THE USE OF DIRECT REACTIVE FLUORESCENT DYES FOR THE CHARACTERIZATION OF BINDING MEDIA IN CROSS SECTIONAL EXAMINATIONS

by Richard Wolbers* and Gregory Landrey**

A brief review of current methods and materials used for media characterization on small cross-sectioned samples of painted or varnished structures is presented. Both the limitations and advantages of these techniques are discussed, along with general criteria for the successful performance of such stains. Several fluorescent reactive dyes are currently available to meet these requirements. Their application, and usefulness as microscopic reagents is presented in a case study type of format. Painted and varnished structures of all types are covered by these examinations.

Current interest in, and techniques for, the micro-chemical characterization of binding media in small samples removed from artifacts or paintings seem to derive from a very few seminal sources within the conservation field itself(1,2,3). Where credit is acknowledged, contemporary publications in both architectural and fine arts preservation point to Joyce Plester's article which appeared in Studies in Conservation, 1956, as a key source work(4). In it she provided an excellent review of sampling techniques, mounting materials and micro-chemical tests available at the time for characterizing under the microscope binding materials, and indicated something of its history, and both the benefits and limitations of such applied techniques. The methods, at least, have remained largely unchanged since Plesters' work. Current architectural practice standards for instance still call for solubility-type tests in the characterization and description of certain historical paint and varnish. types(4,5). In terms or fine arts, only a handful of biological stains suggested in the literature have either augmented or supplanted the two originally found useful by Plesters(2,3). But sampling, mounting and examination techniques really have changed very little from those described by Plesters. The reasons however, for taking samples or doing some form of cross-sectional analysis, both visually and with micro-chemical tests or probes remain as valid and largely the same as those originally set forth by Plesters.

In terms of understanding the complex visual phenomena presented by the surface of a painting or artifact, a small sample can provide a wealth of information of both a technical and visual nature, within certain limits. It does this by revealing what materials are present, how they've changed with age, and how it is that certain effects are generated either by design or deterioration. A small cross-sectioned sample yields a certain amount of contextual information that might be eschewed by other forms of more sophisticated analysis. Certainly with the advent of Fourier Transform Infrared or even more elaborately hybridized instrumentation, media analysis at the microscopic level has, to some extent, been trivialized(6,7). Small samples, commensurate with the amounts which might be safely removed from a painting or other delicate structure can now be taken and analyzed by anyone of a variety of instrumental methods. Yet it is the very arrangement of these materials, layer on layer, layer into layer, the aging effects within a given layer, I trace amounts of additives and so on, which also provides useful information, for interpreting and characterizing a painted structure. As an artifact of a certain maker or level of technology, a good deal of physical information can. be posited in an organic material. The natural oils,

* **Associate Paintings Conservator**
** **Furniture Conservator, Winterthur Museum, Winterthur, DE 19735.**

resins and proteins that form either individually or in combination the basic traditional art or finish making materials bear also within their primary chemical structures the hallmarks of the chemical processes of their manufacture, manipulation, handling, construction, and, of course, age. Visualizing these materials and their interrelationships by using micro-chemical reagents can extend our ability to answer the still fundamental questions of what was used when, to what purpose, by whom, and to add to our basic lexicon of information, more than might be found in other routine types of examination I techniques.

Solubility type tests per se can be helpful in media characterizations only to the degree that materials and more particularly their solubility parameters remain fairly well defined, and distinct from one another. Materials are inevitably compounded however, they age, crosslink, etc., and, in short, are complicated even from the outset in composition, and there can be a tremendous amount of overlap in terms of exhibited solubility parameter. Thus, solubility in Dimethylformamide (DMF) or aqueous basic solutions has been used by some as a criterion for an oil bound composition. Its just as true though that, as extremely polar solvents, they would as readily solubilize most of the natural polymeric materials likely to be found in paints and varnishes, including collagen and milk derived proteins(8,9). Certainly these materials can be sorted through one from another, and visualized independently by taking advantage of the affinity of specific functional groups for certain highly colored biological stains. Plesters introduced the idea of using Nile Blue as a general stain for oils and Acid Fuschin as a general stain for proteins(10,11). As a relatively non-polar material Nile Blue retains a strongly hydrophobic character and exhibits a concomitant affinity (depending on . the carrier solvent) for oil or oil-like hydrophobes. But it is also conceivable that in aqueous or partially aqueous system it can dissociate to a limited degree into a weakly anionic material which can be non-specifically associated with, or be adsorbed onto weakly cationic material. Acid Fuschin is essentially the Di-sodium salt of a tri-sulfonated derivative of a pararosanilin type. It is a fairly soluble in water, is highly colored, and if dissolved in water would tend to be strongly anionic in character and tend to associate with any oppositely charged basic material in a given sample, depending on the surrounding pH and small ion concentration in solution. In the case of a protein bearing sample any of the basic amino acids which might function as weak cations could adsorb the stain and be made visible by it. It was pointed out as early as 1926 by Pischinger(12) however that the uptake of acidic or basic stains onto the oppositely charged groups of proteins from aqueous solutions was a function of the pH or small ion concentration in that solution. Indeed, a variety of staining effects could be achieved, and some selectivity in staining, by delivering any given stain in a series of pH graded buffer solutions. Lowering the pH of a solution containing an acidic stain tends to diminish its anionic character slightly making it more hydrophobic, while at the same time tends to promote protonation, and an increasing cationic character to : proteinaceous materials. To maximally protonate and therefore make available for staining as many basic groups on that protein as possible, fairly acidic solutions were, and are, still often used to deliver acidic dyes. Elizabeth Martin in her article, “Some Improvements in the Techniques of Analysis of Paint Media” (Studies in Conservation. Vol. 22, 1977, pp. 63-67), attempted to exploit this phenomenon to differentiate between proteinaceous binding materials in paint structures. But the trade-off is a more and more non-specific staining or deposition of the acidic stain on the sample, as it losses its charge, along with the desired staining effect on the substrate. The problem then becomes one of “destaining” or washing off the non-specifically absorbed stain while leaving it behind selectively adsorbed onto the groups it was meant to associate with. Again, if staining is a function of pH, destaining can produce a variety of effects depending on the pH and solvent strength of the destaining solution. Results may vary depending on the length of time of destaining, and on the complex nature of

the substrate; if nothing else, paint cross sections, despite being carefully ground or polished, tend to be, on a microscopic scale, still very granular, porous, substrates which don't lend themselves to efficient washing. In histology, tissue, samples containing proteins can be carefully fixed(13) (i. e. denatured, and bound to a solid matrix) and copiously washed before examination to minimize the effects of non-specific staining. The methods of general histology however do not necessarily transfer without modification, given the same type of stains available, to paint cross-sectional analysis. Acidic or even neutral aqueous staining systems tend to swell, and solvate proteins; without prior fixing their loss is inevitable during staining and destaining procedures, and can seriously compromise an unequivocal reading of the final stain deposition and its interpretation.

These and other technical problems were described in great detail in Johnson and Packards work of 1971; in essence, they introduced Ponceau S(14) and Sudan Black B(15) as cross-sectional media stains for proteins and drying oils, respectively. Both are Diazo type dyes; Ponceau S is the tetra salt of a 3, hydrozyl-diazotetrasulfonate. In a dilute, weakly acidic aqueous solution it is a strongly colored (red), weakly anionic material. Again, any material with a cationic character under these conditions can conceivably adsorb the dye and be made visible by it. As a protein stain then, it should function well in theory. Johnson and Packard did note a sensitivity of certain materials to dissolution in the acidic staining solution; when this occurred they recommended that the stain Coomassie R 250,(16) which is entirely soluble in a dilute neutral aqueous solution, (presumably because of the higher pK of the ionizable sulfonate groups on it) be used instead of Ponceau S. In either case, stains were applied in aqueous systems and then were washed or destained in water as well. Aged samples seemed to fair better through staining and de staining without any fixing procedures;"mode1" or fresh materials used as test substrates required fixing in 3% Acetic Acid or heating to 98 ºC prior to staining to preserve them through the staining or destaining procedures. Presumably in age, proteinaceous binding materials undergo a variety of reactions that could leave them less soluble in aqueous systems. The loss of certain polar groups through deamination or decarboxylation can occur(17,18); cross-linking could also occur which might make these materials more resistant to swelling and solvation in aqueous systems(19). These effects have to be variable though, and must depend a good deal on the vagaries of what materials are present and the environment and treatment history the paint or finish have been subject to. When does a given material reach a level of insolubility in aqueous staining and destaining solutions to remain intact and reliably retain a stain to reflect its presence on examination without fixing? Fixing procedures using fairly acidic incubations or heating prior to staining may change the sample or remove materials from which might change or limit its characterization on examination. Either Ponceau S or Coomassie R250 as the brightly colored sulfonic acid derivatives of certain dye-types are only soluble in aqueous systems as long as they're sulfonic acid groups are dissociated or charged; hydrophobic interactions in a non-specific fashion can be forced with these stains if the hydrogen ion or small cation concentration around them rises appreciably; water washes alone, no matter how copious, may not be enough to break these kinds of hydrophobic interactions and successfully destain dyes adsorbed to substrates in this fashion. Sudan Black B, as with the earlier Nile Blue, is soluble in a variety of relatively non-polar solvent systems and can conceivably function as a lipid or hydrophobe stain. Johnson and Packard applied Sudan Black to test oil samples in a dilute solution in an ethanol:water system (3:2) and destained in a slightly more polar mixture of the same two solvents (Ethanol:Water (2:3)). The authors admit to an intrinsic variability in the staining and destaining process. The staining and destaining solutions tended to wash away the oil substrates if left in contact with them too long. Again, the success or the unequivoca1ity of this kind of staining technique

is probably as much a function of the degree of cross1inking (and therefore solubility) of the oil sample to be stained, other properties in age, and the materials which are present with it in the sample, as it is in choosing the proper solvent strength in designing an appropriate staining and destaining solution for a particular sample.

It's a curious position Johnson and Packard take in relationship to the overall success or failure of a particular staining procedure. One of the "disadvantages" of Sudan Black B was its relative transparency, i.e. its lack of coverage of pigment particles within an oil bound paint layer. Ponceau S was seen as superior because the stain could not only be picked up by a proteinaceous binder or component in a paint layer but it also "covered" pigment particles present in that layer and minimized their presence visually to simplify reading where the stain was ultimately deposited. The color of an applied stain can be problematic on certain paint layers as Johnson and Packard point out. A blue dye, for instance, adsorbed onto a blue pigmented layer is difficult if not impossible to discern, at least at low magnifications. With visible light type stains, this would seem to imply that at the very least, a variety of colored stains (depending on paint colors present) should be available, or employed in, the routine examination of media in cross-sectioned samples to avoid the possibility of missing the presence of certain materials in certain layers. But the fact that Ponceau S is adsorbed by both pigment and binder in a layer is not an advantage but more indicative of a general problem with the non-specific adsorption of this dye onto a material which shouldn't have retained it in the first place. The need for specificity cannot be understated--media stains should of course be adsorbed by binders only. And to guarantee the most consistent sort of results, that adsorption should take place in solvent delivery system which won't disturb either the pattern distribution or localized concentration of a stained material in the original sample. Ideally, staining should be independent of substrate concentration or color, and minimally effected by the presence of other materials likely to be present initially or develop with age, or result from treatment of a painted structure.

