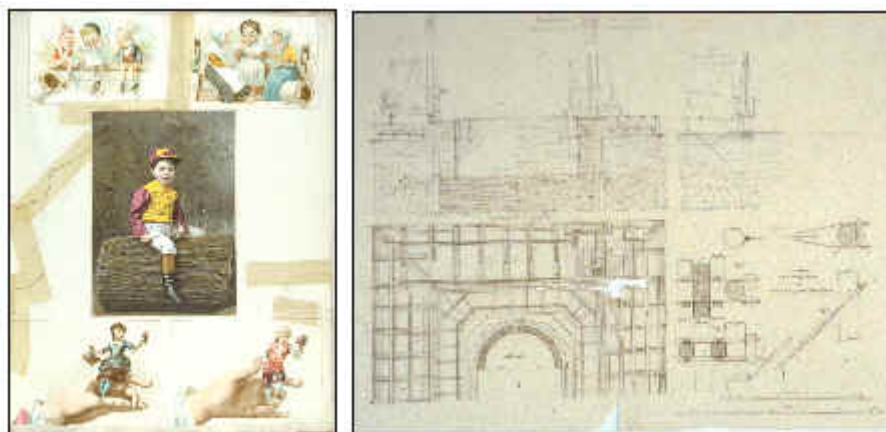


RELACT

HISTORY, TECHNOLOGY, AND TREATMENT OF SPECIALTY PAPERS FOUND IN ARCHIVES, LIBRARIES AND MUSEUMS: TRACING AND PIGMENT-COATED PAPERS

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ABSTRACT

Museums, libraries, and archives contain large collections of pigment-coated and tracing papers. These papers are produced by specially formulated compositions and manufacturing procedures that make them particularly vulnerable to damage as well as reactive to solvents used in conservation treatments. In order to evaluate the effects of solvents on such papers, several research projects were designed to consider the variables of paper composition, properties, and aging, as well as type of solvent and technique of solvent application. This paper summarizes findings for materials characterization, degradative effects of aging, and some effects of solvents used for stain reduction, and humidification and flattening, of pigment-coated and modern tracing papers.

Pigment-coated papers have been used, virtually since the beginning of papermaking history, for their special properties of gloss and brightness. These properties, however, may render coated papers more susceptible to certain types of damage (surface marring, embedded grime, and stains) and more reactive to certain conservation treatments. Several research projects have been undertaken to characterize paper coating compositions (by SEM/EDS and FTIR) and appearance properties (by SEM imaging of surface structure and quantitative measurements of

color and gloss) in order to evaluate changes that might occur following application of solvents used in conservation treatments. Samples characterized include both hand-coated and machine-coated papers. A statistical study was designed to provide reliable data on the effect of two treatments which have been used for cleaning dirt, stains, or accretions from coated papers, namely aqueous immersion and blotter-poulticing, followed by air or blotter-drying.

Tracing papers, also called transparent papers, require specific chemical and physical properties, such as translucency and whiteness, produced by overbeating paper pulp or by acid immersion, coating, or supercalendering the paper sheet. Unfortunately, such papers are exceptionally susceptible to degradation (discoloration and embrittlement), while also prone to loss of translucency and dimensional stability when treated by solvents used in conservation. An initial project characterized selected modern tracing papers using SEM/EDS, FTIR, UV Microscopy, GC-MS, etc. A second project compared effects of aging on some chemical and physical properties of tracing papers. A third project examined the effects of four commonly used stain-removal solvents (water, ethanol, acetone, and toluene) applied by three different treatment techniques (suction, immersion and poultice) to several modern tracing papers. A fourth project examined the effects of treatment techniques (including Gore-tex) used to flatten transparent papers. The effects of solvents and techniques were evaluated by, among other things, SEM/EDS and imaging of surface and cross-sectional distortions in texture, porosity, and distribution and character of inorganic components; UV microscopy of organic binder disruption and migration; and mechanical measurements of tensile strength changes in the machine direction of the papers.

I. PIGMENT-COATED PAPERS:

Pigment-coated papers provide a smooth, white ground for metal point drawings and ink illustrations; an inert ground capable of maintaining registration despite multiple inkings for chromolithographs or off-set lithography; and a luminous, sharp background for letterpress and other relief and intaglio prints, halftone photomechanical prints, bookplates, and photographs. Such papers can pose special problems to conservators, since their surfaces may be more easily marred by scratches, absorbent of stains, and retentive of dirt [1-9]. In addition, pigment coatings and binders may be reactive to solvent treatments. These papers are produced by modifications to standard papermaking practices, including sizing, coating, and calendering [10-32], in order to have specific properties of smoothness, brightness, gloss, opacity, and ink receptivity, required especially by the printing trade [33-63].

Papers may be coated in any number of ways for any number of reasons. Consequently, such papers may be called many things in literature relevant to conservation, including, for instance, prepared-ground paper, prepared paper, clay-coated paper, pigment-coated paper, color-coated paper, coated paper, enamel paper, surface-sized paper, etc., which may be one-side coated, two-side coated, light weight coated, hand-coated, brush-coated, machine-coated, or off-machine coated, etc. The following review of the literature attempts to define some of these terms and provide a brief historical overview of materials and techniques used in formulations (dates provided serve only as an approximation, since they may change depending on reference and geographical sources).

A. Characterization of Pigment-coated Papers

Pigment-coated papers generally consist of a paper base covered by a mixture containing at least a binder and inert pigment (Table I). The earliest examples may have originated from China, where paper surviving from 450 CE is reported to have a starch sizing and gypsum surface treatment [16]. During the Tang Dynasty (CE 618-907) papers were coated with white mineral powders and wax, which filled interstices between fibers in order to increase water repellency and smoothness for fine calligraphy [20]. By the 8th century, Arab cultures had reportedly modified paper with talc, gypsum or chalk, which could also be mixed with rice starch to coat the paper for increased whiteness [10, 12].

During the middle ages, papers were coated with white pigments to provide an appropriate surface for metal-point drawings, executed with a metal stylus made of silver or copper, which before the discovery of graphite represented the only "dry" medium available for very finely detailed drawings [2]. Coated or prepared-ground papers had the additional advantage of being "erasable" in that media could be scraped and/or burnished away (or coated over) if changes were desired. To prepare such paper, coating material, mixed with approximately two parts water, was poured on and hand-bushed evenly over the paper, which was then loft-dried [23]. Burnishing, usually by hand with agate stone, created different surface effects, such as increasing smoothness by evening out surfaces, saturating color by compressing pigment, and creating luminosity from increased gloss. Early treatises on recipes for prepared papers include ground bone ash, powdered cuttlebone, or gypsum, mixed with aqueous binders of glue or gum, or with linseed oil [15, 19, 24, 29]. A treatise on Persian paintings reportedly suggests a two-layered ground consisting of plaster, glue and grape teacle topped by lead white and oil varnish [7]. By the 16th century, coatings were applied to the backs of playing cards, to improve strength and durability. By the mid-16th century (1540) hammer-glazing had replaced hand-burnishing [23]. In the mid-18th century (1764), a coating mixture containing lead white, plaster of Paris, lime size, and nut or linseed oil was patented by George Cummings [19]. There is some reported use at this time of zinc white (1775), a very white, bright and opaque pigment [21, 22]. After the turn of the century, in 1827, enamel paper was made with lead white, isinglass, gum, and animal size, several coats of which were applied and then burnished by plating or running the coated paper, in contact with a steel plate, through a press [19, 22]. High gloss could also be imparted by burnishing wax and rosin-treated paper by calendering in 1830 [19].

The early 19th century witnessed the development of several new coating mixtures. The most popular mixture, introduced around 1807, was a combination of casein and animal glue with China Clay or kaolin (hydrated aluminum silicate extracted from feldspar in granite, with traces of muscovite mica and potassium in primary or residual sources, or yellowing titano-ferrous impurities in secondary or transported sources) [12]. Clay coating made paper whiter, heavier and more receptive to ink. The end of the century (1879) marked the introduction of a pigment coating used for the production of high gloss art and off-set printing paper, satin white (from slaked lime treated with paper makers' aluminum sulphate). Satin white has a high pH, enabling it to augment clay and to be used in binders of gum arabic, casein, soy protein, hydroxyethylated starch, or carboxymethyl cellulose to provide a satin-like gloss following relatively light calendering [21]. It has a high gloss and bright color, but because it is expensive, has a high adhesive demand, and is difficult to handle, it is used today primarily for off-machine coating of specialty papers [14]. The last

decade, 1890, marked the increased use of baryta (specifically precipitated barium sulfate from barite). Baryta, or barium sulfate, co-precipitated 7:3 with zinc sulfide forms lithopone, which became a substitute for lead carbonate. Barium sulfate itself comes in two forms, either as the natural mineral barite or as the artificial blanc fixe, which may be derived from baryte or witherite (a barium carbonate ore in England and Europe). Baryta, or blanc fixe, makes a brighter, denser, and less porous coating, used for special grades of chart papers and for photographs, although it is now being replaced in part by titanium dioxide [14, 21]. Another, lesser used, pigment was calcium carbonate (natural ground chalk and limestone from calcite or precipitated as aragonite). The 20th century ushered in several new materials, starting with the introduction in 1906 of titanium dioxide (made from ilmenite, a double oxide of titanium and iron, processed by sulfuric acid or chlorine, and occurring as either anatase or rutile, which has greater opacity, preventing show-through). Titanium dioxide is so opaque and white that only a small amount is needed [21]. It may be bulked up by calcined clay or substituted 25-50% by synthetic silicas and silicates [12, 21]. Also used during the early part of the century were binders of rubber latex (1927), peanut and soy proteins (1937), and pigments such as precipitated calcium carbonate (1925), diatomaceous earth (1938), and zinc oxide (1933), used for early photocopying paper. By the middle of the century, fluorescent whitening agents (stilbenes, salicylates, benzophenones, benzotriazoles and others) [3, 21, 26], and acrylic gessos [8] had been developed, and there was more use of talc (hydrated magnesium silicate with hydrophilic, hydrophobic, and oleophilic properties), used to control wax-like pitch from sulphite wood pulp [21]. Resin binders included urea and melamine formaldehyde resins (1946), polyethylene resins (1946), acrylonitrile, acrylic emulsions (1952) and polyvinyl alcohols [9], as well as latexes of rubber, butadiene-methacrylate and styrene-butadiene (1947) [21].

