

## CONSERVATION OF THE SHROUD OF TURIN

ALAN D. ADLER  
and  
LARRY A. SCHWALBE

**Introduction**

**Nothing lasts forever!** All material objects do deteriorate with time (e.g., people, mountains, and statues). While the identification of the Shroud of Turin as the actual burial cloth of Christ is an issue of severe polemic, there are, nevertheless, many who unreservedly view the Shroud as a symbol of their faith. These people deserve the very best advice that science can offer for the preservation of this unique and remarkable relic. It must be strongly emphasized that one is not simply interested in the preservation of the linen cloth, but equally concerned with the preservation of the images found on that cloth. The pressing need for a conservation program and some of the issues involved have been previously reported by the authors.<sup>1,2</sup> Some further matters bear consideration.

In order to design a conservation program, it is first necessary to identify unequivocally the chemical structures involved in the object one desires to conserve, i.e., here, the images on the cloth.<sup>2</sup> Unfortunately, for the Shroud of Turin this is a subject of prolonged strong controversy.<sup>3,4</sup> There are those who contend that the Shroud is a 14<sup>th</sup> century painting made with iron oxide as the pigment, held to the cloth with a proteinaceous binder for the body images, and with some mercuric sulfide admixed with this "paint" to produce the blood images.<sup>5</sup> On the other hand, there is a large corpus of evidence that the Shroud is definitely not a painting; that the body images have been formed by some as yet unidentified process producing a dehydrative oxidation of the cellulosic surface of the linen cloth itself and with the blood images having been formed by the cloth enfolding and contacting a wounded human male body, thus transferring blood derived materials to the surface of the cloth.<sup>6,7,8,9</sup>

This difference of opinion must be resolved before a serious conservation program can be undertaken. A number of relatively noninvasive, non-destructive modern analytical methods and techniques could be used onsite to accomplish this, although a minimum amount of some specific designated sample material might be required for offsite analysis in order to remove all ambiguities in the identification. The body image is only found on the top surface of the cloth, i.e., one to two fibers deep, as evidenced by the

observation that the body images, unlike the blood images, cannot be seen in a transmitted light photograph.<sup>6,7,8</sup> Further, since the chromophore itself is only a thin layer on the surface of these fibers,<sup>5,6,7,8</sup> it is easy to estimate that the concentration of the chromophore is only of the order of a part per billion of the total cloth. Therefore, the instrumental methods employed should emphasize surface techniques and reflection rather than transmission methods.

Such instruments could be left onsite to be employed in an ongoing monitoring program designed to continuously check the condition of the Shroud and its stability.<sup>1</sup> It must be noted that a considerable amount of research will be required in order to design such a monitoring program to assure that the Shroud and its images are in fact being preserved. There are several physical, chemical, and biological processes that can lead to various types of deterioration of the cloth itself and/or the images found on its surface.

### CONSERVATION PROBLEMS

- Ionizing radiation
- Non-ionizing radiation
- Mechanical stress
- Humidity
- Pressure
- Temperature
- Biology
- Chemistry
- Miscellaneous Factors
  - Debris
  - Protection
  - Archiving

### Ionizing Radiation

Although it will be a considerable period of time before the accumulation of its damaging effects are evidenced (on the order of millennia — barring a nuclear catastrophe), exposure to ionizing radiation arising from nearby sources of natural radioactivity and cosmic radiation must be considered, as it influences display and storage considerations. The energy of primary-cosmic radiation varies from a few Bev to the order of several Pev.<sup>10</sup> In particular, the high energy end of the cosmic radiation spectrum can produce secondary ionization covering areas of the order of 10 square feet, i.e., air showers. These in turn will induce extensive *Bremsstrahlung*, in metallic materials near or about the Shroud that will slowly but surely destroy the integrity of the cloth through the ion and radical chemistry induced by the chemical bond breakage such radiative interactions produce (as the strengths of these bonds are only of the order of 4 to 5 ev). Therefore, as only low atomic number materials would be indicated, glass would be the preferred construction material employed in all supporting and containing

structures. To minimize cosmic ray exposure, all display formats should place the plane of the cloth perpendicular to the earth's surface. Appropriate shielding should be considered and tested (bearing in mind the problems of possible earthquakes). The amount of such radiation should be assessed and monitored routinely. Note that plastic type construction materials should be avoided in the immediate vicinity as they invariably contain low molecular weight diffusible structures that can chemically react adversely with the cloth and especially the images.

