Detecting Individual Paints in Mixed-Media Paintings

The Challenge of Conserving Mixed-Media Paintings

Conserving modern and contemporary mixed-media paintings is made difficult by the impossibility of visually identifying individual paints in the mix. Furthermore, because paints have different chemical and physical properties, traditional single-media conservation techniques may cause unwanted damage and irreversible changes to the surface of a mixed-media painting.

Mixed-Media Test Panels with Known Ratios of Acrylic, Alkyd, and Oil

A 2008 research project at the Smithsonian's Museum Conservation Institute explored procedures that could be used to detect each paint component in a mixed-media painting. This study used Grumbacher oil, Winsor & Newton Griffin alkyd, and Golden acrylic emulsion in weight ratios of 25:75, 50:50, 75:25, 90:10, and 100.

Samples were prepared from drawdowns on Mylar sheets and left to age in an indoor environment with stable temperature and humidity. These experimental test panels were used to develop and refine the testing procedures and provided an excellent resource for studying the aging behaviors of mixed media.

Tests

In our studio, examining and interpreting the spectra of the binder media alone using Fourier Transform Infrared Spectroscopy (FTIR) is the first step in paint identification and is a straightforward process. While carbonyl peaks overlap, especially as oil paint ages, the fingerprint and C-H regions are readily distinguishable. The analysis can be completed in one to two minutes.

For mixed paint binders, however, FTIR analysis is less straightforward. Pigments and fillers make infrared identification of individual paints more difficult to confirm. Infrared spectroscopy of mixed-media paintings may provide information on multiple components of a paint mixture, but peak overlaps can prevent observation of some less prominent peaks from different paints.

Thus, microtesting of physical properties, such as melting points and solubility (often used in forensic and pharmaceutical laboratories), is standard procedure in our protocols and is used to establish safety limits for temperature and solvents for treatments such as lining and cleaning. Our solubility test is adapted from the National Bureau of Standards Special Publication 480-40, Paint Solubility Test, prepared for the National Institute of Justice, issued in 1982. We used a Fisher-Johns melting point apparatus for our melting point tests.

We performed the first full-scale investigation of paint mixtures at various ratios in the summer of 2012. It included assessments of gloss, color, melting point, solubility (under visual and 3D microscope examination), FTIR, and gas chromatography-mass spectrometry (GC-MS). Preliminary results indicated that it is not possible to visually identify paints by color or gloss, and that even FTIR identification is not completely reliable. Pyrolysis-gas chromatography/mass spectrometry using tetramethylammonium hydroxide (Py-GS-MS using TMAH) can successfully identify all components, but is not always accessible or affordable for practicing conservators.

Findings from this study demonstrated the feasibility of using microsamples of paint to microscopically observe melting points and solubility, and integrating FTIR analysis in the test protocol to detect single-component paints in mixed media.

In the second phase of our investigation, carried out in 2013, we employed paint samples we had prepared in 2008, but expanded the investigation to include commercial household paint samples. The scope of our current investigation is smaller and focuses on establishing testing criteria and standardizing reagent concentrations and other parameters for tests of melting points and solubility. When followed rigorously, with controlled time and temperature, these procedures can be used to classify paints by their chemical reactivity and physical properties, and thus characterize individual paint components in mixed media.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Instrument: Thermo Nicolet 6700 FTIR spectrometer. Resolution: 4 cm-1. Sampling accessory: Golden Gate ATR with diamond crystal, single bounce, 45º. Detector: DTGS. Number of scans: 128. Correction: ATR corrected. Samples for ATR-FTIR were placed directly on the diamond crystal of the ATR accessory. For small samples, a piece of aluminum foil backed the sapphire anvil to eliminate any sapphire absorption in the IR spectrum. Samples of medium alone were also available for FTIR analysis.

