Filogamo and Zina [60] similarly reported seeing granular particulates but apparently nothing resembling red corpuscles. Photomicrographs [8] of the "blood" stains reveal amorphous red–orange encrustations between the fibers and in the crevices, with higher concentrations in the valleys at the intersections of warp and weft threads. In some areas it appears as if similar material once on the crowns of the threads had either fallen away or had been mechanically eroded to leave exposed the red–orange stained fibers that are now seen. The color of the individual "blood"-stained fibers is not strictly uniform; colors range from orange–red to yellow–orange.

Heller and Adler [40] reported that under 250–1000× magnification the "blood"-stained fibrils on the tape samples appear either garnet red or brown in color depending on the light source and whether they are observed by reflection or transmission. Generally, the stain appears to surround or coat the fibrils; in some cases, the coatings have become detached and appear as "blood sherds". Heller and Adler examined one of the tape samples, which contained a small, brown crystallite in addition to the "blood"-stained fibrils, by microspectrophotometry in the visible range (400–650 nm). They reported that the crystallite and stained fibrils showed intense Soret absorption (400–450 nm), which indicates the presence of a porphyrinic material.

No more definite material identification was made from these measurements. Characteristic visible band features can be obscured by scattering and absorption processes in both the stain and the cellulose substrate material. The data do suggest the presence of hemoglobin, however. To test this hypothesis, they treated the samples first with a strong reducing agent (97% hydrazine vapor) to reduce the iron to the iron(II) state and then with a strong acid (97% formic acid vapor) to displace the iron. Under near-u.v. radiation, the treated sample "blood" fibrils were seen to fluoresce in the red, confirming the suspected presence of porphyrin and, therefore, also blood in the "blood" areas. Recently, Heller and Adler [37] have also detected bilirubin with a modified Jendrassik method and albumin with bromocresol green; both findings corroborate their earlier conclusion.

It was mentioned earlier that yellow fibrils were observed on tape samples from both "blood"- and pure-image areas. It is important to reiterate here that the respective yellow discolorations differ in several respects. First, those from "blood" areas exhibit a deeper yellow discoloration. (It is probable but not entirely certain that this corresponds to the "shiny honey-yellow" color that Frache et al. [59] reported for the interior fibers of the "blood" threads.) Second, the yellow color in the "blood" areas is clearly a coating that yields positive tests for protein whereas the yellow body-image fibrils do not. The evidence would imply different origins for the two yellow discolorations. It would seem that the yellow material in the "blood" areas derives from blood serum directly.

Radiography and x-ray fluorescence

The radiographs [10] revealed no readily apparent high-density structures that might correspond to the visible "blood" stains. However, the x-ray fluorescence studies [9] indicated iron concentrations 20–40 $\mu g\ cm^{-2}$ above measured or inferred background levels in the "blood" areas. Morris et al. [9] found these numbers to be generally consistent with the expected quantities of iron in comparable blood stains; however, their measurements could not differentiate between actual blood and iron-based pigments because x-ray fluorescence detects only element concentrations without regard to molecular arrangement.

The excess "blood" iron was the only detectable spectral characteristic that clearly differentiated these stains from the non-"blood" areas. In particular, Morris et al. noted that no potassium signals could be found in any of the "blood" area data. In whole blood, the potassium K_α peaks are typically an order of magnitude smaller than the iron K_α peaks. They are still smaller for blood soaked into a cellulose substrate. Therefore, even if potassium signals were present, they would probably have remained undetected within the substantial noise level in the low-energy range of the x-ray fluorescence spectrum. Heller has suggested that because potassium compounds in blood are quite soluble, they may have been dispersed in the presence of moisture. The failure to detect potassium, therefore, is felt to have no significant bearing on the question of whether the "blood" stains contain blood.

Photoelectric spectrophotometry

Gilbert and Gilbert [12] presented reflectance and fluorescence results from four different "blood"-stain areas. Their relative reflectance data, referenced to the same mean clear-area spectrum, show moderately strong absorption in the wavelength range 320–550 nm. A reflected-density curve was calculated from an average of these relative-reflectance spectra. The averaged density appears to be quite uniform in this short wavelength range, which suggests that no identifiable structures are common to the rather noisy individual spectra. The absorption is weaker at longer wavelengths, but there is a rather interesting reproducible feature at 600–630 nm.

