AN ALTERNATE HYPOTHESIS FOR THE IMAGE COLOR

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The outstanding characteristic of the Shroud image is the ***discontinuous*** distribution of the color on the surface. Color appears predominantly on the highest parts of the threads in the weave, as can be seen from the excellent photomicrographs taken by Mark Evans of STURP. Copies of Evans' collection are available from the Shroud web site (www.shroud.com). I would especially recommend ME-029, a 64X magnification of the image area near the nose. You can see specular reflection (a shine) on many of the parts of the thread that descend to go under the adjoining thread in the weave. Image areas other than the nose and feet show almost completely discontinuous color. This observation would seem to rule out any hypothesis for image formation that involved simple diffusion, capillary flow, or radiation.

Pellicori and Evans made an extensive study on contact and material-transfer hypotheses [Archaeology 1981, 34, 34-43). Their observations make it difficult to accept any image-formation hypothesis that is based solely on any material-transfer mechanism, but their observations also suggest the probable importance of catalysts for the image-forming process.

STURP members reported microscopic observations of single fibrils with image color on one end only where the fibril had been on top of the thread. Then Jumper, Adler, Jackson, Pellicori, Heller, and Druzik [ACS Advances in Chemistry No. 205, Archaeological Chemistry ill, Joseph B. Lambert, Ed., Copyright 1984] stated: "Because the yellow fibrils comprising the body-only image are confined to the uppermost portions of the threads of the cloth, mechanisms that would evidence migration by capillary action can be excluded ...We really do not have a satisfactory, simple explanation for how the body image got on the cloth."

A partial explanation for the discontinuous and superficial nature of the image color and its chemistry might be found in a study of the technology of the production of the cloth. The technology coupled with Pellicori's observations might explain the nature and distribution of the color of the image.

The technology of the Shroud strongly indicates a very mild bleaching technique in agreement with the methods described by Pliny [Pliny the Elder, AD 23-79, Natural History, ca AD 77, Book 19 §48] and in use, with some minor differences, until after the last crusade (AD 1291). It also supports an hypothesis about the "banded" appearance of the cloth (visible bands of lighter or darker weave).

The first reports of the use of a "spindle wheel" came from Persia in AD 1257, although it was probably used in the East before that. Linen made before the advent of the spinning wheel was spun by hand on a spindle whorl. When the spindle was full, the spinner emptied it by wrapping the thread around his arm the same as we roll up a long extension cord. Each hank of thread was bleached separately, and each was a little different; indeed, different parts of the same thread show slightly different colors a little like variegated yarn.

The warp thread was protected with starch during the weaving process, making the cloth stiff. The final cloth was washed in a solution made with the juice from what Pliny called "struthium" to make it more supple. We found that struthium is the Saponaria officinalis plant. A conservator at the Museum of Egyptology in Turin (Anna Maria Donadoni Roversi) had used Saponaria to clean and preserve museum specimens.

Commercial production of linen started during Medieval times, and the linen looks much different than the Shroud. Medieval linen was spun to great lengths on the spinning wheel, and it was bleached as the cloth. Most commercial bleaching took place in "bleach fields" in the Low Countries, the genesis for the name "Holland cloth" that is applied to the backing on the Shroud. Considerable material was lost during the bleaching process, and the newer linens are less dense, as can be seen with the Holland cloth. The newer linens are also homogeneous. They do not show bands of different thread in the weave.

Modern linen has a matte finish as a result of vigorous chlorine bleaching, and it is almost always treated with fluorescent fabric brighteners.

We could find very little confirmatory evidence for the use of Saponaria on the Shroud. The age of the cloth and damage during the fire of 1532 make some chemical testing difficult. More work needs to be done. However several circumstantial bits of evidence that Saponaria might have been present early in the history of the cloth should be mentioned. Saponaria is hemolytic, which could explain why the old blood stains are still red on the Shroud. We found that Saponaria was used in clinical chemistry to hemolyze blood for laboratory analysis. The process releases the hemoglobin. Hemoglobin is quite stable, and an observation of red blood would suggest either painting or hemolysis. Diane Soran (deceased) of Los Alamos tested hemolysis on Saponaria-washed cloth before we went to Turin. The blood stays red. It is still red on those 24-year-old samples. This observation supports an hypothesis that Saponaria was on the cloth at the time of image formation.