The 19th and 20th century also fostered the development of new coating application techniques. In the last quarter of the 19th century, as hand-made paper was replaced by machine-made paper, hand-coating and hand-brushing were replaced by automated "off-machine" coating processes. Off-machine coating is carried out separately from the papermaking machine. One of the earliest examples employed a single-surface brush-coating machine (1852) which used a splatter brush to apply to the paper the correct weight of coating material, smoothed by a coarse brush, refined by a firm brush, and finished by badger-hair brushes, followed by festoon-drying [6]. The coating produced was of good quality but poor uniformity when tested by quality-control measurements of "wet thumb" and "thumb rub" tests [23]. By the late 19th century (1880), double-surface brush-coating processes were developed, but as brush maintenance was time-consuming and expensive, brush-coaters were replaced at the turn of the 20th century by roll-spreading coaters (1920), which quickly and evenly metered and spread coating material on paper using rotating rolls. Roll-coaters worked best with starch adhesives. These first high-speed coaters opened the door to mass production of coated papers [13]. Toward the middle of the 20th century air-knife coaters (1940) were developed, which used a stream of air from a transverse nozzle to control both coating weight and spread in one simple operation by leveling off excess coating to form a smooth surface, dried in hot air tunnels. Later developments resulted in the flexible or trailing blade-coater (1950), which utilizes a flexible blade running against paper backed by a rubber roll, followed by drying in air cap driers. More recent developments include extrusion coating, whereby thermoplastic polyethylene resin is melted and extruded in a continuous flow under light pressure through a film-forming slot-die; it is then stretched and rapidly combined with paper between a rubber covered pressure roll

and a water cooled chromium plated steel roll to form a lasting bond with paper [21].

Today, pigment-coated papers account for 20% of all paper sold in the United States. At least ten types of coaters have been developed, including dip, brush, knife, roll, air-brush, spray, extruded, print, cast, and strip coaters. Currently, most coated paper is machine-made, meaning that the coating is applied to the paper as part of the papermaking process. Coated paper may be graded in different ways, including by use or by function, such as coated litho grade (water-resistant sized, one-sided coated paper) or coated book grade (suitable for reproducing halftone photomechanical illustrations) [13, 14]. Examples of U.S. paper grade standards for pigment-coated papers are outlined in Table II.

Modern coatings are composed not only of pigments and binders (90-94% solids and 6-20% binder by weight), but also additives and fluid (water). Ninety percent of today's pigment-coatings use clay, the size of which varies greatly, affecting covering power, brightness, gloss potential, and ink and varnish hold-out. Calcium carbonate is the second most important pigment and is used with clay to increase brightness, opacity and ink receptivity. Some pigments have been put to new uses. Amorphous silicas and silicates, such as diatomaceous silica (Kieselguhr or infusorial earth) from the fossil remains of microscopic diatom plants, are used to reduce gloss and increase resistance to "blackening" upon calendaring. Luminosity is enhanced by fluorescent pigments having an average size of 1 micron, which improve brightness, or by phosphorescent pigments having an average size of 5-10 microns, which create an afterglow (useful for special map and display papers). Sulfides of zinc or cadmium create a short afterglow, while strontium or calcium creates a long afterglow. Finally, plastic pigments have also been developed, such as polystyrene, which is widely used in publication-grade coated papers [12, 13, 20].

Modern coating binders provide bonding strength among the pigment particles and the rawstock; act as a barrier controlling ink absorption and hold-out; and influence the rheology (flow), and water-holding and set-time, of wet coating. Papers with strong binding adhesion are called "hard-sized" while those with weak binding adhesion are called "soft-sized" [13, 14]. The principal binders in use today are classified as either hydrophilic water-soluble colloids based on starch (corn, tapioca, white potato, sorghum, sweet potato, rice, and wheat) and protein (glue, casein, and soy); or resin or "rubber" latexes and resin emulsions in aqueous medium, such as styrene-butadiene, polyacrylate, and polyvinyl acetate (sometimes used with starch and protein) [13, 14, 21].

Starch, because of its low cost, is the prevalent binder in the U.S. today, although to control its high viscosity and tendency to gel, retrograde, and lose strength, it must be modified by oxidation, chemical treatment (hydroxyethylation), enzyme conversion or conversion to dextrans. Oxidized starch (treated with alkaline sodium hypochlorite) is used primarily for off-machine coatings. Chemically modified starch is used for size-press coatings or trailing blade-coaters because of its high viscosity and ink receptivity. Starch converted by enzymes (inactivated by heating to 205-212 degrees F for 10-20 minutes or chemically by phosphates, silicates, acids, formaldehyde, etc.) is the principal binder for machine-coated publication papers because of its low cost and ease of adjustments. Conversion to dextrin is done by dry-roasting starch at low temperatures for British gum, which is the best dextrin for coatings as compared to canary or white dextrin, produced by high temperatures and

acid treatment. Water-resistant starch is required for coated lithographic paper, tag papers, washable wallpaper, fancy wraps, etc. Compared to casein, starch binders can be produced with less foam, odor and spoilage, although the final coating may have a lower bonding strength, water resistance, finish and oil absorption.

Animal glue (bone or preferably hide) is presently used only for coated specialty papers such as playing cards, wallpapers, metal-coated papers, and grades needing high gloss and water resistance. Technical grade gelatin is used with barium sulfate for photographs, with glycerol, sorbitol, and butanol added for conditioning. Glue can be hardened for water-resistance with chrome alum or formaldehyde treatment, although it never becomes as resistant as casein. Casein is today used for off-machine coating of very high-grade printing papers and for machine-coating of paper boards. It is made from curd from coagulated skim milk, acid-separated and alkaline treated, which none-the-less retains some fat that may result in the formation of grease spots. It has a high degree of water-resistance if treated with formaldehyde, zinc salt solution, alum acids, or lime. Soybean protein from soy flour is used in washable wallpaper, and as fluid extender in casein coating mixtures, although it is not as readily waterproofed.

Resin latex or emulsion binders are used for both off- and on-machine coating (generally in combination with starch, soybean protein, or casein), to increase stabilization against mechanical breakdown from high shear on roll-coaters; to improve water-holding properties; and to reduce costs. Latexes can plasticize starch coatings for calendering, flexibility, and wet-rub resistance. Synthetic resin latexes and emulsions have good bonding strength, smoothness, flexibility, dimensional stability, curl resistance, wet-rub resistance, and gloss, and some of these properties even improve with age. Styrene-butadiene latex, which provides a very smooth surface, high finish, and crisp edge when folded, has been used as the sole binder in many European and Japanese mills [23]. These resin and latex binders calender easily because of thermoplastic qualities, but they may also blacken or darken on calendering.

Other binders used in lesser amounts are polyvinyl alcohols, which have high pigment bonding strength but also high cost, and water-soluble cellulose derivatives, which have good bonding strength, flexibility and oil resistance, but high viscosity. Other water soluble resins may include acrylic acid, acrylamide, acrylonitrile.

Modern additives serve many purposes and may include eveners (levelers and smoothers), pigment-dispersing agents (fluidifiers, stabilizers, softeners, plasticizers, lubricants), and anti- and defoaming agents, etc. [14]. Coatings with starch binders may require leveling agents or soaps such as sodium, ammonium or calcium stearates (which also minimize dusting and increase gloss during calendering); fluidifiers and viscosity stabilizers of urea and dicyandiamide, or polyoxyethylene stearate, polyethylene glycol laurate and sulfated oleic acid (used with enzyme-modified or thermochemically-modified starches); softening agents including invert sugar, sorbitol, urea, glycerine, or corn syrup (to increase pliability); and plasticizers or lubricants such as calcium stearate, resin latexes, ethanalamine soaps, alkyd resins, fatty acid esters, soaps, and polyglycols. Coatings with casein, soy protein, resin latex and resin emulsion binders may generate foam, which can form pinholes and craters as air bubbles burst through the coating upon drying. Foam may be composed of fine bubbles, dispersed throughout the coating mixture, or coarse froth along the top of the mixture. Anti-foamers include sulfonated oils, pine oil, amyl

alcohol, skim milk, ether, kerosene, tributyl phosphates, silicones, and other agents which depress surface tension and convert fine foam, which undermines coating weight and structure, into coarse foam expelled from the surface of the coating. Defoamers may be added to coating formulas to lower surface tension if foaming has already begun (0.1-1.0 % total weight of solids; too much can cause problems in printing offset papers) [14]. Latex binders might require stabilizers of anionic and nonionic surfactants such as sodium dodecyl sulfate, polyethylene oxide alkyl, or alkyl/aryl ether.