Certainly, the most highly specific reagents available for the recognition of-certain types of proteins, at least, are antibodies raised against those specific structures in animals(20). Immunoglobulins (antibodies) can, under physiological conditions (pH=7.6, ionic strength equivalent to normal saline) associate with their antigens (target protein structures) and form aggregates in solution and ultimately precipitate en masse with them. For each antibody made there is only one unique portion of a protein that fits it. Conceivably then antibodies can, and have, -, been raised against some of the common proteins found in art or finish making materials, and can "recognize" them. I If brightly colored dyes or fluorescent materials are coupled to purified antibodies, both a high degree of specificity and visibility as reagent stains can be achieved. The notion to use fluorescent antibodies as microscopic media stains was advanced by both Johnson and Packard and later Talbott(21). Practically speaking, while antibodies are highly specific reagents, relatively long incubation times are required both for reaction and destaining(22). Again, in normal histology, fluorescent antibodies are applied in buffered saline solutions, pH 7.6, i.e. normal physiological conditions, to previously fixed tissue or cell samples on glass slides. After about 30 minutes the samples are copiously washed with a higher ionic strength buffered saline solution, again at a pH of 7.6. Uptake of an antibody is a function of antibody concentration, substrate concentration, pH, ionic strength, time of staining, and so on. But more than anything else, two factors have made the direct application of these histology techniques for antibody staining hard to transfer to paint cross-sectional analysis; 1) the long exposure of unfixed protein containing samples to high ionic strength aqueous staining and de staining solutions, and 2) the precipitation-like reaction between antibody and antigen.

Antibodies are “sticky” molecules; they have a large hydrophobic tract of amino acids at one region of their structure; they tend to aggregate once they’ve bound to an antigen by coalescing together at this region, non-specifically(23), and its this potential “stickiness” or hydrophobicity which makes them poor reagents, at least without modification. They can be adsorbed onto pigment and inert materials as well as hydrophobic substanced, and these kind of non-specific interactions cannot easily be “destained” or broken by aqueous saline washes. Antibodies can be made less “sticky” by mildly reducing them, enzymatic degradations, where whole anti bodies can be sp1it into smaller fragments (light and heavy chains) and the “sticky” portions (heavy chains) can be separated away. The so-called “light-chains” of immunogloblins carry the structures which recognize other specific protein segments and these, if coupled with a dye or fluorochrome could prove to be useful in media analyses in the future(24). Fluorescent materials in general are much easier to see at low concentrations under the microscope than visible light stains because they can readmit a good deal of the absorbed light energy that impinge on them. But again, for any stain to be unequivocal in its reading it has to be applied to a general mixture of materials without disturbing them, be picked up on one component in that mixture specifically, and then be easily washed off the rest without affecting their disposition. Where proteins have been present in a sample, acidic dyes, and more specifically, the sulfonated derivatives of highly colored materials. have been used to mark or stain them by adsorbing onto them through weak ionic sorts attractions. The sodium salts of these dyes form anionic species in solution and the basic amino acids on the proteins where protonated, act like weakly cationic substances. Both stain and protein have to be in aqueous environments for the adsorption to occur. But the problem remains, how to deliver the stain and not wash away the protein at the same time? Certain organic functional groups--acid chlorides, isocyanates, sulfonyl chlorides, azides, diazonium chlorides, etc.--react spontaneously in non-aqueous environments with primary, uncharged amines to form condensation products covalently bound to the amino bearing moiety(25). Fluorescein(26), Rhodamine B(27), and a number of related fluorochrome structures have been derivatised to produce just such reactive dyes, which have the capacity to covalently bind to free amino groups and couple to them. Practically speaking, such a reactive fluorochrome can be delivered to a protein containing sample in a non-aqueous solvent--one hopefully which is a poor solvent for the protein to be stained itself or any other material for that matter to be observed, present with it--and allowed to react to form a fluorogenic adduct to the protein, marking it and making it visible under specific illumination conditions. Lissamine Rhodamine Sulfonyl Chloride(28) in a dilute solution in acetone (.25g/l00ml) has been used by us as a marker or stain for proteins, as has fluorescein isothiocyanate (FITC), (.25g/l00ml in acetone). Samples are cast into small polyester blocks (Bio-Plast, Ward’s Natural Scientific, Inc.), ground to reveal a cross-sectional presentation and then the dilute stains delivered by pasteur pipette onto the exposed sample, The carrier solvent (acetone) evaporates immediately and the samples are cover-slipped without rinsing, with a slow evaporating aliphatic hydrocarbon solvent (Shell Solv) and examined under the appropriate excitation wave length light for the dye being applied. The unreacted portion of the applied stains are soluble in the coverslipping medium, and by dilution, become invisible under the microscope; that portion of the stain which has reacted with available amino-groups fluoresces brightly even at relatively low concentration on the substrate. Since the sample is essentially bathed in a monochromatic light for exciting the fluorochrome, during examination intrinsic color in the sample tends to become gray-like or dark and the fluorescence of the dye brightly visible on the sample. The fluorescence colors of Lissamine and FITC are bright red and yellow-green respectively; since very few of the materials of traditional finish or paint construction fluoresce with these particular colors intrinsically, they’re reading is usually uncomplicated by other in-situ materials. The natural resins, such as dammar, mastic, rosin,

and shellac of course do fluoresce intrinsically or can develop an auto-fluorescence on aging; the same can be said for proteins and carbohydrates generally speaking. They tend to (save for shellac) fluoresce with a blue-white color under long wave ultraviolet light illumination. Again, the color of a reactive fluorochrome can be selected to avoid confusion with these observed properties of certain materials. Where these materials do not exhibit a background fluorescence before staining, a dye called Fluorescamine(29) has also proven a useful fluorogenic marker for proteins; in the presence of a free amino group the fluorescamine molecule bonds in a non-aqueous environment to the free amine. Structurally, this bonding allows a lactone ring to close within the molecule of the dye, imparting a blue-white fluorescence to it. Where it reacts, the fluorescent adduct to the protein is seen; the unreacted material remains unfluorescent and therefore invisible under near ultraviolet examination. Typically, only about a .25g/100ml in acetone solution of fluorescamine is necessary for staining. The stain is applied, carrier solvent allowed to evaporate, the sample is cover-slipped in Shell-Solv, and then examined immediately. No staining/destaining cycle is necessary for a reading. Again, by selecting a carrier solvent to deliver the stain which is a poor solvent for the proteinaceous substrate, its chances of remaining intact in both amount and distribution in the sample are greatly increased over aqueous based stains. Emulsion-type binders or coatings of the simplest type; i.e. protein and oil mixtures, may stain better if dyes are delivered in less polar solvent systems than water as well, because of the increased wetting onto these materials that may be substantially hydrophobic in character. Johnson and Packard noted a kind-of “speckled” staining pattern for Ponceau S on layers they deemed protein and oil emulsion types; it’s probably just as likely that the “speckled” deposition of the stain might be a water-spotting kind of phenomenon, i.e. a lack of wetting onto a non-polar surface by a polar substance, and not, as they suggest, a reflection of the micellular structure of the emulsion itself.

As general lipid (drying-oil) stains, two fluorochromes, or fluorogenic materials have proved useful; Rhodamine Band 2,7 Dichlorofluorescein(30). The former forms a brightly red-orange fluorescene in non-polar type environments. As with fluorescamine, in an aqueous environment the structure of Rhodamine B is a soluble, highly colored but non-fluorescent entity. In a relatively non-polar environment a hetero annular ring closure within the molecule takes place to produce a fluorescent moiety. When Rhodamine B is allowed to “dissolve” in a drying oil structure then, it fluoresces brightly. Again, by selecting a carrier solvent which dissolves the dye, wets efficiently onto an oil containing sample, and doesn’t dissolve it, Rhodamine B can be delivered to and stain for an oil component down to only trace amounts of that material in both a quantitative as well as a qualitative sense. 2,7 Dicholorofluorescein is simply used when a different fluorochrome color is required, for counterstaining, or higher visibility. It fluoresces a yellow-green color dissolved in an oil containing material. Its affinity is purely by solubility parameter only and ,functions much like the oil stains discussed earlier.

Reducing sugars, by virtue or their slight redox potential have been visualized by us on cross sections in a kind of reverse fluorescence type reaction. Compounds similar to substituted tetrazoles can exhibit very high sensitivity to even the mildest of reducing agents. When reduced they can revert to highly colored formazan-like compounds(31). Triphenyl-tetrazolium Chloride (TTC) is soluble in a fairly wide range of non-aqueous solvents(32). If it is dissolved in methanol (.1g/100ml) for instance and delivered to a sample containing a reducing sugar (gum, starch, etc.), it can convert upon evaporation of the carrier solvent to a formazan product on exposure to a slight amount of atmospheric moisture. Where a naturally aged gum or starch component is auto-fluorescent, this appears to darken the sample where the reac-

tion takes place, when the sample is viewed under the proper excitation wave length light. Parenthetically, while its never been explicity state, mounted sample grinding should not be done in water, if those materials sensitive to water, i.e. proteins, gums, and water soluble resins hope to be preserved through the sectioning and grinding process.

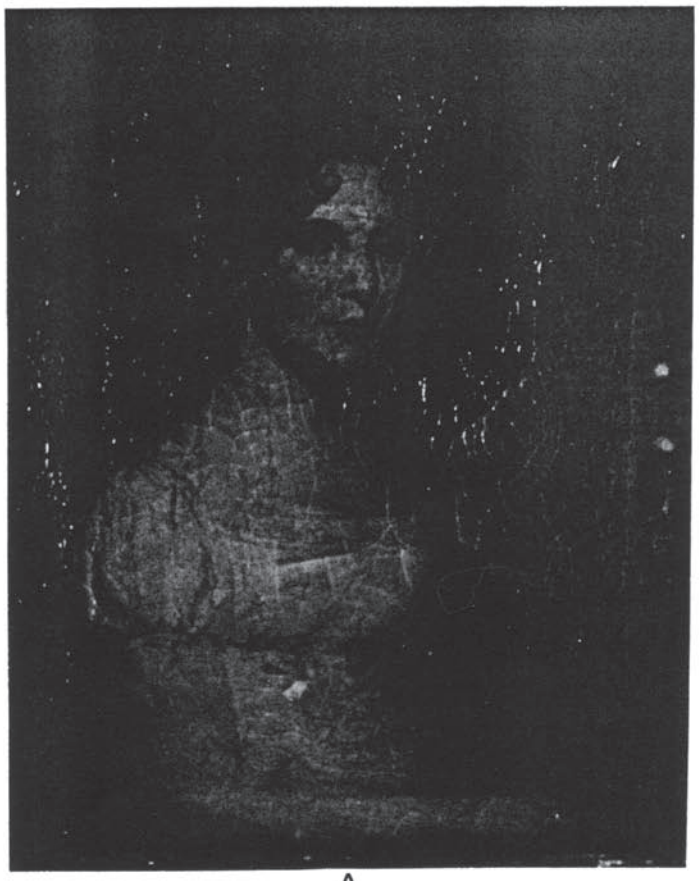
Martin has suggested Bromcresol Purple (.1% in ethanol) as a color indicator for natural resins, by virtue of any resin acids which might be present in a particular material. The author points out as well that oils to some extent contain free acidic groups as well, although to a lesser extent. To these materials one must add proteins and some sugar or polysaccharides as well; and along with the variety of materials which contain acidic functional groups, it should be pointed out that even within the limited group of natural resins which form the basis for traditional coating materials, a fairly wide range of acid containing material is possible as well(33). Dammarolic acid may represent only 1% of total we1ght of certain dammars; on the other hand elemolic acid may constitute upwards to 30-40% of gum e1emi. These numbers, of course, certainly change with manufacture, age and treatment history of the mater1a1. One feature of some of the natural resins exploited by us in terms of a fluorescent staining-type reaction is the formation of the hexachloroantimonate salt of a carbonium ion generated by stenols in the presence of antimony pentachloride(34). The hexachloroantimonate fluoresces a bright blue-white in color under long wave ultraviolet light illumination. In the presence of naturally aged, autof1uorescing resins only an increase in fluorescence is noted, not a distinguishing fluorescent color; on the other hand, resinous materials which are not autof1uorescent can be made visible this way, as can some asphaltic material apparently by virtue of its highly polycyclic core or aspha1tene material. The antimony pentachloride can be delivered to a sample as a 20% solution in chloroform; the chloroform volatilizes away , immediately, and excess antimony penta- and tri-chloride sublimates away. The sample is wiped cleaned and coverslipped with Shell-So1v as described above.

