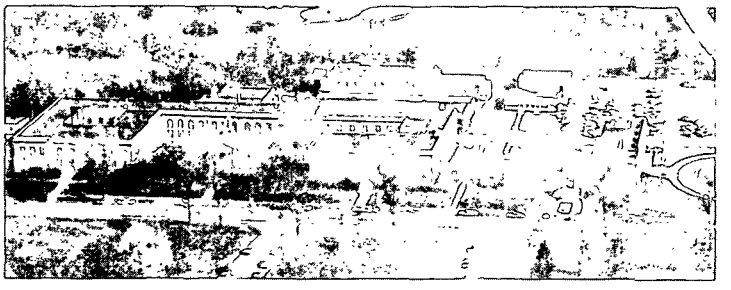

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X-RAY DIFFRACTION/EDXA/SEM

RUSSELL A. PARHAM AND JACK D. HULTMAN

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X-ray diffraction/EDXA/SEM: A more comprehensive approach to pigment characterization

Russell A. Parham and Jack D. Hultman

INTRODUCTION

The increasing use of polymeric pigments, microcapsules, and other non-crystalline materials in today's paper pigment and coating systems creates a complex substrate for characterization by the paper scientist. The use of data from x-ray diffraction combined with that from a scanning electron microscope equipped with an energy-dispersive x-ray analyzer can give a comprehensive picture of the morphology and composition of such pigment formulations.

The present paper provides a number of illustrations of the use of these methods.

The second part of this paper was presented at the Workshop on Scanning Electron Microscopy and the Law, Chicago, IL, April, 1975.

X-ray diffraction/EDXA/SEM: A more comprehensive approach to pigment characterization

Russell A. Parham and Jack D. Hultman*

Abstract

The increasing use of polymeric pigments, microcapsules, and other non-crystalline materials in today's paper pigment and coating systems creates a complex objective for characterization by the paper scientist. Only by using data from x-ray diffraction (XD) combined with that from a scanning electron microscope (SEM) equipped with an energy-dispersive x-ray analyzer (EDXA) can a comprehensive picture of the morphology and composition of such pigment formulations be obtained. Both EDXA/SEM and XD have their weak points, but in combination, they represent a very powerful tool for the analysis of both crystalline and noncrystalline pigment systems. Even with these tools at hand, the complete clarification of a multicomponent pigment system on an undefined base sheet can be a difficult task. However, at present, the EDXA/SEM/XD combination is probably the most informative and expedient means by which to study pigments in paper.

INTRODUCTION

The majority of coating and filler pigments commonly used in the paper industry are crystalline and are thus usually identifiable by their characteristic x-ray diffraction pattern (1,2). Such pigments

*R. A. Parham, Research Associate, and J. D. Hultman, Research Fellow, Division of Natural Materials and Systems, The Institute of Paper Chemistry, Appleton, WI 54911. The skillful assistance of Hilkka M. Kaustinen is gratefully acknowledged.

include clay minerals (kaolinites, bentonite, attapulgite, talc), calcium carbonates, hydrated alumina, barium sulfate, some satin whites, calcium sulfate, titanium dioxides, and others. Despite this very useful analytical advantage, however, there are two serious deterrents for relying upon pigment analyses solely by x-ray diffraction. First, any amorphous pigments are not detected, including calcined clays or alumina, some satin whites, zeolite, precipitated and diatomaceous silica, and others. Also, the more recently introduced polymeric pigments (3, 4) as well as most microencapsulated materials on paper (5) go "unseen." Second, the interpretation of diffractograms for a multicomponent system can be complex and may lead to erroneous interpretation unless other supportive methods are employed. Unfortunately, most alternative methods also retain either analysis ability or time, sampling statistics, and/or contamination intolerance as a disadvantage for use in routine applications. Furthermore, some of these methods are not at all amenable for in situ studies.

The present communication illustrates how some of the above shortcomings can be surmounted, or at least minimized, by combining x-ray diffraction (XD) data with that from an energy-dispersive x-ray analyzer (sis) (EDXA) that is interfaced to a scanning electron microscope (SEM). The EDXA permits rapid detection of noncrystalline pigments which escape the XD system; the SEM yields visual data missed by both systems.

TECHNIQUES

Methods used in the XD analysis of paper pigments are generally known and can be considered to be essentially those outlined by Garey

and Swanson (1). For SEM/EDXA examination, specimens are mounted on carbon planchets with organic adhesive and coated with carbon (6). If high-resolution micrographs are required, an additional coating of Au/Pd may be necessary, but this should be done on a matched sample. Details on preparation of various specimens are found in the literature (6-9).

APPLICATIONS

Amorphous Pigments

Shown in Fig. 1A-1C are EDXA spectra of an American coating clay, a filler-grade clay, and an English coating clay, respectively. All of these are relatively well refined, indicated by the almost identical Al and Si peaks typical of pure kaolinites. A small amount of additional Si contaminant is evident in Fig. 1B and 1C. However, if a significant fraction of Si contaminant is present (e.g., quartz), and/or if amorphous silica (Fig. 1D) is added purposely to the clay system, the resulting Si peak will be substantially higher than for Al.

[Fig. 1 here]

Amorphous pigments may also be discerned visually in the SEM (6), but when these materials (e.g., SiO_2, diatomite, zeolite) are present in complex formulations, the assignment of Na, Mg, Al, Si, S, Ca, etc., to specific pigments is ambiguous. Here neither the SEM and/or EDXA will resolve the enigma, and only with added data from XD can such formulations be meaningfully established. For very complex formulations — for example, those containing calcined clays (which appear amorphous to XD) or those with special chemical additives or optical brighteners — it should be noted that a definitive compositional analysis may be

exceedingly difficult to obtain via any combination of analytical procedures.

