


Insight into Sam Francis' painting techniques through the analytical study of twenty-eight artworks made between 1946 and 1992

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Abstract The present paper proposes an overview of the painting materials experimented with over the years by Sam Francis, leading figure of the post-World War II American painting, through the analytical study of an extended number of paint samples supplied by the Sam Francis Foundation. In total, 279 samples taken from twenty-eight artworks made between 1946 and 1992, were analyzed by Raman, FTIR and Py-GC/MS techniques. The obtained results revealed the Francis' preference in terms of pigments, i.e., phthalocyanine blues and greens, and outlined unconventional combination of binder media.

1 Introduction

Unanimously recognized as a major figure of the American painting from post-World War II and generally presented as an Abstract Expressionist, Sam Francis (1923–1994) was also one of the most talented colorists of his generation. Francis was established in Southern California, but spent numerous long journeys in different places around the world, including Paris, Bern, Mexico City, New York and Tokyo.

Throughout his career, the exploration of colors to express his thought and emotions was of primary concern to him. The Francis's colors, literally described as vivid,

saturated, pure, vibrant intense and rich, largely contribute to the unique character of his work¹ [1]. This peculiarity explains the interest in conducting an extended analytical study on the Francis' painting materials.

This would be highly informative on the pigments and the binding media at the origin of his singular color shades. On the other hand, most of the Francis' paintings exhibit highly chromatic surfaces, showing for some of them, bronzing, fluorescence or opalescence effects. As a consequence, retouching paint losses from Sam Francis works may become a challenging task, the degree of the color matching required in the imitative technique being particularly difficult to attain, in the presence of such surfaces. The use of pigments chemically similar to the original ones is often necessary for matching painted surfaces involving pigments with high color strength [2, 3], like most of the modern synthetic organic pigments (SOPs) [4, 5].

Therefore, the characterization of the Sam Francis palette over the years would contribute to the improvement of technical art history, but it would be also useful for paintings conservators dealing with Francis' works. *Sam Francis: The Artist's Materials* (upcoming Getty publication) offered the opportunity for in-depth analyses of hundred paint samples.

The present study focuses on 279 paint fragments, sampled from twenty-eight Sam Francis' paintings made on canvas, paper or masonite hardboard (pressure-molded wood fibers used for numerous applications since 1930s and employed here as painting substrate), between 1946 and 1992. All the samples were supplied by the Sam Francis Foundation and the Beyeler Foundation and were investigated in the Getty

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Conservation Institute laboratory, by means of three complementary analytical techniques, pyrolysis–gas chromatography–mass spectrometry (Py–GC/MS), micro-Raman spectroscopy (μ -RS) and micro-Fourier transform infrared spectroscopy (μ -FTIR). The Raman spectroscopy is known as a very efficient technique for identifying most of SOPs in paint systems. Examples of Raman spectra recorded on dry pigment references and/or obtained from paint samples can be found in the literature [6–9]. On the other hand, the Py–GC/MS and FTIR methods provide essential information concerning the binding media [10, 11].

2 Experimental

The Raman analyses were performed with a Renishaw inVia Raman micro-spectrometer coupled to a Leica DMLM microscope. Micro-paint fragments were sampled with sterilized scalpel blade. All the samples were individually analyzed after being placed on a microscope glass slide. For each paint fragment, five spectra from different pigment grains were recorded in the spectral range of 100–2700 cm^{-1} by using a diode laser with a wavelength of 785 nm and a 50 \times objective. The Raman spectra were acquired with a laser power reduced at 0.1–0.5 %, 10- to 30-s integration time and 3 accumulations.

The FTIR spectra were collected with a Thermo Nicolet Avatar 360 FTIR spectrometer using a germanium crystal and equipped with a microscope. The samples were placed on a Diamond window and individually analyzed in transmittance mode in the 4000–650 cm^{-1} range, with a spectral resolution of 4 cm^{-1} . The Raman and FTIR results obtained for the Sam Francis' paint samples were both interpreted by using spectral databases as well as reference spectra reported in the literature.