Other additives might include smoothing agents, improving flexibility and preventing pinholes, such as pine oil (also a preserving agent) and sulfonated oils (0.1-0.5% total volume of coating mix; too much can cause oil spots). Carboxymethylcellulose can control viscosity and minimize binder migration. Amines increase gloss. Wax emulsions (paraffin or microcrystalline) decrease dusting during calendaring, and increase water repellency, flexibility and gloss. Carnauba wax may be used with friction calendaring for high gloss. Shellac dispersed in ammonia has been used in paper coating formulas to increase water resistance [14].

Modern finishing may include varnishing with a clear spirit varnish to improve durability, to protect a final printed surface, and to increase luster. However, the amount of varnish gloss depends on the hold-out quality of the coating, which is enhanced by a binder having good film-forming properties (such as casein as opposed to starch) and a less absorbent pigment (such as fine clay rather than calcium carbonate).

Modern coated papers, formerly flint and friction calendared (which used talc as a finishing pigment) [14], are today usually supercalendered (sometimes with emulsions including wax, soap, or polyethylene), which subjects the coating to pressure-polishing, improving smoothness and gloss, with the least reduction in bulk and light-scattering coefficient. The level of gloss is influenced by the supercalendering process (type of calender used, i.e. having stacks of 10-12 soft cotton-filled rollers; number of nips through which the sheet is passed; pressure, ranging from 400-2000lbs per linear inch; speed of about 800 m/min. or more; and temperature, since heat increases supercalendering action by softening the web and plasticizing the binder); the binder (amount, higher ratios lower gloss; and type, starch being dull while resins and latexes are glossiest, although they have a tendency to "blacken" from too close compression and loss of light-refracting pigment surfaces); and pigment (moisture content, which along with heat serves to soften and plasticize the coating so that supercalendering does not crush the paper structure below, although high moisture can also cause "blackening"; shape, as in clay's plate-like particles; and size, the finer, the higher the gloss in general) [13,14]. Calendaring lowers the strength of coated papers one wax level in the TAPPI Standard Dennison Wax Pick Surface Strength Test, and can cause unwanted patterns of ridges and valleys if coatings become over-plasticized, as with some high speed roller-coating systems.

Another polishing technique is cast-coating, which can be done on or off the papermaking machine. It requires pressing a freshly coated paper against a highly polished nickel or chromium plated drier; after the paper dries, it is stripped off (wax is sometimes added to aid in stripping). The technique, low-speed and high-cost, can be used with greater amounts of binder but yields a soft porous surface, susceptible to marring [14].

Variables of furnish (distribution, size and orientation of pigment particles and distribution, type and amount of binder, etc.) and formation (the processes described above), affect the structure of the coating, which in turn affects the optical properties of the coating [13, 14]. Unfortunately, the structure and optical properties of a coating may also change as a result of degradation and subsequent conservation treatment, affecting the ultimate appearance of the coating.

B. Deterioration

Typical forms of deterioration found in pigment-coated papers include abrasion, flaking, fingerprint and oil stains, water damage, foxing, adhesive and tape accretions and staining [1,2,4,6,8]. Objects such as Victorian chromolithographs occasionally undergo yellowing and flaking of the varnish or glaze finishing, printing ink, and coating. Blocking is a particular problem with these objects as well as with clay-coated bookplates, occurring when moisture, trapped in books and scrapbook albums, softens the coating binder. Flaking of ink can occur if the coating finish is such that there is little penetration by linseed oil printing inks, preventing secure bonding [23].

C. Treatment Research

Treatments published in the conservation literature have included the use of organic and aqueous solutions applied by steam, brushes, and poulticing for the removal of extraneous accretions [4,5,6,8]. Similar treatments used by the authors have been found to be very successful. However, preliminary testing [1] on a variety of pigment-coated samples (App. A), indicated that organic and aqueous solutions may cause the break up of pigment coatings. Consequently, questions remain as to whether modern pigment-coated papers (App. B), treated by various aqueous solvent application techniques (App. C), could cause changes in appearance of the coating with respect to 1) surface structure as observed by SEM imaging, 2) brightness as measured by colorimetry, and 3) gloss (App. D). In response to these questions, several on-going research projects were developed [6], one of which is described in Table III.

Machine-made pigment-coated (machine-coated) papers were characterized based on manufacturers' information (App. B), and analysis of binders (FTIR) and pigments (SEM/EDS, see Table IV). These were compared to the elemental composition of common coating pigments in Table I. Table I also indicates the refractive index and general size of pigment particles as used in the paper coating industry, which along with particle shape contribute to the brightness, gloss, and opacity of the final coat. For instance, refractive index (n) influences a pigment's ability to refract light, contributing to opacity, which is important for reducing print show-through in modern papers. Size (microns or μm) also affects a pigment's ability to refract and reflect light, and as the particle size decreases, opacity increases [14]. Particle size also affects surface smoothness and contributes to gloss, depending on porosity, compactness, etc. A size of 0.12 μm may be best for ink holdout, while 0.2 μm might be best for gloss, but 0.5 μm may have the best combination of gloss and light scatter [21].

Based on the comparison of elemental compositions shown in Tables I and IV, the modern machine-coated papers can be divided into three groups. The first group ("B") is made primarily of barium sulfate (Ba, S), perhaps with talc (Si, Ca) or gypsum (Ca, S). The second group ("K" and "L") contains primarily clay (Al, Si, K)

and gypsum (Ca, S). The third group (the remainder) contains primarily clay (Al, Si) and talc (Ti, Ca) or titanium dioxide and calcium carbonate. The pigment-coating compositions of these papers were compared with the composition of several pigment-coated chromolithographs undergoing contemporaneous conservation treatment [6]. Based on these comparisons, one paper from each of the three groups was chosen for treatment trials and testing. The three selected modern machine-coated papers, designated by the codes "B," "S," and "L," are described in Table V and Appendix B.

The treatment trials compared effects of water applied by two techniques that might be used to remove accretions. The two treatment techniques were immersion and poulticing with a damp blotter (Table III). These two treatments were selected to represent differences in amount of solvent absorption, exposure time to solvent, and direction of application and evaporation. For example, aqueous immersion may result in greater penetration, longer exposure, and more lateral movements of compounds as compared to aqueous poulticing. Details of the procedures used are outlined in App. C. Half of the samples were exposed to a five minute immersion treatment in deionized water, while the other half of the samples were poulticed with a damp blotter for five minutes. Half of the treated samples were air-dried and the other half was dried in a blotter press. Changes in the papers after treatment were assessed by SEM imaging and by measuring optical properties of color/brightness and gloss (App. D).

D. Conclusions

Aqueous immersion and blotter-poulticing, followed either air-drying or blotter-drying, of three different types of modern machine-made, pigment-coated papers, caused changes in surface appearance and significant reductions in gloss and brightness (increased darkening and yellowing). The greatest structural changes, as observed by SEM imaging, occurred in the blotter-poultice samples, especially for less glossy papers. The greatest unit reduction in gloss, as measured instrumentally, occurred in the glossiest paper and was most irregular for the poulticed samples. Findings suggest that while aqueous blotter-poulticing and blotter-drying may be appropriate for some pigment-coated papers, other procedures might cause less surface change to highly glossy coated papers.

Table I: Some common coating pigments and relative purpose, with elemental composition, refractive index (n) and average optimum particle size in microns (um), brightness, and pH [compiled from: Beazley, Casey 1961, Kouris]

PIGMENTS	Al	Si	K	Ti	Ca	S	Ba	Zn	Pb	n	um	Bright.	pH
barium sulfate (baryte or blanc fixe) {weight, purity, brightness, finish}	-	-	-	-	-	+	+	-	-	1.64 1.65	0.11 - 0.54	95-98	3.5
calcium carbonate (precipitated or ground) {opacity, brightness, dull finish, ink affinity}	-	-	-	-	+	-	-	-	-	1.66	0.1-10	93-98	7-10
calcium sulfate (gypsum or pearl white, crown filler, alabastine, etc.)	-	-	-	-	+	+	-	-	-	1.52	0.2		
calcium sulfite {brightness, absorbency}	-	-	-	-	+	+	-	-	-		6.5	92-96	8-9
clay (primary or secondary) {body, finish}	+	+	- /+	(+)	-	-	-	-	-	1.55	2.0 0.4-5.0	65-85	4.3-7
diatomaceous silica {dull, abrasive, resistant to blackening}	-	+	-	-	-	-	-	-	-		1-5 X 10-50	65-95	5
lead white (basic lead carbonate, hydrocerussite)	-	-	-	-	-	-	-	-	+	1.80 - 2.08			

satin white (calcium sulfoaluminate) {finish, brightness, gloss}	+	-	-	-	+	+	-	-	-		1-2 by 0.1- 0.2		
talc	(+)	+	-	-	(+)	-	-	-	-	1.57	2.0		4-6
titanium dioxide (rutile or anatase) {opacity, brightness, whiteness, smoothness}	-	-	-	+	-	-	-	-	-	2.5- 2.7	0.2- 0.5	97-98	4-6
zinc sulfide	-	-	-	-	-	+	-	+	-	2.37	0.3	94-96	
lithopone (Orr's White, Charlton White)	-	-	-	-	-	+	+	+	-	1.84 - 2.00	0.3- 0.5		
zinc oxide (opacity)	-	-	-	-	-	-	-	+	-	2.01 - 2.03			
polystyrene	-	-	-	-	-	-	-	-	-	1.59	0.5		

