SCIENTIFIC METHOD APPLIED TO THE SHROUD OF TURIN
A REVIEW

Raymond N. Rogers* and Anna Arnoldi**

***University of California**
Los Alamos National Laboratory
Los Alamos, NM

****Department of Agrifood Molecular Sciences**
University of Milan
Milano, Italy

ABSRACT

After 25 years of scientific study, I believe that three statements can be supported on the basis of established laws of science and direct observations on the Shroud of Turin.

1. The radiocarbon age determination made in 1988 used an invalid sample, and it gave an erroneous date for the production of the main part of the cloth.

2. The hypotheses that have appeared since the announcement of an AD 1260-1390 date that invoke radiation of different kinds to explain the image and the date can be categorically discarded.

3. The characteristics of the image can be explained by reference to highly probable, well-known chemical reactions. No miracles are necessary to explain the image.

INTRODUCTION

The Shroud of Turin first came to public notice and was documented early in the 14th Century in France when its custodian claimed that it was the shroud of Jesus. It has been fiercely controversial ever since.

It has very seldom been displayed to the public, and it has been more an object of veneration that of study. Reports on it have been more subjective than objective; however, its religious concomitant does not eliminate the possibility of making truly scientific studies on it. It exists as a material object, and anything that can be observed and measured can be studied by objective methods

The Shroud is a large piece of linen that shows the very faint image of a man on its surface. The image appears to show a man who has been crucified, with blood flows in the appropriate positions. These features have been observed by several different, independent scientific techniques.[1]

The Shroud is now preserved in Turin, Italy. A group of scientists produced a plan for study in 1977.[2] This group incorporated as the Shroud of Turin Research Project (STURP). In 1978, the custodians permitted limited scientific studies to be made. Results of those observations are reviewed below.

All methods used to establish basic beliefs are subject to the test of *general reliability*, and they are acceptable only if they yield beliefs which prove to be true. Attempts to develop objective philosophical methods for reaching truth from observations have resulted in the logical approach known as Scientific Method. The STURP plan was based on a rigorous application of this method.

The Bishop of Troyes sent a letter to the pope in AD 1389 claiming that the image had been painted;

therefore, that was the primary question to be addressed during the 1978 STURP studies. However, the scientific observations made in Turin in 1978 can and should be used to test any hypotheses involving the Shroud.

SCIENTIFIC METHOD

A summary of the major elements of Scientific Method in the context of Shroud studies follows.

1) Identify and clearly state the goal. The goals of the different studies on the Shroud are not always clearly stated in writings on the subject, and ultimate goals were never agreed upon by all of the persons connected with STURP. There is a huge difference among the following list of possible goals: 1) test whether the image was a hoax that used known methods for producing an image; 2) estimate the probability that the Shroud is an "authentic" shroud; 3) prove that the cloth had been the shroud of Jesus; and 4) test whether the Shroud proved the resurrection of Jesus.

2) Assemble all pertinent data. Two of the most damaging things a "scientist" can do during the development of a "scientific" study is to include speculations on an equal basis with tested facts and exclude observations he does not like. We have seen both problems in Shroud literature. "I think I see," seems to be accepted by "true believers" on an equal basis with quantitative measurements. Persons who are devoted to "debunking" the Shroud refuse to accept observations that do not further their goals, and persons who want to prove the resurrection refuse to accept observations that seem to conflict with their preconceptions.

3) Hypothesize and innovate. An unproved statement that is intended for study and testing is called an "hypothesis." The Method of Multiple Working Hypotheses[3] encourages a scientist to state as many credible explanations for an observation as possible. This is an enjoyable phase of science; it is perfectly valid to let imaginations run wild. Groups often get together to "brainstorm" all of the hypotheses they can think of. Unfortunately, few attempts have been made to develop multiple, testable hypotheses on image formation. Persons with fixed goals wish to prove their points, and they refuse to "assemble all pertinent data." Hypotheses for image formation were discussed in detail after the STURP observations.[4]

4) Test and confirm. The rigorous application of Scientific Method requires that all hypotheses be tested equally, and they must be tested against the same *comprehensive* set of facts and observations. A person who feels comfortable with Scientific Method enjoys "shooting holes" in his hypotheses. Hard feelings often result when somebody else's favorite hypothesis is picked to pieces, but that is an important part of the "self-correcting" nature of science. An important part of confirmation is prediction. Prediction enables confirmatory experimentation. Hypotheses that can not be used to formulate testable predictions are useless. Miracles can not be tested nor confirmed and are not part of science.

5) Occam's Razor. In any contention, both sides can not be correct; however, both sides can be wrong. Competing hypotheses should be tested with Occam's Razor. We usually state it as, "The hypothesis that includes the smallest number of special assumptions has the highest probability of being closest to the truth." Scientists normally do not consider it possible to prove a truth. A miracle is a "special assumption." If one hypothesis demands a miracle and another can be supported by known science and observations, the miracle should be discarded.

6) The fallacy of the *non sequitur*. After weak hypotheses have been eliminated according to known facts and laws of nature, you hope that at least one remains. After a comprehensive study of the known facts, STURP members reported[1] that, "We really do not have a satisfactory, simple explanation for how the body image got on the cloth."

Many writers who are supporting a religious/miraculous position take that statement to mean something like the following: "If science can not explain the observation, it must have had a miraculous origin." The

Greeks recognized the fallacy of such an "argumentative leap" before 300 BC. The fact that science has not yet found an explanation proves nothing.

ASSEMBLE ALL PERTINENT DATA

The primary goal of STURP was to test the hypothesis that the Shroud's image was painted. Secondary goals were to observe the Shroud's technology and composition so that statements could be made on its "authenticity" (whatever that is taken to mean) and possible age. In order to accomplish the goals, a large number of observations were made before, during, and after the Shroud was made available for study in Turin. Facts were also assembled from literature surveys. Some of these facts will be mentioned to illustrate the process of Scientific Method. The observations and data can and should be used to test all hypotheses on the Shroud. No facts can legitimately be ignored.

1) The fire of AD 1532:
Fortunately for us, the Shroud was nearly destroyed in a church fire in AD 1532. If the image had been painted, some colored material had to be added to the cloth. The pigments and vehicles (glair, gums, glues - oils were not used in the 14th Century, but they were also tested) would have been subjected to a violent "chemical test" during the fire. The temperatures, temperature gradients, pyrolysis products, and water used to extinguish the fire would have changed the chemical composition of most foreign materials. Before going to Turin in 1978, we did many experiments on the stability of the painting materials. All of these pigments and vehicles were tested by applying them to linen and subjecting the samples to different kinds of heating.

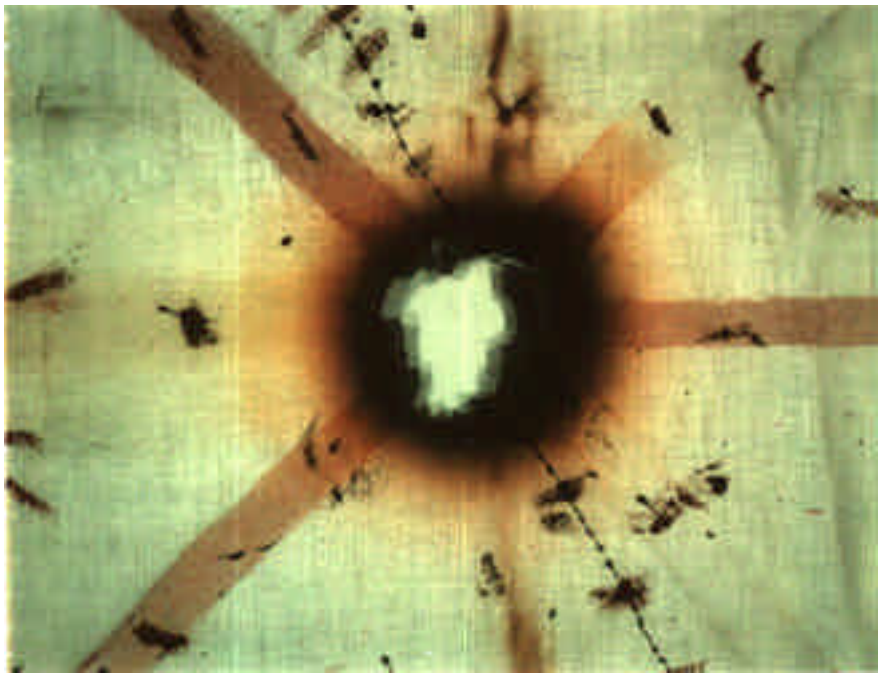

Figure 1: Results of one "burn test." Linen streaked with blood and different painting media with and without pigments was heated intensely in the center while it was confined between two stainless-steel plates (1977).

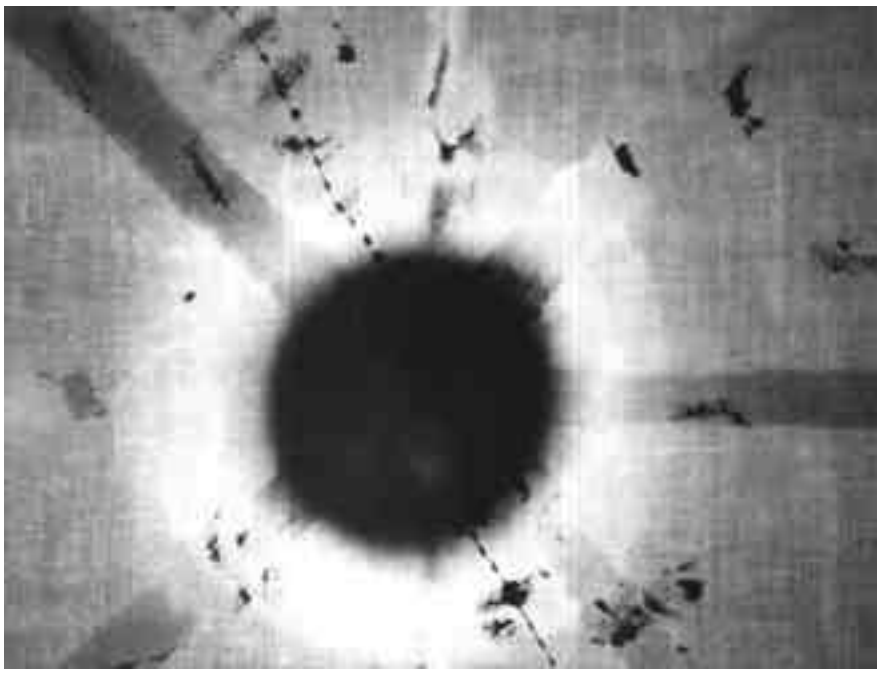

Figure 2: The same sample under UV illumination. The linen was modern and contained "fabric brighteners." Condensed cellulose pyrolysis products form an intensely fluorescent ring around the center of heating.

We had expected hematite (Fe_2O_3) to be the most probable pigment that could have been used to paint the image. The heating tests proved that much of the red hematite was reduced to black magnetite (Fe_3O_4) by the pyrolysis products. No such effect could be observed on the Shroud.

All paints were changed by heat and/or the chemically reducing and reactive pyrolysis products (formaldehyde, furfural, organic acids, CO, etc.). Some Medieval painting materials become water soluble and they would have moved with the water that diffused through parts of the cloth at the time of the AD 1532 fire. Observations of the Shroud in 1978 showed that nothing in the image moved with the water.

STURP concluded that the image was not a painting. Walter McCrone[5,6] insisted that the image was painted with hematite. Several other people have claimed to reproduce the appearance of the image by different "painting" methods, but none have used the observational methods used by STURP to test their hypotheses.

2) Direct microscopy:
The Shroud was observed through a microscope for many hours in 1978, and a large number of photomicrographs was taken.[7] No evidence for fungal attack could be seen. The image is the result of many superficial yellow linen fibers. Although Walter McCrone refused to accept any observations other than his own, and he claimed that the image was painted, he reported that, "Microscopically, the image consists of yellow fibers…and the yellow fibers are the major colored substance in the body image.[5,6]"

During the 1978 observations in Turin, I used a dissecting needle to push some of the individual, superficial, yellow, 10-15-µm-diameter image fibers aside and look under them with a microscope. I could not see colored fibers more than a relatively short distance from the top surface of a thread. Published photomicrographs of the surface show the discontinuous distribution of the color on the topmost parts of the weave. [7] The color density seen in any area of the image appears primarily to be a function of the number of colored fibers per unit area rather than a significant difference in the density of

the color of the fibers. This observation was puzzling, and we called it the "half-tone" effect. No fibers in a pure image area were cemented together by any foreign material, and there were no liquid meniscus marks. These facts seemed to eliminate any image-formation hypothesis that was based solely on the flow of a liquid into the cloth. This also suggests that, if a body was involved in image formation, it was dry at the time the color formed. Diffusion of gaseous reactants or dyes into the cloth would have produced a color gradient (darker on the surface, lighter at depth).

3) Observation of the back surface:
Several STURP members looked at the back surface of the Shroud, and there is no trace of an image on it. Some of the blood flows can be seen on the back surface.

Figure 3: Photographed under pure UV: The image is seen only as a result of background fluorescence. Notice the narrow, vertical dark line to the right of the wrist blood stain. The color density of an image area on the hand is increased where the darker band intersects it. Other bands show the same effect.