Saponaria hydrolyzes to produce some aglycones that are fluorescent, and the non-image part of the Shroud is weakly fluorescent. Unfortunately, we did not have equipment to do a detailed test on the surface of the cloth, and we have not studied how Saponaria fluorescence changes with age.

Saponaria is a potent preservative. Kuszlik-Jockym and Mazur reported that Saponaria glycosides even stopped alcoholic fermentation by yeasts. Roversi said that old cloths tend to be well preserved.

Hydrolysis releases the Saponaria glycoside sugars. Chirva, Kintya and Lazur'evskii [Khim. Prir. Soedin. (1969), 5(1), 59-60] found that two 5-saccharide chains were produced. The following compounds were identified in those chains: galactose, glucose, arabinose, xylose, fucose, rhamnose, and glucuronic acid. Some of the sugars are pentoses, different from the typical six-membered-ring sugars from starch and cellulose. A few spot tests for pentoses on Raes threads from the Shroud were just above the detection limit for the test, but they did not prove anything conclusive.

The sugars of Saponaria are very similar to the mixtures of sugars that are found in plant gums. Such mixtures of sugars are viscous liquids at room temperature. Liquids decompose very much more rapidly than crystalline solids, e.g., cellulose. I developed a method for the determination of chemical rate constants for such materials [J. Chromatog., 48 (1970) 268-276], and I found that furanose pentoses were the most rapidly decomposing sugars of any. For example ribose (mp 86°C) in a liquid phase seems to have an appreciable decomposition/dehydration rate at body temperature that would produce a color in some, perhaps extended, amount of time. I have not yet been able to find reliable kinetics constants for the furanose sugars in Saponaria, but they are probably similar to ribose. The time to coloration would be much shorter at higher temperatures and/or in the presence of catalysts.

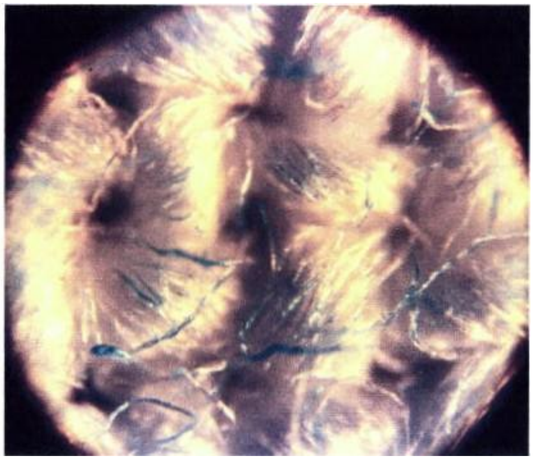
Human sebaceous secretions include free fatty acids, combined fatty acids, triglycerides, and considerable unsaponifiable material (e.g., squalene, hydrocarbons, wax alcohols, cholesterol, alkane-1,2-diols and a significant amount of sterols). Fatty acids are the largest part of sebum, the source of "body odor." Some of these materials should catalyze the decomposition of low-molecular-weight carbohydrate impurities.

Saponaria officinalis is called "soapweed" in some areas. ***It acts as a surfactant: It reduces the surface tension of water making it a good wetting agent.*** The non-polar end of the molecule can penetrate the surface of oily materials while the polar end causes the oil to become suspended in the water. Both hydrophobic and hydrophilic materials that had been on the raw linen would be put into solution or suspension by the Saponaria solution. These properties could be of importance in considering the Shroud.

Roversi told us that, after 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 microsamples from irregular surfaces into sheets of filter paper. It is easy to see that the dry deposits appear on the outer surface of the drying cloth (or paper). This type of process might help explain why the Shroud color is superficial.

Top of experiment with blue dye.

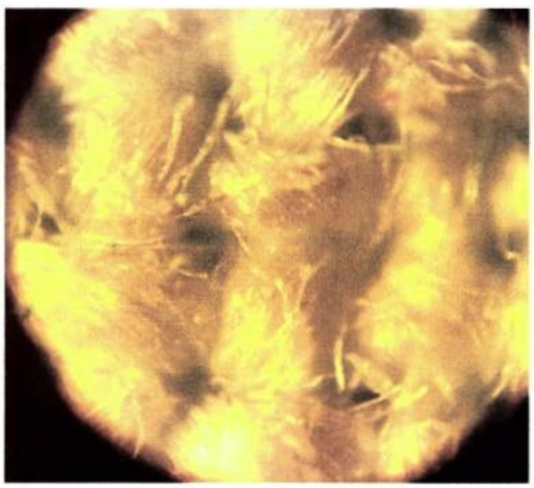
Bottom of experiment with blue dye.