FTIR Analysis of Single-Component Paints (Fig. 1)

Interpretation of single-component paints (acrylic, oil, and alkyd) is straightforward. Carbonyl peak C=O can overlap, especially in aged oil samples. The C-H and fingerprint region are easily distinguishable: alkyd peaks at 1274 cm-1 and oil peaks at 1170 cm-1. However, when pigments and fillers are added, infrared interpretation becomes more difficult.

FTIR Analysis of Alkyd and Oil Paints (Fig. 2)

Differentiating alkyd and oil paint in mixtures would appear to be easy: alkyd peaks at 1274 cm-1 and oil peaks at 1170 cm-1. However, peaks from fillers can obscure these peaks. Silica's 1100–1000 cm-1 Si-O-Si stretch and sulfate's asymmetric stretching band of 1200–1050 cm-1 can overlap these two markers, making it difficult to identify individual paints. 25% alkyd paint has no peaks that can be attributed to alkyd.

As seen in the sample of 75% alkyd: 25% oil paint, peaks from fatty-acid soaps present in the aged oil paint film, at 1540 cm-1, are quite prominent. The main peak in the alkyd paint film, at approximately 1400 cm-1, is actually due to carbonate filler and is not distinctive to alkyd paint. The sample with 25% alkyd: 75% oil paint has no peaks that can be attributed to alkyd paint.

FTIR Analysis of Alkyd and Acrylic Paints (Fig. 3)

With C-H stretching bands of 2986 cm-1 and 2955 cm-1, the overall profile of the C-H stretching region, C=O stretching at 1732 cm-1 and the fingerprint at 1179 cm-1, are indicative of acrylic emulsion. The OH peak of around 3300 cm-1 and

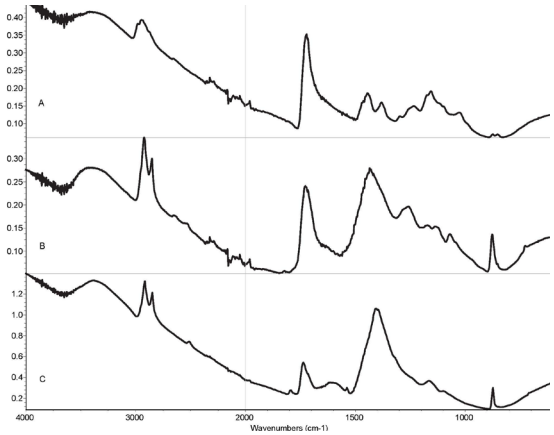

Figure 1. IR absorbance spectra for single-component paints.
A: acrylic; B: alkyd; C: oil.

C=O stretching at 1730 cm-1, peak 1274 cm-1 fingerprint region 1123 cm-1 and 1072 cm-1, are indicative of alkyd paint. Alkyd's fingerprint region peaks of 1123 cm-1 and 1072 cm-1 often mask acrylic's skeletal vibration of 1179 cm-1.

FTIR Analysis of Acrylic and Oil Paints (Fig. 4)

When acrylic and oil paint are mixed, fatty-acid soaps from aged oil paint peak at 1170 cm-1 and dominate the infrared spectrum. An unknown sample with 75% acrylic paint and 25% oil would be difficult to identify as containing acrylic.

However, any sulfate or silicate pigments or extenders ruin quantification due to peak overlaps. Acrylic C–O and C–C stretch also have high absorption in the 1100–1300 cm-1 region and prevent quantification of a mixture of three paints.

As described, when acrylic and oil paints are mixed, fatty-acid soaps formed in the aged oil paint dominate the infrared spectrum. If the acrylic peak at 1170 cm-1 is attributed to oil paint rather than acrylic, even an unknown sample that is 75% acrylic paint and 25% oil paint would be difficult to identify as containing acrylic. Acrylic C–O and C–C stretch also have high absorption in the 1100–1300 cm-1 region and prevent quantification of a mixture of three paints.