4) Bands of different colored yarn (linen technology):
Bands of different-colored yarn can be observed in the weave of the cloth (figure 3). Where darker bands intersect image areas, the image is darker. This proves that the image color is not solely a result of reactions in the cellulose of the linen. Something on the surface of the different batches of yarn produced color and/or accelerated color formation. The observations of bands of color agree with historical reports on the methods used to produce ancient linen. [8]They indicate a very mild bleaching technique, unlike that used after the last crusade in AD 1291.[9]

The warp of ancient linen was protected with starch during weaving and the finished cloth was washed in *Saponaria officinalis* suds. *Saponaria* is hemolytic, which could explain why the old blood stains on the cloth are still red. Diane Soran (deceased) of Los Alamos, tested hemolysis on *Saponaria*-washed cloth before we went to Turin. The blood is still red on those 25-year-old samples. Controls are black. *Saponaria* hydrolyzes to produce some aglycones that are fluorescent, and the non-image part of the Shroud is weakly fluorescent. The image quenches that fluorescence. *Saponaria* is toxic, and it is a potent preservative. A textile conservator told us that old cloths tend to be better preserved than newer

ones. Comparison samples loaned to us by the amazing Museum of Egyptology in Turin were still supple, and several dated to several thousand years BC. *Saponaria* produces four glycosidic saponins, all containing gypsogenin. The glycosides hydrolyze to produce sugar chains[10]. The following carbohydrates were identified in those chains: galactose, glucose, arabinose, xylose, fucose, rhamnose, and glucuronic acid. Pentose sugars with a furanose structure appear to be the most reactive sugars.[11] The *Saponaria* sugars should be quite chemically active. Human sebaceous secretions in sweat are about 28% free fatty acids. They are a source of "body odor." These fatty acids are chemically reactive, and they catalyze many types of reactions. Darker-appearing, pure-image areas did not penetrate significantly more deeply into the cloth than did lighter areas. The effect was much different than that produced by scorching a cloth with a hot statue.

5) Adhesive-tape sampling:
I took samples from the surface of the Shroud in 1978, using tape made specially for the task by Ronald Youngquist of Minnesota Mining and Manufacturing, Inc. The backing of the tape was chosen to be amorphous; i.e., it did not give any birefringence colors under crossed polarizers when viewed under a petrographic microscope. Image fibers on the sampling tapes are lemon yellow (figure 4).

The tapes were applied to the surface of the cloth with a pressure-measuring roller. I had designed the roller to enable semi-quantitative comparisons among sampling areas; however, a surprising feature was observed. The applicator could also be used to measure the force required to *remove* a tape. Much less force was required to remove tapes from image areas than from non-image areas.

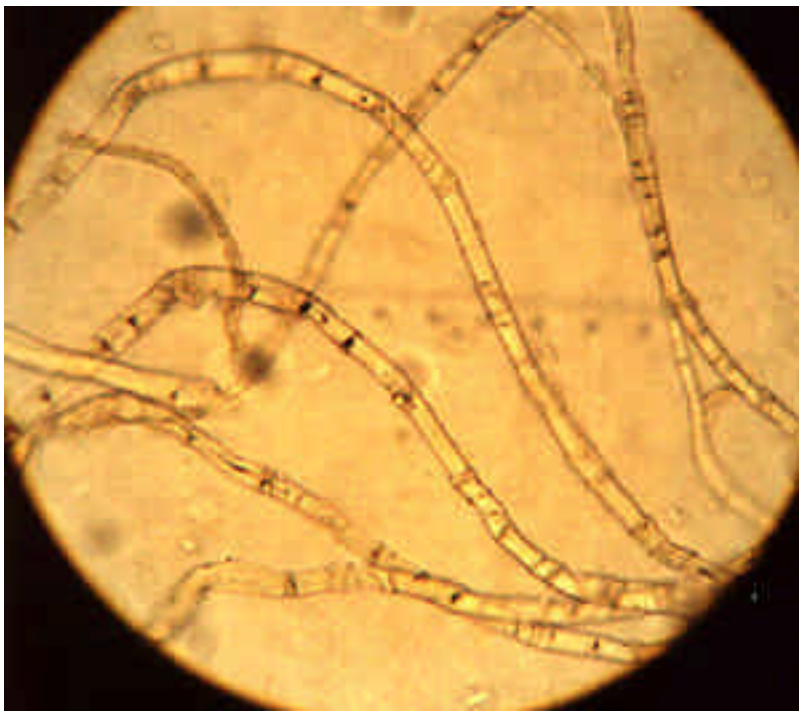

Figure 4: Lemon-yellow image fibers (400X), showing black lignin at growth nodes.

6) Instrumental methods of analysis:
The Shroud was observed by visible and ultraviolet spectrometry[12,13], infrared spectrometry[14], x-ray fluorescence spectrometry[15], and direct microscopic viewing. Later microscopy[4,5,6,16], microchemistry[4,16], pyrolysis-mass-spectrometry[4], and laser-microprobe Raman analyses[4] were used on samples we obtained in Turin.

Many of the pyrolysis fragments observed by pyrolysis-mass-spectrometry would be the same products of thermal degradation whether they came from cellulose, hexose sugars, or starches; i.e., a starch

impurity would not have been detected. UV and visible spectrometry would not see any differences among the carbohydrates. The -OH vibrational states of all of the carbohydrates and water are very broad and intense, and IR spectrometry could not distinguish among them. Laser-microprobe Raman is similar to IR. We were not looking for trace carbohydrate impurities, we were looking for painting-type impurities on the cloth.

The pyrolysis-mass-spectrometry analyses of individual fibers at the NSF Center of Excellence at the University of Nebraska was sufficiently sensitive to detect ppb levels of polyethylene oligomers that came from sample bags, but it did not detect any of the possible pigments or painting media. The pyrolysis-MS analyses did not detect any nitrogen-containing contaminants. This seemed to rule out glair (egg white) as well as any significant microbiological deposits. These results were confirmed by microchemical testing.

7) Chemical tests:
Image color does not appear under the blood stains when they are removed with a proteolytic enzyme[16]. Whatever process produced the image color must have occurred after the blood flowed onto the cloth, and the image-producing process did not destroy the blood. Microchemical spot tests with aqueous iodine indicated the presence of some starch fractions on Shroud fibers. No proteins could be detected in either image or non-image areas; however, they were easy to detect in blood stains.[1,4,16] We have recently found that some plant gum, mordants, and dye(s) coat the yarn of the sample which was taken by Gilbert Raes in 1973 for textile analysis[17]. These deposits are unique to the Raes sample; however, that area was in immediate contact with the radiocarbon sample that was removed for dating in 1988. This fact makes the validity of the radiocarbon sample questionable.

8) Summary of primary observations:
All of the observational methods agreed that no pigments, normal painting vehicles, or natural exudations (other than the blood) had been added to the cloth after its production.

9) The image color resides only on the surface of the fibers:
Heller and Adler found[16] that the image fibers could be decolorized with diimide, a powerful reducing agent. Reduction left colorless cellulose fibers. They concluded that the color was a result of conjugated double bonds, agreeing with the spectrometry of Gilbert and Gilbert[12]. At high optical magnifications, up to 1000X, no coatings could be resolved on the surfaces of image fibers;[16] however, the surfaces appeared to be "corroded." Heller and Adler also reported that "ghosts" of color were stripped off of fibers by the adhesive of sampling tapes when they were pulled out of the adhesive and that the insides of the fibers were colorless. I have confirmed this observation (figure 5). *The color is only on the surface of the image fibers.* Another important observation was that the "ghosts" had the same chemical composition as expected from dehydrated carbohydrates.

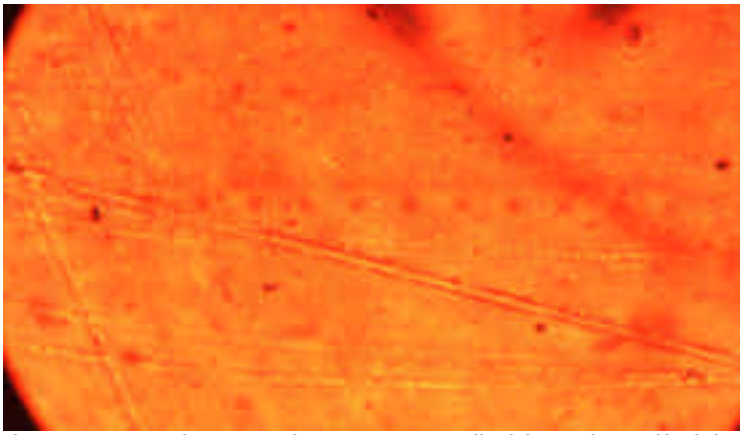

Figure 5: "Ghost" on sample 1EB. The tape was pulled from the calf of the leg. There is no fiber in the horizontal line, proved by rotating the sample between crossed polarizers. Cellulose is birefringent. The line shows a faint-yellow image color.

The STURP observation[16] that the surfaces of image fibers appeared to be "corroded" suggests that a very thin coating of carbohydrate had been significantly dehydrated on the outer surfaces of the fibers. Dehydration causes shrinkage; therefore, any coating of carbohydrate impurities would "craze" during dehydration. Such a crazed coating would be easy to pull off with adhesive, explaining the easy removal of tapes from image areas. *In the context of a discussion on radiation, these observations prove that only radiation-induced reactions that color the surfaces of fibers without coloring the cellulose can be considered.*

10) Image fibers were not scorched to produce the color:
The medullas (tubular voids in the centers of linen fibers) of image fibers do not show any coloration or charring (figure 6). The medullas are usually clean and colorless. Fibers that were scorched during a fire in AD 1532 show some scorching in the medullas.

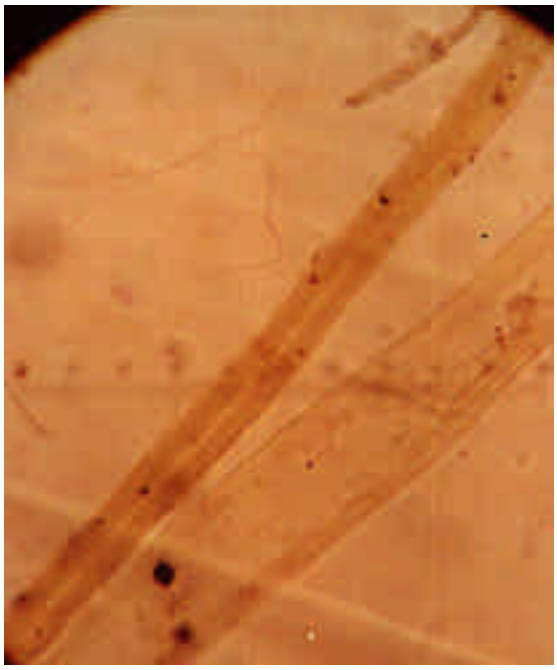

Figure 6: A Colored image fiber from the back image (X400),
showing that the medulla is completely colorless.

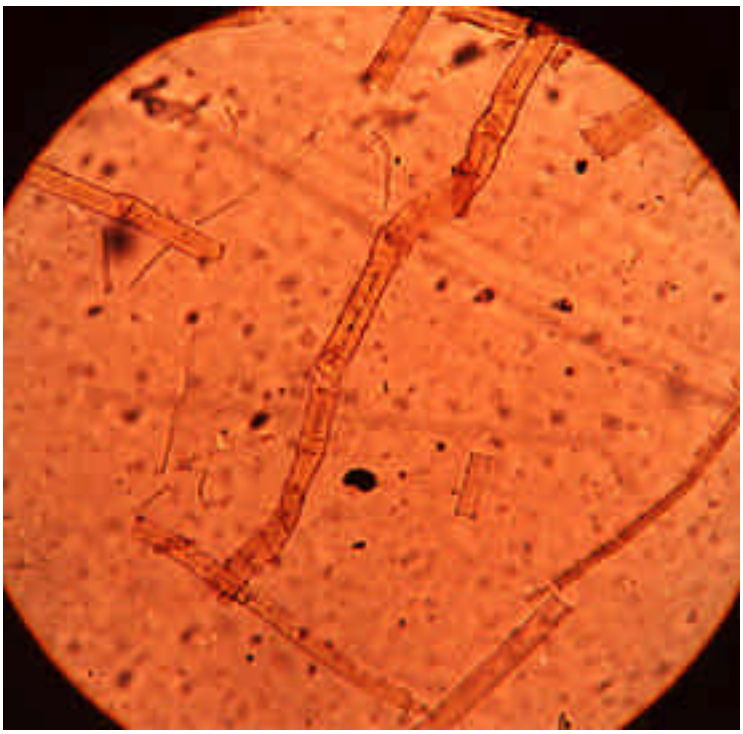

Figure 7: Fiber from a lightly scorched area. The medulla shows darker coloration than the rest of the fiber.

When viewed in parallel light under a microscope, a scorched fiber is colored through its entire diameter, and the medulla usually appears to be darker than the mass of the fiber as a result of reactions at its surface and its shorter radius of curvature (figure 7).

11) Properties of energetic radiation:
If any form of radiation (thermal, electromagnetic, or particle) degraded the cellulose of the linen fibers to produce the image color, it would have had to penetrate the entire diameter of a fiber in order to color its back surface. Some lower fibers are colored, requiring more penetration. Radiation that penetrated the entire 10-15-μm-diameter of a fiber would certainly color the walls of the medulla. All image fibers show color on their surfaces but not in the medullas.

The penetration of forms of radiation into linen is critical to any hypothesis involving radiation. The NIST web site, http://physics.nist.gov/PhysRefData/Star/Text/contents.html , gives comprehensive information on penetration for different forms of radiation, but some scientific background is required to interpret the data and graphs.