Lacking any Saponaria solution, I demonstrated the phenomenon with a very dilute solution of blue dye. I saturated a piece of cotton cloth with the dye solution and put it on a smooth plastic plate. The dye immediately started showing concentration on the top of the cloth as drying started while standing out in room air. After drying for a few hours, the top was colored, with the most dye showing on the highest points and single fibrils of the nap that pointed directly upward from the top of the cloth. The bottom of the cloth was white.

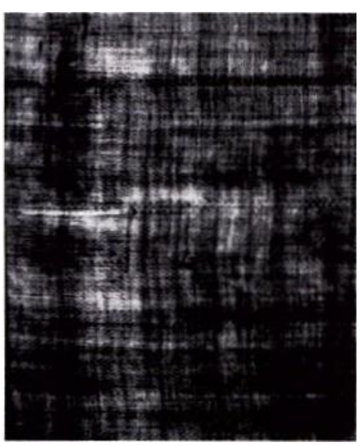
Top surface at 60X

Bottom surface at 60X.



The photomicrographs show that the main concentration of dye on the top surface appears on the fibrils of the nap that are pointing straight up and on the top-most surfaces of the threads (look for patches of little blue streaks on the tops of the threads). The bottom surface is apparently completely free of dye. Even the upward-pointing fibrils of the nap are not colored. Such a process appears to provide one hypothesis for the discontinuous appearance of image color on the Shroud and its shallow penetration into the cloth.

I think that any impurity in solution or suspension in a system with a relatively low surface tension would migrate to the drying surface of a piece of saturated cloth and be left there in a much higher concentration than anywhere else after the solvent dries.



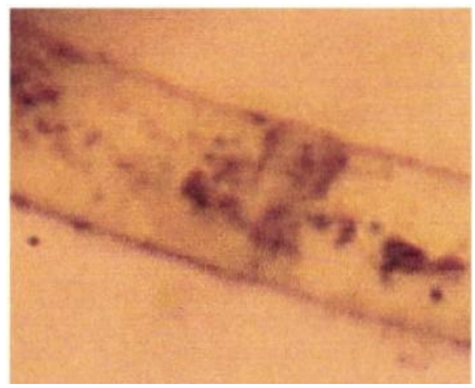
Another observation that is of importance in the context of an image-formation hypothesis is the fact that the process that formed the image produced slightly different densities of color on the different lots of thread. The photograph is taken from D. H. Janney's image-analysis collection, and it shows the area of the image's face. *The density of the image is not simply a function of the chemical properties of cellulose. It also depends on the individual properties of the thread, both warp and weft, used to weave each specific part of the cloth.*

We might hypothesize that the observed effects were caused by differences in the amounts of foreign materials that coated the surfaces of the individual fibrils of the threads as a result of slightly different production techniques. An "impurity hypothesis" immediately suggests possible traces of starch and/or Saponaria on the threads at the time of image formation. Saponaria, being a surfactant, would flow smoothly over the cloth. A dilute solution would form a very thin layer on the upper surface of the cloth. The most soluble fractions of starch should also appear on the top-most surface.

Al Adler surprisingly reported that the centers of the yellow image fibrils were clear. *The cellulose core and medulla were not affected by the image-producing event.* Notice that his report concerned the individual fibrils (approximately 13 μm in diameter) and not the threads.

As a result of Adler's observations, I observed the few fibrils I have left on microscope slides once more. The medullas of image fibrils are largely clear:

A fibril from an image area X100.



A fibril from a scorched area X400.

The medullas of scorch fibrils of the same color are dark. The dark band across the scorched fibril is lignin at the growth joint. It appears that the scorched fibrils colored all of the way through their diameter, but the medullas of the image fibrils were not affected by the image-forming process. That observation supports Adler's observation that all color resides on fibril surfaces, but it still needs confirmation.

Heller and Adler also reported: "The absence of products expected from a high temperature cellulose degradation, however, suggests that the process that formed the final chemistry took place at lower temperatures (less than 200°C), because no pyrolytic compounds were found. The fluorescence of the scorch image areas, however, demonstrates the presence of high-temperature pyrolytic products in these areas."

They also detected "ghost" images of fibrils adhering to the sample tapes after fibrils were pulled from the surface. That observation proves that degraded, colored material on fibril surfaces was easily separated from the cellulose core.