Polymeric Pigments

Use of plastic pigments as a partial substitute for customary inorganics is gaining commercial acceptance (3), and such practice will ultimately necessitate use of the SEM for characterization of papers incorporating these submicrometer particles. Figure 2 illustrates a clay/plastic pigment formulation on paperboard. By routine XD analysis, the polymeric constituent would have never been suspected.

[Fig. 2 here]

Specialty Coatings

While no illustrations are given here, use of the SEM for characterization of more exotic paper coatings such as those composed of microcapsules or those on reproduction papers is well documented (6,8,10-12). In these cases the SEM/EDXA combination is also especially valuable for process and quality control.

The EDXA/XD Approach — An Overview

For comprehensive characterization of paper and paper pigments, combination of data from SEM/EDXA and XD is actually a necessity. Two further cases well illustrate this point.

Figure 3 shows the EDXA data for a paper containing (confirmed by XD) kaolin clay (Al, Si), mica (K, Al, Si), $BaSO_4$, and TiO_2. Note that the Ba peaks cannot be resolved from those arising from Ti. Sulfur is present and evident, but sulfur could conceivably be attributed to some

nonpigment additive or residue in the paper. X-ray diffraction resolved the question, showing both $BaSO_4$ and TiO_2, but had the pigment contained polystyrene spheres, the SEM would have also been a requirement in this analysis.

[Fig. 3 here]

Via SEM/EDXA examination, the paper in Fig. 4 was coated with only $CaCO_3$ and TiO_2 (with a trace of silica). Unfortunately, one interesting feature about the covered base sheet not revealed by EDXA/SEM here but which was obvious by XD was that the sheet contained polyethylene fibers. The SEM was, however, able here to discern the size and shape of the $CaCO_3$ particles, which, although separable by XD into calcite and aragonite forms, cannot be distinguished by XD as to exact particle morphology.

[Fig. 4 here]

Trace amounts and higher concentrations of Cl, S, Ca, K, Al, Fe, Na, etc., in paper but not attributable specifically to the pigment system may plague the interpretation of both simple and complex EDXA spectra. However, the very powerful capability of microarea and particle analysis, along with other fundamental leverages of the SEM/EDXA system, endow the latter with an analytical advantage such that when used in concert with the x-ray diffractometer, probably represents the best instrumental combination presently available with which to study paper pigment systems.

LITERATURE CITED

1. Garey, C. L. and Swanson, J. W., Tappi 43(10):813 (1960).

2. Breunig, A. and Weninger, M., Wochbl. Papierfabr. 102(20):773 (1974).

3. Rossin, E. H., Pulp Paper June, 1974:57.

4. Prachar, M., Papir Celuloza 29(7,8):153 (1974).

5. Chapman, B. S., Paper Technol. August, 1974:231.

6. Parham, R. A., In "Scanning Electron Microscopy/1975." (O. Johari, Ed.), Chicago, IITRI, 1975. p. 511.

7. Klingele, H. and Weigl, J., Wochbl. Papierfabr. 101(7):197 (1973).

8. Judt, M., Pulp Paper Intern. 16(7):43 (1974).

9. Walbaum, H., Tappi 55(7):168 (1972).

10. Baum, G. A., Tappi 57(6):75 (1974).

11. Walbaum, H., Tonelli, J., McIntosh, D., and Deed, L., Tappi 56(5): 86.

12. Windhager, R. and Carter, H., TAPPI Fall Coating Graphic Arts Conf. (St. Charles):31 (1974).

FIGURE CAPTIONS

Fig. 1. Energy-dispersive x-ray spectra of paper pigments. A, An American coating-grade clay. B, An English coating-grade clay. C, Water-washed, filler-grade clay. D, Precipitated, amorphous SiO_2.

Fig. 2. Surface of a paperboard pigmented with clay and polystyrene spheres.

Fig. 3. EDXA spectra of a paper containing, among other constituents, kaolin clay (Al, Si), $BaSO_4$, TiO_2, and a trace of mica (K, Al, Si). A, illustrating Ba L-lines. B, illustrating Ti K-lines.

Fig. 4. An EDXA spectrum from a paper containing polyethylene fibers and coated with $CaCO_3$ and TiO_2. Note also a trace of Si in this formulation.

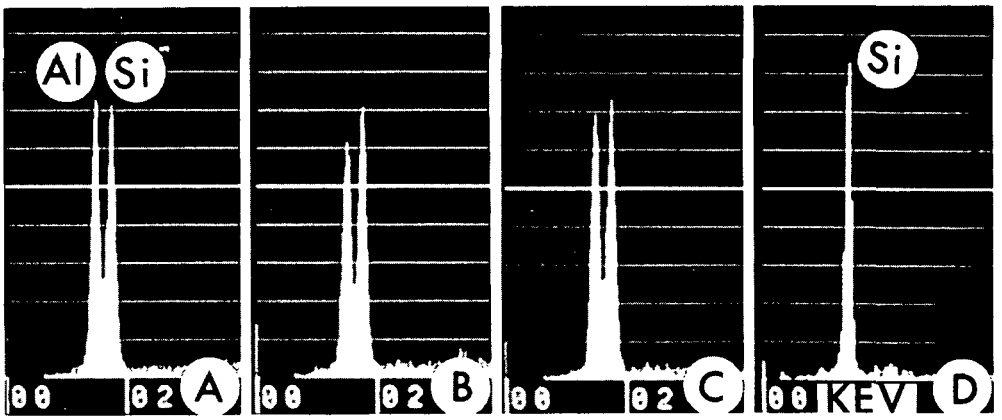

FIGURE 1.

FIGURE 2.