### **Non-ionizing Radiation**

Exposure to non-ionizing radiation, such as visible light, will also lead to either direct photochemical damage to both the cloth and the images or indirectly to similar damage through photocatalyzed reactions brought about by the presence of photosensitizers.<sup>2</sup> Trace transition metal compounds and, particularly, the relatively large amounts of various iron-containing structures present<sup>5,7</sup> can serve as such photosensitizers. Such reactions can strongly affect the images. For example, the red color of the blood has been attributed to the presence of protein-bound bilirubin being admixed with methemoglobin.<sup>7,8</sup> Overexposure to ultraviolet and/or visible radiation could modify this color,<sup>2</sup> as bilirubin can be readily and quickly photodecomposed under a variety of conditions.<sup>11</sup> Alternatively, if the red color of the blood is due to the presence of vermilion, i.e., mercuric oxide, light exposure will blacken the image, as has been evidenced in many older paintings.<sup>12</sup> Until such considerations have been completely assessed, a continuous lighted display of the surface of the Shroud would be inadvisable and the display of a photoreplica should be considered. While a protective ultraviolet filtering glass cover might prove effective, the use of such filters for the visible region would be most unaesthetic. The employment of any possible chemical quenching agents should be disregarded, since there is no way of really predicting what would be the long-term sequelae following their use. Clearly, the Shroud should be maintained, as now, in the dark until such matters are thoroughly investigated.

### **Mechanical Stress**

Various types of mechanical stresses can also lead to damage. Unless properly supported, the cloth can stretch under gravity when displayed vertically and distort portions of the image. This stress can be reduced by horizontal display, but that increases the exposed target area for damage due to ionizing radiation as discussed above. More important, such stretching causes cracking and flaking of any adherent materials such as proteinaceous blood derived materials or pigment binders, whichever is present. (It is of some historic interest to note that Vignon used the lack of such effects on the body images to argue against the Shroud being a

painting.) Low magnification micrographs of the blood image areas of the Shroud already show marked extensive abrasion of this type of damage from past rolling and folding activities.<sup>6,7,8</sup> Moreover, the sampling tapes demonstrate that these abraded materials have become redistributed over the entire cloth surface, leading to some confusion in assigning specific chemical structures to specific parts of the images.<sup>7,8</sup> Folding also produces such stress as evidenced by signs of fatigue, i.e., wrinkles. It should be noted that stressed and/or curved surfaces are more chemically reactive than the unstressed structures, particularly with respect to oxidative reactivity. Ultimately this leads to fractured and broken fibers and therefore deterioration of the integrity of the cloth itself. Therefore, the Shroud should not be kept folded or rolled. The backing cloth and its mode of attachment also contribute to this stress problem. However, a decision about removing or modifying the attachment of the backing cloth is not a trivial problem. This will depend somewhat upon the choices made for display and storage formats. Vibrations will also produce the same kinds of problems, although extended over a much longer period of time. Consideration of antivibration designs should be incorporated into display and storage formats.

### **Humidity**

Humidity control is recommended for similar reasons. Hydration/dehydration cycles will produce the same effects as vibrations, as the cellulose fibers will stretch and shrink as their degree of hydration changes. Further, as the chemical mechanism of formation of one of the suggested chromophores constituting the body images involves dehydrative reaction steps, this must also be given some consideration. For this reason it is not recommended that the cloth be either stored or displayed under vacuum. The extent to which such effects enhance oxidative activity should also be ascertained, as it is well known that drying linen increases the effects of mechanical stress. On the other hand, excess moisture will increase the absorption of ambient air pollutants that can lead to adverse chemical effects.<sup>2</sup> It is readily seen that determining the actual conditions of humidity control for proper maintenance of the Shroud is a matter requiring further investigation.

### **Pressure**

Pressure regulation is also desired. Although the direct effects of small pressure variations on chemical reactivity for the reaction types of interest can be predicted to be negligible, these changes can affect the state of hydration with the subsequent consequences alluded to above. Such small pressure variations can also increase the convective influx of atmospheric pollutants and contaminants by at least an order of magnitude over that expected from simple diffusion. Serious consideration should be given to the possibility

of maintaining the Shroud in a sealed glass container under an inert gas atmosphere, but only after the possible microbiological problems have been determined as discussed below. Some provision for these matters should be made in the proposed designs for any recommended forms of analytical monitoring, e.g., various spectroscopic and electroanalytical methods.