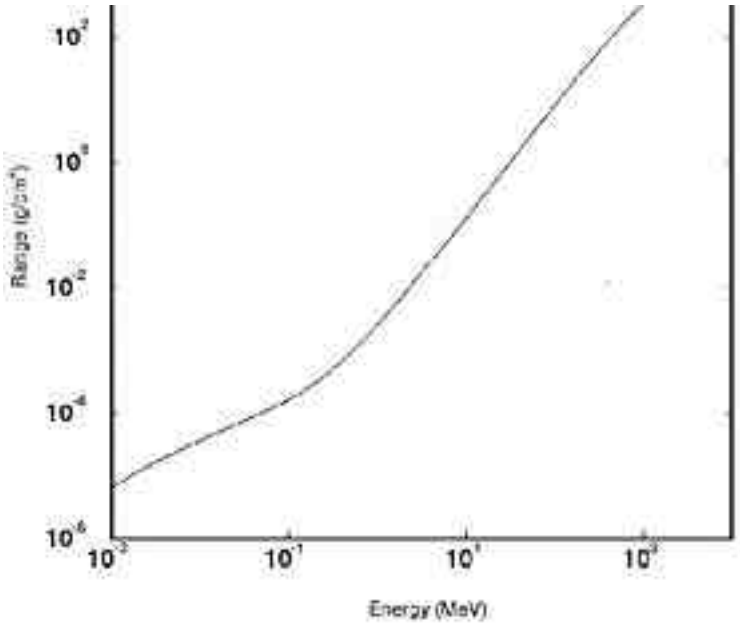

Figure 8: Proton penetration into water as a function of energy.

Rinaudo claimed that, "Protons are indeed the only ionizing radiations to induce mainly acid oxidations[18]." A look at proton penetration data shows that his hypothesis does not and can not fit the observations (figure 8). It is easy to calculate the range in cm from the range in g/cm². For example, 1 cm³ of water weighs 1 gram. A penetration of 1 cm would require roughly 16 MeV of energy (the energy scale is logarithmic). A proton with a few MeV energy would penetrate the entire diameter of a Shroud fiber, coloring the medulla on its way to the farther surface. No radiation hypothesis alone can explain how the entire outer surface of image fibers could become colored without coloring the inside and the medulla.

12) Radiation effects:
When cellulose fibers are heated enough to color them, whether by conduction, convection, or radiation of any kind, water is eliminated from the structure (the cellulose is "dehydrated"). When water is eliminated, -OH chemical bonds are broken. The C· free radicals formed are extremely reactive, and they will combine with any material in their vicinity. In cellulose, other parts of the cellulose chains are usually the closest reactants. The chains *crosslink*.

Cellulose molecules are folded back and forth in a fairly regular arrangement, and they show the properties of crystallinity. This is called a "fibrillar structure." When you rotate the stage of a petrographic microscope with crossed polarizers while looking at a linen fiber, straight lengths changes from black to colored every 90Ķ. The fiber is birefringent and has an ordered structure. When cellulose starts to scorch (dehydrate and crosslink), its characteristic crystal structure becomes progressively more chaotic. Its birefringence changes, and not all parts of a straight fiber go through clear transitions from dark to light at the same angle. Zones of order get smaller and smaller. It finally takes on the appearance of a pseudomorph and just scatters light. A significantly scorched fiber does not change color as the stage is rotated between crossed polarizers.

It is easy to measure the index of refraction of a material and observe changes in its crystallinity with a petrographic microscope. Unfortunately, it is much harder to make measurements on the sampling tapes now that they have started to crystallize. Observations must be made on the specific fibers that reach extinction at the same angle as the tape (while everything is black). The index of refraction of a normal linen fiber parallel to its length is nearly identical to that of the adhesive on the sampling tapes (it nearly disappears). The index across the fiber is appreciably lower than the adhesive. The indices of refraction

and crystallinity of image fibers are identical to unaffected fibers. Bent, crushed, or otherwise damaged fibers show strain dichroism and will give an erroneous index.

Experiments scorching normal linen fibers agree with observations on scorched fibers from the Shroud. As the scorch color deepens, the two indices of the linen approach the same apparent value. The index observed is the average of all of the orientations of the microcrystaline zones in the pseudomorph. Similar fibers have not been observed on image tapes. Other than observing colored medullas, crystallinity and birefringence give good clues for differentiating between scorched and image fibers. The evidence is strong that the image is not a result of dehydration of the cellulose by any mechanism, thermal or radiation.

The observations of colorless cores in image fibers, ghosts pulled from fibers by the adhesive, the reduction of the color with diimide, lack of fluorescence in an image area, and optical differences between image and scorch fibers seem to eliminate any high-temperature heating event or energetic radiation in image formation. **The cellulose of the image had not changed as a result of image formation.** Neutrons produce "recoil protons" when they hit a material that contains hydrogen. The loss of hydrogen also causes crosslinking. Neutrons can not be invoked for a miracle.

13) Low-temperature processes:
Although high-temperatures and energetic radiation must be ruled out for image formation, lower-temperature processes are still possible. All that is required is that temperatures never reach the level where cellulose begins to dehydrate at a significant rate. Cellulose starts to dehydrate rapidly between 275 and 300°C. Many materials color rapidly at temperatures much lower than that. Some claims have been made that thermal radiation (heat/infrared) could not play a part in image formation, because intensity of the radiation follows a $1/r^2$ law. That is not correct. Materials radiate different wavelengths of electromagnetic energy at different temperatures. The wavelengths can be calculated from Planck's Radiation equation. Before a hot surface starts to glow, most of the radiation is produced in the infrared range.

Surfaces radiate different amounts of heat at different angles depending on the electronic structure of the material. G. G. Gubareff, J. E. Janssen, and R. H. Torborg[19] discussed the scientific principles of thermal radiation in rigorous detail. Polished metals radiate and absorb very little thermal energy, and what they do radiate comes off of the surface at a very low angle. Nonmetals radiate much more thermal energy, and most of it comes out 90Ķ to the surface. It is obvious that thermal radiation does not follow a $1/r^2$ law.

You can observe this effect by buffing the surface of a chrome-plated spatula and putting a fingerprint, a spot of syrup, and a smear of clay on the surface. Heat the piece in the dark. As the temperature increases, the first places that you will see glow with radiation will be the print and other non-metallic spots, and they will glow long before the rest of the metal reddens with heat. The glow will be most visible from straight above. When the metal starts to glow, its light will be most visible at a low angle. The emissivity of a human body is like other non-metals or organic materials. Image formation that involves thermal radiation can not be ruled out; however, it can not explain all of the features of the Shroud.

The thermal conductivity of linen is quite low, about 5×10^{-4} cal cm^{-1} s^{-1} $°C^{-1}$; therefore, the temperature gradient extending outward from any heated area will be quite steep: It will be much hotter near contact points and cooler away from them. This is important in considering the chemical rates of processes that can form a color on a shroud that is in contact with a warm body.

14) Other possible sources of color:
We considered iridescence (optical interference in thin layers) and electrons trapped in crystal defects. Those could easily be discarded. All remaining ways must involve chemical changes.

15) Chemistry and rate processes:
All chemical processes occur at some rate at every temperature above absolute zero, -273°C (-459°F), but the rates follow an exponential function as temperatures change. Some rates are very slow at normal temperatures. Cellulose does not scorch at a visible rate at room temperature, but it will char quickly above about 300°C. Other carbohydrates (e.g., starches and sugars) can color at much lower temperatures. A piece of cloth heated to several hundred degrees at a point will start to color, but the color quickly becomes less intense away from the heated point as a result of the low thermal conductivity of cellulose. Several medical investigators have told me that the postmortem body temperature of a person who has died of hyperthermia and/or dehydration often reaches 41°C (106°F),[20] and body temperatures can actually increase slight ly after death. Some bodies have shown temperatures as high as 43°C (110°F). The bodies are quite dry as a result of the hyperthermia. Many bodies are found at high temperature in closed automobiles or lying on the desert in the sun. Materials that are stable at normal room temperatures (about 22°C) can react rapidly at 41-43°C. Many simple chemical processes double (or even triple) their rates for each 10°C (18°F) increase in temperature. A dehydration-type of reaction could be expected to be about three times faster at normal body temperature than at room temperature and *four to nine* times faster at about 41°C.

Chemical rates are modeled with an exponential equation called the Arrhenius expression, $k = Ze^{-E/RT}$, and rates can be predicted from known, measured chemical kinetics constants (k, the rate constant; Z, the frequency factor; E, the activation energy; R, the gas constant; and T, the absolute temperature). Any chemical process involved in image formation will have properties in accordance with this equation. Heat is also transferred by convection. The circulation of air between a hot surface and a cooler one is driven by the differences in density between a hot gas and a cooler gas. Convection cells are small where clearances are small and larger where clearances are larger. Convection also transfers vapors, which can include reactive gases, from one surface to another. Fairly thin stagnant zones of gas form near fixed surfaces. Other gases that approach such zones must *diffuse* through the stagnant gas to reach the surface. Diffusion of gases through other gases is modeled with Graham's Law of Diffusion. The rates of diffusion are inversely proportional to the square roots of the densities of the gases. Diffusion parallel to the surface of a cloth that covers a body can not be instantaneous, and it will be slower for heavier molecules

In the context of image-formation hypotheses that involve reactive gases, remember that cloth is porous. Gases diffusing to the surface can pass through the pores and be lost. This phenomenon will restrict vapor concentrations as a function of the distance from contact points where a body touches a cloth. Cloth surfaces are active and adsorb gases rapidly, a fact that further limits concentrations as a function of distance. John Jackson's mathematical analysis of image resolution[2] suggested that no single, simple molecular-diffusion or radiation mechanism could produce the image observed. However, a combination of systems could offer an explanation, e.g., anisotropic heat flow by radiation from the body to the cloth, attenuated heat-flow in the cloth, gaseous diffusion, convection, surface properties of cloth, and the dependence of chemical rates on temperature.

16) Summary:
Some type of carbohydrate dehydration reaction seems most probable as an explanation for the image color; however, *the color appears only on the surface of individual fibers*. The color of the image does not involve the cellulose. Energetic radiation absolutely can not be used to explain the properties of the image. *That statement does not suggest a miracle.*

TEST ALL HYPOTHESES WITH THE SAME FACTS

I. The Radiocarbon Date of 1988

The 1988 radiocarbon age determinations were the best that could have been obtained anywhere in the world. Effects of sample-preparation methods were studied and careful statistical analyses were made. Damon, et al., reported[21] that "The age of the shroud is obtained as AD 1260-1390, with at least 95% confidence." Unfortunately, that date does not reflect the STURP observations on the linen-production technology and the chemistry of the fibers from the tape samples.

In many cases where questions arise, an appeal is made to "authority." There can be no question about the authority of the radiocarbon investigators; however, true scientists like to see all loose ends questioned and tested. Persons who object to having their results tested can not be considered to be rigorous scientists. Rigorous Scientific Method should be applied in an attempt to resolve the age questions.

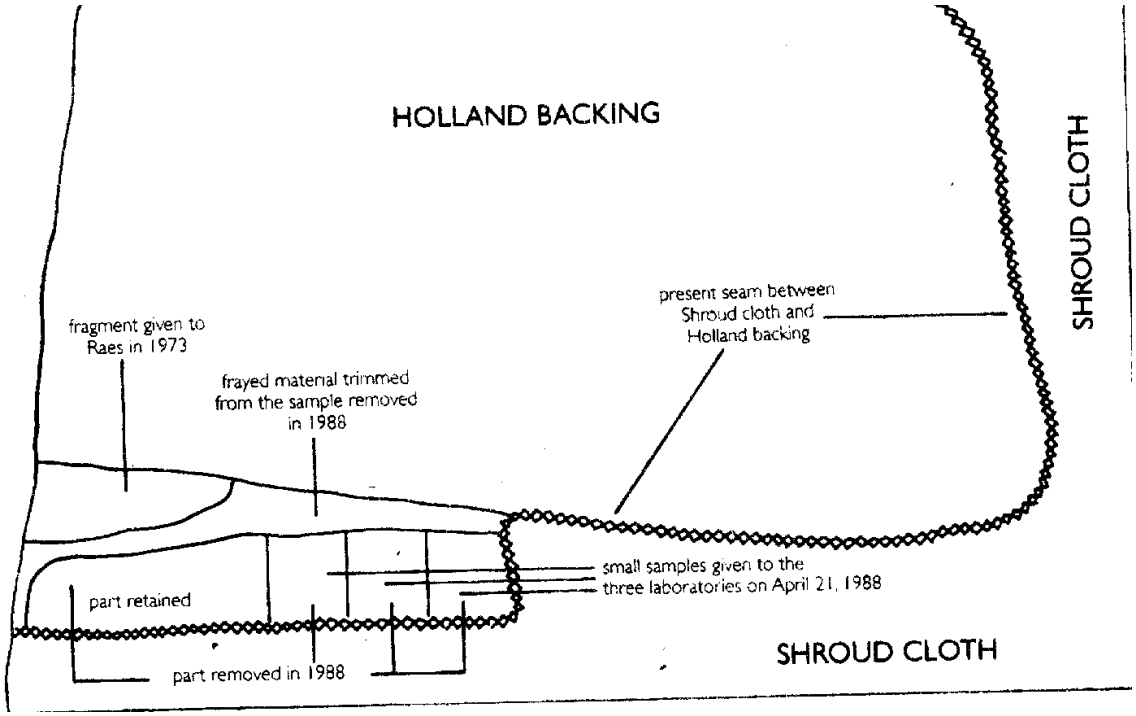

Figure 9: Locations of Raes and radiocarbon samples (bottom margin of cloth is to left). There should be compositional similarities between them. Retained samples should be studied by chemistry and microscopy.

The 1988 sampling operation was described as follows[21]: "The shroud was separated from the backing cloth along its bottom left-hand edge and a strip (~10 mm x 70 mm) was cut from just above the place where a sample was previously removed in 1973 for examination. The strip came from a single site on the main body of the shroud away from any patches or charred areas." The location of the sample is shown in figure 9.