Summary

Interpreting single-component paints (acrylic, oil, and alkyd) is straightforward. However, when pigments and fillers are added, infrared interpretation of individual paints becomes more difficult. Chalk's characteristic CO_3^{2-} stretching band of 1490–1370 cm-1, calcium sulfate's characteristic asymmetric SO_4^{2-} stretching band of 1140–1080 cm-1, and silica's asymmetric Si-O-Si stretching band of 1100–1000 cm-1 often obscure the telltale peaks of individual paints, and overlapping peaks can inhibit identification.

Infrared spectroscopy of mixed-media paintings may provide information on multiple components of a paint mixture, but peak overlaps will prevent seeing some less prominent peaks from different paints.

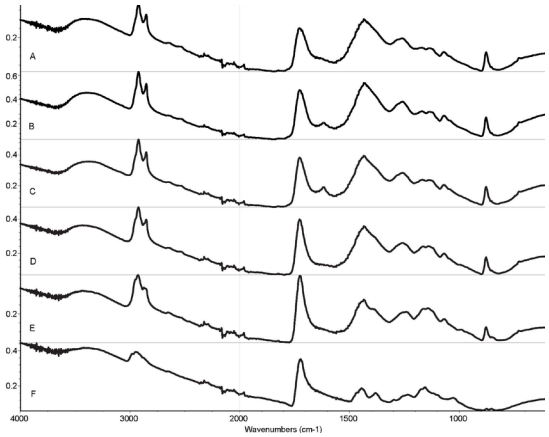

Figure 2. IR absorbance spectra for alkyd/acrylic mixtures.
A: 100% alkyd; D: 50% alkyd, 50% acrylic;
B: 90% alkyd, 10% acrylic; E: 25% alkyd, 75% acrylic;
C: 75% alkyd, 25% acrylic; F: 100% acrylic.

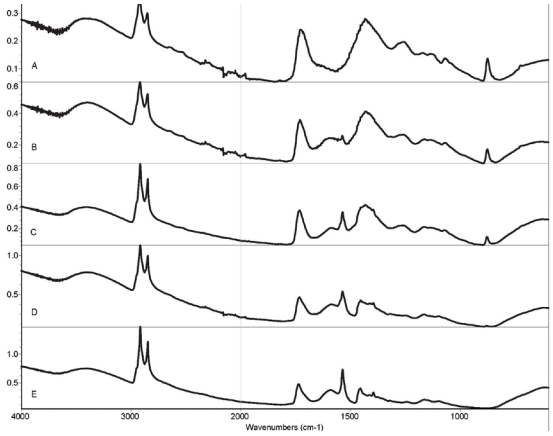

Figure 3. FTIR absorbance spectra for alkyd/oil mixtures.
A: 100% alkyd; D: 10% alkyd, 90% oil;
B: 75% alkyd, 25% oil; E: 100% oil.
C: 50% alkyd, 50% oil;

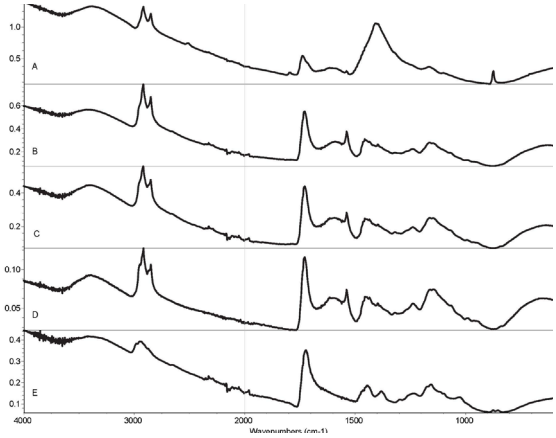

Figure 4. FTIR absorbance spectra for oil/acrylic mixtures.
A: 100% oil; D: 25% oil, 75% acrylic;
B: 75% oil, 25% acrylic; E: 100% acrylic.
C: 50% oil, 50% acrylic;

Melting-Point Tests

Melting-point tests were conducted on a Fisher-Johns melting point apparatus, with a small hotplate heating area connected to a thermometer that can measure up to 210°C. All paint samples were exposed to a temperature range of 30°–210°C. An 18-mm circular cover glass was placed between the heating area and the sample to keep the heating area clean. A rotary knob on the apparatus controlled the speed of heating. The melting point apparatus was placed under a microscope to observe sample reactions. Two metal needles were used to manipulate the samples and test their behavior under pressure.