## Temperature

Temperature maintenance is imperative. Small variations in the temperature can enhance all the pressure, humidity, and mechanical stress effects previously discussed. Further, small temperature variations can have pronounced effects on chemical reaction rates, particularly under various types of catalyzed conditions. The problem of the continuous thermal oxidation of the cloth background has been previously reported.<sup>2</sup> If the body image chromophore has been produced by an oxidative mechanism, the subsequent thermal oxidation of the non-body image background to the same degree of color saturation will lead to the apparent disappearance of the body images. They will no longer be distinguishable from the nearby surrounding cloth background. Using literature information on chemical reactivity of this type, it was shown that this process could be expected to require as long as a millennium to be manifested. However, it was also shown that it could happen in one to two decades, if steps are not taken to prevent various types of predictable catalytic phenomena from occurring, as would be expected from interactions with various air pollutants, light, radiation, etc.<sup>2</sup>

It should be noted that simply placing the cloth in an inert gas atmosphere with the exclusion of oxygen will not immediately stop all this activity. Previous chemical reactions on the cloth, e.g., the retting process in manufacture of the linen, the known historic fire and its extinguishment, and previous display and storage procedures, have left a variety of chemical structures on the surface that can act as oxidants and also as catalysts. For example, the acidic structures produced by previous oxidative activity can strongly promote various types of autocatalysis. As much of this sort of material resides in the scorch marks, a very difficult problem is presented. Should they be removed or chemically treated in some fashion? How to deal with it without defacing the cloth or producing new problems will call for some extensive basic research. The recent strong concern by library conservators over the rapid degradation in books of acidic paper, another cellulosic material, should give us some pause for thought.

Although it would be expensive to maintain, some form of cryogenic storage and display could minimize these effects by slowing the rates of chemical reactivity. A research program should be initiated to find an appropriate temperature that will compromise

expense with some designated degree of preservation. An interesting advantage arises here if the blood images are partially comprised of mercuric sulfide as has been suggested.<sup>5</sup> This chemical compound exists in two forms, the usual red colored structure associated with the mineral cinnabar, frequently used as a medieval artist's pigment (vermilion), and a black colored form to which it can convert, especially at elevated temperatures.<sup>13</sup> Such a possible discoloration of the blood images would be more than effectively prevented by the use of cryogenic conditions. However, such conditions would not prevent the photodecomposition of either bilirubin or the vermilion, as discussed above. This illustrates the importance of unequivocally determining what these chemical materials really are before attempting to design an appropriate conservation program.

## **Biology**

An electron microscope examination of the dusts and pollens removed from the Shroud by G. Riggi by a microvacuuming technique at the time of the 1978 testing has revealed that some species of mites are resident on the cloth. Lichenothelia have recently been both observed in and cultured from Shroud samples and may even have affected the radiodating of the cloth.<sup>14</sup> Arachnids have also recently been observed in one of the tape samples.<sup>15</sup> Information on what other types of fungi, molds, and other species of microorganisms present that should be considered in a conservation program is entirely lacking. A thorough microbiological study to assess such matters should be undertaken, especially to determine what the activities of such organisms might do to the stability of the materials found in the various images, e.g., any proteinaceous structures or partially degraded cellulosic structures. For example, if obligate anaerobes are present it would be strongly inadvisable to place the Shroud in an inert atmosphere, as that would stimulate their activity. This determination of what flora and fauna are already resident on the Shroud is absolutely necessary to any considerations for a proper conservation program.

No insecticides, pesticides, fungicides, fumigants, detergents, or similar materials should be applied to the cloth to generally remedy any projected problems in these regards, as such chemical structures will invariably act as photosensitizers, oxidative catalysts, or reactants or ligands for some of the proposed chromophores. Such remedial treatments should be employed only after extensive research into all possible long-term consequences.

## **Chemistry**

It has already been seen that most of the chemical problems that will be encountered in a conservation program for the Shroud of Turin can be met by controlling the physical factors involved such as temperature, pressure, radiation exposure, and humidity.

Conjugated carbonyl groups, one of the postulated image chromophores, are readily reactive with a wide variety of other organic functional groups. Restriction of air-borne pollutants and contaminants from further contact with the cloth is probably one of the most pressing matters to be investigated. How to deal with problem materials now present on the cloth will also require a considerable amount of thought and original research. Contact with plastic materials should be strongly avoided as their volatile effluents will be reactive with the chemical structures postulated to be of importance on the Shroud. Further, one rigid rule that must be followed with no exceptions whatsoever is that no chemical materials will be applied to the cloth without the most searching investigations into the possible risks involved, especially for the future. One should adopt the simple rule that any material giving off a detectable odor should be excluded from contact with the cloth and should not even be employed in the immediate vicinity of the Shroud.