Table II: Examples of Grading Standards in the U.S. [Sources: Casey 1961, 1985]

GRADES	TYPES	USES	RAWSTOCK	BRIGHTNESS (GE)	GLOSS 75° (SEPARATE GRADING SYSTEM)
1	Merchants Grade, coated enamel, coated woodfree	multicolor printing, advertising, brochures	100% chemical pulp (basis weight g/m²=100- 150)	85+	45+ (glossy)
2	Merchants Grade, coated enamel, coated woodfree	multicolor printing, advertising, brochures	100% chemical pulp (basis weight g/m²=75- 150)	83-84.9	25-35 (dull)
3	magazines, catalogs	magazines, catalogs	chemical & mechanical	79-82.9	25- (matte)
4	coated groundwood	magazines, catalogs	mechanical & chemical	73-78.9	
5	publication grade, coated groundwood	magazines, newspapers	mechanical	72.9-	

Table III : Research design for statistical study: treatment testing of selected machine-coated papers

Select Sample Machine-Made Pigment-Coated Papers														
Identify Components by Elemental Analysis														
Treatment Trials (Aqueous)											Untreated			
Immersion						Poultice						Control		
A1		A3		A3		B1		B2		B3		C1	C2	C3
Air	Blot	Air	Blot	Air	Blot	Air	Blot	Air	Blot	Air	Blot			
Evaluate Changes in Appearance (SEM Imaging) and Optical Properties (Color and Gloss) (Note: For each paper type each sample under categories A1-C3 was tested 3 times)														

Table IV: Elemental composition of 8 machine-coated papers based on SEM/EDS

PAPERS	Al	Si	K	Ti	Ca	S	Ba
"B"	-	+	-	-	+	+	+
"C"	+	+	-	+	-	-	-
"F"	+	+	-	+	+	-	-
"K"	+	+	+	-	+	+	-
"L"	+	+	+	-	+	+	-
"Q"	+	+	-	+	+	-	-
"R"	+	+	-	+	+	-	-
"S"	+	+	-	+	+	-	-

Table V: Characterization of selected machine-coated experimental papers

PAPERS	RAWSTOCK (Estimated Percentages)	PIGMENT COMPOSITION		BINDER (FTIR)	BRIGHTNESS (Hunter)	APPEARANCE	85° GLOSS
		SEM/EDS	FTIR				
"B"	100% ground hardwood and softwood (estimate)	Ba, S, Ca	sulfate, some clay	protein, resin	91.66	matte, smooth	18.5
"S"	40% chemical, 50% mechanical wood pulp 10% rag (est.)	Ti, Si, Al, Ca	clay, calcium carbonate	styrene acrylic resin	85.08	matte, slightly rough	11.8
"L"	85% chemical softwood, with some chem. hardwood 15% rag (est.)	Si, Al, Ca, S, K	clay	protein, acrylic	89.65	very glossy, smooth	96.9

E. Appendices

Appendix A: Preliminary Testing: Effects of solvents and application techniques on traditionally hand-coated papers: A survey of traditional recipes provided the basic information for sample preparation. The sample papers were hand-coated with combinations of calcium carbonate, zinc oxide and barium sulfate in binders of gum, glue, and acrylic. A machine-coated paper composed of barium sulfate and calcium carbonate in an acrylic binder was examined and tested as a comparison for a modern pigment-coated paper. The treatment procedures were selected to the effects of 4 solvents--water, ethanol, acetone, and toluene--applied in 3 ways--immersion, poultice (diatomaceous earth), and suction disk--to each of the papers. The results indicated that, among other things, the aqueous poultice applications used in this study could cause cracking of some pigment-coated surfaces, especially the machine-coated sample [1, 6]. The formulas, using reagent grade compounds, for the 6 hand-coated papers were as follows:

1. calcium carbonate:Liquitex rabbit skin glue (1:3) applied in 5 coats
2. calcium carbonate:gum arabic (1:2)
3. zinc oxide:Liquitex rabbit skin glue (2:3) applied in 5 coats
4. zinc oxide:gum arabic (2:3)
5. zinc oxide:Liquitex gel acrylic medium
6. barium sulfate and calcium carbonate:Liquitex gel acrylic medium

Appendix B: Modern Pigment-Coated Papers (Machine-Made): supplied by various manufacturers, who described them as follows:

"B": Machine-made in France as "Special Point d'Argent: Calligraphie" (recommended by manufacturer for silver point drawings)

"C": Machine-made 100% rag paper with neutral pH. Smooth, clay-coated; recommended for silverpoint drawing.

"F": Machine-made glossy, light weight stock, available in 28 colors.

"K": Glossy white text weight paper recommended for illustrations and ink drawings.

"L": Machine-made in Germany; smooth, glossy surface on 2 ply, 10 point card stock.

"Q": Machine-made with fine clay coating. Ivory color, recommended for silverpoint drawing.

"R": Machine-made 100% rag paper with neutral pH. Smooth, clay-coated (2 sided); glossy on one side and matte on the other. Recommended for off-set printing but not silverpoint drawing.

"S": Machine-made paper with smooth clay coating recommended for silverpoint drawing.

Appendix C: Aqueous Solvent Application Techniques:

Immersion Procedure: The samples were immersed in deionized water on a polyester web (nonwoven, with a smooth surface, 5 mil) on a polypropylene screen. The samples remained immersed for five minutes. The screen with web and samples was lifted out of the water and allowed to drain for two minutes. Half of the samples were lifted on the polyester web to an unbuffered blotter on a felt and were allowed to air-dry totally. Appearance measurements (color and gloss) were taken after two days. The other half of the samples were placed onto an unbuffered blotter on a felt and allowed to air-dry for 5-10 minutes until all standing water on the surfaces of the papers evaporated. The unbuffered blotter under the samples was replaced by a dry unbuffered blotter and these samples were then covered with polyester web, unbuffered blotter, and felt, and were blotted with hand pressure. Both top and

bottom unbuffered blotters were changed and the ensemble was placed for five minutes in a "press" under a felt and 1/2 inch thick piece of plexiglas (less than 1 PSI). The unbuffered blotters were changed again after one hour and returned to the "press". The polyweb and unbuffered blotter were changed the next day and returned to the "press." Appearance measurements (color and gloss) were taken after two days.

Poultice Procedure: The unbuffered blotter used for poulticing was dampened by immersing it on a screen in a tub of deionized water. The screen was removed and the unbuffered blotter was drained on the screen for two minutes. A piece of 4 mil polyester film was placed on the unbuffered blotter resting on the screen and then the unbuffered blotter was flipped over so that the polyester film was on the bottom. The unbuffered blotter was allowed to sit for five minutes to enable standing water to evaporate for more even moisture distribution. The unbuffered blotter was then flipped over onto the samples, which were against a Formica countertop, and the polyester film was removed. A felt and a 1/2 inch thick piece of plexiglas were placed on the unbuffered blotter-poultice for 5 minutes. After the plexiglas, felt, and damp unbuffered blotter were removed, the wet samples were exposed to the air for two to five minutes, until all standing water on the surfaces of the papers evaporated. Half of the samples were left to air-dry totally. Appearance measurements were taken after two days.

The other half were moved to a blotter "press" made up, from the bottom up, of the formica counter, felt, unbuffered blotter, polyester web, sample, polyester web, unbuffered blotter, felt, plexiglas (less than 1 PSI). The samples were left overnight in the press. The next day the polyester web and unbuffered blotter were changed and the ensemble was returned to the "press." Appearance measurements were taken after two days.

Experimental Conditions and Labeling:

(Each treatment trial was conducted three times and each resultant sample was measured three times for statistical accuracy)

MODERN PIGMENT COATING S L B

Control (C) 1=C 14=C 27=C

Immerse/airdry (IAD) 2=IAD.1 (3 meas) 15=IAD.1 (3 meas) 28=IAD.1 (3meas)

3=IAD.2 (3 meas) 16=IAD.2 (3 meas) 29=IAD.2 (3 meas)

4=IAD.3 (3 meas) 17=IAD.3 (3 meas) 30=IAD.3 (3 meas)

Immerse/blotter (IBD) 5=IBD.1 " 18=IBD.1 " 31=IBD.1 "

6=IBD.2 " 19=IBD.2 " 32=IBD.2 "

7=IBD.3 " 20=IBD.3 " 33=IBD.3 "

Poultice/airdry (PAD) 8=PAD.1 " 21=PAD.1 " 34=PAD.1 "

9=PAD.2 " 22=PAD.2 " 35=PAD.2 "

10=PAD.3 " 23=PAD.3 " 36=PAD.3 "

Poultice/blotter (PBD) 11=PBD.1 " 24=PBD.1 " 37=PBD.1 "

12=PBD.2 " 25=PBD.2 " 38=PBD.2 "

13=PBD.3 " 26=PBD.3 " 39=PBD.3 "

Data: Gloss, 85 degrees (Standard Deviations)

ABSOLUTE: S L B

Control (C) 1 = 11.8 +/-0.4 14 = 96.9 +/-0.3 27 = 18.5 +/-0.2

DELTA:

Immerse/airdry (IAD) 2-4 = 6.2 +/-0.3 15-17 = 31.4 +/-2.5 28-30 = 5.4 +/-1.2

Immerse/blotter (IBD) 5-7 = 5.8 +/-0.3 18-20 = 27.9 +/-1.0 31-33 = 3.7 +/-0.4

Poultice/airdry (PAD) 8-10 = 5.3 +/-0.5 21-23 = 30.4 +/-13.8 34-36 = 5.2 +/-0.9

Poultice/blotter (PBD) 11-13 = 4.1 +/-0.7 24-26 = 22.2 +/-6.2 37-39 = 3.5 +/-0.4

Appendix D: Instrumental Analysis:

SEM: SEM imaging and SEM/EDS analysis were carried out on a Jeol JXA - 840 A scanning electron microscope with Tracore Northern TN 5502 energy dispersive x-ray analysis system. For imaging the samples were mounted on aluminum stubs and gold coated. For elemental analysis the samples were mounted on carbon stubs and carbon coated.