Py–GC/MS analyses were performed on a Frontier PY-2020D micro-furnace pyrolyzer interfaced to an Agilent 7890A GC/5975C inert MSD. A J&W DB-5MS-UI capillary column (30 M \times 0.25 mm \times 0.25 μm) attached to a Frontier Vent-Free adaptor was used (40 M effective column length), with helium set to 1 ml/min. The split injector was set to 320 $^{\circ}\text{C}$ with a split ratio of 50:1. The GC oven temperature program was 40 $^{\circ}\text{C}$ for 2 min and then 6 $^{\circ}\text{C}/\text{min}$ to 320 $^{\circ}\text{C}$ with 9 min isothermal. Samples were placed into 50- μl stainless steel eco-cups prior to analysis and pyrolyzed at 550 $^{\circ}\text{C}$.

3 Results and discussion

The pigments and the binding media identified by Raman, FTIR and Py–GC/MS techniques are listed in Table 1. Pigments are presented through their *Color Index Generic*

Names [12]. The blue, red, yellow, green, orange and purple pigments corresponding to primary and secondary colors, the other pigments and the binding media are discussed separately. Despite the complementary character of the analytical methods applied in this study, the potential presence of additional compounds undetected through RS and FTIR spectroscopies has to be considered. In addition, the obtained results did not always lead to the pigment identification. For example, the pigments contained in the fluorescent pink paint samples, which have in common their high Raman fluorescence, remain unknown. Further investigations, i.e., μ -XRD (X-ray diffraction) and/or scanning electron microscopy–energy-dispersive spectroscopy (SEM–EDS) measurements, should be conducted for this purpose.

3.1 Blue

As one can see in Table 1, regardless of the decade of application, the support and the binder media, Francis achieved his characteristic blue shades through the use of phthalocyanine blue (PB15) and/or ultramarine (PB29). However, few other blue pigments, including cobalt blue (PB28), Prussian blue (PB27) and indanthrone blue (PB60), were also punctually detected. Prussian blue was found in two early works only, the first one is *3 Blue* from 1952 (oil on canvas) and the second one is *Blue, Black and Yellow* from 1958 (watercolor on paper).

About phthalocyanine blue, alpha and beta CuPc pigments, respectively, introduced on the market in 1935 and 1952, were found in separate samples in relatively equal proportions. Previous studies have shown the presence of both types in pre-mixed blue paints found in Francis studio (Santa Monica) after his death [13, 14]. The alpha and beta crystal forms were discriminated by using the RS polymorphic markers reported in Defeyt et al. [15].

The bronzing effect observed in several sampled blue surfaces can be attributed to the presence of PB15-based paint films. The characteristic red bronzing phenomenon reported for CuPc blue pigments is related to their high coefficients of light absorption (pure pigments appear almost black) and refraction in the long-wave region of the visible spectrum. Note that bronzing effects typically occur in over-pigmented paint systems [4, 16].

3.2 Green

The Raman results obtained from the green paint samples, reported in Table 1, revealed an extensive and uninterrupted use of CuPc green pigments, all along Francis' career (see Table 1).

Those include PG7 and PG36, which are both halogenated copper phthalocyanines derivatives. The green

Table 1 Overview of the pigments and the binding media successfully identified in the paint fragments, taken from twenty-eight Francis' works, and investigated by Raman, FTIR and Py-GC/MS techniques