Unfortunately, the sample was approved at the time of sampling by two textile experts, Franco Testore, professor of Textile Technology at the Turin Polytechnic, and Gabriel Vial, curator of the Ancient Textile Museum, Lyon, France. No chemical or microscopic investigations were made to characterize the sample. I believe that was a major disaster in the history of Shroud studies

Samples:
Professor Gilbert Raes of the Ghent Institute of Textile Technology cut a small sample from the cloth in 1973[17]. He found that the samples contained cotton, and he reported that the cotton was an ancient Near Eastern variety, *Gossypium herbaceum*, on the basis of the distance between reversals in the tape-shaped fibers (about eight per centimeter). I can not confirm the identification of the cotton variety; however, I can confirm the presence of cotton in the Raes sample. The cotton is important. Cotton was almost unknown in Europe until about AD 1350[9], when "there was widespread belief that it was the fleece of miniature sheep that lived in trees." Crusaders helped spread knowledge of cotton through Europe. There were still legal disputes over whether cotton was a kind of linen as late as AD 1631.

As part of The Shroud of Turin Research Project (STURP), I took adhesive-tape samples from all areas of the Shroud in 1978[4]. The tape was produced specifically for the project by Ronald Youngquist of the Minnesota Mining and Manufacturing Corporation. He used an amorphous, pure-hydrocarbon adhesive that would not contaminate the Shroud or the samples, and the adhesive could be removed by washing with xylene. The tapes were applied to the surface of the Shroud with a pressure-measuring applicator to enable semi-quantitative comparisons among samples. The Shroud was badly damaged in a church fire in AD 1532. Nuns patched burn holes and stitched the Shroud to a reinforcing cloth that is now known as the Holland cloth. I also sampled it in 1978. The Holland cloth provides an authentic, documented sample of Medieval linen.

In 1980, I received several threads from the 1973 textile sample[17] from Professor Luigi Gonella, Department of Physics, Turin Polytechnic. I now have them numbered and identified as the "Raes threads." I archived remaining tape samples, Holland cloth samples, and Raes threads after STURP disbanded. The samples are still available for independent scientific testing of the observations reported here.

Observations:
Visual comparisons among samples were made with a Zeiss petrographic microscope.

(A) Cotton is not evenly distributed throughout the cloth. Cotton fibers are easy to find mixed intimately with the linen fibers of all of the Raes threads. Figure 10 shows a heavily encrusted cotton fiber on the surface of one of the Raes threads. It can be identified by its flat, tape-like shape, the presence of one reversal, and the absence of the bamboo-like growth nodes of linen. When the cotton fiber was drawn out of the thread, it showed reversals about 1.2-mm apart. Cotton is not a simple surface contaminant: It occurs throughout the Raes threads. Fibers retained on the sampling tapes can be differentiated according to their relative indices of refraction compared with the index of the tape's adhesive. The two indices of cotton are close to that of the adhesive. Birefringence is first-order white. The index of linen across the fiber is appreciably lower than that of the adhesive.

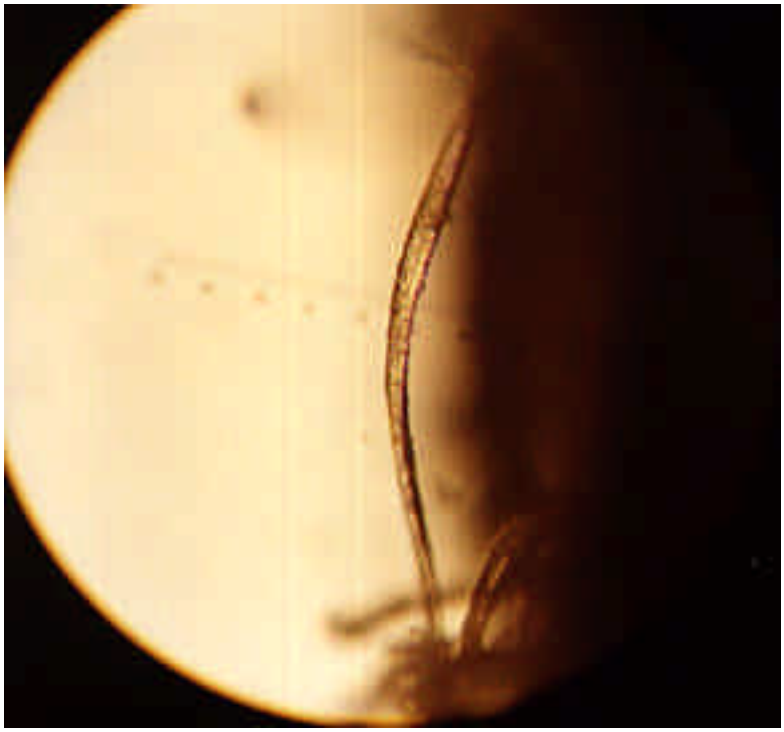

Figure 10: Heavily encrusted cotton fiber emerging from Raes #14 (400X).

I did not attempt to make a quantitative cotton comparison between Raes threads and Shroud tapes, because there was too little cotton of any kind on Shroud samples. We had been puzzled by the Raes report at the time of the 1978 STURP observations in Turin. We could not find more than traces of cotton on the cloth. The Shroud appeared to be pure linen. We used cotton gloves during the STURP studies of 1978 to protect the relic, and they could have been responsible for the traces of modern cotton found on a few Shroud sampling tapes. Samples from the main part of the cloth are significantly different from the Raes samples with regard to cotton content.

(B) Amounts of lignin differ between Raes samples and Shroud fibers. The linen fibers found on Shroud tapes average about 13-µm diameter, and they are round in cross-section. They show periodic growth nodes, and they look like microscopic lengths of bamboo. Figure 4 shows several linen fibers that were pulled from the image at the back of the ankle. It is a completely unpolarized photograph. There is no dichroism or birefringence color. These fibers are characteristic and representative of image fibers. There are dark deposits of lignin on most of the growth nodes. Absolutely no cotton could be found among the hundreds of fibers on this tape sample.

Very little lignin is visible at the linen growth nodes of the Raes and Holland cloth samples. Lignin is a dark, complex natural structural polymer that is found in all woody plants. Its composition and structure are specific to a given plant, but phenolic units are common to all lignins. It is not a polysaccharide (polymer composed of sugar units) like starch and cellulose. Linen is bleached to remove lignin; however, it is unusual to find a Shroud fiber without some significant deposits of lignin.

(C) Quantitative evaluation of lignin. Simple microscopic viewing is not sufficient to prove differences among the samples. In order to obtain quantitative data, I counted hundreds of growth nodes in each sample and noted which showed traces of lignin. The table shows that fibers from the Raes threads, Holland cloth, and modern linen show very little lignin at growth nodes, and the amounts of lignin in those samples are quite consistent.

SAMPLE	NODES WITH LIGNIN (%)
Modern Commercial	55, very light
Raes Threads	40, light
Holland cloth	60, light
Right Foot, Dorsal Image	54, heavy to moderate
Finger, Frontal Image	80, light
Ankle, Dorsal Image	100, heavy to moderate
Scorch control	39, heavy to moderate

Notice that the numbers refer to percentages not numbers of growth nodes observed. No samples of the Holland cloth or Raes threads had heavy deposits of lignin. Unlike the Raes and Holland cloth samples, the fibers on the Shroud tapes vary greatly in amounts of lignin. A large number of observations shows that lignin ranges from heavy to nil, depending on the location from which the sample was taken. There is an explanation for this observation.

(D) Lignin amounts vary among Shroud locations. X-ray-transmission[4,22], contrast-enhanced, ultraviolet[23], and transmitted-light photographs of the Shroud all show specific, discrete bands of yarn with different x-ray densities and corresponding color densities (figure 3). Both warp and weft yarns show this property. Some areas show darker warp yarns and some show darker weft yarns. In some places bands of darker color cross. In other places bands of lighter color cross. The effect is somewhat like a plaid. Many photographs of the Shroud can be viewed on the Shroud web site: http://www.shroud.com.

Linen is bleached to remove the lignin in an attempt to render it pure white. The more quantitative the bleaching process the whiter the product. The bands of different color on the Shroud are the result of different amounts of lignin left from the bleaching process. The tape samples reflect this variation as observed differences among quantitative measurements of lignin on the fibers.

A conservator at Turin's Museum of Egyptology, Anna Maria Donadoni[24], pointed out locations where batches of yarn ended in the weave and new yarn had been inserted in order to continue weaving. The yarn ends were laid side by side, and the weave was compressed with the comb. The ends are often visible, and the overlaps appear to correspond to zones of different color in the weave.

I believe that the observations of bands of different colors agree with Pliny the Elder's description of ancient linen-production technology[8]. Ancient linen yarn was spun by hand on a spindle whorl. When the spindle was full, the spinner prepared a hank of yarn for bleaching by the fuller. Each hank of yarn was bleached separately, and each was a little different; indeed, different parts of the same hank show slightly different colors, a little like variegated yarn. The warp yarn was protected with starch during the weaving process, making the cloth stiff. The final cloth was washed with "struthium," *Saponaria officinalis*, to make it more supple.

Medieval linen was bleached as the whole cloth. Most commercial bleaching took place in "bleach fields" in the Low Countries, the genesis of the name "Holland cloth" for the Medieval backing on the Shroud. Considerable material was lost during the bleaching process, and the newer linens are less dense than ancient linens, as can be seen by comparing the Holland cloth and patches with the main part of the Shroud. The newer linens are also homogeneous. They do not show bands of different-colored yarn in the weave.

A phloroglucinol-hydrochloric-acid reagent detects vanillin (4-hydroxy-2-methoxybenzaldehyde) with great sensitivity. Fresh lignin evolves vanillin in the reagent. You can often smell the vanillin that is evolved from the lignin of warm pine-tree bark. The lignin loses vanillin with time and temperature. The lignin on older samples of linen gives progressively weaker tests for vanillin as age increases. The lignin on Shroud samples does not give the test. That fact could indicate either significant age for the Shroud or accelerated aging of the lignin as a result of heating during the fire of AD 1532. Differences between amounts of lignin on linen fibers in the Raes samples and on Shroud fibers are significant. There is probably a similar difference between the radiocarbon samples and the main part of the Shroud.

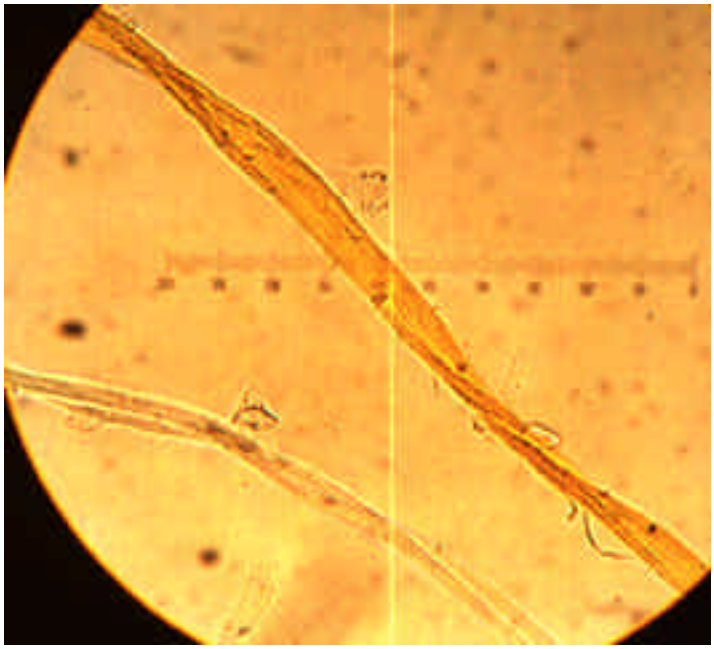

Figure 11: Two cotton fibers (X400) from a Raes thread, one nearly colorless from inside and one encrusted and red from outside.

(E) Raes threads show a yellow-brown coating. All Raes threads show colored encrustations on their surfaces. Some sections of medulla contain some of the material, showing that it had been able to flow by capillary attraction as a liquid. The encrustation is not removed by nonpolar solvents, but it swells and dissolves in water. There was absolutely no encrustation on either the Holland cloth or fibers from the main part of the Shroud (figure 4). The encrustation is unique to the Raes samples. Any retained samples of the material dated in 1988 should be tested for this encrustation.

Figure 11 shows two cotton fibers from Raes thread #5. One of the fibers was taken from inside the thread, and it is nearly colorless. The other fiber was taken from just under the outer surface of the thread, it is deeply colored, and it shows gelatinous material adhering to its surface. A marked difference between inside and outside fibers is characteristic of Raes samples.

The outside of Raes thread #14 showed the heaviest encrustation and deepest color of any of the samples. The encrustation is heaviest on cotton fibers, it is the vehicle for the yellow-brown color, and it suggests that the cotton was added to enable better control of dyeing or staining operations. When I teased threads open at both ends with a dissecting needle, the cores appeared to be nearly colorless. This observation suggests that the color and its vehicle were added by wiping a viscous liquid on the outside of the yarn in order to match the color of new material to the old, sepia color of the Shroud. The yellow-brown encrustation shown in figure 12 swelled and became more transparent as it soaked.