As general classes of materials, the organic structures which have formed the basis of traditional western art or finish making binders lend themselves to examination not only by their interaction with visible light, but ultraviolet and infrared interactions as well. As early as 1911 (Stube1) and 1913 (Wasicky) investigators attempted to classify organic materials by their uautof1uorescent properties(35). The discovery of certain synthetic fluorescent dye types predates even these studies (Fluorescein, 1871, and Rhodamine, 1887) by a good margin(36). With the introduction of the first true1y fluorescence microscopic apparatus by Hemstadt and Lehman in 1911, the examination and selective staining of microscopic samples began in earnest. Early landmark papers on either autof1uorescence or fluorescent staining have to include Bommer (1929), Haitinger and Hamperl (1933), Haitinger (1938), Eichler (1934-35), and Haitinger and Lins (1934-35). Through this series of works one can track the progressive developmental use of fluorochromes to selectively stain and make visible certain organic structures, and the recognition of critical staining factors with regard to stain concentration, staining times, pH, and secondary or multiple fluorochroming(37). The first use of a fluorescent-antibody reagent is surprisingly early as well (Coons, 1941)(38). FITC as a specific relative derivative of fluorescein for labeling proteins in It nonaqueous environments is first introduced by Rinderknecht in 1960(39); Fluorescamine by Undenfriend (1972)(26); and Lissamine Rhodamine Sulfonyl Chloride in 1958 (25) . By car e full y a d apt i n g their use to the special requirements of paint cross-sectional examinations, conservators or conservation scientists may realize some of those benefits, directly or indirectly stated in the above discussion. That is, as aids in visualizing the presence and contextual relationship between materials, their quantity, location,

interaction, and change with age and treatment. The following case studies are offered as examples of how this kind of information has been utilized by us in either apprehending or conserving certain painted or finished structures.

CASE STUDY #1

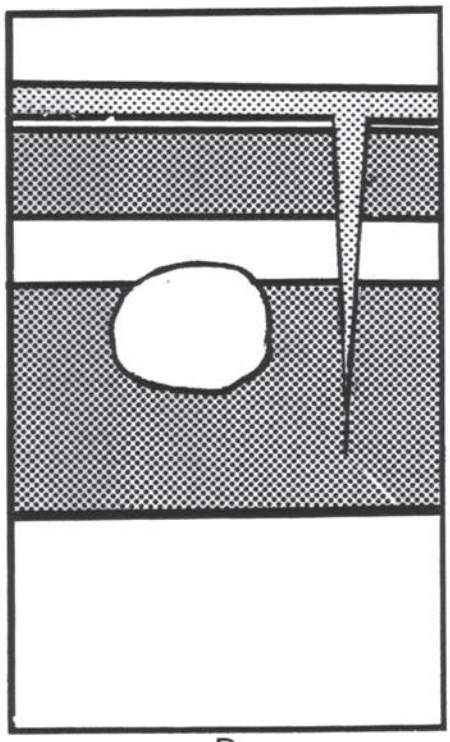
A 25" x 30" Portrait of Anna Ross Hopkins by Jacob Eichholtz (1813) descended through the sitters family and was bequeathed to the Heritage Center of Lancaster County, Inc. in 1967(Fig. lA). On examination in the studio, the overall appearance of the painting was very dark; the uppermost surface coating was extremely yellowed with age and grime laden. On examination in cross section(Fig. lC) the uppermost surface coating exhibited a bright red fluorescence when stained with a .25% Rhodamine B solution in Ethanol, indicating a relatively high oil content to that layer. As part of the treatment course, a Lipolytic enzyme/detergent solution was used to hydrolyze and subsequently solubilize the surface coating. Two features of the painting structure, revealed in cross section, made the choice of this approach to cleaning a logical one. 1) - The uptake of the dye (Rhodamine B) is proportional to the content of the oil component of the surface coating; it's - possible to quantitate this uptake by directly measuring the fluorescence produced by the stain in a non-polar environment, by means of a micro-spectrophotometer, or by adapting to the task any general micro-photometry system, with a variable format diaphragm, and a capacity to measure - at individual or restricted wave lengths, peak fluorescent emissions. Even qualitatively, the indication from the cross section for a substantial oil component made it feasible to approach its removal with the enzyme/detergent system (Fig. lD, shaded portions are oil containing layers and were positive with Rhodamine B). 2) While very thin, an original varnish layer, composed of primarily a natural resin lay underneath the uppermost oil containing coating. - It autofluoresced only weakly overall, but in most cases appeared to form a continuous film of material between - paint and the most recent coating, and could act as an effective "mask" or "stop" for the enzyme to protect the original paint from enzymatic hydrolysis. Its autof1uorescence was used to distinguish and characterize the older original varnish layer, and indicate a very low oil additive or modifier in it, making it a poor substrate (and a good barrier) for a Lypolytic enzyme treatment (Fig. 1B) is the surface coating partially removed from the painting in the lower right corner).



A

B

C



D

FIG. 1

CASE HISTORY #2

A general paint survey was performed on the exterior decoration of The Willows, Fosterfields, Morristown, New Jersey, an estate constructed in the mid-1850's by General Joseph Revere, grandson of the Revolutionary War hero. General Revere, an artist as well as a soldier, is generally credited with much of the original interior - decoration; the dining room is elaborately decorated with trompe l'oeil murals and fauxbois trim elements. While - little was known of the exterior decoration history, the trustees of the estate were interested in both the original as well as the exterior decoration during the 1890's, during the tenure of one of the estates subsequent owners. In cross section, the original exterior appeared to be a complex layered construction of base coat(s) of a proteinaceous binder, followed by layers of oil paint and toned resin varnish to build a visual presentation that was additive rather than direct. As an example, Figure 3A shows the bottom of a sample removed from an engaged column on one of the porches on the house; here the bottom brown layer (base color) is covered with a red layer, and a highly weathered thin black layer. Under ultraviolet illumination the red layer splits into two distinct layers (Fig. 3B), the uppermost of these autofluoroescing brightly. When stained with Rhodamine B (.25% in Ethanol) Fig. 4C), the red layer picked up the dye and fluoresced a bright red orange in its binder. A small band of autofluorescing unstained material surrounding the black pigment particles on top of the red layer remained negative for oil or protein stains, yet clearly indicated a black glaze-like material, that was distinct from what might have been otherwise mistaken as a grime layer. Schematically this is represented in Figure 4D in the layer labeled (2) as a non-staining material at the top of this layer. Part of the increased fluorescence and oil penetration in the top of layer (1) is due to the immediate application of oil bound material onto this relatively porous base coat. The layer marked (A) is a filler (Calcium Sulfate) used in preparing the wood substrate prior to painting. The layering of a thin black glaze over a red opaque layer would produce a brown layer in overall appearance; color restoration to this original scheme would have to mimic the effect of both layers and not simply, a priori, proceed from the assumption that the bottom-most continuous paint layer was the original presentation surface. A Leitz Orthoplan Microscope fitted with an SP-MPV (Leitz, also) Micro-Spectrophotometer was used to reconstruct the original color by measuring the combined visible light spectrum of the two layers simultaneously. Media

