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Revising Walter C. McCrone's Dates for Pigment Use

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Through trade and technology, the pigments that have been available for artists' palettes have shifted through time. Dr. Walter C. McCrone published several papers about the usefulness of a pigment timeline, most notably in "A Scientific Study of 'Marcus Aurelius Between Philosophers,'" published in *The Microscope* (1). This paper discusses the prominence of forgeries and describes paintings as time capsules that can be decoded by referencing the origin dates of their materials and their first use. Using the microscope and his ability to distinguish artist pigments, McCrone was able to narrow the date and provenance of paintings and artifacts based on the pigments that he identified.

The history of pigments available to artists is a well-researched subject, used by art historians, art conservators and microscopists. McCrone himself condensed some of the most common information into a useful table, largely using Gettens and Stout's *Painting Materials* (1966) as a reference. McCrone's list is published in the article mentioned above and in his book, *Judgement Day for the Turin Shroud* (2). He found this organized, quick-check table handy, and even today it is shared in each of the pigment identification courses taught at McCrone Research Institute in Chicago.

McCrone did not only distribute his pigment list to students; many examples exist where he used pigment dates as evidence for and against an art works' authenticity. In an article published in *The Microscope*, McCrone used his list to fortify an argument for the authenticity of a painting attributed to Giorgione (1477–1510). He found that the pigments used in *Marcus Aurelius Between Philosophers* were indeed common to late 15th century paintings and were consistent in "particle size, the presence of mineral impurities and the absence of later common pigments," (1).

In another article, he uses an artifact's pigments against it, such as in his examination of the *Vinland Map*. This map of North America was thought by some scholars to have been made by the Vikings in 1400. This would be a remarkable piece of history if it were genuine, but McCrone found that the maker of the map had drawn lines using a yellowish variety of titanium white (TiO_2) — a material unknown until 1916 (3).

While McCrone's list is useful, it required some updating. Many respectable books about the history of pigments have been written since McCrone's publication, and a wider survey of the literature is due. An effort has now been made to compile new information about pigments and create an annotated list of their first use dates.

In addition to being a more comprehensive survey of available literature, some other changes have been made. For example, on many pigment dates, McCrone used the shorthand "before 1300." Contemporary records from before that time are rare, often making it difficult to pinpoint a first-use date. However, pigment literature today will often mention the earliest artifacts discovered to contain the material, as well as references that ancient historians, like Pliny, who sometimes describe a mineral's mining or manufacture. Therefore, efforts were made in the new table to use this information to make "before 1300" more specific.

Other specifications include regional variations on which pigments were available to whom and when.

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Cochineal is an example of these important details. It is a red dye made from the insect in the suborder Sternorrhyncha. This dye was used in ancient Peru, but European art makers did not know or have access to it until Spanish explorers brought it back in 1549. Pigment dates concern scholars of European and American art alike, and a pigment timeline with only one date would ring false to one of them. The updated pigment table includes a Remarks column to address these discrepancies.

Remarks also included in the passing of time between when a material was first discovered to when it was put into full manufacture. In some cases there may have been the possibility that an artist had access to a laboratory or been given a sample of a pigment before it was mass-produced. In other cases, a pigment could have been produced in one medium (watercolor, for example) but was not manufactured in another medium for many years (as was the case with oil). The Remarks column makes these changes clear for a pigment's history.

New pigments were also added to McCrone's original list. Pigments from around the world were included, such as Maya blue and Han blue, and some coloring agents that are important, but not necessarily used in painting, are also worth mentioning: Tyrian purple (dye) and sepia (ink) are among them. Also included are newly developed pigments that have recently come into artistic acceptance. Manufactured, organic pigments especially fill this category. Many of these synthetic pigments have replaced traditional pigments in modern tube colors, even those labeled to be the same color. These additions expand McCrone's list for slightly broader use by analysts who specialize in different geographic regions, mediums and eras.

The updated table will be a useful quick-reference to professionals examining and identifying pigments. If any of these specialists happen to read this article and find discrepancies or exclusions of pigments vital in their field, please contact the author. This list, like McCrone's original, will always be subject to alteration and expansion.

The author would like to acknowledge the McCrone Research Institute in Chicago for suggesting this research project and assisting in its production. The table has already been used to great advantage in courses covering the microscopy of paint, pigments and other artists materials.

REFERENCES

1. McCrone, Walter C. "A Scientific Study of 'Marcus Aurelius Between Philosophers,'" *The Microscope*, **42 (3)**, pp 111–119, 1994.

2. McCrone, Walter C. *Judgement Day for the Turin Shroud*, Chicago: Microscope Publications, 1996.

3. McCrone, Walter C. "Vinland Map," *The Microscope*, **47 (2)**, pp 71–74, 1999.

See Dates for Use of Artist Pigments tables on pages 35–39, and table references on page 40.