It might be possible to develop an alternate, testable hypothesis for the color on the image fibrils that is based on the presence of impurities on their surfaces coupled with the diffusion of catalysts, as discussed by Pellicori. Such an hypothesis would have to assume that the impurities on the fibrils colored more easily than the cellulose of the linen.

The color formed by the dehydration (caramelization) of any type of carbohydrate impurity (e.g., starch and/or sugars) would be the result of the same kinds of conjugated structures as produced by cellulose, and *the color would appear on the surface of the fibrils only*. All of the analytical tests described by Heller and Adler would apply to these impurity colors. All colored fibrils should color to approximately the same degree, depending on the amount/thickness of the impurity layer, explaining the "half-tone" effect STURP reported.

Slightly different amounts of impurities might be expected to concentrate on the different hanks of thread used in the weave, depending on the difference between the surface tension of the washing solution and the surface energy of the specific piece of linen thread. This would explain the "banded" appearance of the Shroud. There might be little or no contribution from the cellulose in the production of the color. The deposition of an impurity as a result of washing would help explain the fact that colored fibrils appear predominantly on the very tops of the top-most threads on the Shroud.

We expected to find starch on the Shroud, so we did not specifically look for it. That was an unfortunate oversight. Starch is a very complex carbohydrate, and not all sources give exactly the same material. The starch might have given us information on its source and the provenance of the cloth.

Starch consists of two main polysaccharides (shorter chains with the same general structure as cellulose). Starch "toasts" much more easily than cellulose, giving the familiar colors from yellow through brown. One of its components, amylose, dissolves in water to give a clear blue color with iodine. The other dissolves only in hot water to form a paste, and it gives a violet color with iodine. Some of it should have remained after the stiff cloth was washed immediately after manufacture. When we were testing for sulfoproteins in blood areas with an iodine-azide reagent (it bubbles vigorously when sulfur is present), we got a reddish background. The color should have suggested some polysaccharide impurities to us. We should have tested for starch and other polysaccharides.

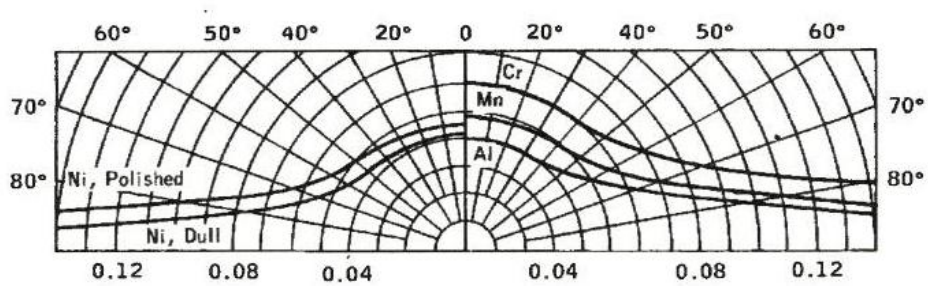
Aging processes might be expected to have changed the composition of the surface of the Shroud since the image-forming event. Age and/or heating in the fire of 1532 have certainly changed the lignin, and it would certainly change other impurities that are less stable than either lignin or cellulose. Tests of image-formation hypotheses would need fresh material.

Some powerful and sensitive surface-analytical techniques are now available for looking at molecular structures. Electron Spectroscopy for Chemical Analysis (ESCA) can give direct information on the chemical bond types on a material, and it can be applied to small samples. Such information would be invaluable in testing both primitive linens of modern manufacture and samples of the Shroud.

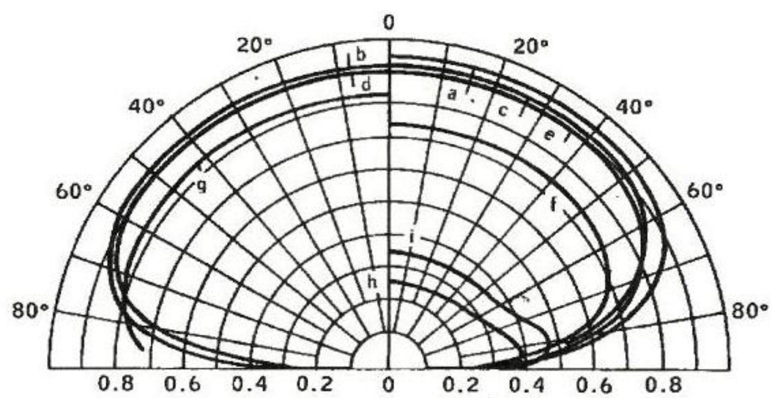
The lignin on linen that has been bleached by primitive methods can easily be detected with a very sensitive chemical test under a microscope. The test involves the evolution of vanillin from the lignin. The few uncontaminated Shroud fibrils we had for testing did not show that test, even though you can see lignin at the growth joints. Preliminary tests showed that lignin gives increasingly weaker tests as it ages over many centuries.