Pellicori [13] has examined the absorption characteristics of whole blood with a Cary 14 spectrophotometer to compare with the Turin results. He found a strong absorption band at 400–420 nm that corresponds to the Soret band, and weaker bands at 530–580 and 625 nm. These effects are far more pronounced in transmission than in reflection; only the weakest band at 625 nm could conceivably correspond to the small structure seen in the Turin data. He also measured absorption spectra for Fe_2O_3 and blood after baking at 60°C for 7.5 h to simulate aging. None of these data resembles the Gilberts' Shroud "blood" absorption spectra in detail, but that of Fe_2O_3 approximates them most nearly. The Gilbert "blood" spectrum is shown along with that for Fe_2O_3 in Fig. 5; the two reflectance curves are quite similar over the greater part of the wavelength range, although the curious "blood"-stain feature at about 630 nm is not observed for Fe_2O_3.

Heller and Adler [40] have noted that there is no specific spectrum for blood per se: the spectral characteristics depend on the chemical state (coordination and decomposition) of the hemoglobin and also on its state of aggregation. They pointed out the strong resemblance of the Gilberts' "blood" data to those for "perturbed" acid methemoglobin, which is a chemical state of blood in which the iron in the hemoglobin has been oxidized [61]. Cameron and George [62] have published absorption spectra for acid methemoglobin in the range 480—640 nm. These data strongly resemble the Gilberts' curves and even include the small absorption structure at about 630 nm. Recent microchemical tests [37] reveal the presence of bile pigments (i.e., decomposition products of porphyrin) in some of the "blood" artifacts. Their presence could account for some of the non-heme peaks seen in the spectral data. Independent measurements on methemoglobin samples by both Adler and Pellicori have shown strong Soret absorption, an observation that is in agreement with the microspectrophotometric results. Pellicori [13] feels that the absence of the Soret peak in the Gilbert reflectance data was due to low signal-to-noise ratios in this wavelength range.

Photoelectric and photographic fluorescence

The Gilberts' spectra show no detectable "blood"-stain fluorescence. The "blood", like the other stains, reduces the background fluorescence but apparently without shifting the maximum to longer wavelengths as observed for image and scorch areas. (According to our earlier interpretation of this effect, the absence of a shift in the fluorescence peak is consistent with the nearly constant absorption characteristics of the "blood" in the 400—600-nm range.) Although the photoelectric fluorescence results are consistent with the nonfluorescent properties of hemoglobin, they have given little specific information about the "blood"-stain composition.

The u.v.-fluorescence photographs of Miller and Pellicori [14] reveal an interesting effect in several nominal image areas where "blood" flows are present: the dark "blood" regions are partially surrounded by margins that appear to fluoresce as intensely as do the non-image background areas. Weaver [3] has published four of these photographs along with drawings to illustrate the "light-colored" margin locations at the side wound, the "nail" wound in the wrist, and the "blood" flow at the right foot on the dorsal image. (At other "blood" locations, such as the flow across the back and the left dorsal foot region, no fluorescent margins are seen.) This unexpected effect is most clearly visible under the special conditions described above, and it is unfortunate that this observation was made only after the direct examination period. Neither photomicrographs, spectral reflectance, nor quantitative fluorescence data are available from these regions to aid our interpretation. Multispectral analysis of these areas has not yet been done.

There are several possible explanations for these light areas. They could represent a direct attempt by an artist to represent blood serum and were perhaps more recognizable at the time the image was produced. A second possibility is that the effect was accidental; the light areas could have resulted either from a non-pigmented vehicle in the paint used to represent blood or from actual blood serum flowing into the cloth ahead of the red cells or away from them in the case of clot retraction. Miller and Pellicori [14] suggested that the non-pigmented fluid itself may be fluorescing; they demonstrated that blood serum on linen does fluoresce moderately.

