Identification of Synthetic Organic Pigments and Dyes in Modern Art (pre-1920)

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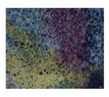
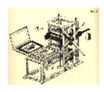
INTRODUCTION



The identification of synthetic organic pigments and dyes in modern works of art is an important step in order to evaluate their aging behavior, since they can considerably affect the properties of the paint layers [1].

Since the first synthesis of mauve in 1856 that marked the start of the modern synthetic dye industry, a number of soluble salts of acid dyes were transformed into insoluble salts or lake pigments by reaction with water-soluble salts of calcium, barium or lead, whereas basic dyes were treated with tannins or antimony potassium tartrate to also yield pigments. Since then and to the present date, over 500 synthetic organic pigments have been developed for different applications, and among these, about 160 have been used as artist's materials. More than 100 synthetic organic colorants, both pigments and dyes, were mentioned as lithographic ink components until the 1920s [2].

Early Lithographic inks generally consisted of a colorant or mixture of colorants (dye/s and/or pigment/s), a 'varnish' or carrying vehicle, and several additives or modifying agents [3].
Color lithographic inks, often undergo bleeding, offsetting or sinking into the paper substrate during aqueous conservation treatments, even though they are oil based and specifically formulated to resist water during the printing process. Testing routinely performed by conservators prior to treatment does not provide an accurate picture on the solvent sensitivity of the ink [4], therefore the identification of the pigments and dyes is a crucial step in the design of a safe conservation intervention.



In this poster, a compilation of reference spectra of red and orange pigments and dyes first synthetized before 1920, and recommended in early manuals of lithography, is presented. This period is chosen as a focus since it was one of intense experimentation, during which the number of synthetic organic pigments and dyes commercially available grew substantially and allowed lithographers to achieve hues not accessible using inorganic pigments alone [3], though often times at the expense of the weather fastness on the ink used.

Synthetic organic pigments (red, orange, blue, green, yellow, black) belonging to the **xanthene, anthraquinone, anthanthrone, azo, thiazol, quinoline, nitro, nitroso,** and **azine** groups were available in the 1890s, while thioingoid pigments were first synthetized after 1905 [2].
Pigments and dyes containing a xanthene ring (XR) can be identified by the XR's characteristic vibrations in the Raman spectrum [6]. In Rhodamine 6G (PR 81), the XR stretching gives rise to intense Raman bands at ca. 1513 and 1360 cm^{-1} and weaker peaks at 1645, 1590, 1569 cm^{-1}. Other characteristic bands appear at ca. 1313 cm^{-1} (CH deformation); 1268 cm^{-1} (XRS and C-O-C stretching); 931, 768, 610 and 403 cm^{-1} (XR deformation); and 354, 313 and 266 cm^{-1} (XR torsion). Alizarin (1,2–dihydroxyanthraquinone) lakes, prepared from natural madder as coordination complexes with aluminum and calcium, are the oldest known metal complex pigments [7]. Strong bands have been reported at 1659, 1587, 1569, 1191, and 470cm^{-1} for the normal FT-Raman spectrum of the solid [8]. Azo colorants were among the earliest to be synthetized in the second half of the 19th century, and have developed to this date into the largest class of colorants [2,7]. For the general azo group, the following characteristic Raman bands are expected [9]: the N=N stretch between 1450 and 1380 cm^{-1}; the C-N symmetric stretch between 1200 and 1130 cm^{-1}; the C-N symmetric bend between 1200 and 1160 cm^{-1}, the azobenzene ring vibration at ca. 1490 cm^{-1} and the aromatic quadrant stretch at 1600cm^{-1}. PR88 (4,4',7,7'-tetrachlorothioindigo) was discovered in 1907 and it is to this day for printing inks [2,7]. Characteristic Raman spectra of thioindigo has been obtained using a 1064nm excitation [10].