FTIR: FTIR analysis was carried out on a Mattson Cygnus 100 Fourier Transform Infrared Spectrophotometer with a Spectratech IR-Plan Microscope. Surfaces were analyzed by reflectance, or alternately micro samples were removed and pressed into thin films in a diamond anvil cell for analysis by transmission.

Colorimetry/Brightness: Color (specular reflectance included) was measured with the HunterLab Ultrascan Spectrocolorimeter (D_{65} , 10° observer, diameter of area of view 1.2 in) using the CIE $L^*a^*b^*$ color notation, where L^* represents the degree of brightness (100 white, 0 black), a^* the degree of redness (positive numbers) or the degree of greenness (negative numbers) and b^* the degree of yellowness (positive numbers) or the degree of blueness (negative numbers). Three measurements were taken per sample and averaged. Brightness (Table V) was calculated for the untreated papers by the following equation: $B = 0.01L^2 - bL/70$. The brightness values quoted in Tables I and II are according to a GE Brightness Meter, which was an instrument used to determine the reflectance at 475 nm, using a tungsten source. The two sets of values are comparable, with the exception that the Ultrascan measurement will be higher when there are optical brighteners in the paper.

Gloss: Gloss was measured with a Dr. Lange Labor-Reflektometer RL at angles: 20° , 60° and 85° . Three measurements for each angle were taken per sample and averaged. TAPPI gloss, quoted in Tables I and II, requires measurements at 75° (TAPPI T480). For this experiment, the three angles (20, 60, 85) were judged to be more descriptive of the changes. Values for TAPPI gloss would be expected to fall between those for 60° and 85° ; nonetheless, the two methods cannot quantitatively be compared.

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II. MODERN TRACING PAPERS

Tracing papers have been used as supports for a wide variety of materials in museums, libraries, and archives, including architectural drawings and fine arts paintings. They are frequently used as a support for technical drawings by designers, architects, and engineers. Subsequently, the tracings are often handled directly by workers or historians, since such drawings can not always be effectively reproduced by photographs, facsimiles, or microfilm. This is because legibility may be impaired by faded or smudged design media which might also be erased or added, indicative of significant changes in the evolution of design concepts; reproductions may also fail to accurately portray the variety of media representing different design elements and stages; finally, notations in the margins or on the reverse of the drawings are occasionally cropped in reproductions. Tracing papers are also used as supports for paintings by artists attracted by both the paper's translucency and its relatively low cost. In these cases, the paper is in danger of damage not only from handling, but also from exhibition, especially if improperly displayed. Unfortunately, the composition, size, age, past use, and fragility of tracing papers, compounded by handling and exhibition, makes them particularly vulnerable to deterioration. To correct damage and deterioration problems, such papers frequently require conservation treatment.

Conservation treatment of tracing papers is complicated not only by diverse and sensitive media, but also by the very nature of the paper supports, which are produced by specially formulated compositions and manufacturing procedures to achieve specific chemical and physical properties, such as translucency, whiteness, and smoothness. However, special formulations and procedures may render these papers exceptionally susceptible to surface marring, embedded grime, discoloration, and embrittlement. Tracing papers can absorb extraneous material, like resins and oils from tapes and other adhesives, causing embedded stains that are difficult to remove. Often the papers are extremely hygroscopic, which makes them particularly susceptible to planar distortions and dimensional changes. Different manufacturing processes may also render the papers extremely sensitive to conservation treatments (Baker et al. 1989). For instance, the translucency of tracing papers may be affected by solvents used for treatments, such as washing or deacidification (Flieder et al. 1988, Glaser 1988, Yates 1984); consolidation or lining with aqueous, solvent-activated or thermoplastic adhesives (Bachmann 1983 & 1986, Bush 1986, Jirat-Wasiutynski 1980, Hoffenk de Graaff 1982, Saucois 1981, Steinkellner 1979, Stone 1987); stain-removal (Flieder et al. 1991); or humidification and flattening (Flamm et al. 1990, Hofmann et al. 1992, McClintok 1986, van der Reyden et al. 1992b).

To reduce the hazards of solvent treatments, conservators often select from a variety of application techniques, as, for instance, in the case studies of two paintings on tracing paper from the collection of the National Museum of American Art, Smithsonian Institution. The sensitive nature of a gouache and enamel painting by J.C. Huntington on tracing paper required removal of adhesive using the application of various solvents (ethanol and acetone) in a poultice (Fuller's Earth), followed by flushing on a suction table with warm ammonia water to remove residual

adhesive and subsequent staining. A second painting, by William H. Johnson, required aromatic solvent vapors to soften and aid removal of residual tape adhesive. The painting was then flattened following humidification in a humidification chamber and stretch drying. In order to evaluate the effects on tracing papers of various types of solvents and solvent application and evacuation techniques, employing immersion baths, poultices, suction tables, and humidification chambers, several research projects were undertaken.

A. Characterization of Modern Tracing Papers

Considerable conservation literature exists on analysis and treatment evaluation of historic tracing papers (Flieder et al. 1988, Flamm et al. 1990, Mills 1986, Richardin et al. 1990), but less information is available on modern tracing papers (Rundle 1986, van der Reyden et al. 1992a & b). Since 1987, the Conservation Analytical Laboratory has been engaged in research characterizing several types of specialty papers, including coated and transparent or tracing papers, to enable conservators 1) to categorize, non-destructively if possible, the nature of various types of specialty papers, in order to anticipate potential changes to properties from aging and solvent treatment, and 2) to formulate treatments selecting solvents and application techniques appropriate to specific types of specialty papers (Baker et al. 1989). The ongoing work with respect to tracing papers is divided into four interrelated projects outline in Table I.

General terms used to describe tracing paper in the conservation literature include transparent paper, translucent paper, oiled paper, onion skin paper, and waxed paper. The US Federal Specifications for Tracing Papers (UU-P-561H 1972) recognizes four classifications or types of tracing paper, each type being characterized by fiber composition (rag or chemical woodpulp) and specific degrees of whiteness, translucency, strength, and permanence. Commercial manufacturers of modern tracing papers tend to categorize their products into groups referred to as natural tracing papers, vegetable parchment papers (also called genuine parchment paper or pergament), imitation parchment papers (pergamyn or glassine), or prepared tracing or vellum papers. Each of these papers is made by either 1) processing the fiber pulp stock or slurry by overbeating to break down fiber structure and reduce porosity to eliminate light scattering air/fiber interfaces, and/or 2) processing the formed paper sheet to fill such interfaces with material having a refractive index similar to paper fibers. This latter process requires either immersion of the paper sheet in acid, calendering of the sheet, and/or applying a transparentizer (coating and/or impregnating agents) to the sheet. Fiber processing is the primary procedure used to make natural tracing paper (highly overbeaten pulp), while sheet processing is primary to producing vegetable parchment paper (immersed in acid); imitation parchment paper (highly calendered); or prepared tracing paper or vellum paper (both impregnated with transparentizers). Papers representing each of these categories, selected for the current study, were examined by SEM imaging (van der Reyden et al. 1992a), and their general characteristics are outlined in Table II and described below (Bolam 1962 & 1976, Casey 1980-83, Horie 1987, Kouris 1990, Mosher 1950, Roth 1963, Vaurio 1960, Vincent 1932, Yates 1991).