Dates for Use of Artist Pigments

PERIOD\ DATE	PIGMENT	END DATE	REMARKS	REFERENCES
Paleolithic	**Hematite:** Fe_2O_3			A
Paleolithic	**Sienna:** raw, burnt, $Fe_2O_3 \cdot xH_2O$			A
Paleolithic	**Ochre:** yellow, red, brown, $Fe_2O_3 \cdot xH_2O$			A, G
Prehistoric	**Carbon Black:** flame (lamp), carbon			G
Prehistoric	**Lamp Black:** carbon			G, A
Neolithic	**Kermes:** dye	1549	Use ended with cochineal.	A, B
Ancient	**Chalk:** $CaCO_3$, whiting		Ground, especially Northern Europe.	A
Ancient	**Charcoal:** carbon			A
Ancient	**Dragon's Blood:** resin		Used in illumination.	H, A, G
Ancient	**Graphite:** carbon			A, H
Ancient	**Green Earth:** terre verte, Fe, Mg, Al, K silicate			A, B, G
Ancient	**Maya Blue:** indigo on a base of palygorskite		Widely used in the Americas by the Mayans, Toltecs, Mixtecs and Aztecs	A
Ancient	**Vermilion:** cinnabar, HgS		China, Greece and Assyria	C, A, B, G
Ancient	**Orpiment:** As_2S_3	Phased out in 1800s	Egypt, 3100 B.C.	C, A, B
Ancient	**Egyptian Blue:** $CuO \cdot CaO \cdot 4SiO_2$	800s	Egypt IV Dynasty; later replaced by smalt and cobalt; synthesized in 1959	A, B, G
Ancient	**Realgar:** As_2S_2		Egypt New Kingdom	B
Ancient	**Egyptian Green:** $CaSiO_3$, Cu		Egypt VI Dynasty	A
Ancient	**Malachite:** $CuCO_3 \cdot Cu(OH)_2$	Rare after 1800	Evidence in Egypt and China	C, A, B
Ancient	**Azurite:** $2CuCO_3 \cdot Cu(OH)_2$	Rare after 1600s	Egypt	A
Ancient	**Gypsum:** $CaSO_4 \cdot 2H_2O$		Egypt	A
Ancient	**Madder:** 1,2-dihydrozyanthaquinone•$Al(OH)_3$, dye		Egypt; a lake pigment was later created in the middle ages	A, B
Ancient	**Naples Yellow:** antimony yellow $Pb_3(SbO_4)_2$		First used in Egyptian glass; European ceramics in 15th century; paintings ca. 1630; modern tube colors are mostly imitations	G, B, C

PERIOD\ DATE	PIGMENT	END DATE	REMARKS	REFERENCES
Ancient	**Woad:** dye		Europe	B
Ancient	**Minium:** red lead, Pb_3O_4		First evidence in Greece; China 5th century	C, A, B, H
Ancient	**Verdigris:** $Cu(C_2H_3O_2)_2 \cdot Cu(OH)_2$	1928	Greece; rare after 18th century	C, A, B
Ancient	**Indigo:** $C_{16}H_{10}N_2O_2$	1800s	First evidence as pigment in Greece; dye in Egypt, 1500 B.C.	C, A, B
Ancient	**Umbers:** raw, burnt, $Fe_2O_3 \cdot MnO_2 \cdot xH_2O$		Evidence on paintings at Ajanta, 300 B.C.; European use in 1400s	C, A
Ancient	**Copper Resinate:** copper green glaze, Cu salts in balsam		Difficult to identify early use through examination	C, A, B
Ancient	**Ivory Black:** carbon		First evidence is Roman	A, G
Ancient	**Massicot:** PbO		Painting pigment in 1400s; ceramics earlier	C, A
Ancient	**Han Blue:** and purple, $BaCuSi_4O_{10}$, $BaCuSi_2O_6$		China	A
Ancient	**Lead White:** $2PbCO_3 \cdot Pb(OH)_2$		Greece	A, H, B
1200 B.C.	**Tyrian Purple:** dye		Pre-Roman	A, G
600 B.C.	**Litharge:** PbO		A dryer in 17th century oils	A, C
100 B.C.	**Lead-Tin Yellow:** $PbO \cdot SnO_2$	1750	First in glass; pigment in Europe ca. 1300s; rediscovered in 1940	A, B
300	**Mosaic Gold:** SnS_2		First in China; in Europe by 15th century; replaced by modern bronze powders	A, B, G
500s	**Ultramarine:** lapis lazuli, Na,S, Al silicate	1800s	First use in Afghanistan; Europe in 1100s	C, A, B
700s	**Gamboge:** gum resin		Japan and China; not in Europe until after 1300	A, B, G
700s	**Vermilion:** dry process, HgS		China earlier	B, G
1400s	**Black Chalk:** or black earth		For drawing	C, A
1400s	**Indian Yellow:** Mg or Ca euxanthate	1890	First use in India; Europe 19th century illegal after 1890	A, B
1400s	**Saffron:** organic dye, no mordant		Dye since 2nd century B.C.; first evidence of painting in 1400s	A
1400s	**Bone White:** $Ca_3(PO_4)_2$ (calcined bone)		Medieval illuminations	C, A
1439	**Shell White:** eggshell and gofun		Japan; eggshells used in Europe before 1584	A, B
1500s	**Van Dyke Brown:** coal			A, B