Work	Blue	Green	Orange	Yellow	Red	Purple	Others	Binding media
<i>The Secret Room</i> , 1946, SFF.5	PB28, PB15			PY34			PBk6, PW21, iron oxides	Egg Tempura, Colophony and Protein
<i>After de Chirico</i> , 1946, SFF.9	PB29	PG7			Litharge		PBk6, PW6 (anat.), PW21, iron oxides	Drying Oil
<i>Untitled</i> , 1947–1948, SFF.44	PB29	PG7		PY37	PR83		PBk6, PW1, PW6 (anat.), PW21, iron oxides	Drying Oil and Elemi
<i>Untitled</i> , 1947–1948, SFF.46	PB15				Litharge		PBk6, PW1, PW6 (anat.), PW21	Drying Oil and Colophony
<i>3 Blue</i> , 1952, SFF.119	PB15, PB29, PB27			PY34	PR49:1		PBk6	Drying Oil, Beeswax and Mastic
<i>Untitled</i> , 1957, SF57-017	PB15, PB29	PG7			PR144	PV23		pMMA/nBA
<i>Untitled</i> , 1958, SF58-011	PB29						PBk6, PW18, PW21	pMMA/EA
<i>Round the World</i> , 1958–1960, SFF.275	PB29, PB60, PB15	PG7		PY37	PR104, PR49:1, PR2, PR52:1		PBk6, PW18, PW6 (rutile and anat.)	Drying Oil, pBMA, pMMA/EA
<i>Blue, Black and Yellow</i> , 1958, SF58-297	PB27, PB15		PO62	PY1, PY3	PR173		PBk6, PW18, PW21, PW6 (anat.)	Plant Gum
<i>Untitled</i> , 1960, SF60-023	PB29	PG7		PY3	PR3, PR7, PR207			Acrylic
<i>Blue Balls VIII</i> , 1961–1962, SFF.358	PB29, PB15	PG7			PR146	PV23	PW18, PW6 (rutile and anat.)	pBMA, pMMA/nBA, pMMA/EA
<i>Untitled</i> , 1963, SF63-074	PB29, PB15	PG36		PY3, PY37	PR144	PV16	PBk6, PW6 (anat.)	pMMA/EA
<i>As For Appearance IX</i> , 1963–1965, SFF.406	PB29, PB15	PG8		PY37			PBk6, PW6 (anat.)	Oil, Drying Oil, pMMA/EA
<i>Untitled No. 24</i> , 1965, SFF.426	PB29	PG7		PY1	PR7, PR112, PR194	PV23	PW6 (rutile)	PVA, pMMA/EA
<i>Untitled</i> , 1968, SFP66-20	PB29	PG7			PR2, PR7	PV23	bone white, PW18, PW6 (rutile)	pMMA/EA, pMMA/BA, pBMA
<i>Colors in Four Corners</i> , 1970, SFF.538	PB15	PG7, PG8		PY1	PR176	PV23	PW18, PW21, PW6 (rutile and anat.)	PVA, acrylic
<i>Untitled</i> , 1973, SF73-063	PB15	PG7			PR188	PV19	PBk6	Shellac, Drying Oil, Protein, pMMA/EA, pBMA
<i>Untitled</i> , 1973, SFF.630	PB15	PG7		PY83, PY97	PR112, PR122	PV23	PW18, PW6 (rutile and anat.)	pMMA/EA, pMMA/nBA
<i>Untitled</i> , 1973, SFF.589	PB15	PG7		PY83	PR112, PR122, PR176	PV23	PW18, PW6 (anat.)	PVA, pMMA/EA, pMMA/nBA, p2EHA
<i>Untitled</i> , 1974–1976, SFF.655	PB15	PG7, PG18	PO43	PY1, PY83	PR176, PR7, PR170	PV23	PW18, PW6 (rutile)	pMMA/EA, pMMA/nBA
<i>Untitled</i> , 1977, SFF.679	PB29, PB15	PG7	PO43	PY16, PY83	PR112	PV23	PW18, PW6 (anat.)	pMMA/EA
<i>Blue Jade</i> , 1982–1983, SFF.854	PB15	PG36		PY12, PY74	PR22	PV23, PV19, PV15	PW18, PW21, PW6 (rutile)	pMMA/EA, pMMA/nBA