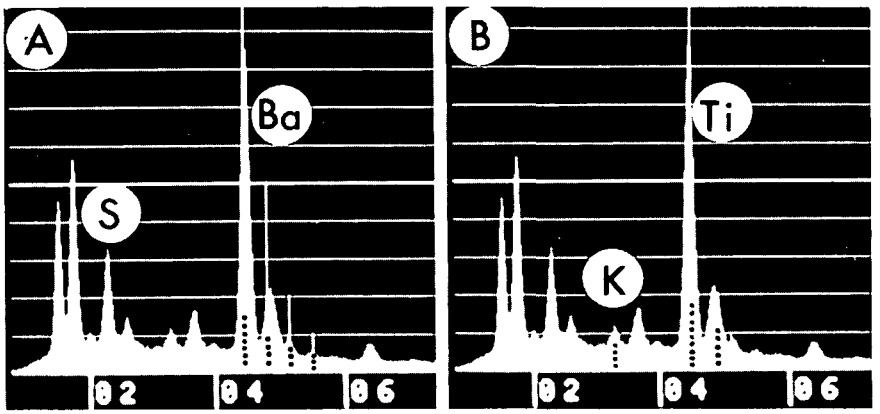

FIGURE 3.

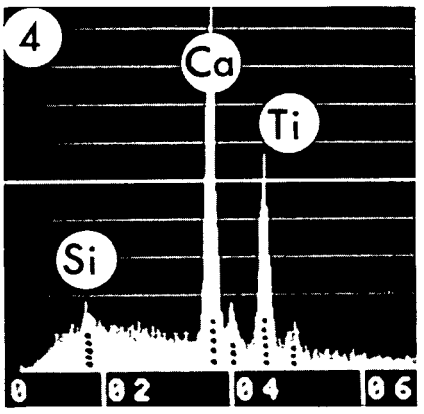

FIGURE 4.

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ON THE USE OF SEM/X-RAY TECHNOLOGY FOR IDENTIFICATION OF PAPER COMPONENTS

R.A. Parham
The Institute of Paper Chemistry
Division of Natural Materials and Systems
Appleton, Wisconsin 54911

ABSTRACT

The characterization of paper components in a manner that is both meaningful and easily interpreted by nontechnical people is a common objective in any legal debate centered on the question of document validity or source. Analytical techniques heretofore utilized in this endeavor include X-ray diffraction, thin-layer and gas chromatography, and a variety of spectroscopical and microscopical methods, as well as neutron activation analysis, the choice being largely determined by whether the constituents are organic and/or inorganic. The size, shape, and arrangement of paper constituents is also of paramount importance in document descriptions. Due to the physical nature of paper products, paper analysis, at least to the point of matching or mismatching two specimens, is, in many instances, demonstrated most suitably via SEM and energy-dispersive X-ray analysis (EDXA). The data produced from SEM/EDXA of paper fibers, pigment systems, printing inks, specialty coatings, and various defects are of considerable value. Other cases, especially complex pigment systems, show the SEM/EDXA combination to be insufficient for complete sample characterization, requiring supplementary data via X-ray diffraction. Element mapping of inorganic constituents in some inks can facilitate immeasurably the demonstration and distinction of some counterfeit items. And, in situations where proper assignment of responsibility for surface defects in large quantities of paper is the question at hand, the SEM/EDXA system is often the most logical tool with which to begin the investigation. Frequently, it is sufficient to elucidate and pinpoint the cause.

KEY WORDS: Scanning Electron Microscopy, Electron Probe Microanalysis, Fibers, Pigments, Inks, Paper, Forensic Science

ON THE USE OF SEM/X-RAY TECHNOLOGY FOR IDENTIFICATION OF PAPER COMPONENTS

R. A. Parham

Division of Natural Materials and Systems
The Institute of Paper Chemistry
Appleton, Wisconsin 54911

Introduction

The identification of paper components is normally an integral part of any judicial proceeding involving forgeries, counterfeiting, certificates, securities, contracts, wills, stamps, works of art, messages, or documents of any type where validity may be questioned.[1] Also included here may be inks, writing instruments, and/or printing processes. Characterization of a seemingly simple but yet so potentially complex a specimen as a sheet of paper may necessitate clarification of physical parameters (texture, basis weight, thickness, strength, quality), chemical composition, as well as paper optical properties (color, whiteness, opacity, fluorescence), some of which are obtained only by destructive means. The experimental schemes involved here are outlined in other texts[1], standard methods[2], and various articles[3-7]. Numerous analytical techniques are applied in such work, but in some instances it is only via the SEM, especially when the latter is equipped with an x-ray analyzer, that the needed data can be provided in a conclusive and easily interpretable manner. Other cases, however, show the SEM/x-ray system to be inconclusive. The aim of this paper is to illustrate some of the advantages as well as shortcomings of the SEM/EDXA (energy-dispersive x-ray analysis) combination as a means of characterizing paper constituents which are subject to scrutiny by the document examiner.

The Problem

Forensic studies of paper commonly involve (1) the possible identification (matching or mismatching) of two paper specimens and/or (2) the origin of the paper. Objectives for examination are paper watermark, fibers, pigments, inks, and any other constituent that can be identified as to chemical composition and chronological utility. With almost 6000 plants in the U.S. alone making or converting paper products, and each of these using any combination of various chemical additives or process variables, the document examiner may sometimes be confronted with an almost impossible task. Armed with a variety of analytical procedures, however, he can often match beyond a reasonable doubt and sometimes on a quantitative basis, the "fingerprints" of two paper samples. Designation of paper source is usually more difficult if not sometimes impossible.

SEM/EDXA Applicability

Paper constituents may include a spectrum of both organic and inorganic materials. Optical light microscopy, infrared spectroscopy, gas and thin-layer chromatography, and pyrolysis gas chromatography are very useful for organic "fingerprinting." Inorganics are best handled by either arc-emission spectroscopy (metallics), neutron activation analysis, x-ray diffraction (crystalline organic and inorganic materials), or EDXA (or a wavelength spectrometer) in conjunction with an SEM. Materials of interest here include fibers, filaments, and/or extruded plastic sheets, chemical additives (rosin, starch, protein, alum, wax, asphalt, synthetic resins, latex, etc.), pigments (fillers and coatings), dyes, inks, and a host of potential process variables.