Another suggestion is that image is not present in these areas and that background fluorescence is being observed. If this is the case, the non-pigmented flow may have eradicated an existing image or it may have reduced or altogether prevented image formation. Heller considers the first possibility to be rather unlikely. In view of the conclusions that the "blood" is blood and that the image is a cellulose degradation effect, there seem to be no likely reactions capable of eradicating the image in any way resembling the spot tests with strong reductant mentioned earlier. The second possibility is more plausible and all the more interesting because it is difficult to reconcile with the image as an artistic production. It would be quite difficult to paint blood onto a cloth before image production with sufficient accuracy to index with every desired image location after image production. It seems more logical that an artist would have superimposed the blood on an existing image.

At this time, the fluorescent blood-margins are not well understood, but it would seem that they derive in some way from blood serum that had been isolated by clot retraction, probably before it was applied to the cloth. The "blood" areas, particularly in these peripheral regions, should be a subject of considerable interest in future studies.

Conclusions

The evidence seems to be sufficient to conclude that the Shroud "blood" areas are blood. The presence of protein, bilirubin, and albumin, the optical absorption and fluorescence characteristics of individual fibrils, and the iron concentrations determined by x-ray fluorescence, all support this hypothesis. This contradicts earlier tentative conclusions [59, 60] that were drawn mainly from the negative results of less sensitive tests.

At this time, the most interesting unanswered question is whether the blood or the image was applied first. So far, the results of most tests have provided little information pertaining to this problem. Conclusions have been drawn only for rather specific instances. For example, if the blood had been applied initially and the image then scorched, there might be burnt blood similar to that seen near burned areas from the 1532 fire. The fact that the blood areas are not obviously scorched argues against this particular hypothesis. Future studies should be directed at this problem.

CLOTH CHARACTERISTICS

There are two objectives in our attempt to establish a broad scientific data base for the Shroud. The first is to learn about the origin of the cloth and how the image was created. The second and perhaps more important objective is to evaluate the current physical condition of the Shroud and to support valid recommendations for its preservation.

Although the first of these has been dealt with, concern over proper and immediate conservation measures is justified. In 1978, the backing cloth was partially removed from the Shroud in the vicinity of the dorsal foot region. The reverse side of the Shroud appeared whiter than the image side. Evidently, the topside has darkened, and there is some fear that progressive deterioration and soiling will decrease the relative contrast between the image and background. Riggi found both fungi and spores in his vacuumed-material samples. Also, the atmospheric conditions of the urban environment in Turin could be particularly damaging to the image and fabric. To our knowledge, only Curto [33] and Pellicori [13] have published any specific recommendations toward conservation. Members of the Shroud of Turin Research Project hope that their contributions will aid and interest textile conservators and others qualified to address the problem.

Observations on fabric and thread

The following discussion concerns specific observations of the fabric and threads. The 4.3 × 1.1 m Shroud appears to consist of two panels of visually identical linen material joined together lengthwise by a seam which is 4—5 mm wide. The image is located wholly on the larger "main" section of the cloth. Apparently sewn to this main section is the so-called side strip that varies in width between 7.8 and 8.4 cm. The 1973 Turin Commission Report [5] contains some documentation on the cloth. Delorenzi [63] recorded visual observations of the patch and repair stitching, and Raes [64] reported his work on samples of extracted material.

Raes examined two threads (1 warp and 1 weft) from the main portion of the cloth and a triangular-shaped sample (about 40 mm wide × 42 mm high) of the fabric that had been removed from one end of the Shroud along the edge (see Figs. 1 and 7). The triangular-shaped sample evidently consisted of two pieces: one from the main section and one from the side strip. Raes reported both pieces to have the same herringbone 3:1 twill weave but, because this type of weave is not particularly distinctive, could not determine where or when the cloth had originated. Weft threads from the two pieces were found to differ somewhat in diameter although the number of weft threads per centimeter were virtually identical. Raes was unable to tell whether or not the main cloth and side strip were of different manufacture because of the short thread lengths that were available to him.