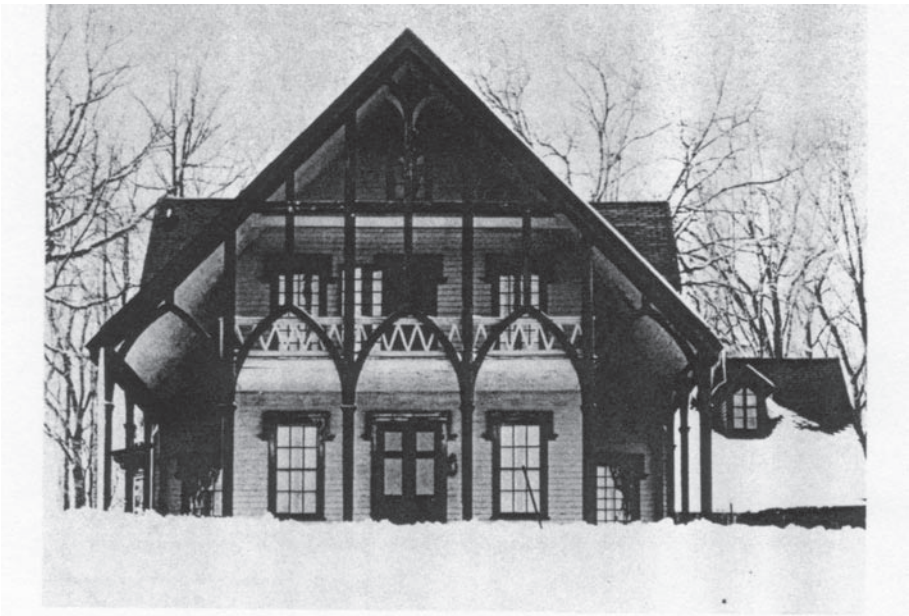
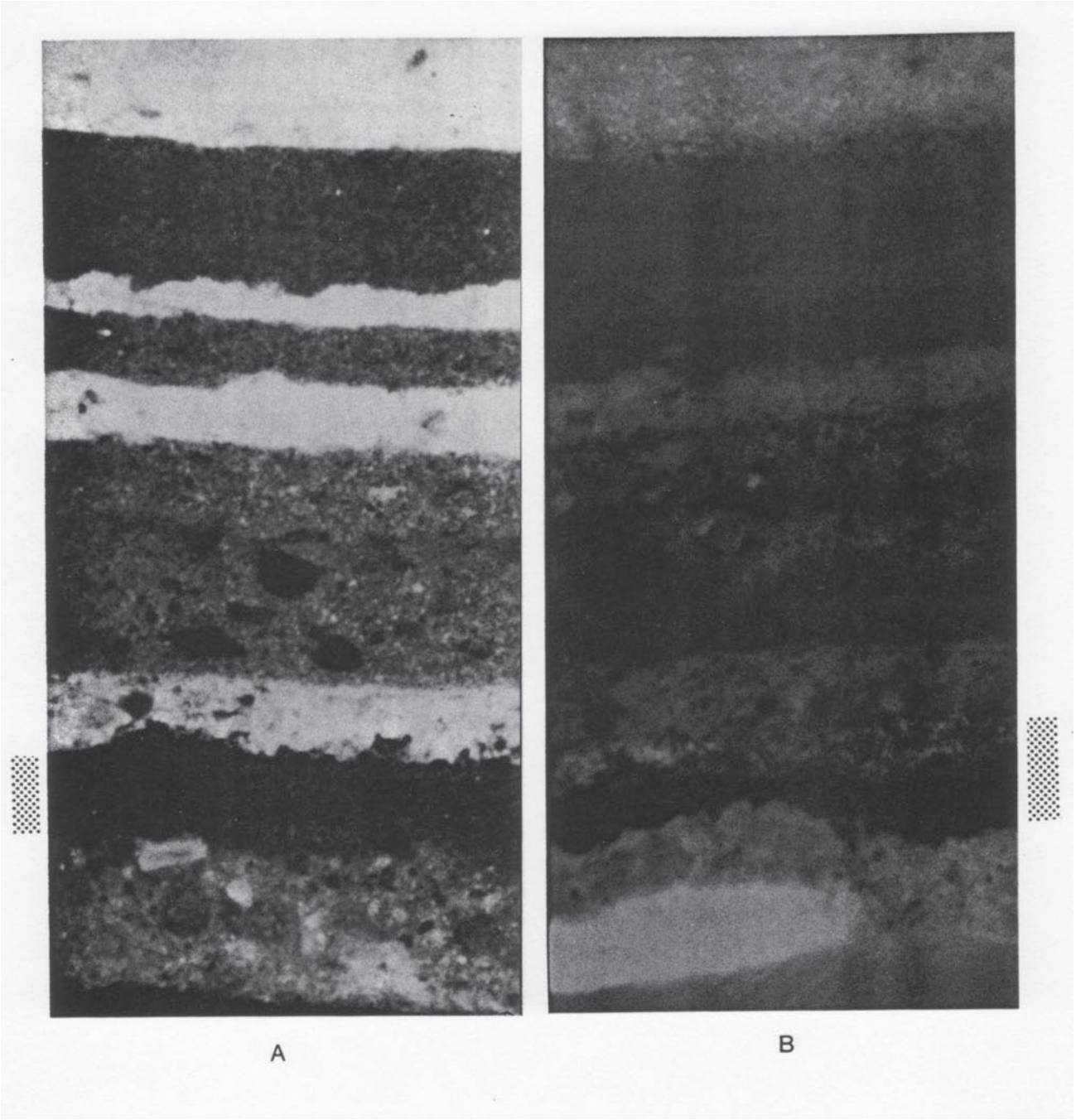


FIG. 2

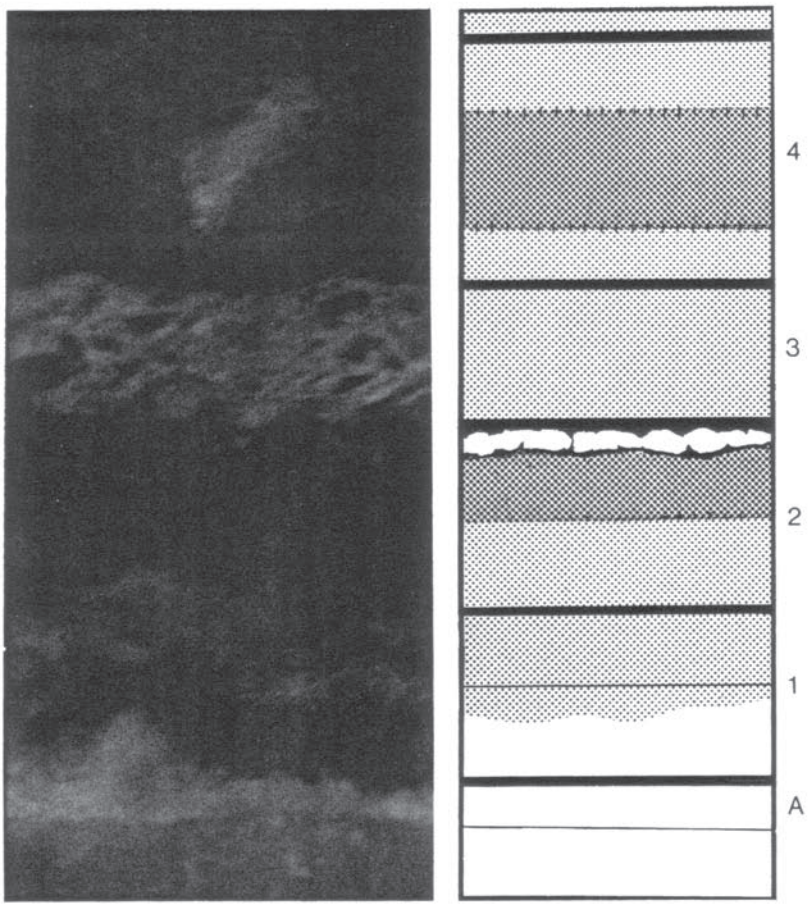


A. Sample WIL32.800x,tungsten/halogen

B. Same. UG1 excitation. 430nm suppression

FIG. 3

staining with FITC (.25% in Acetone) and Rhodamine B helped locate later paint layers which appear to be similar to emulsion type paints (linseed oil and casein) introduced by about the mid-1870's commercially Figure 5, Layer 2 (40). This aided in making sense of the paint chronology and appearance for The Willows before the turn of the century(4l).

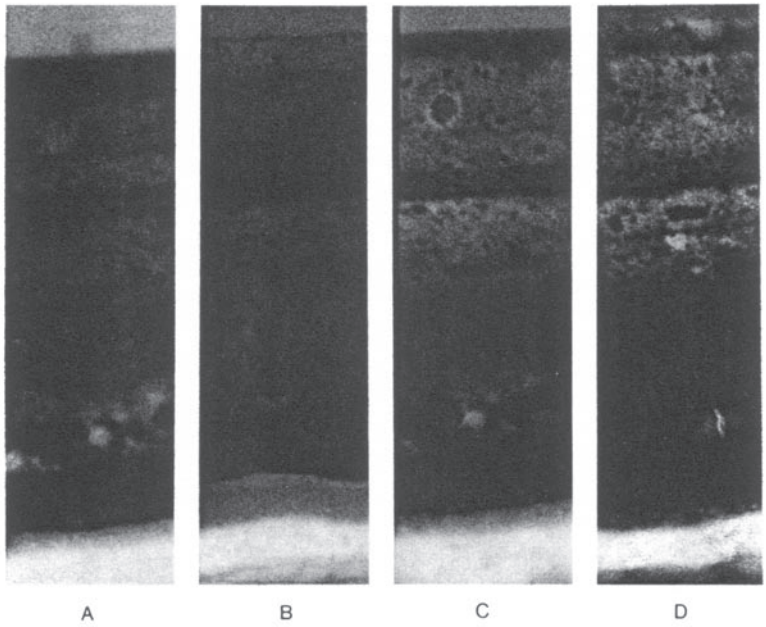


C. Stained. .25% Rhodamine B in ethanol (WIL32 sample)

D. Diagramatic view of (C)

FIG. 4

41).



A. Unstained. UG1 excitation, 430nm suppression, HBO200W Hg lamp 400ASA Daylight Ektachrome (800 x).
B. Same, Stained with RhodamineB..2S%in ethanol (Sigma)
C. Same. Stained with FITC. .25%, in acetone (Sigma).
D. Same. Stained with (C) then (B)

FIG. 5

CASE STUDY #3

A po1ychromed bust of George Washington (Fig. 6), once belonging to the Philadelphia Hose Company (c.1880's), was acquired by Winterthur (WM63.733) and displayed above the main entrance to the Museum. In appearance, a rapid darkening of all the paint media, especially in the figures It face was noted. In cross section (Fig. 8A), the construction was straight forward; wood substrate was coated with creosote, the paint applied in flat monochromatic colors over this, and a thin natural resin varnish applied overall. The accumulation of grime and the yellowing of the surface coating alone were not sufficient to explain the darkening effect in appearance. When stained with antimony pentachloride (20% in chloroform) diffusion of the natural resin (compr1s1ng the surface coating) into the oil paint, as well as substantial diffusion of a SbC1S positive material from the asphaltic' creosote layer under the oil paint and into it was noted (Fig. 8B). Schematically, Fig. 8C, the extent of diffusion is denoted by the shaded portions of the diagram from layers (the surface coating) and (3-the creosote) into the paint layer (2). A solvent sensitivity of the paint was observed to the solvent mixtures required to remove or reduce the surface coating, probably due to the extent of diffusion of surfacing resin and the material coming from the creosote. In treatment, aqueous resin-based detergents were used in place of the normal course of solvents to minimize swelling and partially solvation of the upper portion of the oil bound film (Fig. 7).