Melting-Point Characteristics of Acrylic, Alkyd, and Oil Paints (Table 1)

The melting behaviors of acrylic, alkyd, and oil paints are highly distinct. Alkyd and oil paints cannot approach the softness and elasticity of acrylic emulsion paint. Moreover, alkyd paint starts to soften at lower temperatures than oil paint (alkyd: 30°–40°C; oil: 40°–100°C) and loses softness at a very specific temperature point (100°–110°C). Oil paint typically chars and discolors at 120°–140°C. The degree of charring is age-dependent: fresh oil paint will char and turn brown-black at a lower temperature than aged oil paint, which chars at around 180°C or above.

Melting-Point Characteristics of Acrylic Paint

The acrylic paint samples we analyzed were soft and elastic. Probing left a dent that would return to its original shape when the pressure was released. All of the samples immediately reacted to rising temperature with increasing softness and elasticity. This behavior intensified at higher temperatures, but no other changes were seen. At 210°C nearly all the samples were still very soft and very elastic. No changes in color appeared.

Melting-Point Characteristics of Alkyd Paint

The alkyd paint samples were essentially hard and non-elastic. Probing with a needle left a dent that did not bounce back. However, all of the samples showed clear softening and elasticity at temperatures of 30°–40°C. This behavior increased up to a point, but at around 100°–110°C the samples lost elasticity and became increasingly hard and brittle and would break when poked with a needle. At 210°C all samples hardened and became quite brittle. No color changes were observed.

Melting-Point Characteristics of Oil Paint

Oil paint samples ranged from soft (but non-elastic) to very hard and brittle, depending on the age of the sample. Most samples started to soften at 40°–100°C. At 120°–150°C the oil paint samples started to congeal and become increasingly brittle (one sample congealed at 90°C). This was typically accompanied by a color change. Lighter-colored samples yellowed then turned brownish. Darker-colored samples became darker. Color changes were not noticeable in very dark-colored samples. In oil paint, these color changes mark the beginning of charring, a process that is complete at higher temperatures than could be measured in our study. Melting-point characteristics of oil paint are highly variable, depending on the degree of dryness and oxidation. Some samples became hard and brittle and changed color significantly at 210°C, while others remained soft even while becoming brittle and changing color.

Melting-Point Characteristics of Mixed Media (Table 2)

Our observations suggest that a mixture of two paints will exhibit the characteristics of both types of paint present. These dual characteristics were seen in each sample tested, especially upon exposure to mid and upper temperatures. Noting this, it is possible to see that certain combinations encourage certain types of paint to be more prominent. Oil will darken at high temperatures. Alkyd alone will harden but not darken at 110°C, but these reactions require a higher temperature when alkyd is mixed with another type of paint. Acrylic will turn soft and react to probing with a fine needle only at 210°C. Fortunately, in tests the melting-point characteristics of one type of paint will not be dominant. Thus, if conservators carefully examine paint reactions at both lower and upper temperature ranges, they can be confident that a melting-point test will not falsely indicate the presence of only one paint when, in fact, there are mixed media.

Summary

Melting point tests cannot provide the weight ratio of the mixture. However, the individual paint melting behavior is noted in the mixture. Acrylic emulsion and alkyd paint have predictive and consistent melting behaviors. Acrylic emulsion will soften at 30°C and remain soft without drying or darkening at 210°C. Aged and young acrylic paint behave similarly. Alkyd paint will harden but not darken at 110°C and remain that way up to 210°C. This is true for aged and young alkyd paint. The melting-point characteristics of oil paint are age-dependent. At 30°C oil paint is hard. It will soften at around 60°C and melt at 120°–160°C, depending on the age of the sample. It will char and darken at 160°–210°C.