Figure 12: Heavily encrusted fibers from the outside of Raes #14 (400X) mounted in water

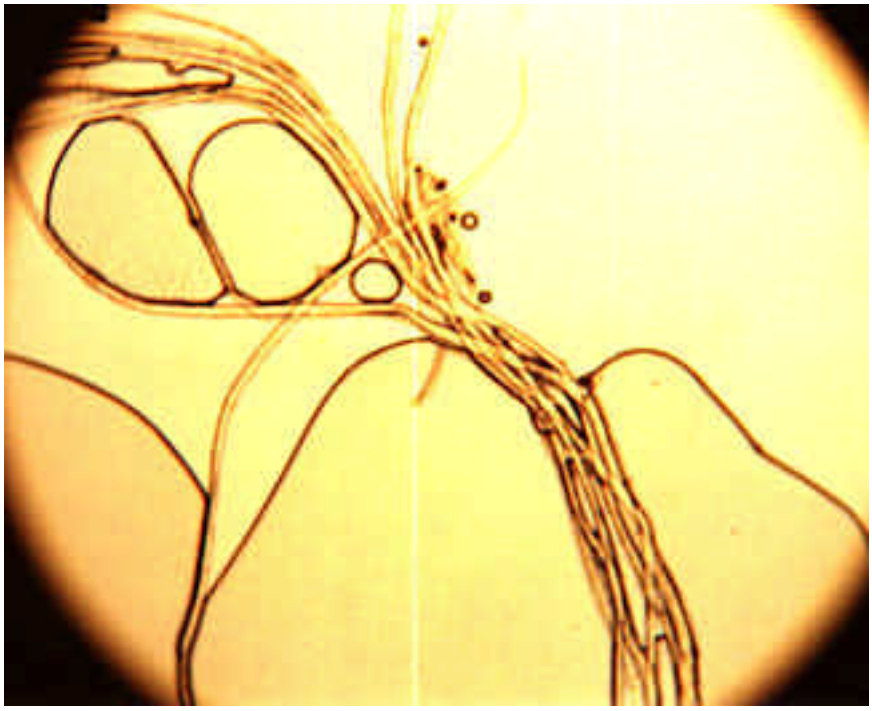

Figure 13: The same fibers shown in figure 12 mounted in 6N HCl. Notice the bright yellow color

The color instantly changed to bright yellow in 6N hydrochloric acid (HCl), and the coating was reduced in density as the fibers were soaked in the acid (figure 13). The natural dye extracted from Madder roots was important in the Near East for thousands of years. It appeared in Italy about the time of the last Crusade, but it was not until the 16th Century that it appeared in France and England. The first European book on dyeing was published in AD 1429[9].

Spots of colored dye on a mordant are called "lakes." Bright red lakes of dye were found on many of the most-colored Raes fibers, indicating that at least some Madder root dye was used and that some of the color appeared on a hydrous-aluminum-oxide mordant. Some purpurin appears in Madder root extract, and it reacts much the same as alizarin. Hydrous aluminum oxide is instantly soluble in 6N HCl, and alizarin is bright yellow in acid (figure 13).

Alizarin is used as an acid-base (pH) indicator in chemical analysis. It is yellow below a pH of 5.6 and red above a pH of 7.2 (figure 14), changing to purple above 11.0 (figure 15). This agrees with observations on the coating. Madder root dye is a highly probable contributor to the color of the coating. No dye could be detected on any image fibers.

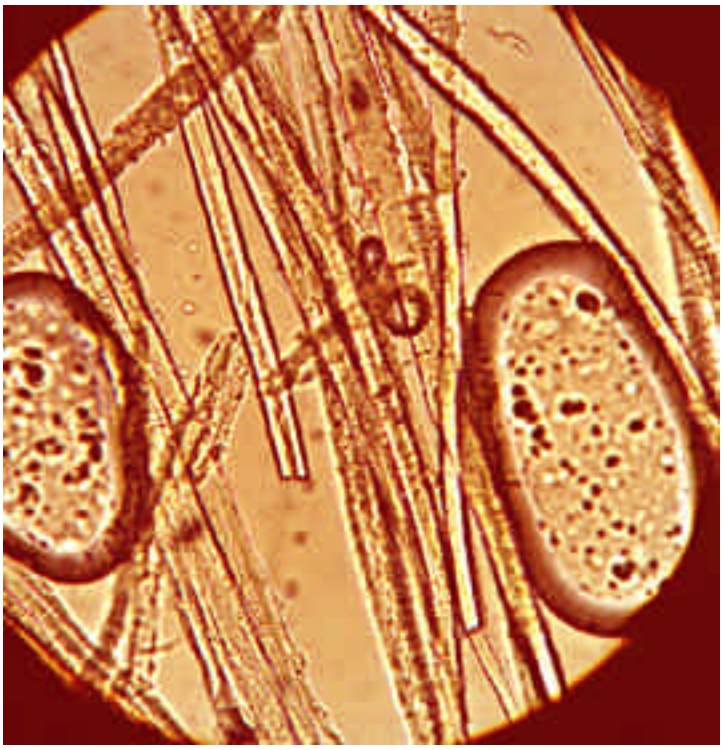

Figure 14: Surface fibers from Raes #14 reddened in NaHCO3 at a pH of 8.0

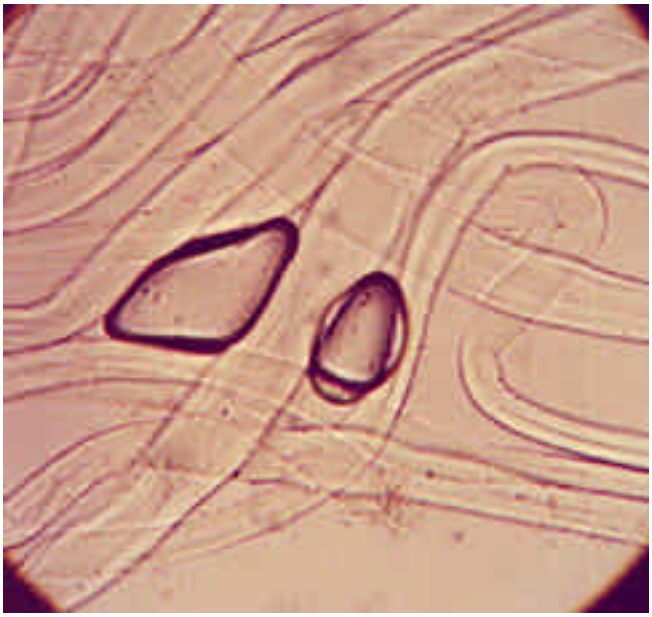

Figure 15: Surface fibers from Raes #14 turned purple by soaking in a high-pH medium, 2N NaOH

The color changes of the dye in the gum coating do not provide a definitive proof that it is alizarin/purpurin. Many dyes show similar color changes with pH, and this observation should be confirmed with spectrophotometry and additional chemical tests. The barrier to confirmation at present is the critical lack of samples. The samples that can be sacrificed weigh micrograms, and the dye probably weighed no more than nanograms. Confirmation may be difficult; however, the important point is that a dye similar to alizarin had been added to the gum coating on the Raes samples. They were colored for a purpose using technology that was not used in Italy before the 13th Century or in France before the 16th Century, about the time the time the Shroud was moved to Turin from France.. The gum coating is not biogenic.

Other mordants produce different colors with Madder, including blues with calcium compounds. A few blue lakes can be seen on Raes fibers. The color suggests traces of alizarin on crystals of calcite in the threads. They are all removed by 6N HCl. A mixture of mordants with alizarin and purpurin can produce almost any desired shade of yellow or brown. In agreement with observations on the individual threads, I could not detect any significant amount of dye on fibers from the insides of threads.

The gummy coating was totally hydrolyzed by concentrated HCl and 2N NaOH. That fact and its solubility in water suggest that it is probably a polysaccharide and not a denatured protein. The fact that some hydrolyzed in 6N HCl suggests that it is probably a polypentose, composed of five-carbon sugar units. However, not all of the polysaccharides on the fibers were removed by concentrated HCl. Higher-molecular-weight starch fractions are much more difficult to hydrolyze than are polypentose-containing plant gums. Some starch could be detected on HCl-cleaned Raes fibers with an aqueous iodine reagent.

I arranged two heavily-encrusted fibers from the outer surface of Raes #5 across each other and covered them with a cover slip. The dry fibers were nearly opaque as a result of the coating. I then ran aqueous iodine solution under the cover slip by capillary flow. The iodine quickly turned the coating bright yellow, indicating a plant gum. The coating swelled and partially dissolved in the water. I let the water and iodine evaporate overnight. The redeposited, colorless, gelatinous material is clearly visible along the fibers in figure 16. The iodine was in simple solution in the gum. It did not produce the yellow color by iodination or iodine-catalyzed dehydration reactions. The horizontal cotton fiber in figure 16 shows a deep-red coloration. When tested with iodine, normal soluble starch turns blue. Starch that is soluble only in hot water turns red. The higher-molecular-weight, hot-water-soluble starch is the last to wash out of a cloth.

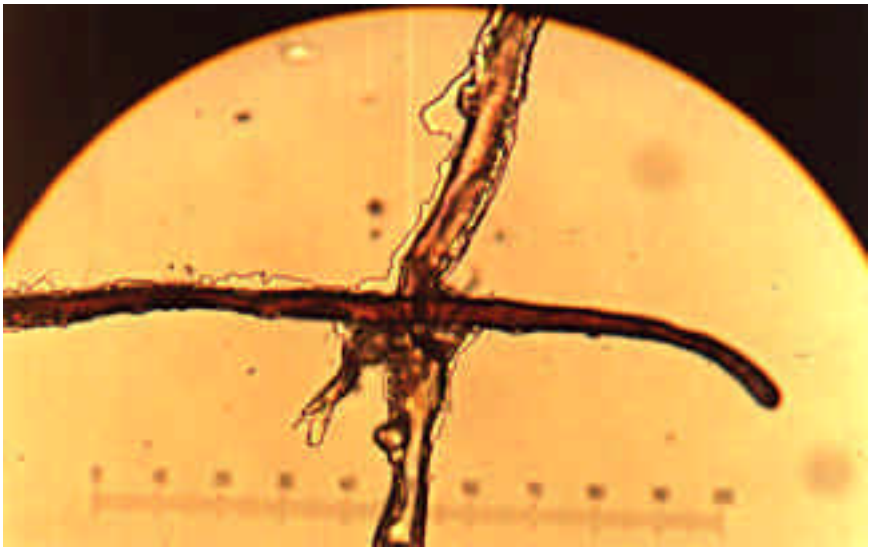

Figure 16: Encrusted cotton fibers from the outer surface of Raes sample #5 (400X) after treatment with aqueous iodine and drying

The encrustation on Raes samples is almost certainly a plant gum. The gum does not appear on any of the other linen samples that are associated with the Shroud of Turin. It is highly probable that the alizarin-dyed, gum-coated yarns extend into the adjoining radiocarbon samples.

L. A. Garza-Valdes was allowed to observe fibers from a part of the radiocarbon sample that had been retained by Giovanni Riggi di Numana after the sampling operation. He reported seeing a coating on the fibers[25]. Although he has misinterpreted the coating, his observations increase the probability that the radiocarbon sample has properties identical to those of the adjoining Raes sample. The gum is probably the same age as the Raes threads, and it should have had no effect on the age determination. In any case, it would also have been removed by the cleaning procedures used on the dating sample. However, the presence of a gum coating on retained 1988 radiocarbon-dating samples would prove that the samples were not representative of the main part of the relic's cloth. Such a lack of association would prove that the radiocarbon date is invalid.

The relatively easy water solubility and hydrolysis of the encrustation suggests gum Arabic. It is obtained from *Acacia senegal*, and it is mostly composed of pentose-sugar units. It turns bright yellow in aqueous iodine, as observed on the Raes threads. Gum Arabic has been used for thousands of years, and it is still used in inks, textile printing, and the adhesive on postage stamps.

Figure 17: Raes thread #1 showing an end-to-end splice.
The two ends show different colors and amounts of coating.

(F) The Raes samples show a unique splice. Raes thread #1 (figure 17) shows distinct encrustation and color on one end, but the other end is nearly white. The photograph was taken on a 50% gray card for color comparison. Fibers have popped out of the central part of the thread, and the fibers from the two ends point in opposite directions. This section of yarn is obviously an end-to-end splice of two different batches of yarn. No splices of this type were observed in the main part of the Shroud.

(G) Other observational methods show anomalies in the ^{14}C sample area. The specific area where the radiocarbon sample was obtained was photographed in 1978 with low-energy x rays at high resolution[4,22], a pure ultraviolet source[23], and by transmitted 3200°K illumination. All of these photographs were available before the Shroud was sampled for radiocarbon analyses. I believe that the sampling area was one of the worst that could have been chosen.

While making the UV photographs (figure 18), the source was heavily filtered to exclude visible light and the camera was heavily filtered to exclude any effect of the UV on the film. All that appears on the film is the result of pure fluorescence. The small, triangular,white area in the lower left quadrant is the place where the Raes sample was cut in 1973. The normal non-image cloth shows weak fluorescence (upper right). When image appears on the cloth (figure 3), it quenches the fluorescence and gives it a brown color.

Figure 18: UV fluorescence photograph of the 14C sample area. The small, white area is the location of the Raes sample, which adjoins the radiocarbon sample. © 1978 Vernon D. Miller

Figure 19: Transmitted-light photograph of the same area. © 1978 Barrie M. Schwortz

The radiocarbon sample area (figure 9) is darker than normal, a fact that is not the result of image color or scorching. The cloth is much less fluorescent in that area, brightening into more normal fluorescence to the right. The photograph proves that the radiocarbon area has a different chemical composition than the main part of the cloth, and it is truly anomalous.