More recent data have provided supplementary information. The radiograph, shown in Fig. 7, suggests that the side strip either is, or at least was, at one time an integral portion of the full cloth. In this particular area, there are alternating high- and low-material-density "bands" that evidently correspond to weft lots of different weight used in the weaving. (The visible-light transmission photographs of Schwortz also clearly show these struc-

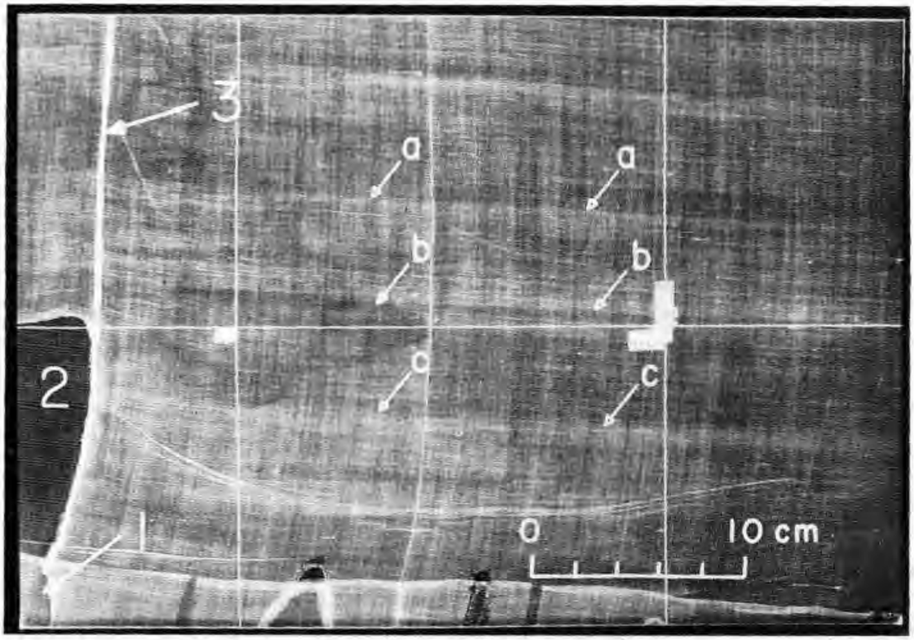

Fig. 7. Radiograph of the Shroud area indicated at the bottom of Fig. 1. The area labeled 1 in this figure is where the Raes [64] fabric sample was taken. The area labeled 2 designates a cutout portion of the Shroud where only the backing cloth is present. Alternating high- and low-density bands, orientated horizontally in this figure (three boundaries are indicated by the arrow sets labeled a, b and c), are continuous through the seam (3) and suggest that the so-called side strip either is or was at one time an integral part of the main section of the Shroud.

tures.) The density variations of the material are apparently associated with the Shroud, because they are not visible in the cut-out portion in which only the backing cloth is present. The distinct weft structure is continuous across the seam joining the two panels and strongly suggests that the side strip and the main section were of a single manufacture. A more careful examination of the seam needs to be made to determine whether the side strip was actually detached.

The Raes report contained two further, rather interesting findings that have been confirmed by J. L. Janney and other members of the Project team. First, the Shroud threads were spun in the Z-direction, which is apparently somewhat unusual. Egyptian linen, for example, was typically spun in the S-direction to conform to the natural twist that flax assumes upon drying [65]. (Raes observed that the linen thread used to sew together the two pieces of his fabric sample was spun in the S-direction.) Second, Raes found small traces of cotton fibers included in both warp and weft threads from the main-cloth section. He was able to identify these from the number of reversals per centimeter as *G. herbaceum*, a common Middle East variety.

The small quantities of cotton present suggested to him that perhaps the Shroud linen had been spun with the same equipment used previously for cotton. The observation of cotton-fiber inclusions is particularly interesting, because it would suggest a Middle-East manufacture. Beyond this, however, neither observation is sufficient to locate the Shroud's origin unambiguously.

Carbon-14 and areal cloth densities

It is clear that none of the available data provide any substantial clues to the actual age of the Shroud. Lack of this fundamental information has, in fact, been the greatest obstacle in interpreting the results fully. The only universally accepted technique for obtaining a satisfactory age for objects of this sort is the carbon-14 method. However, Shroud custodians have been reluctant to sacrifice the rather large amounts of material required for conventional ^{14}C testing. Earlier recommendations and decisions to postpone these tests were quite justified at the time.