Solubility Tests (Table 3)

For the solubility tests, each sample was placed in the depression of a porcelain plate that was positioned under a microscope. The depression was then filled by syringe with one of the testing solvents (acetic acid 10%, sodium hydroxide 30%, xylene, and isopropanol) until the sample was immersed in the solvent. The sample was left in the solvent for 5 minutes and observed visually, after which it was probed with a needle to look for changes in consistency.

Immersion Solubility Tests of Oil Paint

Sodium hydroxide 30%: Oil paint reacted to sodium hydroxide 30% by becoming partially soluble to soluble. In most cases, after being placed in the solvent the binder began to leach, appearing as a yellowish ring around the sample. After 5 minutes of exposure to the solvent, the samples seemed not to have changed in structure, yet they disintegrated when poked with a needle.

Xylene: Exposing oil paint samples to xylene resulted either in non-elastic softening or no reaction at all, depending on the age and degree of oxidation of the oil paint. Younger paint tended to soften, while aged paint showed no effect on exposure to xylene.

Acetic acid 10%: Exposing oil paint samples to acetic acid 10% resulted in non-elastic softening.

Isopropanol: Exposing oil paint samples to isopropanol caused no reaction.

Table 1. Melting-point characteristics of acrylic, alkyd, and oil paints.

	30°C	110°C	130°C	210°C
Acrylic	Soft and elastic	Soft and elastic	Soft and elastic	Soft and elastic
Alkyd	Remains non-elastic	Hardens; does not darken	Hardens; does not darken	Hardens; does not darken
Oil	Remains hard	Softens	Melts, darkens, then hardens	Hardens, darkens, then chars

Table 2. Melting-point characteristics of mixed media of acrylic, alkyd, and oil paints.

	30° C	40° C	50° C	60°C	110° C	120° C	130° C	150° C	160° C	210° C
75% alkyd 25% acrylic	soften	soft			hard & some softness no darkening					
90% alkyd 10% acrylic	hard	soften	soft	soft	hard & some softness no darkening					
50% alkyd 50% acrylic	soften	soft				hard some softness no darkening				
75% acrylic 25% alkyd	soften	soft				hard some softness no darkening				
75% acrylic 25% oil	soft	soft		soften	soft				soft & harden	soft, non elastic, darken
50% oil 50% acrylic	soft	soft		soften	soft			darken, very soft		
75% oil 25% acrylic	soft	soft	soften	soft			melting w/some softness			soft, deformed mess, darken
75% alkyd 25% oil	hard	soften	soft				harden brittle and no darkening			
90% oil 10 % alkyd	hard	hard	soften	soft				melting	melting	dry out & darken

Table 3. Solubility of single-component paints.

	Acetic acid 10%	Sodium hydroxide 30%	Xylene	Isopropanol
Acrylic	Becomes soft and elastic, then swells	No reaction	Becomes soft and elastic, then swells	Becomes soft and elastic, then swells
Alkyd	No reaction	Becomes partially soluble, then completely soluble	Becomes soft, non-elastic	Becomes soft, non-elastic
Oil	Becomes soft, non-elastic	Becomes soluble	Aged sample: no reaction Fresh sample: becomes soft, non-elastic	No reaction

Immersion Solubility Tests of Alkyd Paint

Sodium hydroxide 30%: When exposed to sodium hydroxide 30%, alkyd paint reacted with partial solubility. Similar to oil paint samples, the paint binder leached during exposure, creating a yellowish ring around the sample. The samples retained their shape until they were poked with a needle.

Xylene: Alkyd paint samples reacted to xylene with non-elastic softening. A few of the samples also reacted with slow, minor swelling during exposure.

Acetic acid 10%: Exposing alkyd paint samples to a 10% acetic acid solution caused no reaction.