Natural tracing paper is usually made from highly overbeaten chemical wood pulp. The natural tracing sample in our study is characteristic in that it is made from chemical woodpulp (bleached kraft) processed by overbeating fibers in a large

volume of water (c.6% fiber content) at a high temperature (c.80 degrees centigrade) to soften the fibers and increase fibrillation. This fiber processing, compounded by machine calendaring, results in the total collapse of interfiber pores and voids, making the paper highly translucent, with a relatively matte surface. This paper contains many additives intended to modify various functional properties pertinent to coating processes (such as dispersion, foam control, viscosity adjustment, leveling of wet film, water retention, etc.); to printing processes (dry pick, dry rub, wet pick, wet rub, and ink holdout or acceptance); and to special requirements (water and grease resistance, stiffness, folding endurance, gloss, opacity, and color). Additives in this natural tracing sample include sulphamic acid (to control sizing, flocculation and algae growth during processing); artificial clay (containing magnesium silicate with 6% sodium fluoride); rust inhibitors (polyacrylate and phosphates); and defoaming agents. Foam or bubbles, formed during processing, can be prevented by anti-foamers or controlled by defoamers. Early anti- and defoamers included skimmed milk, pine oil, kerosene, animal fat, and vegetable oil. Defoamers, like the blend of hydrocarbon and non-ionic emulsifiers used in this sample, are surface-active agents that weaken the walls of small bubbles, causing them to merge into larger ones, which then become buoyant enough to rise to the surface. Saponified oils may serve as antifoamers, defoamers, film levelers, and plasticisers. Talc (silicate platelets) controls pitch from the woodpulp, and along with calcium carbonate and sand, serves also as an extender to reduce the volume of polymer additives, in this case acrylonitrile. Acrylonitrile can increase stiffness and solvent resistance. Butylacrylate may improve aging, smoothness, and brightness. The final paper has a surface size of styrene maleic anhydride compound (which can increase resistance to water, oil and grease, and insure gloss ink holdout), and modified starch. Starch can be modified in several ways to improve handling properties. The larger, branched, and amorphous amylopectin component of starch forms a weak film, while the linear amylose component forms a strong film that absorbs up to four times its weight in moisture. Amylose can be used as an humectant to prevent brittleness at low relative humidities, but degrades by photo-oxidation and hydrolysis on exposure to ultraviolet light, breaking chains and producing organic acids. Starch can be modified (depolymerized), by enzymes or by hydrolysis and oxidation at high temperatures, to form more soluble gums and dextrans. Dextrin is made by treating raw starch with acid or alkali followed by dry roasting at 250-400 degrees F. Starch can be commercially oxidized by treatment with sodium hypochlorite (followed by pH adjustment); sodium bisulfite (to take up unused chlorine); washing and filtering.

Parchment paper is a generic term that can refer to either genuine vegetable parchment paper or to imitation parchment paper, each of which is made in distinctly different ways. Genuine vegetable parchment paper is usually made of slightly beaten chemical wood pulp (Kraft or sulfate hard and soft wood in the case of our sample). It is transparentized by momentary immersion in baths of diminishing strengths of acid (such as sulfuric or zinc chloride), which swell and partially disperse wood fibers, leaching out short chain beta-cellulose and gamma cellulose, forming an amyloid gel. Translucency is achieved when washing and neutralization reconstitutes, solidifies, and reprecipitates the cellulose and gel. During drying, the dispersed short chain polysaccharides form membranes that are deposited on and around the remaining fiber structure, effectively dispelling air within the interfiber voids. This process bonds the fibers into a grease and solvent resistant paper having high initial wet strength. This parchment paper sample, which is also coated with silica on one side, is recommended by the manufacturer for off-set lithography and silk-screen printing. Imitation parchment paper, such as glassine, is made of chemical woodpulp

(sulfite) that undergoes prolonged beating (20-30% fiber content in water) to fibrillate and partially "gelatinize" the fibers. Translucency is enhanced when the sheet, dampened to 10-30% moisture content, is supercalendered under high pressure (c.2000-3000lbs/linear inch) and heat (surface roll temperature of 180-200 degrees C), generating steam that dries the paper to a 5-7% moisture content and expels air, causing further collapse of the paper structure. Multi-nip off-machine supercalendering with 14-20 rolls increases the imitation parchment paper's density and gloss, as the paper is pressed and "molded" or "replicated" against smooth iron rolls and less smooth cotton-filled rolls. This results in "two-sidedness" or different smoothness and optical properties on either side of the paper. The top side tends to be smooth owing to a higher concentration of fines or loading materials which otherwise pass through the wire or underside of the paper, increasing the ratio of fibrous furnish on the underside. Supercalendering imitation parchment paper causes the top side to become highly glazed as fines and filler are molded smooth, while fibers on the underside of the sheet become flattened.

Transparentizers are used to make vellum papers, prepared tracing and recently developed "self-healing" tracing papers, which are usually made from slightly beaten cotton fibers. The low fibrillation of cotton fibers, combined with their twisted structure, prevents close conformation, resulting in the scatter of light at the fiber/air interface around voids or pores. To achieve translucency, pores must be filled by impregnation and/or coating with transparentizers having a refractive index similar to cellulose. Resins are added either to the fiber pulp slurry (wet-end additives) to improve wet and dry strength (by preventing water from penetrating and breaking hydrogen bonds), and stiffness (by increasing adhesion between fibers), or to the surface of the formed paper sheet to improve water and scuff resistance. Additives in our vellum sample include melamine and urea formaldehyde resins, which are formed by creating water-soluble oligomers of formaldehyde combined with melamine or urea, cross-linked by acid catalysts and/or heat to become hard and stiff. Melamine resins have the greatest chemical resistance to yellowing. Melamine formaldehyde is a wet-end additive that is highly substantitive, having a good affinity to all paper-making fibers. Urea formaldehyde can be modified with butanol to create organic soluble oligomers, which are more flexible than the unmodified polymers, although they can be decomposed, by concentrated acids and alkalis. The formaldehyde resins, which require an acid pH on the paper-making machine for reasonable cure rates, also improve dry pick, dry rub, and abrasion resistance. Our prepared tracing sample, has a coating that is pitted by minute air pockets or "pin-holes" that may result from foaming of the coating during processing, which can produce gas spheres of air 1-100um diameter. As mentioned before, surfactant defoamers encourage the bubbles to merge and rise to the top. According to the manufacturer, this paper has been transparentized by an aromatic solvent based synthetic resin and top coated by styrene and cellulose esters. Esters, formed from organic alcohols and acids, are weakly polar and hydrophilic, and provide toughness, clarity, or antistatic properties in coatings. Coatings can be economically thickened with fillers such as precipitated silica and fumed silica, which can also increase strength and hardness and serve as flattening and matting agents. The thickening effect is greatest when the filler is well dispersed in non-polar solvents for anionic polymers and polyacrylics, which have the best long term stability. Alkali silicates, among the most common fillers in paper coatings, are made from various proportions of silica sand and soda ash, which are smelted and dissolved in water, forming "water glass". Silicates are also used for water retention important for "print-on" coating systems. This prepared tracing sample also has an internal and external size of starch. Recently, continuing developments in paper manufacture

have resulted in new categories of tracing papers, including "rag-free" vellum papers and "self-healing" tracing papers made of solvent based "mobile" transparentizer resins, recommended by manufacturers for diazo copies.

B. Deterioration

Federal Specifications UU-9-561H 1972 requires that, following dry oven accelerated aging at 100 degrees C for 72 hours, tracing papers undergo 1) no subjective change in color, 2) no increase in opacity greater than 9% points for chemical pulp and 3-7% points for rag, and 3) no decrease in mechanical properties as measured by fold endurance greater than 50%. Our accelerated aging conditions of 90 degrees C, 50%RH for four weeks employs increased humidity levels and exposure times which may engender more extensive hydrolysis and oxidation. This may account for the change, exceeding the Federal Specifications, which occurred for some properties of some of the samples tested under our admittedly more severe conditions (van der Reyden et al. 1992b).

C. Treatment Research

Samples of modern tracing papers were selected representing four primary categories (natural tracing papers, vegetable parchment paper, imitation parchment paper, and prepared tracing or vellum papers). Characterization was done for furnish materials (using fiber microscopy and staining, SEM/EDS, FTIR, and GC/MS), for formation procedures (SEM imaging and UV microscopy), and for properties (color, opacity, gloss, mechanical strength, dimensional stability, and pH).

Evaluation of the effects of accelerated aging on the properties of the selected papers was undertaken by measuring changes after aging in color, opacity, gloss, mechanical strength, and pH. Accelerated aged samples were also used to simulate aged or old papers for treatment and further testing.

Evaluation of the effects on tracing papers of four commonly used stain-removal solvents (water, ethanol, acetone, and toluene) applied by three different treatment techniques (immersion, poultice, and suction disk) included measurement of properties as well as subjective observation of overall appearance (color, opacity, gloss, ringing) in visible and ultraviolet light, and tracking dislocation of furnish materials by SEM and UV microscopy.

Effects of Humidification and Flattening: Evaluation of the effects on tracing papers of three humidification techniques (using immersion, humidification chamber, and humidification pack) and two flattening techniques (suction table and blotter press) included measurement of changes in opacity, gloss, mechanical strength, and dimensions, as well as SEM surface imaging.

Conditions of testing and analysis are listed in the Appendix.

Aqueous and non-aqueous solvents are used in conservation treatments of tracing papers to aid in the removal of adhesives and stains, and in humidification prior to flattening. However, solvents may also interact with the special additives and morphologies characteristic of tracing papers. For instance, water, ethanol, toluene, or acetone may affect the morphology of coatings and impregnates used to

transparentize tracings by causing crazing or dissolution of the polymeric films. This in turn increases permeability, enabling the solvents to affect the morphology of the paper structure itself by debonding, swelling, and altering porosity of the paper. The nature of the interaction of the solvent with the paper substrate is determined by several factors, and a review of a few of these might aid in interpreting the findings of this project. For example, the degree of interaction is affected by the solvent solubility parameters. On the other hand, the speed of interaction may be dictated by structure and evaporation rate of the solvents. Some solubility and evaporation rate parameters for the solvents used in this project are summarized in Table III.