In recent years, however, new methods have been developed that require only minute samples. Purser et al. [66] have provided an excellent review of the latest ultra-sensitive particle identification techniques and their capabilities. In particular, they described the Rochester tandem Van de Graaff system that operates on essentially the same principle as conventional mass spectrometers. The advantage of this system is that negative ions are accelerated to MeV/amu energies and can provide high resolution and transmission with exceedingly low background levels. Accelerator carbon-dating techniques have demonstrated accuracies (± 150 years for 2000-year-old samples) that are similar to those of the more familiar radioactive counting methods but are orders of magnitude more sensitive. Purser et al. quote sensitivities of $1{:}3 \times 10^{15}$ for ^{14}C in natural carbon and can date milligram-weight samples in a few hours. Measurements on a 2000-year-old Egyptian bull mummy cloth have given accurate results [67] and demonstrate that this technique could be readily applied to similar samples from the Shroud.

Given that milligram-weight carbon samples are sufficient for reliable dating measurements, these numbers are now related to areal cloth dimensions. An indirect estimate of the areal weight density of the Shroud can be made by measuring those of modern linen with comparable thickness, weave density, and thread diameters. These data are available. Jackson and Rogers measured the fabric thickness of the Shroud at three widely separated points and found it to be $345 \pm 22\ \mu m$. (Measurements of the Shroud plus backing cloth together yielded $615 \pm 29\ \mu m$.) Raes [64] quoted $38.6\ cm^{-1}$ and $25.5\ cm^{-1}$ respectively for the number of warp and weft threads in the weave of the sample taken from the main cloth. Mottern et al. [10] estimated thread diameters to be nominally 0.15 mm. Edgerton prepared samples of linen cloth to conform to the most recent Shroud data (although her thread diameters were larger) and found an areal density of $23.7\ mg\ cm^{-2}$. Edgerton's result agrees remarkably well with the value $23.4\ mg\ cm^{-2}$ that Timossi [68] derived earlier using essentially this same approach.

Other indirect estimates can be made from the 1978 data. Morris et al. [9] measured peak intensities for Compton scatter from the Shroud and backing cloth together. These results gave combined cloth areal densities between 30 and 40 mg cm^{-2} at various locations and an average value of about 35 mg cm^{-2} (see note 9). If this average composite value is multiplied by the ratio of the Shroud to total cloth thickness values quoted above, a Shroud density of 20 ± 5 mg cm^{-2} is found. However, this figure is believed to be low because of the comparatively open weave structure of the backing cloth. Cloth-density ratios derived from the radiographic data combined with the double-cloth values of Morris et al. place Shroud areal densities between 25 and 30 mg cm^{-2} (see note 10). Even allowing for a weight recovery of 20% carbon from a given sample, the estimates show that a radiocarbon date can be easily made with the equivalent of about 1 cm^2 of Shroud material. This amount of fabric has already been removed from the Shroud [41]. While some may argue that intact material should be saved for further non-destructive testing, large amounts of material could be removed from beneath the patches. Mottern et al. presented a radiograph of one of the patched-hole areas that reveals some of the Shroud material that could be recovered; a total Shroud area of approximately 400 cm^2 lies concealed beneath all of the patch work. This is sufficient for literally hundreds of carbon-14 tests with the latest techniques. Any of this material could be removed without affecting the visual appearance of the Shroud or damaging the fabric structure. (Indeed, as a conservation measure, this charred material should be removed to prevent further irreversible soil-contamination of the cloth.)

CONCLUSION

The purpose of this report has been to review the rather substantial collection of available scientific observations on the Shroud of Turin. These are now sufficient to allow some evaluation of selected hypotheses on image formation. Properties of the faint image and its peculiar density shading were noted as the outset. Three-dimensional profiles, generated from the frontal image densities, strongly resemble the human form and suggest that a simple global mapping function may relate the two. Unfortunately these phenomenological studies have implied nothing more definite about the image-transfer process. The faint and apparently negative image characteristics have likewise proven little, although the combined evidence does suggest that rather severe difficulties would have been encountered with conventional painting techniques.