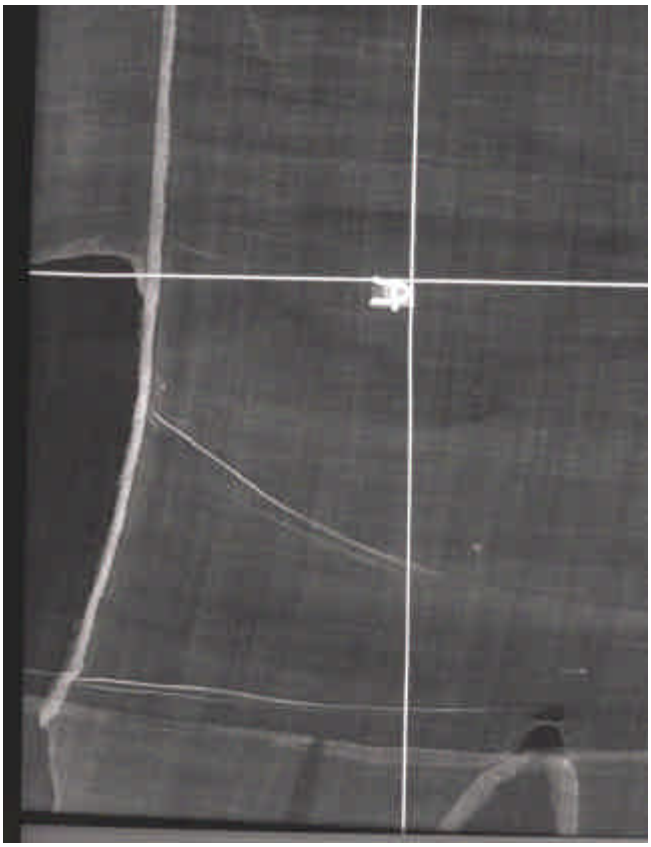

Figure 20: Low-energy, high-resolution x-ray photograph of the radiocarbon-sample area

The transmitted-light photograph (figure 19) shows that the area below the top crease has a different pattern of light and dark bands than the area above the crease. Some vertical bands appear to change in intensity or stop at the horizontal dark band that intersects the top crease. Such an observation would support the hypothesis that some foreign yarns had been woven into the cloth in that location.

The Shroud is dense, making it appear much darker than the Holland cloth. The low-energy, high-resolution x-ray transmission photograph (figure 20) was made in 1978, ten years before the radiocarbon sample was cut. It shows areas of higher density as light-gray streaks. The "banded" characteristic of the cloth is easy to see; however, some bands do not extend from the main part of the cloth into the radiocarbon-sample area: There is a different "plaid" pattern in that area. Area 1 is the Raes sample. The radiocarbon sample was cut from between the Raes sample and the upper double crease (figure 9). Both creases are double on the x ray, because they appear in both the Shroud and Holland cloth; i.e., they formed after the fire of AD 1532. Area 2 was cut off long ago as a "souvenir," and it shows only the Holland cloth backing (low-density, black with no banding). Lines a, b, and c are continuous bands of different density that extend across the cloth. The radiocarbon area shows anomalous banding.

Conclusion on the association between the radiocarbon date and the time at which the Shroud was produced: The combined evidence from chemistry, cotton content, technology, photography, and residual lignin proves that the material of the main part of the Shroud is significantly different from the

radiocarbon sampling area. The validity of the radiocarbon sample must be questioned with regard to dating the production of the main part of the cloth. A rigorous application of Scientific Method would demand a confirmation of the date with a better selection of samples.

II. Pseudoscience

The radiocarbon age determination has led to the formulation of many embarrassing "theories" (really hypotheses) simultaneously to explain both image formation and the unexpected age. Most of these have involved some form of "radiation," and most require a miracle to produce it. Most of the hypotheses about the date and image have had a theological basis, and most such pseudoscience hypotheses claim that "this is the only way it could have happened." They then tend to try to work from the postulated indispensable radiation to a proof of the Biblical resurrection. Goal-directed "theories" and pseudoscience have badly damaged the credibility of rigorous scientific studies on the Shroud of Turin.

Lateral Neural Inhibition

Many observers look at the image for such a long time that they begin to see things that others do not. The phenomenon is responsible for our ability to see figures in clouds. Also, the very faint image is impossible to see at close range. It was difficult to locate desired sampling locations. It is easy to see at a distance of four or five meters (something over 10 feet).

Physiologically, the effect is explained in terms of "lateral neural inhibition": the human eye enhances edge contrasts. The mind plays games with what we think we see. Some devoted observers see images of flowers, teeth, bones, etc. on the Shroud. A statement like "I think I see" is totally unacceptable in a scientific discussion.

Unlikely forms of energy

Some phenomena have been postulated without discussion. I have seen invocations of light, ultraviolet radiation, soft x rays, protons and other ionizing particles, neutrons, and "other perhaps not discovered forms of energy." One hypothesis invoked, "axions resonating in the cavity of the tomb" as an explanation for image formation, and the person had actually purchased an "axion generator" from Russia.

Scientists at the Livermore National Laboratory, MIT, the Lawrence Berkeley Laboratory, and Fermilab are currently working very hard just to detect axions, a very hard, expensive task. The *axion* is an hypothetical elementary particle proposed to explain the absence of an electrical dipole moment for the neutron. It has no electric charge, no spin, and would hardly interact with ordinary matter (electrons, photons, quarks, etc.) at all. It would be very unlikely to cause any chemical effects. Even though the axion -- if it exists -- should have only a tiny mass, axions would theoretically have been produced abundantly in the Big Bang, and relic axions are a possible candidate for the dark matter in the universe. That is the reason they are being studied. They are not even a remote candidate for image production.

Goal-directed pseudoscience

An outstanding example of goal-directed pseudoscience is Antonacci's "Historically Consistent Method[26]." He claims that it "was developed by combining research from scientists throughout the world on all aspects of the body images and blood marks on the Shroud…*This theory (sic) states that if a body instantaneously dematerialized or disappeared, particle radiation would be given off naturally and all the unique features found on the Shroud's body images a nd blood marks would occur"* (emphasis added).

The energy of nuclear weapons is based on the fact that $E = mc^2$; therefore, one bothersome problem with Antonacci's "theory" is that complete conversion of the mass of a normal human body into energy would have the effect of a huge H bomb, on the order of 200-300 *megatons* of TNT. That would have

vaporized a significant fraction of the Holy Land. Antonacci has done severe damage to the credibility of studies on the Shroud.

Failure to test an hypothesis against all data.

A failure to test against all observations can lead to a logically consistent but unsupportable superstructure. For example, L. A. Garza-Valdes and S. J. Mattingly have proposed an hypothesis that a "bioplastic" coating on the Shroud contributed to both the "error" in the ^{14}C analysis and image formation[25,27]. Basing their conclusions on textiles other than the Shroud (e.g., mummy wrappings), they state that[25], "Such coatings have not been previously observed nor confirmed by other investigators," and "Several threads from a putative sample of the linen from the Turin Shroud were examined for the presence of these deposits."

Mummy wrappings have experienced a very different environment than has the Shroud. Mummification technology varied with both time and location; however, the wrappings would have been subjected to a significant amount of protein decomposition products. Color-producing reactions between carbohydrates and proteins and their decomposition products are called Maillard reactions, and they will be discussed in a separate section.

The examination of "the putative" sample from the Shroud was made by Garza-Valdes on the residue from the radiocarbon sample that had been retained by Giovanni Riggi in Turin[28]. Garza-Valdes has not had access to any other samples. On the basis of his observations, he has jumped to the conclusion that "…the individual fibers of the cloth are surrounded by a bioplastic coating." However, the first paper reported that[25]: "It should be noted, however, that the amount of organic contamination to produce such a major change in age is considerable." An addition of about 30% modern carbon would be required to give the error in the age, and more would be required with older contamination. If the effect were integrated over the entire history of the Shroud, a huge "bioplastic" coating would be required.

There are four serious problems with the hypothesis: 1) any organic carbon added must be fairly modern and rich in ^{14}C (it can not be derived from organisms that metabolized original Shroud carbohydrates as the source of their carbon, e.g., fungi); 2) the amount of modern carbon added must be large; 3) several different analytical methods have failed to detect any of the elements other than C, H, and O that are necessary for the growth of organisms, and 4) Madder root dye was identified in the coating on the Raes samples. Some microorganisms do produce large amounts of "extracellular polymeric substances" (EPS) when they are stressed. The EPS are nearly pure polysaccharides. The "bioplastic hypothesis" is perfectly logical, and it can be tested against the wealth of observations that have been made on the Shroud. No such tests were made. Mattingly was so certain of his conclusions that he actually stated: "...the Turin Shroud is completely coated with both live and dead microorganisms. It is not necessary to examine the Shroud linen to make this observation." Rigorous Scientific Method was not applied.

Although they commented on amounts required to change the Shroud's age, Garza-Valdes and Mattingly propose that carbon from times more recent than the 1st Century was added to the Shroud as a product of microbiological action. In order to add more-modern carbon to the cloth, the organisms must fix carbon from the atmosphere (^{14}C is continually replenished by nuclear reactions in the upper atmosphere). In order to grow, they need water and nutrients, e.g., nitrogen, phosphate, sulfur, and trace elements. The elements other than C, H, and O in biopolymers can be detected with great sensitivity.

The Shroud has always been stored dry, and it has usually been stored out of direct light in some kind of closed container, minimizing both the photosynthetic processes that fix carbon dioxide and free access to CO_2.

The STURP tests were planned to test whether anything had been added to the cloth, and observations looked for organic pigments and painting media as well as inorganic pigments. Nothing other than dehydrated carbohydrate could be found in the image area. In addition to sensitive instrumental analytical tests, A. Adler, J. Rogers, and R. Rogers[4,16] spent many hours looking at samples from the

image, blood flows, non-image surface, and scorches under microscopes and running microchemical spot tests. There were no anomalous indices of refraction or impurities. There were no amorphous materials cementing fibers together, except for the blood/serum and some starch and gum on threads from the Raes samples.

Without chemical testing, the alizarin-dyed gum on the Raes sample could easily be mistaken for EPS. The misidentification of the coating and failure to analyze it are probably the source for the Garza-Valdes/Mattingly hypothesis.

Several different, sensitive microchemical tests were used in attempts to detect proteins in the image[16]. Proteins could suggest either protein-containing painting media or bioplastic polymers. Proteins could easily be detected in blood areas. Tests with iodine-azide reagent proved that there were no sulfur compounds on the surface (except in the blood/serum areas). I am not aware of any "bioplastic polymers" that are absolutely devoid of amino acids (proteins) and sulfoproteins.

As scientists, Garza-Valdes and Mattingly should have addressed the detailed analyses that were done during and after the 1978 observations. They did not do any chemical analyses on samples from the main part of the cloth. Mattingly was sent some fibers from the Raes sample by Alan D. Adler, but when questioned about them, he told me that[28]: "I never even looked in the microscope or even handled the thread…I give Garza-Valdes full credit for his hypothesis about the 'bioplastic coating.' It makes perfect sense to microbiologists. Anything with a surface exposure will be coated with microorganisms. I do not even need to see an object to draw that conclusion." Good science requires observations.

In 2001, Mattingly extended the "bioplastic hypothesis" to the problem of image formation[27]. Recognizing that yellow fibers form the image, he said that: "The most readily oxidizable organic materials that contribute to a yellowing appearance are lipids (fatty acids) and some *pigments* (emphasis added) that are susceptible to oxidation by molecular oxygen."

The atmosphere is the source for "modern," ^{14}C-containing carbon. The addition of modern carbon is the only way to decrease the apparent age of ancient carbon-containing materials. The most important organisms that fix CO_2 from the atmosphere are photosynthetic. This is undoubtedly the reason Mattingly mentioned "pigments." Many intensely colored pigments appear in photosynthetic organisms.
The final products of photosynthesis are sugars, polysaccharides, nucleic acids, proteins, pigments, etc. Nature builds flax (linen), trees, grass, and little colored microorganisms by photosynthesis. All of the ^{14}C in our bodies comes originally from photosynthetic processes. The pigments that the photosynthetic organisms use can be detected with great sensitivity by spectrophotometry, STURP used two different systems[12,13], and we did not detect any photosynthetic pigments. If Garza-Valdes and Mattingly had tested the coating, they could have found the alizarin in it. The Method of Multiple Working Hypotheses would have helped avoid error. Alizarin is definitely not one of the pigments produced by microorganisms. Any gum coating that contains alizarin is definitely not a "bioplastic polymer."

Many of the pigments, e.g., porphyrins and carotenoids, are extremely stable. I have observed several in the 11,300-year-old sediments at the site of a mammoth kill in Southern Arizona. If they formed on the Shroud, they would still be there. If the organisms involved in biopolymer production (like fungi) used only the carbohydrates in the Shroud for their metabolic purposes, the biopolymer product would show the same carbon age as the Shroud. The organisms would use fixed carbon (i.e., the sugar units of cellulose) and yield carbon dioxide and cell components. Only part of the metabolized carbon could end up in an EPS layer, and the cloth would tend to disappear much faster than the polymer appeared. Cloth does rot.

All "both live and dead microorganisms" contain proteins, amino acids, and nucleic acids. Algal cells contain 3.9% nitrogen and 3.3% phosphorus. Fungal cells contain about 0.9% phosphorus and 2.9% nitrogen. Compounds containing these elements can be detected by several of the analytical methods we applied. All cells of microorganisms give protein microchemical spot tests.

If there are no detectable amounts of cell components on the Shroud, there can not be much "biopolymer." The color of the image is indeed a result of a thin coating. "Thin" is the important word. Surface cracking ("corrosion" as Adler called it) of the color can be seen, and flakes can be seen in the "ghosts" on the sampling tapes (figure 5). It takes a thickness on the order of a wavelength of light to get an observable change in index of refraction, and observed indices of an image fiber are identical to those of a fiber from the Holland cloth or modern linen. The image-color coating seems to be amorphous, but I have been unable to measure its index. I have been able to measure the index of the gum coating on the Raes sample. The thickness of the image color must be less than a sodium-D wavelength (589 nanometers). Assuming that the image coating could be as thick as 600 nanometers, a 20-÷m-diameter fiber (unusually large) would be less than 1% coating by volume. This is certainly not enough material, even if modern, to cause a significant decrease in the apparent age of the Shroud.