SEM/EDX analysis of paper is restricted to the evaluation of inorganics ($Z > 10$), and due primarily to specimen topography, is mostly qualitative or at best semiquantitative. However, surface detail and particle size, shape, and distribution are easy targets for the SEM over a wide range of useful magnification (5X-30,000X).

Paper Fibers and Sheet Structure

The identification of most paper fibers is best accomplished by light microscopy.[8-11] The major benefit gained from use of the SEM here is only to elucidate fiber surface architecture, interfiber bonding, or other fiber ultrastructure. Highly topographical materials, however, such as some plastic papers (Fig. 1,2) or nonwoven sheets (Fig. 3), demand the SEM.

Paper Pigments

Inorganic mineral (and some organic) pigment is used on/in many papers for either creating a smooth and receptive surface for printing, coloring or whitening the base sheet, or imparting opacity, and such materials may comprise from 5-30% of the paper's dry weight. Individual pigment particles are in the range of 0.1-5.0 μm and thus require electron optics for accurate designation of particle size, shape, and distribution.

General Pigment Morphology

The SEM — both magnification- and resolutionwise — is the ideal instrument for ascer-

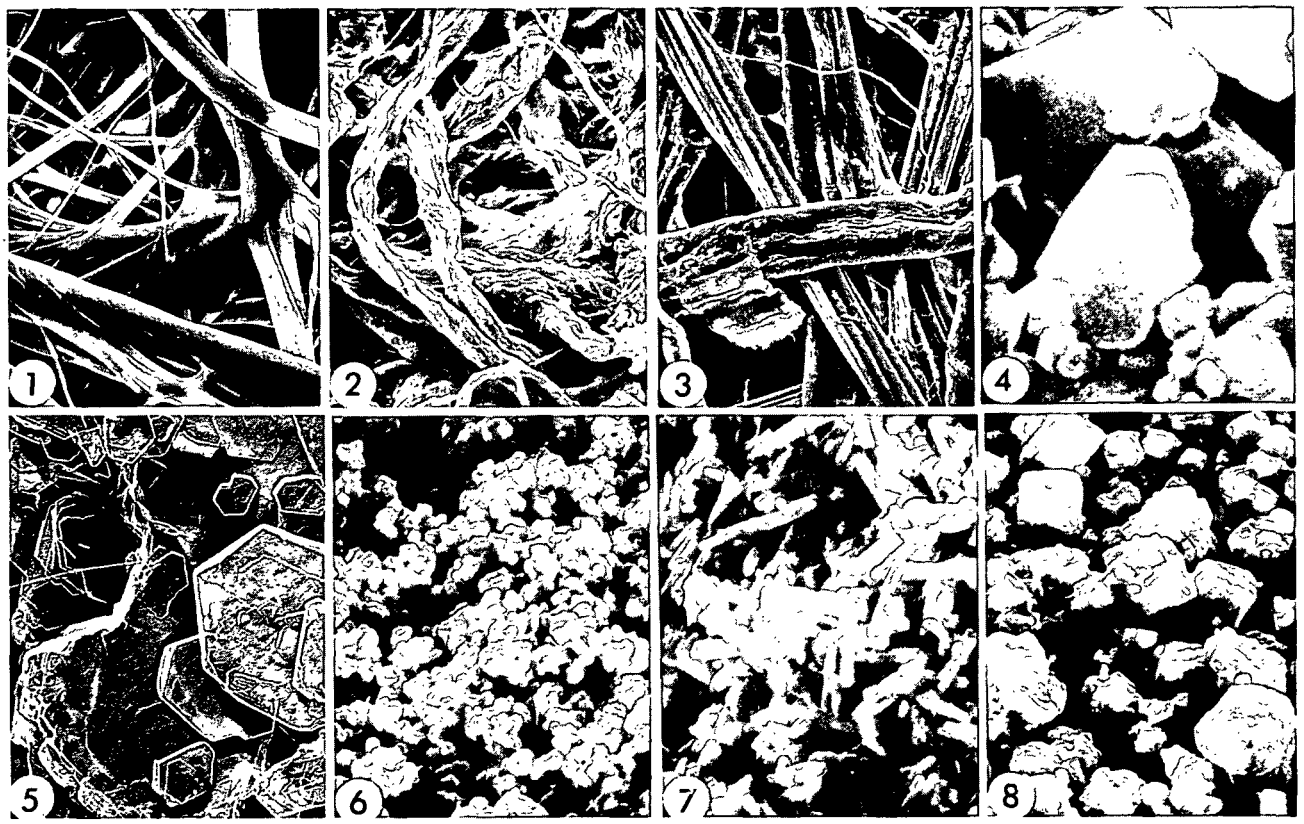

Fig. 1. Paper of polyethylene filament (width of micrograph is 108 μm).
Fig. 2. Specially processed polyethylene pulp (108 μm).
Fig. 3. Nonwoven facial tissue of wood and rayon fibers (108 μm).
Fig. 4. Kaolin clay platelets (1.35 μm).
Fig. 5. Same as Fig. 4. Surface replica. Transmission electron micrograph (2.25 μm).
Fig. 6. TiO_2 particles (5.4 μm).
Fig. 7. Precipitated, aragonite $CaCO_3$ (5.4 μm).
Fig. 8. Precipitated, special type of calcite $CaCO_3$ (7.7 μm).

taining the characteristic morphology of paper pigments and their distribution. Figures 4-15 well illustrate this point for a variety of pigments and some special products. Accurate assessment of these parameters as well as their variability is a prerequisite in the determination of whether or not two paper samples can be deemed identical.