FIG. 6

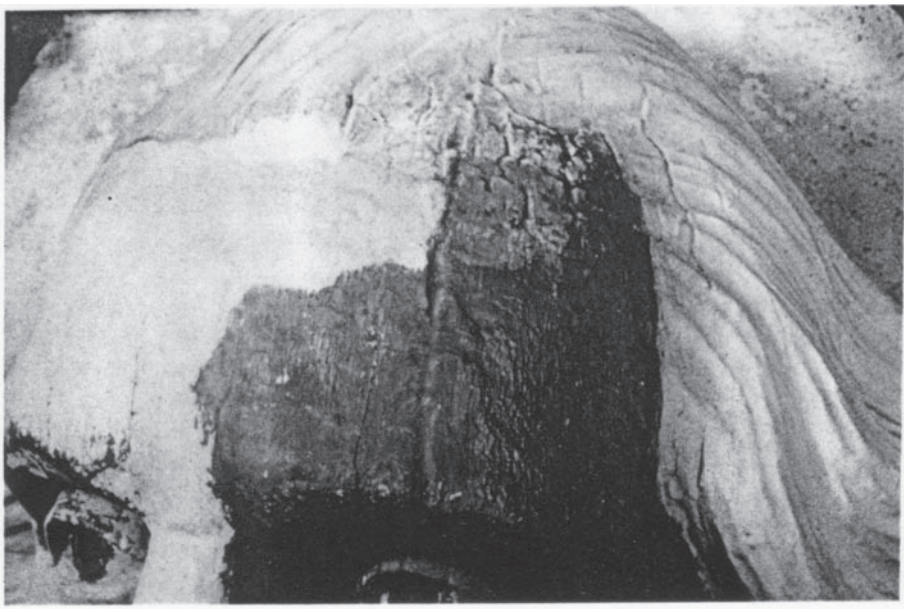
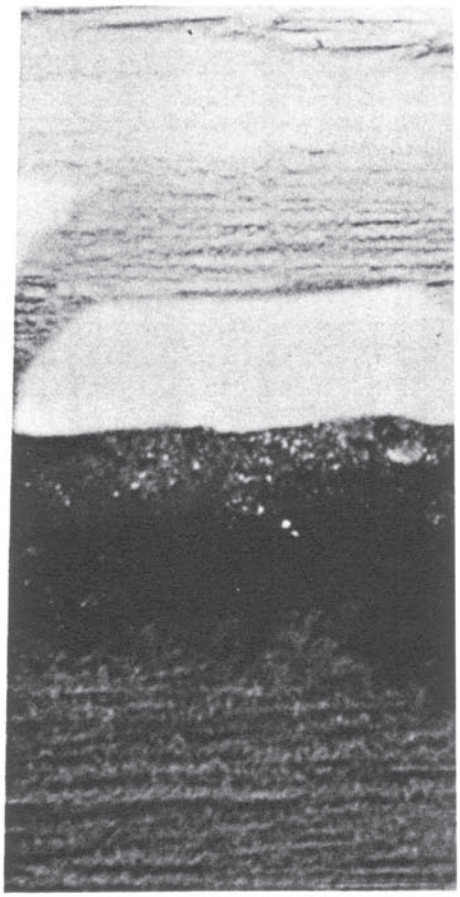
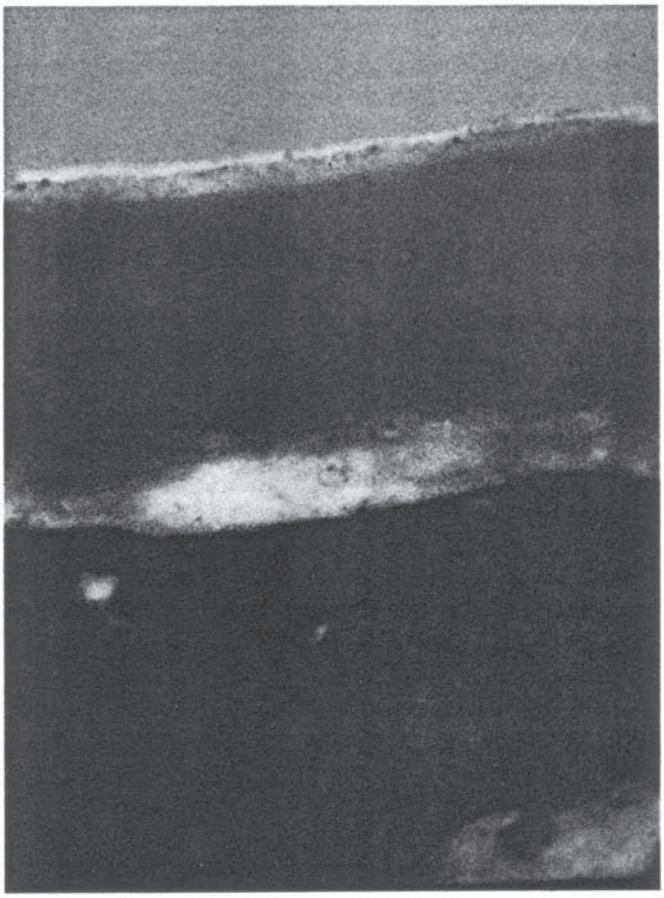


FIG. 7





A. (above) Washington polychrome sample-normal light (400x)

B. (u.r.) same, UG1 excitation, (800x), stained with 20% antimony pentachloride in chloroform, 430 nm suppression

C. (right) diagramatic view of (B). The shaded portions represent $SbCI_5$ positive material.

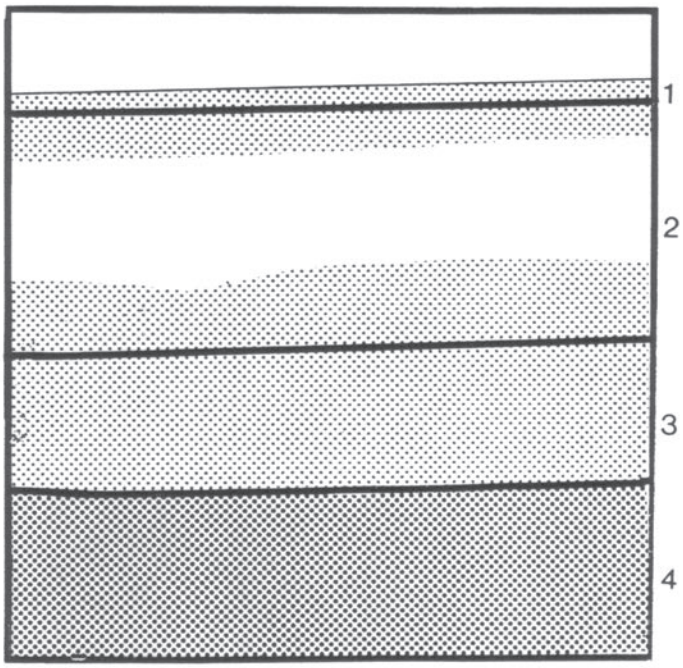


FIG. 8

CASE STUDY #4

An empire bureau in 1830 by Walter Pennery, a Philadelphia cabinetmaker, was purchased by Winterthur in 1980 (WM 80.116, Figure 10) (42). A macro-examination of the finished revealed a crazed but fairly thin resinous coating. Sections of the finish protected from the environment exhibited a highly lustrous surface much like that of a French polish coating(43). On examination in cross section (Figure 11) several important finish characteristics were revealed when stained with a .25% Rodamine B solution in ethanol. A bright red fluorescence in the area of the finish/wood interface (Figure II, 2) indicates . The presence of a fatty acid material such as would be found in an oil. It is known that coating the wood with(44) an oil prior to the application of a resinous finish was done in the period that this piece was made. The bleeding of this material into the porous structures of the wood and the lower finish layers clearly illustrates the unique interaction of individual finishing components revealing a rather complex coating structure. The saturation of the finish into the micro-structure of the wood suggests that this surface coating is the first one applied to the object. The fine layering of the finish visible in cross section would be consistent with a French polishing system. The faint red orange fluorescence may indicate the use of oil as a lubricant in the padding on process. The treatment for this finish will entail a cleaning with a non-ionic surfactant, light mechanical abrasion and a padding on a thin shellac layer to recreate a French polish surface. This approach is based on both micro-analysis and its art historical context to render the piece more true to its original visual impact while minimizing interference with the existing coating layer.

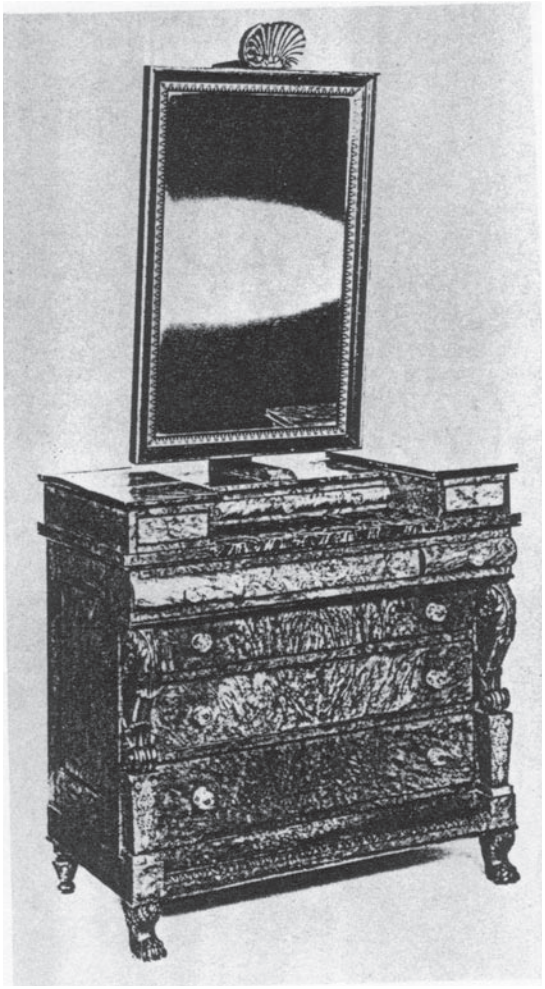
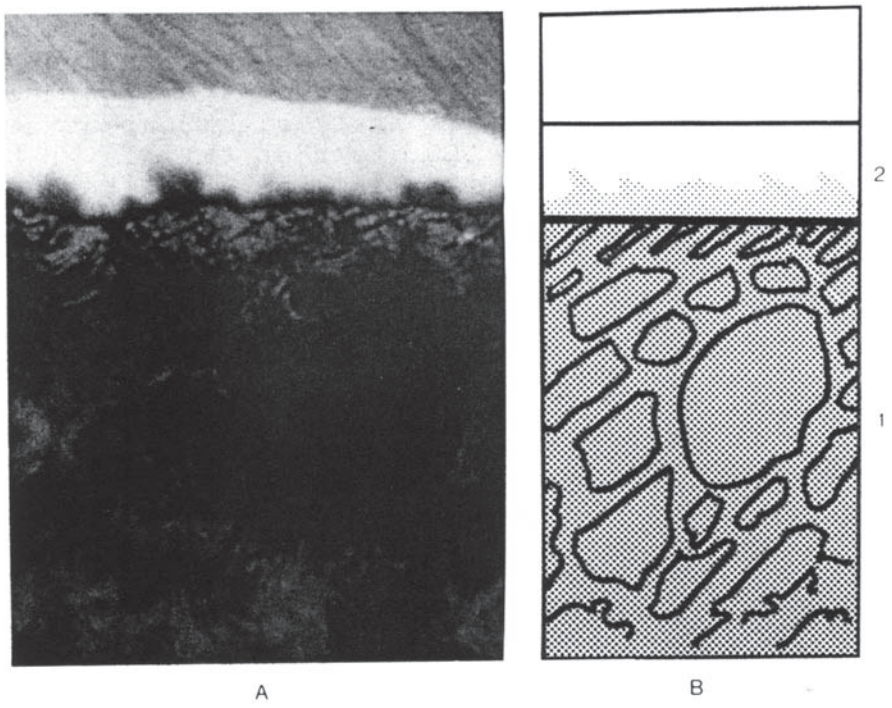


FIG.10

CASE STUDY #5

This painted armchair is likely to have been made in the Baltimore, Maryland, area around 1815 (WM 59.571, Figure 12). The three chinoisere scenes on the crest rail, splat, and the tablet about the front stretcher make the painted decoration of particular interest(45). Prior to treatment, the macro-examination of the chair gives the viewer a rather flat almost mono-chromatic impression of the surface detail except for the/chinoisere. It appeared that there was a disfiguring coating of some sort hiding geometric paint schemes, color varieties and gilding. The cross sections (Figures 13-15) revealed a highly complex paint and varnish structure visible when stained with a .25% Rhodamine B solution in ethanol (Figure 15). The original structures seen have included layers of ground, pigment, metallic coatings, toned varnish, varnish grime, and a/, later oil based coating. The cross section viewed under transmitted light (Figure 13) shows only three distinct layers: (1) paint, (2) a metallic coating most likely a “bronze powder”, and (3) a varnish layer. A limitation of using just transmitted light is evident here. The varnish layers are not distinguishable in the way that they are under ultraviolet light, particularly with a reactive fluorescent dye.