The coating on the Raes samples can easily be observed with a normal light microscope with sodium-D light; however, it can easily be missed when normal procedures are followed. The usual immersion oil used by microscopists has an index of 1.515, because a normal microscope slide is made of crown glass with an index of 1.517 at 589 nanometers. The index of the coating on the Raes samples varies a little, but it is very close to 1.515: It can be completely invisible on a normally prepared slide. Water with an index of 1.33 can not be used as an immersion liquid to enhance contrast, because the coating swells and dissolves. Erroneous measurements will result.

The thickness of the coating on the Raes yarn varies greatly. Cotton fibers tend to have much thicker coatings than linen fibers; however, I would guess that the coating does not average more than about 2 µm thick. It would contribute only a few percent to the weight of the Shroud. That would not produce a significant error in the age determination. In any case, the gum would have been removed by the methods used to clean and prepare the radiocarbon samples for analysis.

I believe that the "bioplastic hypothesis" can easily be disproved. The most probable misunderstanding/misidentification that generated the hypothesis was the presence of the gum-dye coating that is unique to the area of the Raes and radiocarbon samples. This coating was probably mistaken for a "bioplastic coating." Unfortunately, the hypothesis was developed without a rigorous application of Scientific Method.

Conclusion:
I would like to urge persons tempted to call on "science" to prove their point to please use complete, rigorous science. Anything less is scientifically embarrassing and counterproductive to Shroud studies. One recent paper states: "There is a problem with scientists when a non-scientifically explainable phenomenon arises, namely the Resurrection of Jesus Christ." I contend that it is not a problem with scientists. The main problem is the prostitution of science. Science is based on observations of nature: Religions are "revealed."

TEST AND CONFIRM

A large number of attempts have been made to reproduce the image by different methods, and many "theories" (hypotheses) have been proposed. Some of the proposals have actually involved natural processes such as the "vaporographic" theory of Vignon. Some have been far removed from known reality; e.g., postulating that the image results from "… a burst of energy that can be wide-range-light, UV, soft x-rays or other *(perhaps not discovered for now)* [emphasis added] that came from within the corpse." All have failed when compared with observations and measurements on the Shroud.

Attempts to reproduce the image.

(1) Pellicori of STURP studied contact and material-transfer hypotheses[13], and no image-formation hypothesis that is based solely on a vapor-diffusion and/or material-transfer mechanism can be accepted. Vapors and liquids penetrate the cloth: materials that will color the surface will also diffuse into and color the inside of the cloth.

(2) Image-formation hypotheses that are based solely on any kind of electromagnetic energy must also be ruled out. I have already discussed the Lambert/Bouguer law with regard to intensity versus penetration; however, radiant energy either ablates the surface of a cloth subjected to an intense pulse of energetic photons or; delivered more slowly, it colors the entire facing surface (not just the highest parts). A "flash-of-light" hypothesis had been proposed before the STURP study, but it keeps reappearing[26]. We tested the hypothesis with different-length bursts of laser radiation at different wavelengths. Long-wave radiation was not sufficiently energetic directly to produce a color (why they put red screens inside clothing-shop windows). Lower-energy photons can not directly induce dehydration. In order to do that, the energy of a photon must be higher than the bond energy of a -OH bond. Indirect dehydration is caused by radiant heating the material above the temperature at which the dehydration reaction occurs rapidly. That is a relatively slow process. Very intense, 50-ns-long bursts of UV ablated the cloth surface, and the samples were reduced to a cloud of very fine particles. We could not get a color with a "flash of light."

(3) Hypotheses based on ionizing and/or non-ionizing particles suffer from the same problem as photon-energy transfer: The entire facing surface is colored. Image color appears on the Shroud only at the highest parts of the weave. Rinaudo's photographs[18] (e.g., figure 21) compared with Evans' photographs[7] (figure 22) illustrate the difference. Rinaudo claims that his sample is "…very similar to body image on the Shroud photographed by Vernon Miller." It is not. The entire surface is colored. Rinaudo did not make a rigorous attempt to test his hypothesis.

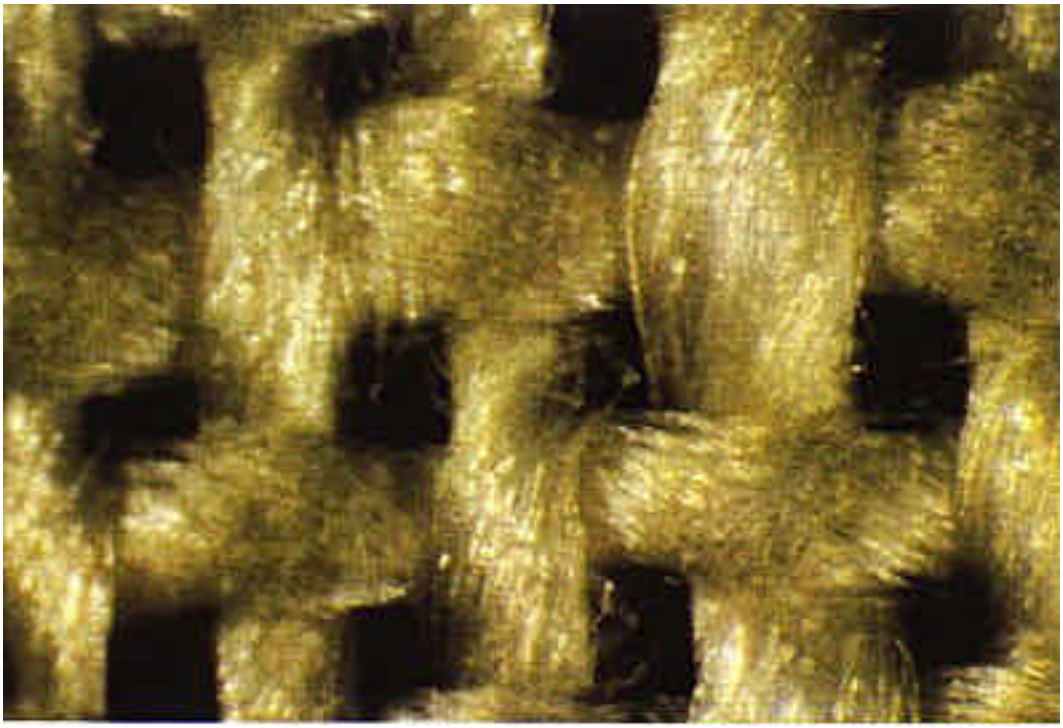

Figure 21: Rinaudo's proton-irradiated linen

Figure 22: Dark image at bridge of nose on the Shroud. © 1978 Mark Evans

(4) Scorching by contact with hot irons, statues, etc., must be ruled out, because heat flow by conduction penetrates a cloth. Different colors can be seen as a function of the depth into the cloth, and fibers are colored through their entire diameter. The medullas of scorched fibers are colored. The Shroud image is entirely different. If a scorching event involves confinement, as with a hot iron, the scorch is fluorescent. The image does not fluoresce.

(5) The flame from a very high-temperature torch can be used to "paint" an image, and the scorching event is open to the air. The scorch does not fluoresce. The flame is repelled from the surface of a cloth by the ablation of the material, and the color does not penetrate very far. However, all fibers that were pointing upward in the nap of the cloth are burned by the flame, and individual fibers are colored all the way through.

(6) A corona discharge charges the surface of an insulator like dry linen, and maximum charge concentrations are observed at points. These charges repel electrons; therefore, upward-pointing fiber ends would not char. I could not produce any colors by this method.

Requirements for a logical hypothesis:

A logical hypothesis for image formation must accept the laws of physics and chemistry and explain all of the STURP observations, as follows:
1) No added material scorched in image areas or was rendered soluble.
2) Direct microscopy showed that the image resided only on the topmost fibers at the highest parts of the weave.
3) The color density of the image depends on the batch of yarn that was used in its weave.
4) Adhesive-tape samples show that the image is a result of concentrations of yellow fibers.
5) The color of image fibers was often stripped off of their surfaces, leaving colorless cellulose fibers. The color resides only on the surface of the fibers.
6) Reflectance spectra and x-ray fluorescence show that the image is not painted with any of the expected pigments, including iron oxides.

7) The image spectra were essentially identical to those from aged linen and light scorches. The structures of all forms of dehydrated carbohydrates would be very similar, containing complex systems of conjugated double carbon bonds. Cellulose is not unique.
8) Chemical tests showed that there is no protein painting medium or protein-containing coating in image areas.
9) The color can be reduced with diimide, leaving colorless cellulose fibers. The color resides only on the surface of the fibers, and it is the result of conjugated double bonds.
10) The image of the back side of the body shows the same color density and distribution as the front.
11) The image does not fluoresce, although scorch margins from the fire of AD 1532 do fluoresce.
12) Microchemical tests with iodine indicated the presence of some starch fractions on the cloth.
13) The medullas of colored image fibers are not colored: *The cellulose was not involved in the color-producing chemistry of the image.*

The requirements make it apparent that no single, simple hypothesis will be adequate to explain all of the observations made on the Shroud.

Hypothesize: A complex, natural hypothesis for image formation.

The fact that the color resides only on the fiber surfaces leads to the hypothesis that the color formed as a result of chemical reactions involving impurities on the surface. The spectra strongly suggest that the impurities were carbohydrates that dehydrated as a result of the image-formation process. The hypothesis on carbohydrate impurities is supported by observations of traces of some starch fractions on image fibers.

No protein impurities were found in image areas. Although scorch fibers show darkened medullas, the cellulose of image fibers was not colored. This proves that any impurities that produced the color had to have undergone low-temperature chemical reactions.

Cellulose dehydration follows known chemical rate laws. Cellulose is a very large polymeric chain made from glucose (sugar) units that are linked glycosidically. The glucose units exist in the "pyranose" form, rings containing five carbon atoms and one oxygen atom. Pyranose structures appear to be much more stable than are the other common sugar structure, furanose rings. Pyranose systems seem to have an activation energy for dehydration of about 27 kcal/mole, while furanose systems seem to be much less stable with an activation energy of about 19 kcal/mole[11]. Because chemical rates are exponential with temperature, cellulose would react much more slowly than other carbohydrates.

In developing an hypothesis, I had to search for low-temperature chemical processes that produced the observed type of color. The processes had to involve only impurities and reactants that were either detected on the cloth or could logically be expected from the history of linen technology[8,9] before about the 16th Century.

The bleaching methods used after about AD 1200 made it difficult to identify probable carbohydrate impurities; however, Pliny the Elder's history[8] suggested that we could expect traces of all of the carbohydrates that are found in crude starch. In addition, we might expect traces of the glycoside sugars from *S. officinalis* [10] (e.g., galactose, glucose, arabinose, xylose, fucose, rhamnose, and glucuronic acid). Dehydration-rate calculations made direct dehydration of any carbohydrate impurities, even pentose sugars, seem very unlikely. Temperatures on the order of 100°C would be required to give a color in any reasonable amount of time.

A person hoaxing the Shroud image could not have lived long enough to produce a room-temperature image. Using a cloth washed in a low-surface-tension solution containing pentose sugars (e.g., a *Saponaria* solution) and dried in the sun, a non-metallic statue at a temperature above 100°C might have worked. Such an hypothesis could and should be tested; however, using Occam's Razor, another hypothesis seemed more probable.

Maillard reactions30,31] are extremely complex, fast, color-producing reactions that involve several reaction paths and products. Starting with a complex mixture of carbohydrates, there could be thousands of products. Just one example of a product, the most intensely colored from reactions between xylose and L-alanine, is shown in figure 23[32].

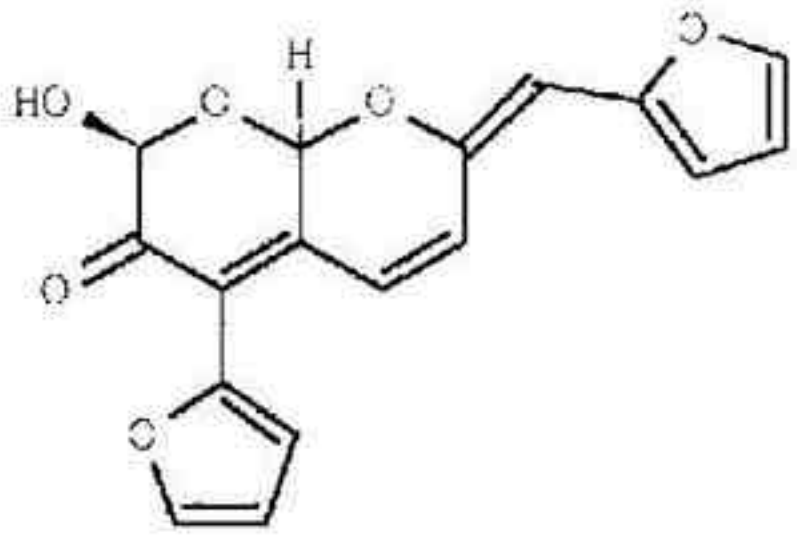

Figure 23: Example of an intensely colored Maillard reaction product.
The color is a result of conjugated double bonds.
The product does not contain any nitrogen.

A fascinating requirement for an hypothesis involving Maillard reactions is that amino groups ($-NH_2$) are needed to react with the carbohydrates. The potential source of amines involves support for the hypothesis that the Shroud is a real shroud. The Maillard Reactions are some of the most studied reactions in food chemistry[30,31]. They involve the condensation of amino groups (the -NH2 groups in amines, proteins, peptides, etc.) with reducing sugars and reducing polysaccharides such as some starch fractions. All reducing sugars and polysaccharides take part in the reactions. The reactions occur at significant rates at much lower temperatures than the caramelization (dehydration) of any of the sugars.