PERIOD\ DATE	PIGMENT	END DATE	REMARKS	REFERENCES
1549	**Cochineal:** carminic acid		Ancient Peru; Europe in 1549	A, B
ca. 1550 (Europe)	**Smalt:** Co, K silicate glass	Less after 1825	13th century in near East	A, B
1600s	**Asphaltum:** bitumen, hydrocarbons		Ancient protective coating; used as pigment with rise of oil	A, G
1600s	**Blue Verditer:** $2CuCO_3 \bullet Cu(OH)_2$		Before 1600; small recipes differ from manufactured verditer	C, A
1687	**Vermilion:** wet process, HgS		Little impact before 19th century	A, B
ca. 1700	**Prussian Blue:** $Fe_4(Fe[CN]_6)_3$			A, B, H
1778	**Scheele's Green:** $CuHAsO_3$	Rare after 1870s	Discovered in 1775	A, B
1778	**Sepia:** organic ink		Drawing and watercolor only	C
1780s	**Zinc White:** ZnO		More common after 1842; mineral known since brass	C, A, B
1781	**Turner's Yellow:** $PbOCl_2$	Obsolete in 1928		A
1782	**Barium Sulfate:** $BaSO_4$ (Barite, mineral)			A, B
Early 1800s	**Chrome Green:** Prussian blue and chrome yellow			A, B
Early 1800s	**Mars Pigments:** synthetic ochres, iron oxides		Yellow at 1780; red by 1835; violet by 1841	A, C
Early to mid-1800s	**Barium Sulfate:** $BaSO_4$ (precipitated, blanc fixe)			H
1803	**Cobalt Blue:** $CoO \bullet Al_2O_3$ glass		Known since 1777	A, H
1809	**Chrome Red:** $PbCrO_4 \bullet Pb(OH)_2$			C, A, B
1810	**Barium Sulfate:** Syn. $BaSO_4$ (blanc fixe)			A, G
1814	**Chrome Yellow:** $PbCrO_4$		Recognized as pigment in 1804	A
1814	**Emerald Green:** $Cu(C_2H_3O_2)_2 \bullet 3Cu(AsO_2)_2$	1960	Discovered between 1798 and 1812	B, A, H, C
1826	**Alizarin:** natural, 1,2-dihydroxyanthraquinone			B
1828	**Ultramarine:** synthetic, Na, S, Al silicate			A, H
1835	**Cobalt Green:** Rinmann's green, zinc green, $CoO \bullet xZnO$ glass		Known since 1780s	A, G
1836	**Strontium Yellow:** $SrCrO_4$		Not common until late 19th century	G, C, H
1840	**Cadmium Yellow:** CdS		Discovered in 1817	A, B