Pigment Identification

The vast majority of pigments presently used in the paper industry are identifiable in a fairly rapid fashion via nondestructive x-ray diffraction (XD).[12] With proper standards, semiquantitative data are obtainable on concentrations as low as 0.5-2%. However, a serious limitation of the XD approach is that only crystalline materials are "seen"; amorphous pigments such as zeolite (sodium silicoaluminate), precipitated and diatomaceous silica (SiO_2), some calcium sulfates and sulfites, polystyrene latex, and any calcined (oxidized by heating) kaolin clays or (once-hydrated) alumina are not detected. In addition, spectral peaks from underlying cellulose, polyethylene, polypropylene, or other substrates may interfere with diffractogram interpretation. With an SEM/EDXA system as an ancillary tool, it is possible to detect and identify all the above pigments (see Fig. 4, 11, 16, 17). All crystalline pigments are also detectable via SEM/EDXA, and characterization of simple pigment systems is straightforward, e.g., kaolinites, TiO_2, $CaCO_3$, SiO_2, and others. However, for multiphase systems (e.g., Fig. 18) potentially containing both crystalline and amorphous materials, the combined data from XD and EDXA may sometimes still be inconclusive. One must then resort to additional methods of analysis (wet chemistry, emission spectroscopy), and a working knowledge of paper coating practices is almost essential. A saving grace in

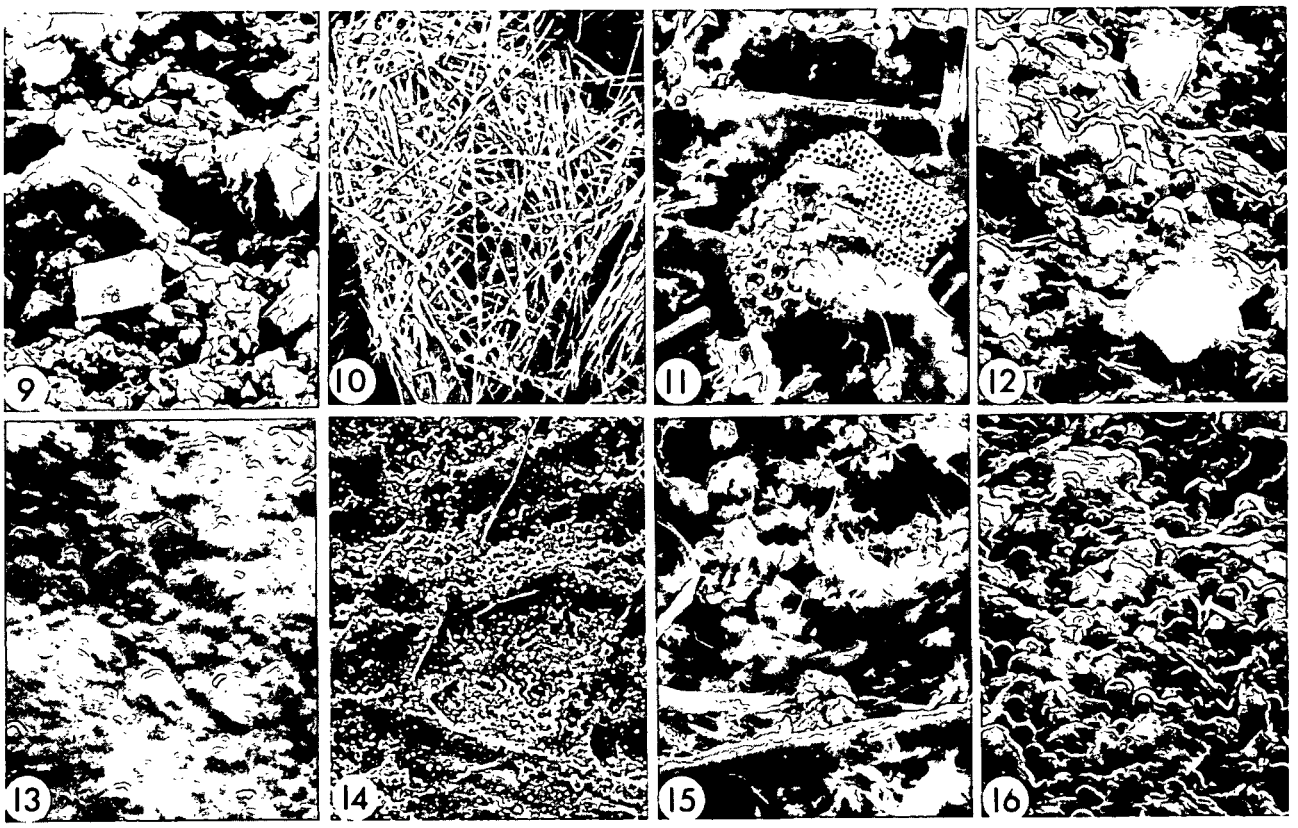

Fig. 9. Natural ground $CaCO_3$ (27 μm).
Fig. 10. Potassium titanate needles (27 μm).
Fig. 11. Diatomaceous silica (27 μm).
Fig. 12. Normal air-dried coating of clay-starch (9.8 μm).
Fig. 13. Coating dried in high velocity, hot air (7.7 μm).
Fig. 14. TiO_2 pigment on paper surface (108 μm).
Fig. 15. Cigarette paper; $CaCO_3$ filler (36 μm).
Fig. 16. Coating with clay, $CaCO_3$, TiO_2, and polystyrene spheres (6.7 μm).

forensic applications is that (probably) illustrating the same composition both microscopically and elementally for two papers, but not necessarily having a complete component analysis, is sufficient to label two samples as identical. Otherwise, a complex pigment system could be a very difficult forensic objective.