A. Empire bureau sample (800x) UG1 excitation stained with Rhodamine B 430nm suppression.

B. Diagram of (a) OH containing portions are shaded.

FIG. 11

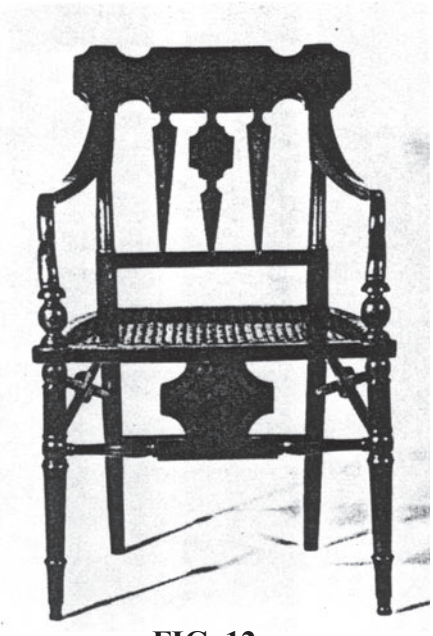


FIG. 12

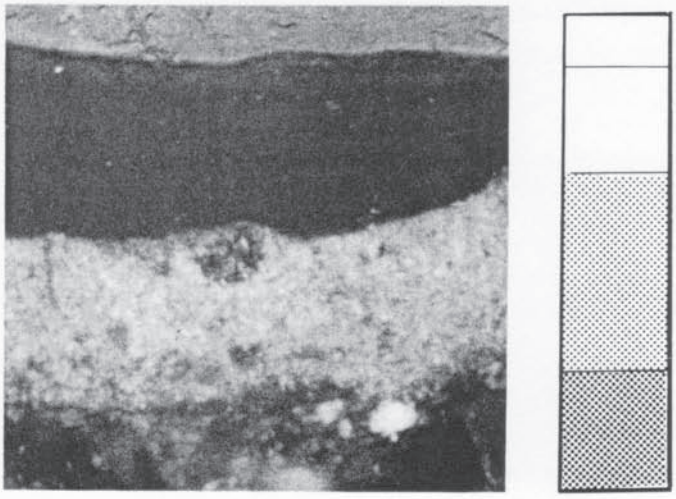


FIG. 13

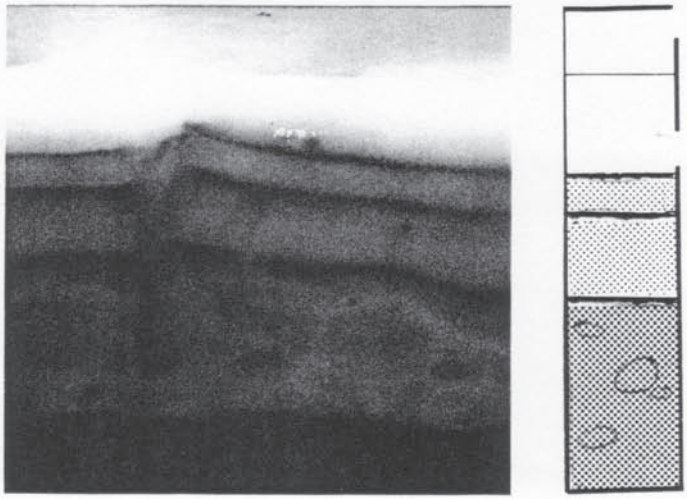


FIG. 14

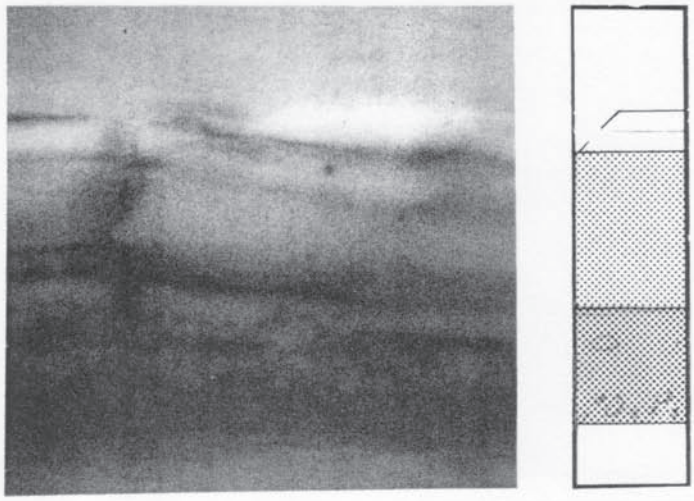


FIG. 15

In the interpretation of the unstained cross section viewed were ultraviolet light (Figure 14), the question came up as to why there are dark zones between the varnish layers (1). A grime layer, which will not fluoresce under these conditions, does not explain this phenomena since these strata are part of the original surface coating. The answer may well lie in the fact that a weak acid, such as acetic acid is known to have been used in varnishing processes between coats to prevent the next coat from crawling(47). Such a technique would cause a darkening of the surface of each coat. Suggesting this possibility is quite reasonable in light of the information rendered in use from fluorescent microscopy and the study of paint and varnish techniques contemporary with the piece.

The cross section stained with Rhodamine B is most revealing (Figure 15). The upper two layers (3) can be differentiated from the rest of the structure in composition and stratification characteristics (also visible in Figure 14, 2). It is this component of the surface coating that was suspected of obscuring the varnish and paint scheme beneath it. The red orange fluorescene.' indicated that there was a relatively high concentration of a drying oil present. It is likely that this layer had been applied to add gloss and color saturation to a somewhat degraded surface. The high oil content of the added layer explains the darkening that has occurred as this "reviver" aged causing the loss of visual detail. Because of a true grime layer between this later addition and the top of the original structure, it appeared logical that this section could be safely separated from the original structure with an enzyme/detergent system. The #1; cross section in Figure 15 shows this cleaning procedure in process. Part of the disfiguring layer has been removed with the enzyme/detergent without affecting the original surface structure even in the area of the crack. The cleaned part of the cross section can be seen on the left while a part of this obscuring layer can still be seen on the right (3).

The cleaning of the chair revealed extensive use of toners in the varnish layers to give a three dimensional affect through shadowing and to create an appearance of antiqued bronze in the gilded areas(48). These critical aspects of f' the chair's original paint scheme would have been altered or obliterated if a solvent based cleaning system had been used. Understanding the nature and interrelationship of r the layers, what the original structures were and what materials were present proved crucial to designing a cleaning system specific to the object that would serve to enhance the appearance of the piece while leaving the original surface coating intact.

CASE STUDY #6

The Du Pont Dining Room of the Winterthur Museum has what appears to be a set of sixteen American Federal style side chairs dating from about 1800 with a New York provenance (WM 57.838.4, Figure 16). Closer examination of the pieces does indicate that there are actually four distinct groupings of chairs(49). A micro-analysis of a finish cross section revealed even further how the chairs have significant differences in the composition and layering of the surface coating. Used in a comparative sense, fluorescence microscopy can further our understanding to what extent objects, or what particular parts in an object, may have had varying histories of care, use, and origin as evidenced in the record of the surface coating.

With this particular side chair, a cross section revealed three distinct parts of the finish stratification when stained with Rhodamine B (.25% in ethanol) (Figure 17). The lower layer (1) fluoresces moder-

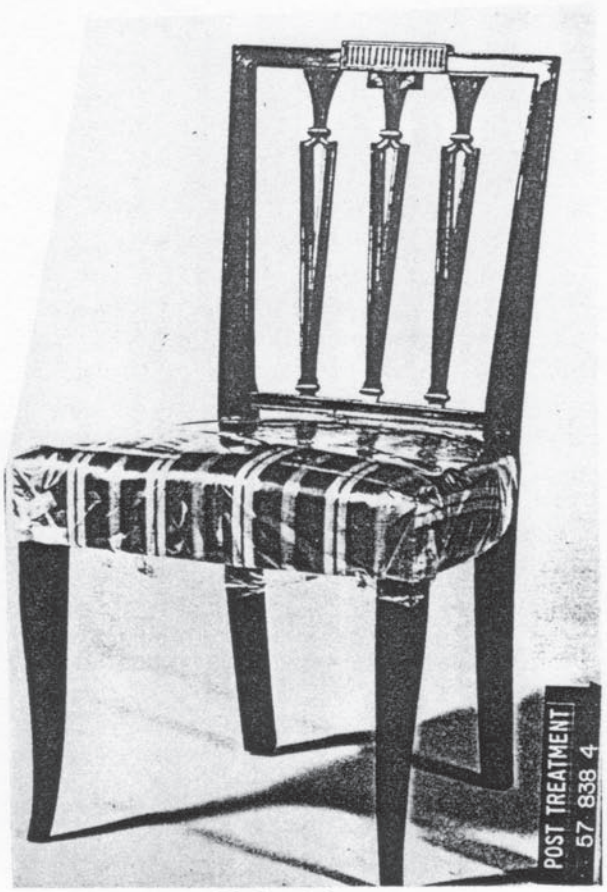


FIG. 16

FIG. 17

ately with some interruption. The middle layer (2) reacts more brightly, having a consistent red orange fluorescence indicating a fatty acid component. The upper non-fluorescing dark section resting on layer (2) is likely a resin coating with some grime apparent on the top. The dark band between layers (1) and (2) may be a result of layer separation.

The major concern about the finish on this chair was the dark and sticky nature of the surface coating. The cross section indicates a grime and resin (3) layer deposited on and integral to an oil based layer (2) that is different in composition and stratification from the earlier layer (1). The information gleamed from this cross section supported a limited treatment of cleaning with a non-ionic detergent pirmari1y to remove grime without affecting the lower strata. This was successfully carried out followed by a rubbing with rottenstone and whiting to created a polished surface properly prepared for a bees and carnauba wax coating(50).

CASE STUDY #7

Whether or not a finish is original is a question often asked about objects of reasonable age. The likelihood of a resinous surface coating lasting for several centuries is low(51). However, our response is often subjective with the lingering question of whether of not some of the original finish materials might still exist under subsequent finishes and polishes(52). Concerns about the original surface coatings on this Federal style sofa (WM 57.863, Figure 18) dating from about 1805 were raised at the treatment proposal stage(53). A cross section (Figure [\ 19) from an area covered over by later upholstery revealed some critical information. The layering viewed under ultraviolet light without stain indicates that stratum (1) is one layer rather than the two actually present. The bottom layer (1) has small red pigment particles while the layer above it (2) has larger black pigment particles. This suggests that this varnish layer was intended to tone the wood to a particular color. The top be contemporary coatings even though of varying composition. The macro-examination shows the finish to be mainly transparent with a reddish cast covering a birch (Betula spp.) seat rail to make it look like mahogany. This evidence was used as part of the proposal suggesting that the birch seat rail of the sofa was originally exposed and finished to match the more prominent mahogany (Swietenia spp.) woods found : elsewhere on the piece.