### **Miscellaneous Factors**

There is a relatively large amount of extraneous debris found on the surface of the Shroud,<sup>5,7</sup> e.g., wax, red silk fibers from the backing cloth, occasional traces of various types of artist's pigments (ascribed to either the artist who painted the Shroud itself<sup>5</sup> or alternatively to artists making copies of the Shroud and then sanctifying the copy by contacting it to the original<sup>7</sup>), pollens, hairs, insect parts, etc. Some of this material has historic value and context.<sup>15,16</sup> However, the traces of artists' pigments present could become more finely dispersed over the surface of the cloth<sup>17</sup> and, as these can act as photosensitizers, they present a conflict of interest between conservation and historical investigation. A decision will have to be made as to whether any of it should be selectively removed or all of it left where it is. It is recommended that any such designated removals be accomplished by a selective microvacuuming technique.<sup>15</sup> Leaving it all where it is will also place some constraints on storage and display geometries, unless the recommendations for antivibration designs are incorporated.

The design of display and storage facilities must take some other more practical factors into account. Protection against damage from fire, severe storm, flood, and earthquakes must be considered. Unfortunately, one must also incorporate strong measures to guard against possible acts of vandalism and/or terrorism. A sense of the historic background should also be provided. Last, but certainly not least, it must be aesthetically pleasing. Placing the Shroud in a deep underground facility would solve many of the problems raised here, but it is unlikely that anyone would consider this a satisfactory solution.

### **Archiving**

Hopefully, a successful program of the sort envisioned here will

make the Shroud available to the public in some acceptable form for many millennia. However, unforeseen and unimaginable events can intervene no matter how carefully one plans for the future. Therefore, the present conservation plans should incorporate a variety of archiving programs to deal with any unanticipated contingencies. These should include a complete video scan of the cloth at low magnifications, preferably with appropriate spectral data for each pixel, and complete sets of large-scale photographs at a large variety of selected wavelengths from the ultraviolet through the infrared. A library of source materials should be established. Consideration should be given to the preparation of an atlas in both hard and computer formats.<sup>18</sup> Such reference sources would permit a great deal of scholarly research to be conducted on the Shroud without the necessity for direct examination. It must be recognized that it is important to foster such continuous research interest in the Shroud.<sup>1</sup>

## **Conclusion**

A number of serious issues affecting the conservation and preservation of the Shroud of Turin have been raised in this article. Problems affecting the cloth itself are not really pressing. Less assurance can be given for matters concerning the stability of the body image; some studies should be initiated now if some anticipated problems are to be avoided in the near future. However, the blood images present a different story - the damage here is already extensive and requires immediate attention. History will hold those of us interested in this remarkable cloth responsible for recognizing that now is the time to initiate such a broad and comprehensive program.<sup>1,2</sup> TEMPUS FUGIT!

## **Dedication**

This paper is respectfully dedicated to the memory of Father Peter Rinaldi, S.D.B. - a scholar, a gentleman, and a friend. Almost seventy years of his life, from the age of fourteen, were devoted to the cause of the Shroud of Turin, setting an example that few can hope to emulate. The conservation and preservation of this cloth was always of paramount interest and concern to him.

ALAN D. ADLER, Department of Chemistry, Western Connecticut State University, Danbury, CT 06810

LARRY A. SCHWALBE, Los Alamos National Laboratory, Los Alamos, NM 87545



## REFERENCES

1. L. SCHWALBE, *Shroud Spectrum International*, 35/36 (1990): 3.
2. A. ADLER, *Shroud Spectrum International*, 40 (1991): 22.
3. D. SCAVONE, *The Shroud of Turin*, Greenhaven Press, San Diego, CA (1984).
4. I. WILSON, *The Mysterious Shroud*, Doubleday, Garden City, NY (1986).
5. W. MCCRONE, *Acc. Chem. Res.*, 23 (1990): 77.
6. L. SCHWALBE and R. ROGERS, *Anal. Chim. Acta*, 135 (1982): 3.
7. J. HELLER and A. ADLER, *Can. Soc. Forens. Sci. J.*, 14 (1981): 81.
8. E. JUMPER et al., *Adv. in Chem.*, 205 (1984): 447.
9. J. JACKSON et al., *App. Optics*, 23 (1984): 2244.
10. F. RICHTMEYER and E. KENNARD, *Introd. to Modern Physics*, McGraw-Hill, New York, NY, (1947): 659.
11. A. MCDONAGH, *Ann. NYAS*, 244 (1975): 553
12. M. DOERNER, *The Materials of the Artist*, HBJ, New York, NY, (1984): 72.
13. N. SIDGWICK, *The Chemical Elements and Their Compounds*, Oxford, London (1950): 320.
14. L. GARZA-VALDES, personal communication.
15. P. MALONEY, personal communication.
16. W. MEACHAM, *Current Anthrop.*, 24 (1983): 283.
17. I. PICZEK, personal communication.
18. K. MORAN, personal communication.