Table 1 continued

Work	Blue	Green	Orange	Yellow	Red	Purple	Others	Binding media
<i>Big Red</i> , 1983, SFF.910					PR7		PW18, PW6 (rutile)	pMMA/nBA
<i>Untitled</i> , 1984, SF84-015	PB15	PG36		PY1, PY3	PR9		PW18, PW6 (rutile)	pMMA/nBA
<i>Yellow Lead</i> , 1984, SFF.1072				PY1			PW18, PW6 (rutile)	pMMA/EA, pMMA/ nBA
<i>Untitled</i> , 1985, SFF.1195	PB29	PG7			PR7	PV23	PW18, PW6 (rutile)	pMMA/EA, pMMA/ nBA
<i>Star</i> , 1987, SFP87-74				PY83	PR7	PV19	PW18, PW6 (rutile)	pMMA/EA, pMMA/ nBA
<i>Untitled</i> , 1992, SFF.1662	PB29	PG7				PV15	PBk6, PW18, PW6 (rutile)	pMMA/EA, pMMA/ nBA

The blue, red, yellow, green, orange and purple pigments, the other pigments and the binding media are presented separately in the table. The use of the Color Index Generic Names (see main text) to indicate the pigments appeared as the most appropriate option. For acrylic resins, acronyms (see main text) are favored. The title and the date of the work are followed by the reference attributed by the Sam Francis Foundation (SFF.xxx or SFyear-xxx)

shade is achieved by substituting a certain number of H atoms by halogens in the CuPc molecule (chlorine and bromine). PG7 is a copper polychloro phthalocyanine containing 14–15 chlorine atoms commercially available since 1936, while PG36 is a copper polychlorobromo phthalocyanine containing 4–8 bromine atoms and 8–2 chlorine atoms, introduced on the market in 1959. PG7 and PG36 provide, respectively, bluish and yellowish green shades [4, 17]. Both pigments can be readily discriminated by using RS [18]. RS measurements performed on the green samples most often led to the PG7 identification.

An additional organometallic green pigment, ferrous beta nitrosonaphthol (PG8), was identified in two polyvinyl acetate (PVA)-based paint samples. PG8 is commonly used in emulsion paints and exhibits dull yellowish green shades close to olive hues [4].

Viridian (PG18), which is one of the major inorganic green pigments found in modern and contemporary painting, was only detected in combination with PG7 in a sample from a 1970s acrylic painting (SFF.655).

3.3 Orange

Perinone orange (PO43) was identified in several orange samples taken from both, fluorescent and non-fluorescent areas. For the first ones, the daylight fluorescence effect probably results from the admixture of fluoragents with the perinone compounds. Some other orange areas are based on diarylide yellow (PY83), a disazo yellow pigment providing a yellow reddish hue [4]. Disazo and monoazo orange pigments, respectively, disazopyrazolone (PO34) and benzimidazolone (PO62) were punctually identified as well.

3.4 Yellow

The presence of yellow inorganic pigments, including chrome yellow (lead chromate, PY34), iron oxides and cadmium yellows (Cd sulfide PY37 and/or Cd coprecipitated with Ba sulfide), was exclusively observed in the paintings made before the 1960s. Actually, on the basis of the investigated samples, yellow SOPs, primarily Hansa Yellows (PY1 and PY3), appeared quite later on Francis' palette, starting in the early 1960s. From that moment the painter made a continuous and an extensive use of monoazo yellow pigments (PY1, PY3, PY74 and PY97). However, PY12 and PY16, which are both disazo yellow pigments, were also detected, but in much less proportion.

3.5 Red

The analytical study of the red samples revealed the use of at least twenty different red SOPs (see Table 1). Among these, eight individual naphthol red AS pigments, PR7, PR112, PR170, PR188, PR22, PR9, PR2 and PR146, which represent a specific monoazo subgroup, were identified, PR7 and PR112 being the most frequently found. Note the identification of azo reds belonging to other subgroups, including beta naphthol toluidine (PR3), BONA calcium salt (PR52:1), barium lithol pigment lake (PR49:1), disazo condensation red (PR144) and benzimidazolone carmine (PR176).

However, various red SOPs from chemical classes other than azo, such as anthraquinone alizarin crimson (PR83), quinacridone (PR122 and PR207), rhodamine B aluminum lake (PR173) and perinone (PR194), were detected as well. Only paint fragments taken from pre-1960s works pointed

out the use of inorganic red pigments, molybdated lead chromate (PR104) and litharge (lead(II) oxide).