Figure 16 illustrates a case in which SEM/EDXA was unique in its ability to identify all paper pigments — kaolin clay, TiO_2, $CaCO_3$, and polystyrene spheres. The latter would have never been suspected by x-ray diffraction.

The EDXA spectrum in Fig. 18, representing a multicomponent pigment system, fails to resolve the K-lines of Ti (4.508, 4.931 kev) and the overlapping L-lines of Ba (4.465-5.193). Kaolin clay, TiO_2, $BaSO_4$, and satin white (calcium aluminosulfate) were confirmed by XD, here a necessary supplement to the SEM/EDXA combination not only for resolution of Ti and Ba but for clarification of the sulfur and calcium sources.

Specialty Paper Coatings

A very specialized coated paper presently manufactured by several companies incorporates "microcapsules" which contain a colorless dye base or an emulsion of dye particles. These contents are released upon mechanical fracture.[13] Such coatings adorn the carbonless copy papers used throughout the world. These materials, which are accurately described only with the SEM, have been the subject of several potential patent infringements. Features of importance here include microcapsule size, shape, surface features (Fig. 19, 20), whether they are single or in clusters, whether they are applied in 1 or 2 layers or are incorporated into the paper, and whether or not starch grains are used in the coating (see Fig. 21-24).

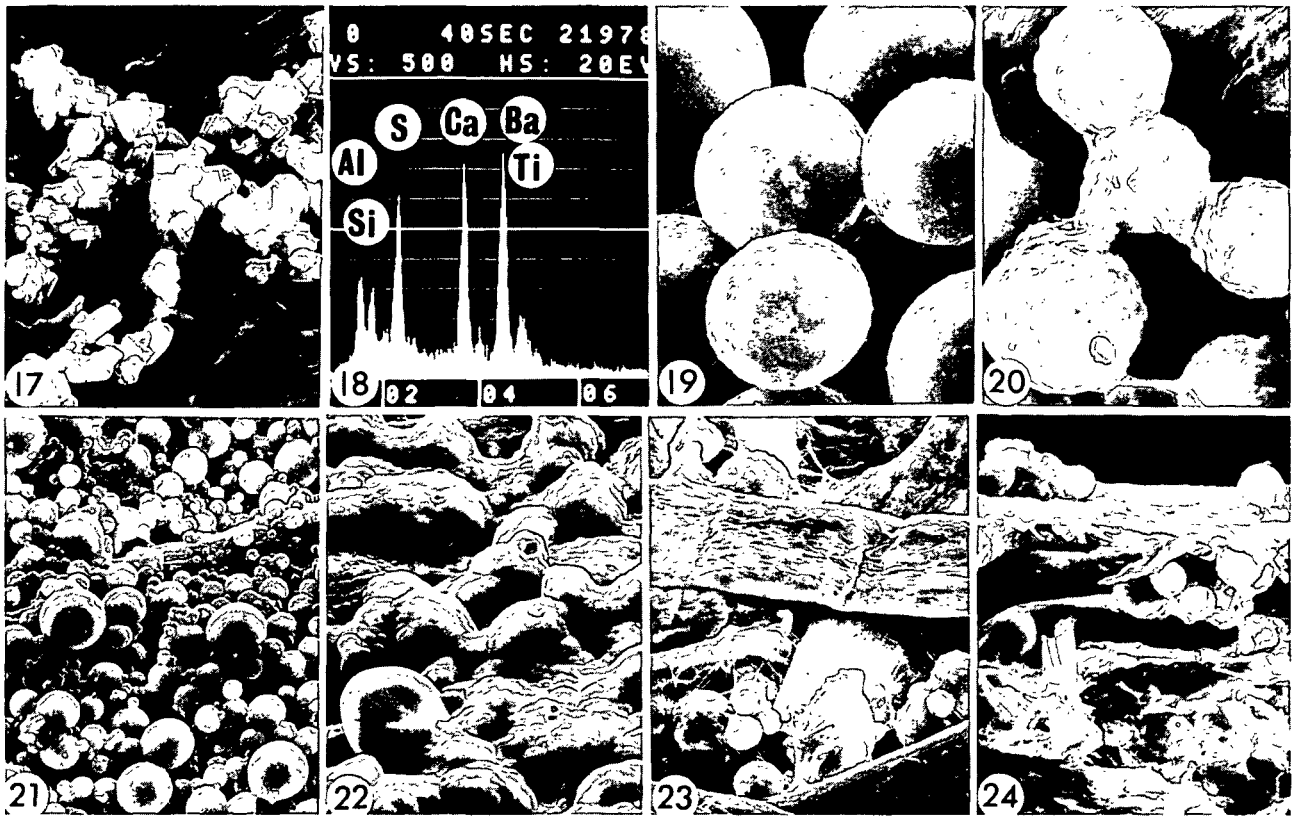

Fig. 17. Hydrated alumina pigment (7.7 μm).
Fig. 18. EDXA spectrum of a coating with kaolin, satin white, $BaSO_4$, and TiO_2 pigmentation.
Fig. 19. Microcapsules. Type A (34 μm).
Fig. 20. Microcapsules. Type B (19.3 μm).
Fig. 21. Carbonless copypaper sheet (54 μm).
Fig. 22. Similar to Fig. 21, except with microcapsule clusters (54 μm).
Fig. 23. Microcapsules incorporated into sheet structure (54 μm).
Fig. 24. Paper in Fig. 23 seen in cross-section after fracture in liquid nitrogen (60 μm).