The lower stratum (1) shows the special relationship that an original coating has with a wood substrate in that there is clear penetration of the resin and medium into the porous cellular structure (1) of the wood that is virtually permanent. The area where the section came from was left intact not requiring treatment. the information gathered from ultraviolet microscopy in this case did not relate specifically to finish cleaning but rather to the original form of the object.

References

1. Plesters, Joyce. “Cross Sections and Chemical Analysis of Paint Samples”, Studies in Conservation, Vol. 2, No.3, April, 1956.

2. Johnson, M. and E. Packard. “Methods Used for the Identification of Binding Media in Italian Paintings of The Fifteenth and Sixteenth Centuries”, Studies in Conservation, Vol. 16, 1971, pp. 145-164.

3. Martin, Elizabeth. “Some Improvements in the Techniques of Analysis of Paint Media”, Studies in Conservation, Vol. 22, 1977, pp. 63-67.

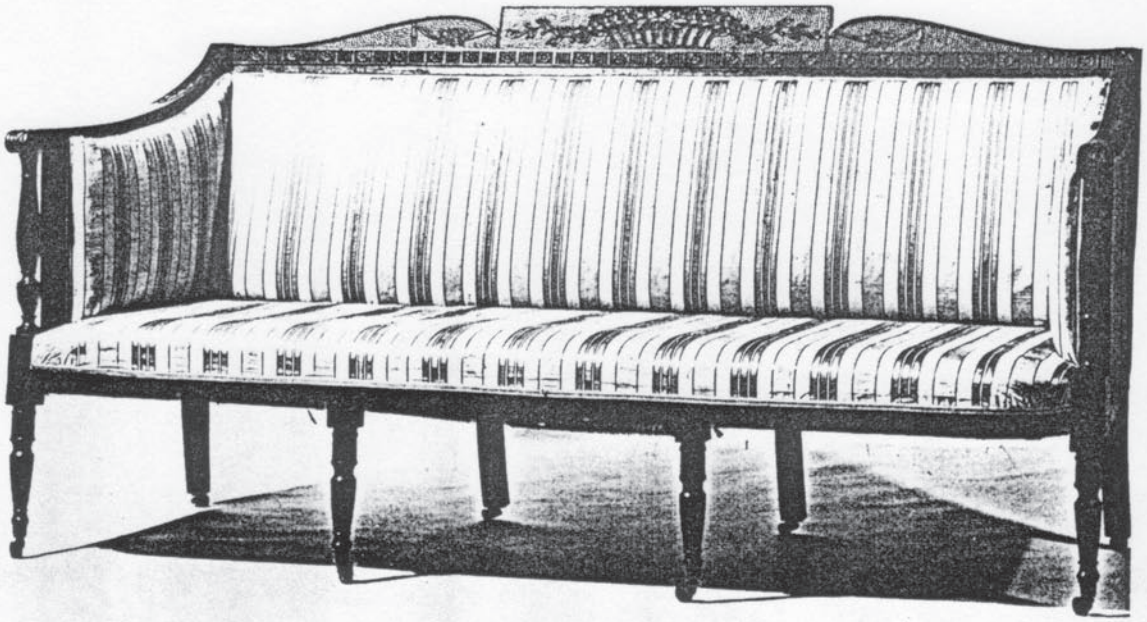
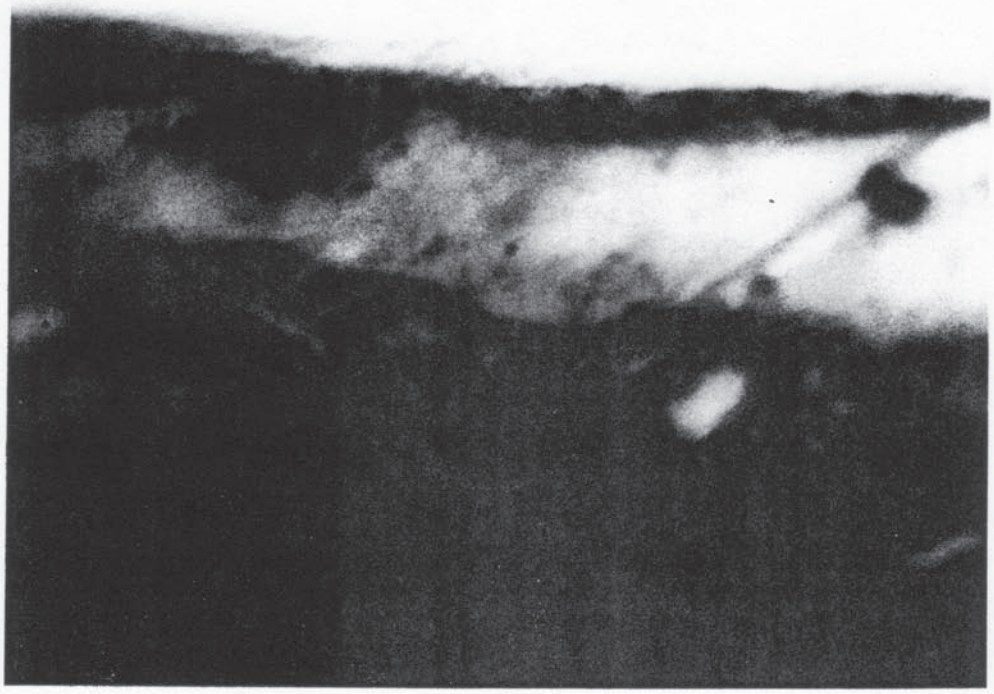


FIG.18



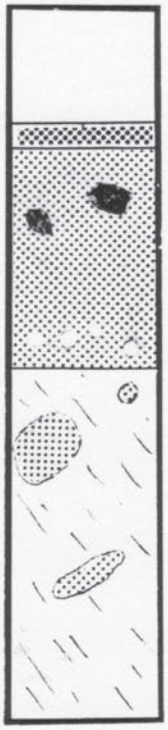


FIG.19

4. Perrault, Carole. “Techniques Employed at the North Atlantic Historic Preservation Center for the Sampling and Analysis of Historic Architectural Paints and Finishes”, Bulletin of The Association for Preservation Technology, Vol. X, No.2, 1978, pp. 6-46. See Appendix ‘LL A for solubility tests for media.

5. Batcheler, P. . “Paint Color Research and Restoration”, American Association for State and Local History, Technical Leaflet 15; History News, Vol. 23, No. 10, October, 1968.

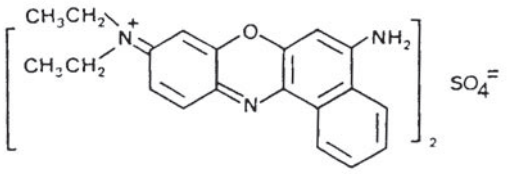
6. Low, M.J.D. and N.S. Baer. “Application of Infrared Fourier Transform Spectroscopy to Problems in Conservation”, Studies in Conservation, Vol. 22, No.3, 1977, pp.116-128.

7. May, R.W., et al. “A Reproductible Pyrolysis Gas Chromatographic System for the Analysis of Paints and Plastics”, Cambridge Engineering Monthly, Vol. 98, 1973, p. 364.

8. Pizey, .J.S. Synthetic Reagents, Vol. 1. New York: John Wiley, 1974, pp. 4-99.

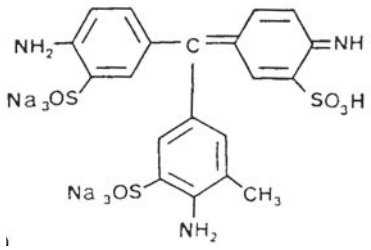
9. Kittilia, R.S Dimethylformamide Chemical Uses/Suppl. Dupont Company, Wilmington, DE, 1967. The Merck Index also noted that DMF is a “solvent for Orlon and similar Polyacrylic Fibers, whenever a solvent with a slow evaporation rate is required, has been termed the universal solvent”. The pH of a .5m solution is 6.7 in water.

10. The structure of Nile Blue is:



J. Histochemistry, 4, 1956, p. 377.

11. The structure of ‘ Acid Fuschin is:

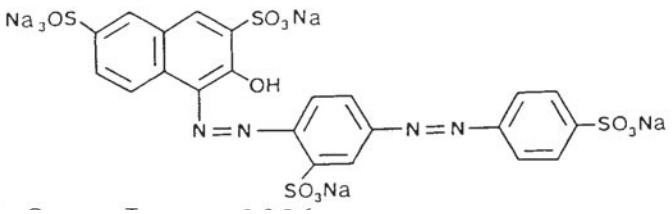


N.Y. Medical Journal, 50, p. 57, 1889.

12. Clark, G. and F. Kasten. History of Staining. v Baltimore and London, Williams and Wilkins, 1983, p. 200.

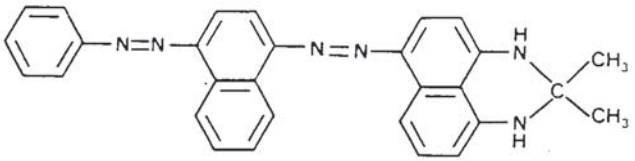
13. Op. Cit., pp. 93.94.

14. The structure of Ponceau S is:



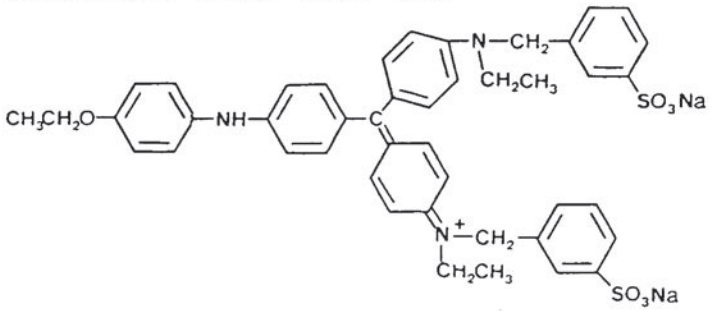
Milwaukee, WI, Aldrich Chemical Co., Inc., 1986 Catalog, p. 1119.

15. The structure of Sudan Black B is:



Milwaukee, WI, Aldrich Chemical Co., Inc., 1986 Cataogue, p. 1208.

16. The structure of Coomassie Brilliant Blue R250 is:



Biochemistry, 20, 1967, p. 150.

17. Morrison and Boyd. Organic Chemistry. Boston, Allyn and Bacon, Inc., 1973, 3rd Edition, pp. 853-854. Describes the relatively mild conditions by which keto acids undergo decarboxylation.

18. Op. Cit., p.898. Amino groups located alpha to a hydroxyl group, can be deaminated through the action of nitrous acid. Primary amines can also react to form unstable diazonium salts as well.