A good example of Maillard reactions is the production of dark beers at low temperatures by reactions between maltose and any reducing starch components and the proteins or amino acids in the wort. Cheaper beers may be colored more rapidly by accelerating Maillard reactions by heating the wort with ammonia. The first steps of the Maillard reactions are rather fast at normal temperatures, and they produce colorless compounds (for examples glycosylated-proteins). The rates are even higher at body temperatures; however, they increase by factors between two and three for each 10°C (18°F) increase in temperature. The colorless compounds are unstable, and they rearrange to give brown polymeric materials, melanoidins (figure 23), most of whose structures are still unknown[30,31]. It takes some time at lower temperatures for the color to appear.

Browning rates depend on pH (the acidity of the system). Rates peak in the neutral to basic pH range, but rates are still rapid in the 3-7 pH range. Human sebaceous secretions are about 28% free fatty acids; therefore, human skin is normally slightly acid, but Maillard reactions are still fast. Many of the final products of Maillard reactions are identical to those produced by caramelization of sugars. The structures that produce the color are conjugated double bonds [30,31,32] (e.g., figure 23), just as hypothesized from the STURP observations[16]. Some of the most important products in color formation do not contain any nitrogen (figure 23). This fact could help explain why we did not observe any nitrogen compounds in image areas.

With regard to the requirement for amine reactants in Maillard processes, decomposing bodies start producing ammonia and amines, e.g., cadaverine (1,5-diaminopentane) and putrescine (1,4-diaminobutane), fairly quickly, depending on the temperature and humidity. A trained cadaver-searching dog can find bodies within a few hours after death. Little decomposition is required.

The ammonia and many of the decomposition amines are volatile and basic (they increase the pH into a more favorable range for Maillard reactions), and they rapidly undergo Maillard reactions with any reducing saccharides they contact. Such sugar-amine reactions offer a natural explanation for the color on the Shroud, and they suggest that the Shroud of Turin was a real shroud. However, identification of a probable chemical process does not explain one of the most perplexing observations on the Shroud, the discontinuous distribution of the color on the topmost parts of the weave.

The fact that color does not penetrate the cloth to any significant depth suggests that any hypothesized impurity had to be concentrated at the top of the cloth with little or none throughout the rest of the thickness. Assumed pressure of a body had no effect on the color density or penetration of image color into the cloth in the area of the back image. This supports the hypothesis that a limited amount of superficial impurities was involved in image formation. There is a simple explanation.

Saponaria officinalis, also called "soapweed," reduces the surface tension of water making it a good wetting agent. Both hydrophobic and hydrophilic impurities on cloth are put into solution or suspension by *Saponaria*. The process is identical to that involved in every laundry day with every kind of soap or detergent.

A textile conservator, Anna Maria Donadoni[24], told us that, after ancient cloth was washed in a *Saponaria* solution, it was "laid out on bushes to dry." Under such conditions, materials that are in solution or suspension in the wash water will concentrate at the drying surface. This is a principle I have used to transfer traces of soluble materials from irregular surfaces into sheets of filter paper for later chemical analysis.

Evaporation concentration can explain the superficial nature of the image. An amine vapor that diffused from a body into the cloth could only develop a low-temperature Maillard color on the surface where saccharides concentrated. The amines do not react with cellulose. The phenomenon can be demonstrated with a simple experiment.

Prepare a very dilute solution of food coloring, and divide it into two parts. Add a drop of liquid detergent to one part. Cut some squares of white cloth that are about 10 cm on a side. Place different numbers of drops of each solution on clean, smooth nonabsorbent plates, and lay pieces of cloth over the drops. Let the liquid evaporate. Different types of cloth will show different degrees of concentration of the dye on the evaporating surfaces.

The Shroud cloth is tightly woven, it is relatively thick, and it does not readily absorb water. With such a cloth, any material that can be suspended by Saponaria will primarily migrate to a drying surface and be concentrated.

The puzzling "half-tone" effect has been mentioned. All of the colored image fibers showed approximately the same color intensity under a microscope. Assuming that the color formed by reactions with a very thin deposit of superficial impurities on the fibers, all of the fibers should have shown identical spectra and roughly the same intensity of color. They did.

Another important observation is the fact that the image-forming process produced slightly different color densities (but identical spectra) on the different lots of yarn[4] (figure 3). The color-density of the image is not simply a function of the chemical properties of cellulose: It also depends on the individual properties of the batches of yarn. The observed effects must have been caused by different amounts of impurities that originally coated the surfaces of the different hanks of yarn as a result of slightly different production conditions.

Slightly different amounts of impurities on the different batches of linen yarn would cause slightly different surface energies. One major linen impurity is "flax wax," and it produces a hydrophobic surface. Liquids wet the threads as a function of the difference between the surface tension of the washing solution and the surface energy of the specific linen yarn. This would explain the "banded" appearance of the Shroud. The original observations and experiments on this phenomenon were done by Benjamin Franklin in 1774[33].

We have now discussed the critical observations on the Shroud, and we can clearly state an alternate hypothesis in accordance with Scientific Method.

Formal statement of the impurity hypothesis for image formation to be tested.

The cloth was produced by technology in use before the advent of large-scale bleaching. Each hank of yarn used in weaving was bleached individually. The warp yarns were protected and lubricated during weaving with an unpurified starch paste. The finished cloth was washed in *Saponaria officinalis* and laid out to dry. Starch fractions, linen impurities, and *Saponaria* residues concentrated at the evaporating surface. The cloth was used to wrap a dead body. Ammonia and other volatile early amine decomposition products reacted rapidly with reducing saccharides on the cloth in Maillard reactions. The cloth was removed from the body before liquid decomposition products appeared. The color developed slowly as Maillard compounds decomposed into final colored compounds.

Test and confirm.

Both starch and cellulose are composed of glucose units; however, cellulose is not a reducing polysaccharide. Crude starch contains a complex mixture of molecular weights as well as some very soluble free sugars: Its reducing carbohydrates rapidly undergo Maillard reactions. One starch component, dextrin, dissolves in water, and it shows reducing properties with Fehling's solution. It is dissolved in a washing solution, and it concentrates at an evaporating surface. I used it to demonstrate the impurity-hypothesis. The Fehling's test uses a fresh mixture of copper sulfate and alkaline tartrate solutions. Add the sample, and heat gently. A reddish precipitate of cuprous oxide proves a reducing saccharide.

Age and/or heating in the fire of AD 1532 has changed the lignin in the cloth[34], and it would certainly change other impurities that are less stable than either lignin or cellulose. Therefore, tests of image-formation hypotheses need fresh material. However, modern linen has been vigorously bleached, and it has been coated with sizing compounds and fluorescent fabric brighteners. It is useless for experimental image-production purposes.

Kate Edgerton (deceased, Norwich, CT) grew flax and made some linen, using both starch and *Saponaria*. Unfortunately, she ironed the samples with a "warm iron" which colored the cloth and changed the *Saponaria* glycosides. Edgerton's samples could be bleached to remove most of the color by soaking in 3.5% hydrogen peroxide. This treatment did not remove the natural waxes.

Because Edgerton's linen was scarce, many preliminary tests were performed on pure-cellulose filter paper. These experiments were done by placing drops of test solutions on a dry plastic plate and laying a piece of Whatman's #4 filter paper over them. The liquid migrated through the paper and evaporated at the surface. No color could be observed in either sunlight or ultraviolet illumination with *Saponaria* alone or with the model saccharides (e.g., levulose, dextrose, maltose, lactose, xylose, dextrin, and soluble starch).

The different samples were treated with ammonia vapor for different times. Light colors developed slowly on the tops of samples that had contained reducing saccharides. A technical grade of dextrin that reduced Fehling's solution was used to test crude-starch reactions. It acts like crude starch without the free sugars and highest molecular weight fractions. Paper was laid over different numbers of drops of dextrin, and the liquid was allowed to migrate into circular spots and evaporate. Samples were then laid over drops of *Saponaria* solution. The *Saponaria* caused the polysaccharides to move radially, as in a

circular paper chromatogram. Treatment with ammonia showed that the Maillard colors were most intense where the dextrin had been concentrated by migration at the *Saponaria*-solution front and on the paper's surface.

Very little color was obtained when the same experiments were repeated with a purified, "soluble" starch or plant gum. The starch gave a bright blue color with iodine and it showed only the slightest reaction with Fehling's solution. The plant gums did not show reducing properties. The effects would have been different after hydrolysis of the materials. It became evident that image-like colors required both saccharides and amines. The following demonstration and figures were made with Edgerton's linen to reproduce effects with a primitive woven fabric.

Figure 24: Evaporation surface of "primitive-type" linen treated first with dextrin, then S. officinalis solution. The Maillard color was developed with ammonia vapor and heating.

A sample of Edgerton's bleached linen was placed on four drops of dextrin solution on a plastic plate. A round spot was obtained. The water was allowed to evaporate from the cloth. No color could be seen on either surface. The middle of the same sample was placed on four drops of Saponaria solution. The wet spot expanded radially through the cloth. The water was allowed to evaporate, and no color could be observed. The sample was then treated for 10 minutes with ammonia vapor. A very light color could be observed on the top surface after standing 24 hours at room temperature.

The same effects as aging can be obtained by heating Maillard reactions. The reaction rates are determined by the Arrhenius activation energies and pre-exponentials of the processes, and the rate is an exponential function of the temperature. Reactions that require years at normal temperatures can be obtained in minutes at elevated temperatures. The rates of different Maillard reactions increase by factors between two and three for each 10ºC (18ºF) increase in temperature. This indicates that they have relatively low activation energies; rates will be significant at lower temperatures. The color shown in

figure 26 developed after a few minutes of heating at 66ºC (150ºF). This temperature is far too low to scorch cellulose.

Figure 25: Maillard-colored fibers (400X) from top of sample in figure 24. Medullas are clear.

Figure 26 shows that the most intense color appears in the ring on top. Some color appears around the ring on the back surface; however, the center of the back is nearly white. Experimental manipulations of concentrations and one-dimensional migration of solutions, as in a large cloth, could produce the same front-to-back color separation and color density as observed on the Shroud.

The fibers on the top-most surface are the most colored when observed under a microscope, and the color is a golden yellow similar to that on the Shroud (figure 25). The coating of Maillard products is too thin to be resolved with a light microscope, and it is all on the outside of the fibers. There is no coloration in the medullas: The color formed without scorching the cellulose. There is very little color on fibers from the middle of the back surface (figure 26).

Figure 26: A nearly-colorless fiber from the middle of the back surface of figure 24. Reactants were concentrated at the evaporating surface.

Several Shroud researchers have wondered why there is no mention of an image on the "cloths" reportedly found in Jesus' tomb. Assuming historical validity in the accounts, such a situation could be explained by the delay in the development of the Maillard reactions' colors at moderate temperatures. No miracle would be required.

Other considerations from physical chemistry:
The chemistry of the color does not answer all questions about how the "photographic" image formed. The image seems to show the body of a man, and it is darkest in areas that should have been closest to the body's surface; however, the "resolution" of the image has been puzzling. I believe that its resolution is a natural consequence of the image-formation process.

Vapor diffusion parallel to the cloth's inner surface would follow Graham's Law of diffusion, and high Maillard reaction rates would limit the spread of reactive amine vapors. Image densities would fall off rapidly away from the body, increasing resolution. Gaseous reactive amines can be lost by diffusion through the porous cloth, reducing concentrations and reaction rates inside the cloth. However, it has long been recognized that the images of the hair, moustache, and beard are anomalous. Figure 26 shows a slightly contrast-enhanced view of the area of the face and hair. The density of the image is greatest in those areas. That can easily be explained by the inhibition of vapor diffusion through a mat of hair. Ammonia is first evolved from the lungs; therefore, amine concentrations would have been highest in the vicinity of the nose and mouth (moustache and beard). The surface area of cloth is large, and higher-molecular-weight decomposition amines adsorb strongly. All of these phenomena would cause a rapid reduction in amine concentrations away from contact points and the nose-mouth area.

Figure 27: Slightly enhanced view of image face. Note increased density in the nose-mouth and hair areas. R. N. Rogers.

Postmortem body temperatures can reach 43ºC (110ºF)[20], and steep temperature gradients would exist across the cloth as a result of the low thermal diffusivity of linen and the angular dependence of radiant heat flow from a nonmetallic surface[19]. The temperature gradients will have a large effect on Maillard reaction rates. I believe that the combination of factors could produce a distribution of reaction products with the appearance of the image; however, the cloth would have to be removed from the body before liquid decay products appeared. This is a testable hypothesis.

CONCLUSIONS

Linen-production technology indicates that the Shroud of Turin is probably older than indicated by the date obtained in 1988. There seems to be ample evidence that an anomalous area was sampled for the radiocarbon analysis; therefore, the reported age is almost certainly invalid for the date the cloth was produced.

The image was definitely not painted.

The observed characteristics of the image rule out any mechanism for color formation that involves high temperatures or energetic, penetrating radiation.

I believe that impurities in ancient linen could have been suspended by the surfactant property of a *Saponaria officinalis* washing solution. They would be concentrated at the drying surface by evaporation. Reducing saccharides would react rapidly with the amine decomposition products of a dead body. This process could explain the observations on the chemistry and appearance of the image on the Shroud of Turin. Such a natural image-production process would not require any miraculous events; however, it would support the hypothesis that the Shroud of Turin had been a real shroud.

The observations do not *prove* how the image was formed or the "authenticity" of the Shroud. There could be a nearly infinite number of alternate hypotheses, and the search for new hypotheses should continue.

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