The primary conclusion is that the image does not reside in an applied pigment. The reflectance, fluorescence, and chemical characteristics of the Shroud image indicate rather that the image recording mechanism involved some cellulose oxidation/dehydration process. It is not possible yet to say definitely whether these chemical modifications were produced by scorching or by some sensitized thermal or photochemical reaction. The fluorescent properties of scorches may eliminate them from consideration, but more detailed investigations are required to rule out scorch hypotheses generally.

Much has been learned about the density shading and chemical properties of the image, but, so far, there are no firm ideas about how the image may have been applied to the cloth. Again, Jackson's three-dimensional studies and the global consistency of the image suggest that some global mechanism was involved; however, nothing more specific can be concluded. Nonetheless, the choices are narrowed somewhat. Resolution considerations and the lack of gross distortion of the image in high profile-gradient regions argue against three-dimensional "hot-statue" hypotheses, although the remote possibility of contact or radiant thermal energy transfer from a flat model cannot yet be dismissed. If the image proves to be a chemically-induced cellulose modification instead of a scorch, it would be seen that the material transfer must have been accomplished by direct contact. (The superficial nature of the image eliminates a vapor diffusion mechanism.) Several contact-transfer models were considered, but none seems totally practical or convincing.

Several important questions about the Shroud have been answered to our satisfaction. For example, it is believed that the "blood" stains are indeed blood. Yet many questions remain. Some of these can be addressed with currently available data (especially in the areas of computer analysis of the image and forensic pathology [69]); others must await the results of future testing. The most important outstanding problems pertain to the image transfer mechanism. Briefly stated, we seem to know what the image is chemically, but how it got there remains a mystery. The dilemma is not one of choosing from among a variety of likely transfer mechanisms but rather that no technologically-credible process has been postulated that satisfies all the characteristics of the existing image.

With all of the questions concerning variations of contrast with time, latent images, artistic styles and techniques, few further definite conclusions are possible without information about the age of the cloth. Given the unique nature and complexity of the problem, the only unambiguous means to establish this is by the carbon-14 method. An objective date, even to within a century or two, is essential for judging the relative likelihood of the many image hypotheses considered here. The additional information will also greatly aid in taking proper conservation measures and in planning future research.

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NOTES

1. The term "image formation" is used here to describe the composite process of image transfer and recording, where "transfer" refers specifically to application mechanisms such as direct contact, diffusion, or radiation, and "recording" phenomena generally pertain to the visible element of the image, i.e., its material composition, whether it be a pigment or an altered cellulose structure on the cloth surface. The latter term will also be used in reference to chemical processes involved in cellulose transformation.

2. For example, Wilson [28] recalled the rumor in 1532 that the Shroud had been completely destroyed in the fire. If this were true, the object we observe today may have been produced sometime before its "reappearance" in 1534 by some Italian Renaissance craftsman. We have neither physical nor chemical evidence to support this rumor. Indeed, the observations of silver fragments and burnt blood [37] as well as the red fluorescence of the pyrolyzed cloth areas [14] are in full accord with the historical documentation of the fire. As another possibility, Gabrielli [29] suspected that the image was produced by some printing technique in the late 15th or early 16th century but before the 1532 fire.

3. This is deduced from direct observations of the underside of the cloth near the dorsal foot region. Gonella has questioned this conclusion on the basis of the discussion presented under the faint image properties because the observation could only be made at close range. However, we were looking specifically for surface discolorations on underside cloth areas that directly correspond to the "top" surface image. Even so, the observation that image discoloration resides only on the top few fiber thicknesses testifies far more strongly to the superficial nature of the image.

4. In 1973, Frei [34] took similar sticky-tape samples, and found and identified pollen from 48 different plants. He stated that some of these plant species are native to central Europe, although others are indigenous only to Palestine and still others to Asia Minor

and the region about Constantinople. Frei takes this as evidence for the Shroud having been in each of these regions during its history and exposed to the environment. Very few pollen were observed on the tape samples taken in the present Project, and no effort was made to identify them.