The effect of solvents on paper composition may also be influenced by how long a solvent is retained in a paper. Solvents retained in coating films may change the dimensional or chemical stability of a film. The retention time may be influenced not only by the evaporation rate, but also by the solvent structure (and concentration, temperature, ambient relative humidity and paper porosity). For instance, based on solvent molecular structure and shape, water, ethanol, acetone and toluene would have respectively increasing solvent retention times, since small solvent molecules which are linear, unbranched, and symmetrical (like water) can pass more easily between polymer molecules than solvents that are larger or branched. However, the speed of evaporation can reduce the normal retention time, so that, for instance, acetone may be removed from paper faster than water and ethanol, even though it is a larger molecule. Likewise, toluene is removed faster than water, due to its higher evaporation rate, even though it is several times larger.

On the other hand, the degree and/or speed of solvent-substrate interaction and retention time may be manipulated by conservators. Conservators can alter this interaction by selecting and controlling any of various solvent application techniques, using for instance immersion, poultice, or suction systems. Such manipulations alter the conditions of solvent concentration; of the direction of penetration, evacuation and evaporation of solvent; and of time and rate of solvent exposure. For example, during conservation treatments, as a solvent volatilizes or evaporates, the resultant removal of heat may lower the temperature of the surrounding area to below the dew point, causing condensation of water from the atmosphere. Water, regardless of whether introduced as condensation or as a solvent, may be absorbed into a polymer film coating and become trapped there as chemically-bound water. Such alteration in hydration state of a film may change its refractive index, and an increase in light scatter causes the film to appear lighter and consequently more opaque, referred to as "bloom." This phenomenon is commonly seen in coatings on furniture and paintings. For instance, acetone, a hydrophilic ketone that can dissolve cellulose derivatives as well as certain resins and waxes, has a high vapor pressure, and its high evaporation rate can cool coating surfaces, causing moisture condensation leading to bloom (Hess 1965, Horie 1987). Under normal circumstances, ethanol at 200 proof is anhydrous and not likely to cause bloom unless it absorbs moisture from the air. Toluene, with an aromatic benzene ring affecting resins and cellulose derivatives, is hydrophobic and a slower evaporator than acetone, and so should be able to dry without bloom. However, if the evaporation rate of a solvent is speeded up at room temperature, for example as a result of application and evacuation of solvent by suction disk, the drop in temperature might reach dew point, causing condensation and bloom. Bloom, resulting from chemically-bound water, may be confused with physical changes in appearance caused by crazing, leaching and precipitation or redeposition of coatings or additives, and fiber debonding and swelling. Crazing is a network of fine cracks or microfissures within a coating. Leaching can be defined as the dissolution, movement, and redeposition or

precipitation of one or more components of a coating leaving a less compact, often porous or uneven surface. Fiber debonding causes the formation or expansion of inter-fiber interstices, increasing refractive surfaces and, hence, light scatter. These variables may be responsible for some of the effects solvents and application techniques have on the properties of tracing papers (van der Reyden et al. 1992b).

D. Conclusion

With respect to properties of appearance of tracing papers, the greatest change in color occurred with aging, the greatest change in opacity occurred with solvents, and the greatest change in gloss occurred following humidification and flattening. Water caused the greatest overall change in properties. The following preliminary observations may aid the conservator faced with the treatment of a tracing paper:

Based on manufacturers' information, literature, and our own findings, there is a great deal of variation and overlap in the furnish and formation procedures for modern tracing papers, and this can make them difficult to distinguish. However, the furnish, formation and properties of modern tracing papers follow certain trends sufficiently different that conservators may be able to determine, with qualifications, whether a paper is characteristic of prepared/vellum paper, a natural tracing paper, a vegetable parchment paper, or imitation parchment paper. This may be done, with varying degrees of accuracy, by several techniques, listed below from least to most complex:

a) observing general appearance (high gloss for calendered imitation parchment paper, high translucency for natural tracing paper, high fluorescence for papers with transparentizers), dimensional stability (greater for coated prepared tracings), reactivity to water (greater for overbeaten natural or imitation parchment papers) or organic solvents (greater for heavily coated prepared tracings), and strength (weaker for overbeaten natural tracings after aging).

b) analyzing fiber content with polarizing light microscope (chemical wood pulp for natural and parchment tracing papers, cotton for prepared tracings) or sheet morphology by SEM.

c) undertaking instrumental elemental analysis using SEM/EDS, FTIR, or GC/MS. In addition to the more frequently used GC/MS, microtome cross-sectioning of samples combined with SEM, FTIR, and UV microscopy appears to have great potential for providing detailed information on composition and distribution of furnish materials in samples.

Accelerated aging under the conditions used for this project causes dramatic differences in the properties of all the samples, sometimes in excess of the standards considered acceptable by the US Federal Specifications. There are significant differences in mechanical properties, before and after aging, depending on whether the samples were transparentized by overbeating or by transparentizing agents. In general, the heavily coated transparent paper samples seem to have better retention of optical and strength properties and dimensional stability after aging as compared with the overbeaten natural transparent and imitation parchment paper samples.

The effects of solvents on the surface of tracing papers vary a great deal and seem to depend first on the composition of the paper, second on the type of solvent, and

third on the application technique. Of the papers studied here, the natural tracing paper was the least affected and the heavily coated paper was the most affected by the various solvents and application techniques. Water effected the greatest changes (increase in surface distortion and opacity and decrease in gloss) and toluene the least. The property most often affected was gloss, which usually decreased. However, the property most severely affected was opacity, which increased in most cases. Dimensional stability was most affected by water. Prepared papers were the most sensitive to tidelines.

Different techniques for humidifying and flattening tracing paper affect properties in different ways. Based on our findings, conservators who must immerse a tracing paper in water might find dimensional changes less severe if the paper is dried in a blotter press rather than on a suction table. Tracing papers with heavy coatings that might soften on exposure to moisture should be humidified in a vapor chamber rather than by prolonged contact with a humidification pack system. This technique, however, might be better for uncoated or lightly coated natural transparent papers, since initial curling is prevented.

The observations stated above must be considered tentative for the following reasons: a) parchment paper samples have not been completely analyzed and tested; b) none of the papers have been aged after treatment to determine the long term effects of treatment; c) no solvent tests have been performed on aged papers; d) techniques of microtomed cross-sectioning and UV microscopy, both promising for characterization of papers before and after treatment, are still being developed, modified, and evaluated; e) a data base of FTIR reflectance spectra for thick coatings, transmission spectra on samples pressed on a diamond cell for medium coatings, and extraction spectroscopy for thin coatings is still being developed; f) multiple papers, such as additional samples of vellum papers, have not been studied; g) the measurements of dimensional and planar changes were non-statistical; and h) there are many other solvents, application techniques, and humidification and flattening techniques and combinations (such as using a drying board or friction drying), that may be used successfully with tracing papers but which were not tested in this project.

Table I: RESEARCH DESIGN FOR MODERN TRANSPARENT PAPERS PROJECT

PROJECT I. CHARACTERIZATION OF EXPERIMENTAL SAMPLES						
SELECTED SAMPLES FOR:	FIBER PROCESSING:	OVERBEATING:	NATURAL TRACING PAPER SAMPLE			
	SHEET PROCESSING:	ACID IMMERSION:	GENUINE VEGETABLE PARCHMENT PAPER SAMPLE			
		CALENDERING:	IMITATION PARCHMENT PAPER SAMPLE			
		COATING AND/OR IMPREGNATING:	VELLUM PAPER SAMPLE			
			PREPARED TRACING PAPER SAMPLE			
IDENTIFICATION OF MATERIALS BY:	GENERAL OBSERVATIONS					
	MANUFACTURER'S INFORMATION					
	ANALYSIS:	SEM IMAGING	SEM/EDS	FTIR	GC/MS	
MEASUREMENT OF PROPERTIES:	APPEARANCE:	COLOR	OPACITY	GLOSS		
	PHYSICAL:	STRENGTH	DIMENSIONAL STABILITY			
	CHEMICAL:	PH				
PROJECT II. EFFECTS OF ACCELERATED AGING						
PROJECT III. EFFECTS OF SOLVENTS & APPLICATION				PROJECT IV. EFFECTS OF HUMIDIFICATION & FLATTENING		
WATER	ETHANOL	ACETONE	TOLUENE	IMMERSION	HUMIDIFICATION CHAMBER	HUMIDIFICATION PACK
APPLICATION TECHNIQUES:				FLATTENING TECHNIQUES:		
IMMERSION	POULTICE	SUCTION DISK	AIR DRY	BLOTTER PRESS	SUCTION TABLE	

Table II: SUMMARY OF GENERAL CHARACTERIZATION OF SELECTED MODERN TRACING PAPERS

		NATURAL SAMPLE	GENUINE PARCHMENT SAMPLE	IMITATION PARCHMENT	VELLUM PAPER SAMPLE	PREPARED TRACING SAMPLE
G E N. O B S.	FIBER TYPE	chemical woodpulp	chemical woodpulp	chemical woodpulp	cotton	cotton
	FIBER PROCESSING	highly overbeaten	slight beating	medium beating	slight beating	slight beating
	SHEET PROCESSING	machine calendered	acid immersed	super calendered	Impregnated and coated	Impregnated and coated
	TRANSLUCENCY	relatively high	medium	medium	relatively low	relatively low
	SURFACE GLOSS	low	low	high	low	low
	FLUORESCENCE	low	low	low	high	high
	DIMENSIONAL STABILITY	medium	medium	medium	high	high
M A N U. I N	ADDITIVES	sulphamic acid; artificial clay; rust inhibitors; defoaming agents; saponified	unfilled	unfilled	melamine formaldehyde, urea formaldehyde	silica, aromatic solvent