Isopropanol: Exposing alkyd paint samples to isopropanol resulted in non-elastic softening.

Immersion Solubility Tests of Acrylic Paint

Sodium hydroxide 30%: Exposing acrylic paint samples to sodium hydroxide 30% caused no reaction.

Xylene: Acrylic paint samples reacted to xylene with elastic softening and immediate, marked swelling.

Acetic acid 10%: Exposing acrylic paint samples to acetic acid 10% resulted in elastic softening and slow, minor swelling.

Isopropanol: Exposing acrylic paint samples to isopropanol resulted in elastic softening and slow, minor swelling.

Immersion Solubility Tests of Mixed Paints (Table 4)

Individual paints in a mixture react independently to solvents. For example, in a 75% alkyd / 25% acrylic mixture, xylene and isopropanol will soften and swell the acrylic paint, but non-elastically soften the alkyd paint. Sodium hydroxide 30% will dissolve the alkyd paint in the mixture but will not dissolve the acrylic paint. These and other telltale signs can alert conservators to the presence of both alkyd and acrylic paint in the mix.

Summary

The solubility test cannot provide weight ratio of the individual paints in the mixture. However, the individual paints in the mixture will react to the solvents independently, and their solubility and chemical properties can be used to classify the paint.

Conclusion

With practice and patience, conservators can perform practical, low-cost tests of melting points and solubility in their studios, and use criteria for chemical and physical characterization to detect individual paints in mixed-media paintings and develop treatment strategies. FTIR can be used as the first step in the identification process or as the final step to backtrack the spectra or sharpen FTIR identification skills. Our modest study aimed to follow the great tradition of "looking into paint" by extending that looking to include alkyd, acrylic emulsions, and modern mixed paints.

Table 4. Solubility of various paint mixtures.

	Acetic acid 10%	Sodium hydroxide 30%	Xylene	Isopropanol
75% alkyd 25% acrylic	No reaction	Becomes partially soluble, then swells	Becomes soft, non-elastic	Becomes soft, non-elastic
75% oil 25% acrylic	Becomes soft, non-elastic	Becomes soft, non-elastic	Becomes soft, then swells suddenly	Becomes soft and non-elastic, then swells slowly
75% alkyd 25% oil	Becomes soft, non-elastic	Becomes soluble	Becomes soft, non-elastic	Becomes soft, non-elastic
90% alkyd 10% acrylic	Becomes soft, non-elastic	Becomes soluble	Becomes soft, non-elastic	Becomes soft, non-elastic
90% oil 10% alkyd	Becomes soft, non-elastic	Becomes partially soluble, then dissolves	Becomes soft, then swells slowly	Becomes soft, non-elastic
50% alkyd 50% acrylic	Becomes soft, non-elastic	Becomes partially soluble	Becomes soft and non-elastic, then swells slowly	Becomes soft and non-elastric, then swells slowly
75% acrylic 25% alkyd	Becomes soft, non-elastic	Becomes soft, non-elastic	Becomes soft and non-elastic, then swells slowly	Becomes soft and non-elastic, then swells slowly
75% acrylic 25% oil	Becomes soft, non-elastic	Becomes soft and non-elastic, then swells slowly	Becomes soft and non-elastic, then swells suddenly	Becomes soft and non-elastic, then swells slowly

Annual Meeting Abstracts

The 2013 WAAC Annual Meeting was held September 8 - 12 at the Asian Art Museum in San Francisco

The papers from the meeting are listed below along with summaries prepared by the speakers.

Building New Expectations: Collections Management in a Multiple Facility Workflow

Kelly Bennett

The Berkeley Art Museum has a longstanding tradition as a highly accessible art collection. Over the last 40 years the majority the collection has been housed in the museum, and the community that utilizes it has come to rely on the immediacy with which their requests can be met. Following alongside other U.S. museums building new facilities, the BAM/PFA remodel has been designed with different priorities for the space available, by housing the majority of the collection in offsite warehouses. Using multiple warehouses will significantly affect the way the staff, the university, and the public interact with the collection.