5. According to Thompson [38], the most important yellow in medieval painting was gold metal. One of the most important services provided by other yellow pigments was to imitate gold and to modify greens and reds. Their least important function was to represent yellow things! Some of the inorganic pigments that were commonly used in the 14th century are yellow ocher (hydrated Fe_2O_3), orpiment (As_2S_3), realgar (As_2S_2), giallulinum (possibly Naples Yellow $Pb_3[SbO_4]$ or massicot PbO), and mosaic gold (SnS_2). Organic dyes include saffron which was often mixed with glair and varnishes. Bile yellows, buckthorn, and weld were used as lake pigments.

6. Morris et al. [9] were concerned that the detected trace elements may not have been uniquely associated with the Shroud. The ambiguity arose because the Holland backing cloth could not be removed from the Shroud for the measurements; technically, their data pertain to the double-cloth system. However, thirteen threads, removed from non-image, non-blood areas of the Shroud in November 1973 [41], were brought to America following the Turin study. X-ray fluorescence measurements were made on these with isotope sources of ^{55}Fe, ^{109}Cd, ^{145}Sm, and ^{57}Co for counting periods of 500—1000 min. These results showed roughly the same relative concentrations of calcium, strontium, and iron that were observed in the original 1978 Turin data. In addition, they showed smaller traces of potassium, chlorine, and possibly lead. The small sizes of the thread samples precluded quantitative estimates for these traces, but the later results suggest that the reported Turin measurements do pertain to the Shroud.

7. The hypothesis that these holes were burned through with a hot poker is probably incorrect. Close inspection of the peripheral areas reveals a foreign material there, resembling pitch. The radiographs also show high density structures that support this observation. This earlier damage may have resulted from burning pitch that perhaps fell onto the Shroud from a torch.

8. Definition on this point is admittedly vague. Certainly, the resolution of the image on the cloth is ultimately limited to about 0.02 cm by the weave structure. However, when the term "resolution" is used here we assume the existence of a uniquely defined parameter that is characteristic of a mechanism of image formation, as yet unknown. Given this assumption, the "resolution" can only be inferred by measuring distances between closely spaced but visually distinct image features; typically the lips have been taken for this estimate. Pellicori [13] quoted 0.5 cm for the minimum resolvable feature; Jackson [50] used 0.6 cm in his theoretical studies. Later, Jackson suggested a parameter that pertains strictly to a model that involves a cloth-draped three-dimensional human figure: d/D where d is the cloth—body distance and D is the distance between two marginally resolved points. He estimates this ratio to be about 1.6 ± 0.8 for the lips. All of these values should be understood as lower bounds; until the image formation mechanism is known, the resolution limit cannot be determined exactly.

9. For the Shroud and backing cloth, Mottern et al. [10] estimated a total density of 66 mg cm^{-2} which is too large. The average density of 35 mg cm^{-2}, quoted here, yields a total weight of 1.66 kg which is more nearly consistent with the value 2.47 kg measured directly by Gonella. The 810-g difference may be attributed to additional, appended material. The Shroud and Holland cloth are surrounded by a blue fabric border. Sewn to this along the length is a piece of red silk (ca. 4.3×1.0 m) that is intended to protect the image surface while the Shroud is stored in its rolled configuration.

10. The film densities of both the backing cloth (through 38 existing holes in the Shroud) and adjacent double-cloth areas were measured from the set of DR films of Mottern et al. [10]. The film density differences, which represent the attenuation caused only by the Shroud material, were typically in the range 0.4—0.5. We then assembled a Balteau radiograph system to duplicate the geometry, inherent beryllium-window filtration,

and atmospheric pressure conditions in Turin. Several calibration curves of DR film density versus cellulose areal density were generated to match nominal film densities (1.8—2.3) of the Turin radiographs at double cloth thicknesses to the corresponding double-cloth weight densities (30—40 mg cm^{-2}) reported by Morris et al. [9]. These combined data then showed the Shroud areal density to be about 25—30 mg cm^{-2}. The close correspondence of these results to those obtained indirectly corroborates the validity of the quantitative elemental concentrations published by Morris et al.

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