More work needs to be done on this observation because it might give an independent estimate for the age of the cloth. Many microscopic samples from widely different parts of the Shroud would be required, because the fire of 1532 would have accelerated the aging of lignin in some areas.

Early in the STURP studies, Kate Edgerton (deceased, Norwich, CT) laboriously made some Roman-process linen that involved both starch and Saponaria. Small samples we got were invaluable for observing the chemical properties of fresh "Roman" linen. We could observe residual lignin at fibril growth joints, and the lignin gave intense spot tests. Unfortunately, she had ironed the woven samples after washing with Saponaria. Spot testing for Saponaria components was very difficult and inconclusive, just as it is with the aged Shroud. She gave us samples of the thread that had been used for the weavings after they were coated with wheat starch of her manufacture and before it was washed with Saponaria, and we could see starch cementing fibrils at 400X. We were not able to test later image-formation hypotheses on her samples, because of the ironing. We could use more samples for additional tests.



Emissivity of Metals as a Function of Direction at about 300 F.



Emissivity of Non-Metals as a Function of Direction at 32-200 F.
(a) Wet Ice (b) Wood (c) Glass (d) Paper (e) Clay (f) Copper Oxide (g) Aluminum Oxide (h) Aluminum Paint (i) Bismuth

Jackson has said that the image could not be the result of a radiant-energy-transfer process, because the inverse-square law precludes the production of an image with "3-D" information "encoded." Actually, the inverse square law holds for a point source but not a curved surface. The emittance graphs are from Gubareff, Torborg, and Janssen [Thermal Radiation Properties Survey, Honeywell Research Center, Minneapolis-Honeywell Regulator Co., Minneapolis, MN, 1960]. You can see that clean metal surfaces (upper) emit most of their energy at grazing angle, and they have very low emittances. That was the reason the hot-statue system failed. It might have worked better with a stone statue. Notice that metal emissivities are only about 0.04-0.05 normal to the surface. Nonmetals emit most of their energy normal to the surface, but the amount of energy transferred is a *function of the angle between the detector and the surface.* It is also important that nonmetal emissivities are more than 10X greater than metals. Emitted energy is not a simple inverse square function of distance, and a large amount of energy can be emitted from a warm nonmetal.

Energy emitted from a nonmetal surface shows about a 4th power relationship to temperature. A little increase in temperature causes a large increase in emitted energy.

I published a method for the determination of emissivities (Anal. Chem. 1966 and Thermochimica Acta 1972), and I do not think we can rule out long-wave heat transfer as contributing to the image-formation process. It could not have been the sole contributor.

Without assuming anything other than an irregular nonmetallic surface and a cloth, heat would be transferred to the cloth by a combination of contact, convection, and radiation. Convection cells will vary in size and efficiency of heat transfer depending on clearance, and clearance will certainly vary with position. Contact points can supply energy that will flow radially from the point by conduction. The thermal diffusivity of cloth is quite low, but it is not zero. Given sufficient data, it should be possible to calculate temperature gradients across a cloth; however, the situation is much more complicated than a simple inverse square law.

With accurate chemical-kinetics values, it should be possible to calculate the temperature of a surface that would be sufficient to caramelize (color) any of the possible sugars or starches on a cloth and the amount of time required to reach any desired fraction of total decomposition.

I believe that a combination of relatively rapidly decomposing impurities on the surface of the cloth with transfer/diffusion of catalytic compounds from a body, as discussed by Pellicori, could explain the observations on the chemistry and appearance of the image on the Shroud. It should explain the shallow penetration of the image, the fact that the color did not penetrate more deeply at presumed contact points, its "half-tone" appearance, and its predominantly discontinuous distribution. Both catalyst concentration gradients and angle-dependent emittance of energy from a body would contribute to the 3-D relief seen in the image.

It is important to notice that this hypothesis does not offer any proof of "authenticity." It is simply an attempt to explain some of the characteristics of what we can observe on the cloth known as the Shroud of Turin.