Inks and Printing

Handwritten and/or printed documents as imaged by the SEM have been discussed to some extent in the literature, mostly with respect to cross-over lines, printing process, and fiber substrates.[3-5] Apparently, letterpress printing yields a very shadowy image, offset lithography hardly any image, and gravure or intaglio very prominent features. Constituents in some pigmented inks which lend themselves to EDXA identification include TiO_2 (white) and colored lead chromates (with Pb, Cr, S). Some of these inks may also contain Cu or Mo. Less frequently, inks may contain the following: Ca, Cl, Cd, Ba, Fe, S, Co, Ag, Zn, Se, Ni, Sb, Mn, Na, or clay (Al, Si). Many more inks (especially black) are entirely organic.[14] Sometimes an inorganic ink constituent is present in sufficient amount to permit distinction via EDX analysis.

Figures 25-26 were evidence in a situation where it was necessary to show whether the high calcium content of a printed document was due to the ink or to the paper. When examined unmetallized with the SEM (Fig. 25), only faint indications of ink were observable. However, an element distribution map of Ca over the same printed area (Fig. 26) demonstrated conclusively that the Ca was concentrated in the ink. Point analyses on and off the inked regions confirmed this finding.

An authentic document can sometimes be distinguished from a counterfeit item via SEM/EDXA by comparing the print topography and/or composition of the inks. For example, the ink lines in Fig. 27 are the result of a gravure or intaglio process (printing from a depressed surface) and show a high concentration of ink around the lines themselves. Since this ink also had a high Fe content, it was possible to delineate the ink location by element mapping (Fig. 28). A matching counterfeit document (Fig. 29) exhibited an entirely different print topography (probably

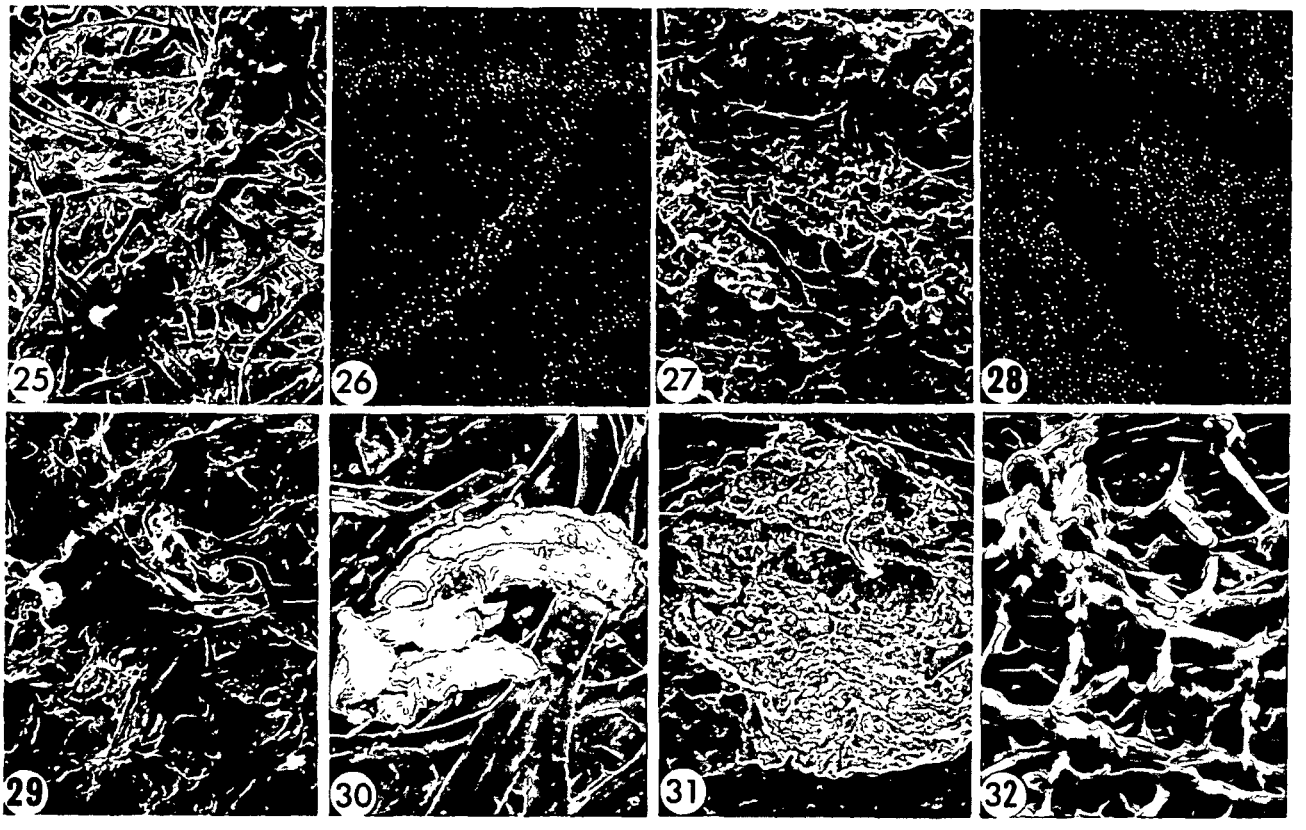

Fig. 25. Unmetallized surface of printed document. Note charging of ink areas (540 μm).
Fig. 26. Element map of Ca over same area as Fig. 25 (540 μm).
Fig. 27. Intaglio-printed, authentic document. Unmetallized (540 μm).
Fig. 28. Element map of Fe over same area as Fig. 27 (540 μm).
Fig. 29. Counterfeit document corresponding to Fig. 27-28. Note difference in print morphology. This paper produced no distinguishable Fe map (540 μm).
Fig. 30. Copper debris on surface of transformer insulator paper (180 μm).
Fig. 31. Crater on printing-grade paper resulting from "picking" during printing operation (200 μm).
Fig. 32. Fungal mycelia on/in coating of polyethylene paper (54 μm).

offset lithography) and very little Fe anywhere on the paper. Point analyses of corresponding regions and other colored inks on the two documents produced further evidence as to their incongruity.