RESULTS

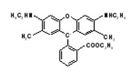
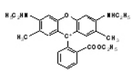
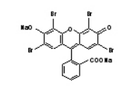
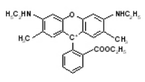
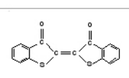
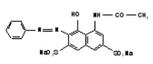
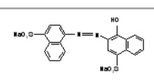
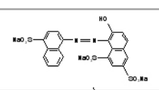
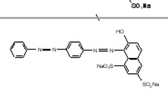
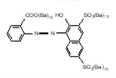
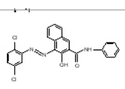
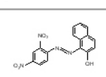
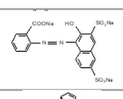
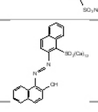
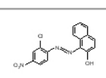
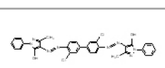
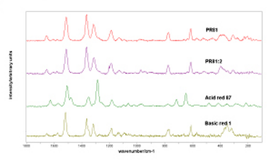
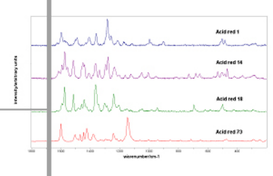
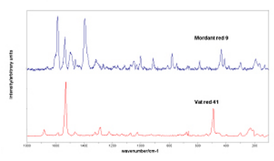
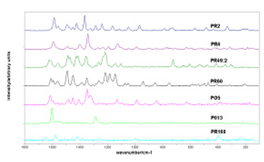
Colorant CI name and group	Classical name	Formula	Date
Xanthene pigments and dyes			
PR81	Rhodamine	Phosphotungstomolybdic acid salt of 	1892
PR81:2	Rhodamine YS	Silicomolybdic acid salt of 	1892
Acid red 87	Eosin Red, Eosine		1871
Basic red 1	Rhodamine 6G		1892
Thiongoid dyes			
Vat red 41	Florescent Red 5B		1905
Azo dyes			
Acid red 1	Acetyl Rose 2GL, Geranine 2GS		1902
Acid red 14	Acid Red B, Acid Rubine		**1883**
Acid red 18	Acid Scarlet 3R		1878
Acid red 73	Scarlet GR, Brilliant Crocein		1882
Mordant red 9	Scarlet 3B		1902
Azo pigments			
PR2	Fast Red F2R		1911
PR4	Permanent Red R		1907
PR60	Pigment Scarlet		1902
PR49:2	Lithol Dark Red		1899
PO5	Permanent Red GG		1907
PO13	Permanent Orange G		1910
Red anthanthrone pigments			
PR168	Indanthren Brilliant Orange RK		1913

Table 1. Summary of the red and orange pigments and dye references recommended in manuals of lithography before 1920. Red and orange synthetic organic pigments and dyes were the first to replace (or to be added to) traditional inorganic pigments in early lithographic inks [5].
Other pigments available before 1920, whose Raman spectra have been previously published are: PR3, PR8, PR22, PR23, PR49:1, PR52:1, PR53:1, PR57:1, PR83 [8,9].

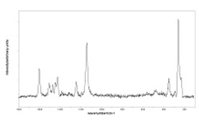








Raman spectra of reference pigments listed in Table 1, λ_0=785 nm , 10mW.



Scala,1893. Raman spectrum of the red ink, showing the presence of Acid Red 73 and vermilion (peaks at 252, 282 and 343 cm^{-1}), λ_0=785 nm.

CONCLUSIONS

Reference spectra for 17 early red and orange synthetic pigments and dyes belonging to the xanthene, azo, thioingoid and anthanthrone groups are presented. This compilation comprises a group of red and orange pigments and dyes first synthetized between 1856 and 1920, a period of intense experimentation by lithographers.
In situ Raman spectroscopy is particularly useful for identifying these colorants in posters without the interference of the complex binding media characteristic of early inks, a task that would otherwise require the use of chromatographic techniques (Py-GC/MS and SEC-FTIR), with the disadvantages of the relatively large sample consumption, extensive sample preparation and the multi-parameter operating conditions.

PIGMENTS vs. DYES

In addition to inorganic, natural organic and synthetic organic pigments, colorants classified as dyes in the Colour Index (CI) were recommended in early manuals of lithography (~pre1920) to be used in inks, and the CI nomenclature is kept here for the sake of clarity, though these dyes were applied as pigments to the paper substrates, that is using a binding medium.

EXPERIMENTAL

The Raman spectra of the pigments samples were recorded with a Renishaw System 1000 spectrometer using A λ_0=785 nm laser. Powers in the order of 10 mW were used, with accumulation times between 40 seconds and 10 minutes. The spectra were recorded using a 1200 lines mm^{-1}grating and a CCD detector, allowing a spectral resolution of ca. 1 cm^{-1} at 1000 cm^{-1}. In the case of the poster examined, the laser beam was focused using a Raman fiber optic probe equipped with a x20 lens, allowing spatial resolution in the order of 5 microns.
Spectra are presented after multipoint baseline corrections were performed. Reference organic pigment samples were obtained from the following manufacturers: Adi Group, Classic Dyestuffs, Clariant, Sun Chemicals, Kremer Pigmente, Sigma-Aldrich and Ciba.
Colorants are referred to by their Colour Index (C.I.) generic names. These are comprised by a letter that relates to the application of the colorant (for example, P stands for pigment), a letter that describes the hue (R stands for red, O for orange) and a number. Some of the classical or early commercial names are also included.

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