19. Metzler. Biochemistry. New York, NY, Academic Press, Inc., 1977, p. 73. Describes the oxidation of cysteine to form the disulfide and hence a cross link in sulfur containing proteins.

20. Op. Cit., pp.284-285.

21. Talbott, R., “The Fluorescent Antibody Technique in the Identification of Proteinaceous Materi-

als", in Papers Presented by Conservation Students at the Third Annual Conference of Art Conservation Training Programmes. Ontario, Canada, Queens University, 1982, p. 140.

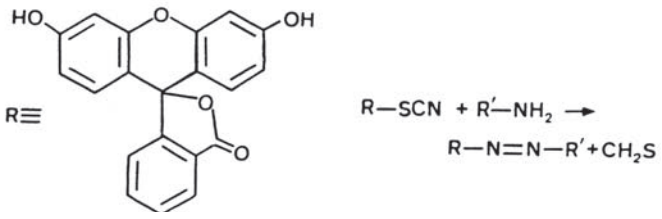
22. Pearse, A.G.E. Histochemistry: Theoretical and Applied, Vol. 1. Edinburgh, Churchill Livingstone, 1980, p. 93.

23. Metzler, p. 285.

24. For the original description of the immunofluorescence technique, see Coons, et al, "The Demonstration of Pneumoccocal Antigen in Tissues by Use of Fluorescent Antibodies", Journal of Immunology, 45, 1942, pp. 159-170.

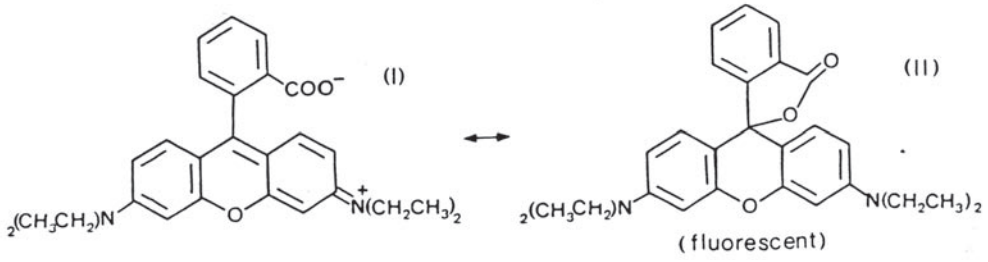
25. Chadwick, et al., "Fluorescent Protein Tracers", Immunology, I, 1958, p. 316.

26. The structure of Fluorescein Isothiocyanate is:



Milwaukee, WI, Aldrich Chemical Co., Inc., 1986 Catalog, p. 669. See also McKinney, R., et. al., "A Simple Method for Determining the Labeling Efficiency of Fluorescein Isothiocyanate Products", Analytical Biochemistry, 14, 1966, pp. 421-478.

27. The structure of Rhodamine B is:

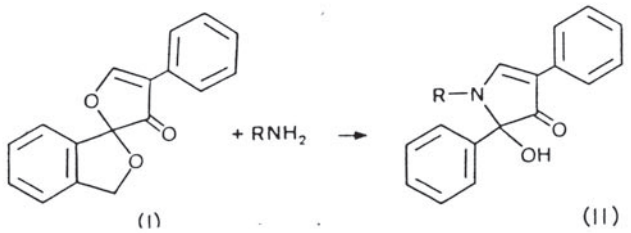


(in aqueous environments) (in non-polar environments)

The acid chloride and sulfonyl chloride have been prepared of (II) above at the 5 carbon.

28. Lissamine Rhodamine Sulfonyl Chloride is a tradename of Imperiral Chemical Industries, Inc.

29. The structure of Fluorescamine is(I):

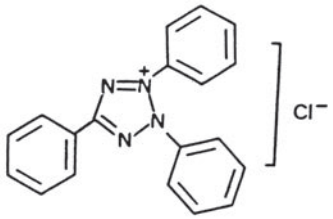


(I) forms a water clear solution in Acetone, and is non-fluorescent; (II) as the amine adduct fluoresces a bright blue white. Weigele, M., Fluorescamine: A Reagent for Assay of Amino Acids Peptides, Proteins, and Primary Amines in the Picomole Range", J. Amer. Chern. Soc., 94, 1972, p. 5927.

30. Sigma Chemical Co., St. Louis, MO, 1987 Catalog, p. 1527, is sold as a general TLC spray reagent for Lipids.

31. Cheng, K.L.,et. al., Editors. Handbook of Organic Analytical Reagents. NY, CRC Press, Van Nostrand Co., 1982, p. 287.

32. The structure of Tripheny1 Tetrazo1ium Chloride is:



Aldrich Chemical Co., Inc., 1986 Catalog, p. 1338.

33. Mills, J. and R. White, "Natural Resins of Art and Archaeology; Their Sources, Chemistry, and Identification", Studies in Conservation, Vol. 22, 1977, pp. 12-31.

34. The reaction is:

$$ROH + 2SbCl_5 \longrightarrow R^+SbCl_6 + SbCl_3 + Cl^- + OH^-$$

Holmes, J. and R. Petit, Journal Organics, 28, 1963 pp. 1695.

35. Clark, History of Staining, pp. 158-159.

36. Op. Cit., pp. 152-153.

37. Op. Cit., pp. 160-162.

38. Op. Cit., p. 146.

39. Rinderknecht, H., Nature, 93, 1962, p. 167.

40. Martens, C. Technology of Paints, Varnishes, and Lacquers. Huntington, NY, Krieger Publishing Co., 1968, p. 4. "The First U.S. Patent was issued 1n 1865 to D. P. Flinn; it covered a water base paint of zinc oxide, potassium hydroxide, resin, milk, and linseed oil" i.e., an oil/protein emulsion system.

41. This study was presented as part ,of a paper, given to the annual meeting of The Association for Preservation Technology in Austin, TX, October 1-5, 1986.

42. Walter Pennery was a "youth apprentice" of John Jamison. See Donald Fennimore, "New Empire Bureau is Exceptional", Winterthur Newsletter (Spring, 1981), pp. 5-6.

43. A French polish coating consisted primarily of shellac thinned in alcohol. The finish would have been applied with a pad consisting of a linen cloth over a woolen wad thinness, light lustre, and a filled grain characterize this finish. This technique of finishing was known in Philadelphia in the 1830's. A journal published in that city in 1837 states "...we were the First to publish any accurate information on 'French Polish' For wood, now become so universally employed". From The Mechanics' Register or Journal of the Useful Arts, Trades, Manufacturers, Science, Etc. (Philadelphia: J. Libby & Co. Vol. I, Number I, February 22, 1837), pp. 28-29. Published by J. Libby & Co., Philadelphia. See also: The Painter, Gilder, and Varnisher's Companion. (Philadelphia: Henry Carey Baird, 1859), pp. 72, 102-105.

44. Sizing the wood before finishing has been a common practice for centuries. Hide glue, oils, and dilute resinous coatings are recorded as having been used for this purpose. In the previously mentioned The Mechanics' Register. (February 22, 1837), p. 28. It is suggested that linseed oil be rubbed onto the wood with pumice stones before rubbing on the finish.

45. Dean A. Fales, Jr., Robert Bishop, and Cyril I. Nelson. American Painted Furniture 1660-1880. (New York, Richard March Publishers, 1981), pp. 136-137.

46. "Bronzing in Wood" is discussed in The Painter, Gilder and Varnisher's Companion, 1856, p. 126. Bronze-powder is described as being laid on with a pencil and burnished.

47. Henley, M.E. and Gardner D. Hiscox. Henley's Twentieth Century Book of Formulas, Processes and Trade Secrets. (New York: Books, Inc., 1967. First Edition 1907). The following reference can be found: "Preventing varnish from crawling-rub down the surface to be varnished with sharp vinegar. Coating with strongly diluted ox gull is also of advantage." p. 717-718. The Painter, Gilder, and Varnisher's Companion Philadelphia: Henry Carey Board & Co., 1883), eludes to the use of such materials to eliminate crawling but states a strong preference for rubbing hard between each coat with just a flannel rag, p. 228.

48. The Painter, Gilder, and Varnisher's Companion, 1883, discusses the toning of gilt decoration for the carriage painter, trade not far removed from the craft of fancy their decoration. This description is given:

“The shade, which seems the most appropriate for gilt is a transparent. brownish color, which is got by mixing burnt terra de sienna with black asphaltum, varnish and enough oil to keep it from drying too quickly”. p.232.

49. The study and treatment of these chairs was carried out by Scott Friedgen-Veitch, Furniture Conservation Technician, Winterthur Museum. The record of this work is on file at the Registrar’s Office of the Museum.

50. Rubbing out a finish when new or to renew an old one has been part of the finishing craft for centuries. A late 18th century American finisher wrote in his personal recipe book: “To polish begin with pomiss [sic] made new, hot beat to a fine powder with rushes, leather and water rub it smooth...with rag and rotten stone and water, polish it like glass...”. From the account book and dairy of Isaac Byington, Bristol, Connecticut, and Bedford Mills, Georgia, 1786-1799, p. 96. Rare Books Room, Winterthur Museum Library. The use of Pumice rottenstone, tripoli and whiting in the 19th century as polishing abrasives is also discussed in The Painter, Gilder and Varnisher’s Companion, 1856, pp. 70, 101.

51. The composition of some finishes was so complex and unstable that their usefulness was short lived. For more information on traditional finishing materials see: Thomas Brachert, “Furniture Varnishes, Surfaces of Furniture”, Maltechnik Restauro (Vol. I-IV, 1978; U Vol. I, 1977). This is a five part series published in German. This author has referred to two English translations by Josephine R. Landrey and Robert D. Mussey. See also: Robert D. Mussey, “Early Varnishes”, Fine Woodworking, (July/August, 1982), pp. 54-57, and Mussey, “Old Finishes”, Fine Woodworking, (March/April, 1987), pp. 71-74.

52. The variety of materials used to revive an old surface coating on furniture was as great as the types of original finishes that might have been employed. As one example, Sarah J. Hale wrote in The New Household Receipt-Book (New York: M. Long & Bro., 1853), “Rubout Linseed oil each day for months...it will require dry rubbing with a linen cloth for about 10 minutes, twice in a week, to preserve it in the highest perfection; which never fails to please your employers...”, p. 20. Other sources record state beer and vinegar as cleaners. More to the point of proper maintenance, Thomas Sheraton wrote in 1803 “And observe, with a ball of. wax and brush kept for this purpose entirely, Furniture in general may be kept in good order.” See Thomas Sheraton, The Cabinet Dictionary, (2 Vols., c “’ London: W. Smith, 1803, Reprint Edition; Charles F. Montgomery, Ed., New York: Praeger Publishers, 1970), p. 289.

53. Montgomery, Charles F. American Furniture: The Federal Period 1788-1825. (New York: Viking Press, 1966), pp. 304-305, Figure 269.

54. Using a stain or colorant in a varnish layer was a common practice at the time this piece was made. “Mahoganizing” with red and black stains was done to imitate a more exotic wood. See Robert D. Mussey, “Old Finishes”, Fine Woodworking, (March/April, 1982), p. 72.