Paper Defects

If present in sufficient number, paper defects may hinder or even discourage use of large volumes of expensive paper products, or, in some cases, may cause failure of component products. The following examples represent instances in which SEM/EDXA was instrumental in elucidating such defects and preventing further arguments and/or legal pursuit by the paper manufacturer, converter, and/or distributor.

Case 1

In the failure analysis of an electrical transformer, SEM/EDXA revealed microscopic pieces of copper clinging to paper insulation wrapping in regions contacting Cu electrodes (Fig. 30). Such debris were not found in those wrapping areas overlapping only paper. It is probable that insufficient cleaning of Cu electrodes prior to transformer assembly was the cause of insulator breakdown and not a property of the wrapping paper supplied to the transformer manufacturer.

Case 2

Small specks (< 0.5 mm) on a printing-grade paper that "picked" away from the paper surface during offset lithography (Fig. 31) were first attributed to special cell types (vessel elements) in the paper pulp. However, SEM/EDXA examination of these defects revealed an extremely high concentration of silicon. The Si source was finally narrowed to a colloidal-silica-based

defoamer used in sheet manufacture. The defoamer was probably applied under improper stress and/or pH conditions, promoting coagulation. Responsibility for the defect was then removed (via the SEM) from the printer, pulpmaker, and defoamer supplier, and transferred accordingly to the paper mill.

Case 3

Unusually dull or nonlustrous areas scattered randomly over a large supply of coated, polyethylene-fiber bookcover stock led to scrutiny with the SEM (Fig. 32). Found embedded in/on the coating surface were masses of fungal mycelia, implying contamination of the product during the coating step and not during sheet manufacture or by subsequent distributors.

Specimen Preparation for SEM/EDXA

Representative samples of a paper in question are usually cut to size with a new razor blade or paper punch and mounted via transfer adhesive (3M No. 465) to the center of a 1-inch diameter carbon planchet (Structure Probe, Inc.). For preliminary study by EDXA, planchets are mounted in a normal SEM specimen holder but then covered with a carbon-coated "doughnut" cap of mylar (organic polyester) plastic. The latter device permits exposure to the electron beam of only the paper sample and protects neighboring parts of the specimen holder from stray electrons and/or scattered x-rays. The EDXA detector (retractable) is also equipped to minimize collection of stray signals by means of a carbon-lined collimator of aluminum. Samples are examined either as is or with a coat of carbon or conducting aerosol (PELCO No. 94) to permit adequate but low-quality imaging by secondary electrons. A light spray with the aerosol obscures detail at higher magnification but has been found to produce no detectable peak in the EDXA spectrum, even when analyzed on a carbon planchet. However, it does contain a mixture of Freons (with Cl and F). After elements of interest are identified employing a 25 kv electron beam, an overvoltage ratio (kv employed/absorption edge energy of element of interest) of about 2.5 is then adopted with an according adjustment in beam voltage. For work strictly via secondary electron imaging, papers are coated sequentially and omnidirectionally in a high vacuum evaporator with carbon and then 60:40 Au/Pd. For specimens incorporating loose fiber networks, a metal sputtering device would probably produce much more satisfactory coatings. However, a light spray with the conducting aerosol followed by metallizing and examination at low kv will often provide acceptable results on these types of specimens.

Conclusions

The information gained from SEM/EDXA of paper is certainly useful and easily interpretable in almost all cases of related forensic endeavor. In some situations, this instrument combination may be unique in its power to provide the needed data. However, in many more cases, especially for complex and multiphase systems, SEM/EDXA is inconclusive. Here, supportive methods of analysis are essential but should be considered in all cases in order to obtain as complete a 'fingerprint' as possible.

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References

1. Browning, B. L., Analysis of Paper, Marcel Dekker, Inc., New York, 1969.
2. TAPPI Standard Methods, Technical Association of the Pulp and Paper Industry, Atlanta, Georgia, 1974.
3. Oron, M., and V. Tamir, "Development of SEM methods for solving forensic problems encountered in handwritten and printed documents," IITRI/SEM/1974, 207-214.
4. Williams, R. L., "An evaluation of the SEM with x-ray microanalyzer accessory for forensic work," IITRI/SEM/1971, 537-544.
5. Taylor, M. E., "Forensic applications of scanning electron microscopy," IITRI/SEM/1971, 545-552.
6. Klingele, H., and J. Weigl, "Scanning electron microscopy — possibilities in paper evaluation," (in German), Wochbl. Papierfabr. 101 (7), 1973, 197-8, 200, 202-203.
7. Parham, R. A., "X-ray/SEM analysis of materials: principles and applications to paper," Paperi ja Puu 55 (12), 1973, 1-9.
8. Isenberg, I. H., Pulp and Paper Microscopy, 3rd Edition, The Institute of Paper Chemistry, Appleton, Wisconsin, 1967.
9. Strelis, I., and R. W. Kennedy, Identification of North American Commercial Pulpwoods and Pulp Fibers, University of Toronto Press, Toronto, Ontario, Canada, 1967.
10. TAPPI, "Qualitative analysis of synthetic fibers," CA Report No. 21, Technical Association of the Pulp and Paper Industry, Atlanta, Georgia, 1969.
11. Battista, O. A., Synthetic Fibers in Papermaking, Interscience Publishers, New York, 1964.
12. Garey, C. L., and J. W. Swanson, "Characterization of filler and coating pigments in paper by x-ray techniques," Tappi 43 (10), 1960, 813-818.
13. Chapman, B. S., "Applications of microcapsules in papermaking," Paper Technol., August, 1974, 231-233.
14. Patton, T. C. (Ed.), Pigment Handbook, Wiley-Interscience Publishers, New York, 1973.