F O		oils; talc; nitrogen polymer or acrylonitrile/ butylacrylate copolymer				
		surface size: styrene maleic anhydride compound, or quaternized polymer; modified starch	unsized	unsized	internal and external size: starch	coating: styrene ester, cellulose ester
A N A L Y S I S	SEM IMAGING	fibers visible on surface but not in cross-section	fibers visible on surface & cross section	fibers pressed & visible in cross sect.	coated surface; impreg. cross.	heavily coated surf.; impreg. cross.
	SEM/EDS	S, Si, Ca, Hg traces: Al, Cl, Na	Si, Ca, Al, S	Al, Si traces: S, Cl, Na, Ca	Al, S; traces: Si, Cl, Na, K, Ca	Al, Si, Cl traces: S, Na, K, Ca
	FTIR	melamine (?) acrylate, oil	NA	NA	melamine, starch, syn. res.	styrene acrylate, res.

						alcohol polymer
	GC/MS	oil	NA	NA	oil	oil, resin

Table III: SOME PROPERTIES OF SELECTED SOLVENTS

SOLVENT	FRACTIONAL SOLUBILITY PARAMETER			EVAPORATION RATE
	HYDROGEN BONDING	DIPOLAR	DISPERSION	
WATER	.54	.28	.18	.27
ETHANOL	.46	.18	.36	2.4
ACETONE	.21	.32	.47	7.8
TOLUENE	.13	.07	.80	2.3

(Information abstracted from Horie 1987)

E. Appendix: Experimental procedures and instrumental analysis

pH measurements: The pH was measured with a Corning Model 12 Research pH meter with an Orion model No. 81-35 flat surface combination electrode. The rinsed electrode, with a pendent drop of deionized water, was lowered onto a square paper sample (1.5 x 1.5 cm) on a polyethylene bag padded with blotters. The pH was recorded after 5 min. The electrode was calibrated with pH 7 and pH 4 buffer solutions before each measurement session. The surface pH of the untreated new and aged controls of each paper type was measured (i.e. 1 measurement for each of 8 samples).

Microscopy: Microscopy was undertaken on a polarized light stage microscope, using transmitted and reflected visible and ultraviolet illumination. UV illumination employed a short pass (Kurz pass) KP 500 excitation filter and a chromatic beam splitter (TK510/K515).

*Microchemical staining: For the iodine potassium iodide test 0.13 g iodine were dissolved in a solution of 2.6 g potassium iodide in 5 ml water. The solution was diluted to 100 ml (Browning 1977, 91).

SEM: SEM imaging and SEM analysis were carried out on a Jeol JXA - 840 A scanning electron microscope with Tracore Northern TN 5502 energy dispersive x-ray analysis system. For imaging the samples were mounted on aluminum stubs and gold coated.

For elemental analysis the samples were mounted on carbon stubs and carbon coated. The new and aged untreated controls and the new and aged treated papers that were flattened on the suction table were observed with SEM amounting to a total of 32 samples.

FTIR: FTIR analysis was carried out on a Mattson Cygnus 100 Fourier Transform Infrared Spectrophotometer with a Spectratech IR-Plan Microscope. The surfaces of the bulk paper samples were analyzed by reflectance; for transmission spectra, fibers were pressed in a diamond anvil cell. To isolate coatings, samples of the papers were extracted with solvents; the solvents were evaporated and the residues analyzed by transmission in the diamond cell.

Gas chromatography: Samples of new natural, prepared, and vellum tracing papers and of the aged natural paper were hydrolyzed in potassium hydroxide (10% in methanol) overnight, neutralized with 3M hydrochloric acid, extracted with diethyl ether, and then taken to dryness in a stream of nitrogen. The sample was redissolved in methylene chloride and then an equal volume of dimethyl formamide-dimethyl acetal was added to form methyl esters. The prepared sample was analyzed on a Carlo-Erba model 5360 gas chromatograph with a 30 m x 0.32 mm DB-1 column. One microliter of the sample plus a comparable volume of methylene chloride was injected. The injector temperature was 300°C. The initial column temperature of 50°C was immediately raised 10°C/min to 320°C. The effluent was detected with a flame ionization detector at 325°C. The chromatograms of the samples and that of a standard solution of methyl esters ("K101") were compared.

Artificial aging: The transparent paper samples were aged for four weeks in the dark at 90°C and 50% relative humidity in an Associated Environmental Systems HK-4116 Temperature/Humidity chamber. These conditions have been chosen as suitable for artificial aging studies [13]. A set of transparent papers was sewn with cotton thread into plexiglas frames so that all four corners were anchored and the samples did not touch one another. However the samples did vibrate in the oven draft.

Colorimetry: Color (specular reflectance included) and total transmission (diffuse plus regular transmission) were measured with the HunterLab Ultrascan Spectrocolorimeter (D_{65} ; 10° observer, diameter of area of view 1.2 in) using the CIE $L^*a^*b^*$ color notation, where L^* represents the degree of brightness (100 white, 0 black), a^* the degree of redness (positive numbers) or the degree of greenness (negative numbers) and b^* the degree of yellowness (positive numbers) or the degree of blueness (negative numbers). Due to irregularities of the transparent papers, the standard deviation for the L^* value of transmission was rather high, sometimes amounting to 0.5. Color and transmission were measured on the new and aged untreated control and the new and aged treated samples that were flattened on the suction table. For color and transmission five measurements were taken per sample and averaged (32 samples).

Gloss: The gloss was measured with a Dr. Lange Labor-Reflektometer RL. Three measurements per sample were taken and averaged at the each of the following angles: 20°, 60° and 85°. Gloss was measured three times on each of the new and aged untreated controls and on the new and aged treated samples that were flattened on the suction table (32 samples).

Tensile tests: The tensile properties were investigated using the Mecklenburg relaxation tensometer with a horizontal load applied in the machine direction to the paper strips. Narrow strips of uniform width were cut with a mat cutter. After measurement of the paper thickness in five places with a micrometer, the paper strips were mounted horizontally in the apparatus exposed to laboratory atmosphere. After an initial equilibration period at a gauge length of 2.5 in, the strip was stretched 0.0025 inch and one minute later the stress sustained by the paper strip was recorded. This process was repeated once per minute until the paper strip broke. Measurements were made on three strips of each paper. From these data, nominal stress (force applied per cross-sectional area of the strip) and strain (change in length divided by gauge length) were computed. Nominal stress was plotted as a function of strain for each paper strip. The new and aged untreated controls and the new and aged treated natural and prepared tracing samples that were dried on the suction table were measured three times each.

Dimensional changes: Dimensions of the samples were measured once per sample in mm (+/- mm) in cross and in machine direction before treatment, after humidification, after one day drying, after two weeks drying and after two weeks storage following drying. The dimensions of all 56 samples including new and aged untreated controls and new and aged treated samples were measured.

Planar distortion: New and aged untreated controls and new and aged treated samples were compared and subjectively ranked in daylight, raking light and transmitted light in a preliminary attempt to evaluate planar distortion. A total of 56 samples was ranked (ranging from 1 for least changed to 5 for most changed). A blind study is planned to provide more statistically accurate data.

Moisture: Moisture content was measured with a Sovereign electronic moisture meter, model 452 A. The samples humidified in a humidification pack were taken out of the pack and placed between polyester film supported by a blotter. The upper polyester film was removed and the surface of the paper measured. The same procedure was applied for the humidity chamber samples. The samples dried out very fast. The measurements had to be taken very quickly. The immersed samples were taken out of the bath and placed on polyester film supported by a blotter. One set of new (120 x 170 mm) and old (90 x 150 mm) untreated papers was cut for this purpose for each humidification technique. Four measurements were taken per paper sample and averaged. A total of 12 samples was measured.

Poultice: Diatomaceous earth (hydrated silica from diatom plant skeletons) was selected for its working properties since, unlike gel poultices (methylcellulose, agarose, starch paste, or hydroxypropylethylcellulose) it can be mixed with aqueous or non-aqueous solvents to form a plaster or paste that absorbs solutes as it dries to a powder, which can then be brushed off. It is more cohesive than fused silica. It is whiter than Fuller's earth, which is formed from hydrated silicates of magnesium, calcium, aluminum, or other metals. It is more controllable than organic solid poultices such as powdered cellulose, paper, or cotton. The diatomaceous earth was saturated with each solvent (approximately 1-2 ml solvent to 0.3 grams earth depending on solvent) and placed on the sample. Contrary to normal practice, the wet poultice was not surrounded by dry poultice, which would reduce tideline formation.

Suction disk: Solvents were applied locally by dropper on a 15 cm fritted glass bead disk (masked off with polyester film), which can reach a pressure of c. 25"Hg [45].

Suction table: The transparent papers were dried under low vacuum on a Nascor dual mode suction table, which can reach a pressure of c. 4.5"Hg.

Humidification Pack: The humidification pack was made up of a damp blotter placed on a polytetrafluorethylene membrane and polyester felt laminate (1/16" thick, produced by W.L. Gore & Associates, Inc.) held in contact with the tracing paper by light pressure, c. 1PSI, for 14 hours. While this may seem a long exposure time, exposure times of up to 72 hours have been found to cause no apparent change in sensitive watercolor media (Flamm et al. 1990.)

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