3.6 Purple

Dioxazine violet (PV23), which exhibits a bluish violet shade unachievable with other pigments [4], is by far the violet pigment predominantly found in Sam Francis' purples. The earliest Francis' work containing PV23 is an acrylic-based painting made in 1957 (SF57-017). In other words, he adopted the novel purple pigment, patented in 1952 [19], soon after its introduction in artists' paints. However, a second purple SOP, named quinacridone violet (PV19) and commercially available since 1958 [19], was identified in two paint fragments. Regarding inorganic pigments, a very punctual use of ultramarine violet (PV15) and manganese violet (PV16) has to be noticed.

3.7 Others

The different extenders and white pigments identified from the paint fragments include bone white, chalk (PW18), blanc fixe (PW21), lead white (PW1) and titanium white (PW6). Titanium white, in both forms rutile and anatase, clearly appears as the predominant white pigments of the post-1950s Francis' palette. Lead white and iron oxide pigments were found in the very early works only. Inversely, almost all the investigated paintings have in common the presence of carbon black (PBk6).

3.8 Binding media

Twenty-one works on canvas, six others on paper and a single one on Masonite were investigated. Among the six works on paper, four were essentially made with acrylic copolymers, pMMA/nBA (methyl methacrylate/butyl acrylate) or pMMA/EA (methyl methacrylate/ethyl acrylate). *Blue, Black and Yellow* from 1958 is the unique case of watercolor painting using exclusively plant gum as binding medium. The paint fragments taken from the remaining work on paper, from 1973 (SF73-063), revealed a very complex and unconventional combination of techniques, involving shellac, drying oil, MMA/EA and BMA (butyl methacrylate) resins and a protein-based binder (see Table 1).

The Secret Room painted on masonite hardboard in 1946 does not differ only because of the support nature. Indeed, this early painting is the unique example of a combined use of egg tempera, colophony and a protein-based binder.

Until the early 1960s, Francis seems have favored modified oil-based paints, especially drying oils admixed with natural resins, for instance colophony, elemi and mastic, or with acrylic polymers. The oldest painting on

canvas, attesting an exclusive use of acrylic paints (MMA/nBA copolymer), dates from 1957 (SF57-017).

The post-1960s Francis production is characterized by the predominance of acrylic paints, preferentially those made of MMA/EA and/or MMA/nBA polymers (see Table 1). These findings are in total accordance with the identification of pMMA/EA in the sixty-four pre-mixed paints from the last Californian Francis' studio [13].

The most heterogeneous mixture identified from painted canvases consists of a blend of shellac, drying oil, protein binder, pMMA/EA and pBMA (SF73-063). In addition, a hybrid polymer made of PVA and acrylic resins was found in three paintings (SFF.426, SFF.538 and SFF.589).

4 Conclusion

The analytical study of Sam Francis' painting techniques through an extended number of paint samples led to the identification of the painter's privileged blue, red, green, yellow, orange and violet pigments, as well as their associated binding media. Although Sam Francis spent numerous long journeys in different places around the world, the analyses performed on 279 paint samples, taken from 29 works representative of five decades, unveiled an extensive and preferential use of some pigments over the years, including ultramarine, titanium white, phthalo blues and greens, azo yellows and dioxazine violet. If Francis' early works remained mainly composed of traditional inorganic pigments, such as lead white, chrome yellow, viridian and iron oxides, phthalocyanine blues were already present on his 1940s palette and can be considered as the first SOPs really adopted by the colorist. On the other hand, a wide range of binding media, including natural gums and resins, drying oils, PVA, alkyd resins and acrylic copolymers, were found. Actually, the conducted material study outlined the usual combination of more than three different binding media in the same painting. The experimental nature of Francis' oeuvre is evidenced by these findings. Furthermore, the identification of the SOPs frequently or occasionally used over the years by this great colorist could be very helpful to conservators in charge of Francis' works for selecting the most appropriate retouching pigments.

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