This presentation will illustrate the significant changes that will be necessitated in collections management, and how they will impact the relationship of the museum with the community. Questions that need answering include: what will it take for BAM/PFA to continue to meet its community's expectations and desires? What new collection management challenges will the museum face, and what institutional priorities will need to shift to maintain a safe environment for the collection?

This presentation will begin with a quick overview of the current management of the collection. This includes curatorial use, educational use, expectations of the university, as well as the museum's relationship with lenders and donors. Next, there will be an overview of the existing/new facilities, outlining resources available during and after the transition to the new museum. This portion will include a description of changes that will occur, specifically the suspension of loans, the closing of the building, and how this period will be used to setup the new workflow. The presentation will also incorporate the handling/movement of the collection, and plans for managing the expectations of the staff and university.

The changing priorities for museums being built in many parts of the U.S. today have dramatically changed the accessibility of artwork. In response, collections management workflows will have to adjust to create a safe and effective new system, as well as maintaining a culture where the community can experience the collection. A multiple facility system opens up new concerns and conservation issues, requiring an institutional shift in priorities to steward the collection. The BAM/PFA has a loyal and committed community that will need to find new methods and techniques to allow them to continue to connect with the artwork.

References

1. Thornton, John I., Shmuel Kraus, Bruce Learner, Beth Hendrickson, Forensic Science Group. Paint Solubility Test. National Bureau of Standards Special Publication 480-40.

2. Fisher-Johns Melting Point Apparatus http://orgchem.colorado.edu/Technique/Procedures/Meltingpt/FisherJohns.html.

3. Derrick, Michelle R., Dusan Stulik, James M. Landry. Infrared Spectroscopy in Conservation Science. *The Getty Conservation Institute*, 1999.

4. Ploeger, R. *The Characterization and Stability of Artists' Alkyd Paints*. University of Torino, Torino, Italy, 2008.

5. Plesters Joyce. Cross-sections & Chemical Analysis of Paint Samples *Studies in Conservation*. Vol. 2 (1956),

San Francisco Rock Posters and the Art of Photo-Offset Lithography

Victoria Binder

Offset lithography was the dominant method of commercial printing of the twentieth century. This workhorse of printing, with its complicated equipment and production sequence, left very little room for artistic experimentation. It was during the nineteen sixties, in the small photo-offset lithographic shops of San Francisco, that commercial need and artistic vision came together in the creation of psychedelic rock posters.

These posters were created to promote music and dance venues featuring many of the greatest rock bands of the sixties. Working under tight deadlines, the artists broke every rule of conventional design, producing works that reflected the visual chaos and revolutionary spirit of the scene. Using sheet-fed offset presses, the small offset lithographic shops affordably produced runs of single-color and multicolored posters in a short period of time. However, unlike larger commercial shops, they were able to provide an environment that was conducive to artistic input.

This presentation examines the process of photo-offset lithography within the context of making early San Francisco rock posters (1966–1968). The materials and major steps of the production sequence for flat multicolor prints are discussed and illustrated with images of original artifacts.

The Conservation of a Human Skeleton Modified for Medical Instruction

Niccolo Caldararo, Claire Antonetti, and Jena Hirschbein

This talk describes the examination and restoration treatment of a male human skeleton that had long been used as a teaching specimen. The treatment would require reassembly and extensive repairs to broken bones due to a fall. Breaks resulted in shattering of the brittle bone material and fragment loss. The skeleton had been previously wired together, had steel inserts for rotation, as well as rods to facilitate weight balance. Bones were first disassembled and catalogued, cleaned and then stabilized using consolidants. Damage to wire or metal-segments was addressed, weak areas of bone were reinforced with metal pins and lost fragments from impact were replaced and secured with adhesive and polymer paste. A new hanging system was suggested that would be more stable. A review of earlier work in the restoration of vertebrate skeletons is provided.