PERIOD\ DATE	PIGMENT	END DATE	REMARKS	REFERENCES
1847	**Antimony Vermilion:** Sb_2S_3			A
1847	**Zinc Yellow:** $ZnCrO_4$		Known since 1809	C, B, H
1850	**Calcium Carbonate:** precipitated, $CaCO_3$		U.S. after 1913	B, H
1851	**Cobalt Yellow:** $K_3Co(NO_2)_6 \bullet H_2O$		Synthesized in 1831	A, F
1856	**Coal-Tar Colors:** mauve, synthetic dye			C, A, G
1859	**Viridian:** $Cr_2O_3 \bullet 2H_2O$		Discovered in 1838; first produced in Paris; reached England in 1862	G
1860	**Barium Chromate:** lemon yellow, $BaCrO_4$		Discovered in 1809	A, B
1860	**Cerulean Blue:** $CoO \bullet xSnO_2$		Discovered in 1805	A, G
ca. 1860	**Cobalt Violet:** $Co_3(AsO_4)_2$ or $Co_3(PO_4)_2$			A, G
1862	**Chromium Oxide Green:** Cr_2O_3		Known since 1809	A, G
1868	**Alizarin:** 1,2-dihydroxyanthraquinone, (synthetic)			G
1871	**Manganese Black:** MnO_2			G, A
1872	**Carbon Black:** commercial channel and soft blacks	Develo	Developed in 1860s	M
1874	**Lithopone:** $ZnS + BaSO_4$		Patented in 1847	A, B
1885	**Red B Naphthol:** para red, PR 1			D, H
1886	**Aluminum Powder:** Al		For frames; paint in 1920	A
1890s	**Manganese Violet:** $Mn(NH_4)_2(P_2O_7)_2$		Known since 1868	C, A, G
1896	**Davy's Grey:** powdered slate			C, A
1905	**Thioindigo Pigments:** red, violet, brown		Not in extensive use until mid-20th century	A, H
1909	**Hansa Yellow:** arylide yellow			A, I, E, F, D
1910	**Cadmium Red:** Cd (S, Se)		U.S., 1919	A, G
1910	**Pyrazolone Orange:** (PO 13)			K, H
1912	**Red Naphthol:** AS, organic			L, H
1916	**Titanium White:** TiO_2		Gained artistic acceptance through 1930s; pure anatase production in1927; industrial pure rutile in 1940s	B, A
1920	**Antimony White:** Sb_2O_3			A, H
1921	**Cadmium Red Lithopone:** Cd(S, Se) + $BaSO_4$			A
1921	**Pigment Green B:** organic		Discovered in 1885	A, E, G

PERIOD\ DATE	PIGMENT	END DATE	REMARKS	REFERENCES
1927	**Cadmium Yellow Lithopone:** Cd (S, Se) + $BaSO_4$		Patented in 1921	F
ca. 1930	**Fluorescent Pigments:** inorganic		First large scale use during WWII	H
1934	**Molybdate Red or Orange:** $7PbCrO_4{\bullet}2PbSO_4{\bullet}PbMoO_4$		Patented in 1930	C, A
1935	**Diarylide Yellows:** organic		Patented in 1912; used mostly in printing	D, F, A
1935	**Manganese Blue:** $Ba(MnO_4)_2{\bullet}BaSO_4$	Rare after 1990	Known since 1869	A, C, G
1935	**Phthalocyanine Blue:** monastral blue, Cu phthalocyanine			C, A, H
1938	**Phthalocyanine Green:** chlorinated Cu phthalocyanine			C, H
1947	**Green Gold:** nickel azo yellow			H, F
1948	**Fluorescent Pigments:** organic (rhodamine, Fluorescein, azosol brilliant yellow)			H
1950	**Mercadian Orange:** (Cd, Hg) S, cadmium mercury sulfide, (mercadmium)			H, A
1950	**Perinone Orange**		Vat dye in 1924	A, E, F
1950s	**Diazo Condensation Pigments:** yellow (also orange, red, brown)			D, F, A
1950s	**Indanthrene Blue:** organic		Dye in 1901	A, F
1953	**Vat Pigments:** pyranthrone orange, perinone orange, indanthrone blue, flavanthrone		Vat dyes earlier in 20th century	A, H, F
1953	**Wollastonite:** $CaSiO_3$, mineral			A, H
1955	**Quinacridone:** magenta and violet		Synthesized in 1935	H, E, F
1958	**Carbazole Dioxazine Violet:** organic (PR-23)		Dye in 1935	H
1960	**Benzimidazolone Reds:** organic			F
1960s	**Nickel Titanium Yellow:** nickel rutile yellow, (Ti, Ni, Sb) O_2			A, G, E
1965	**Isoindolinone Yellow:** irgazin, tetrachloroisoindolinones, disazomethine compounds			A, H, E, F, D
1969	**Benzimidazolone Yellows:** organic			F
1980s	**DPP Pigments:** diketopyrrolopyrrole			F, D, A
1986	**Chromium Titanium Yellow:** (Ti, Sb, Cr) O_2		Known since 1967	E

PIGMENT TABLE REFERENCES

A. Eastaugh, Nicholas, et al. *Pigment Compendium: A Dictionary and Optical Microscopy of Historic Pigments*. Oxford: Elsevier, 2008.

B. Feller, Robert L. (Vol. 1), Ashok Roy (Vol. 2) and Elizabeth West Fitzhugh (vol. 3), eds. *Artists' Pigments: A Handbook of their History and Characteristics,* 3 volumes. (Vol. 1, Cambridge and Washington: Cambridge University Press and National Gallery of Art), 1986; (Vol. 2, Washington and New York: National Gallery of Art and Oxford University Press), 1993; (Vol. 3, Washington and New York: National Gallery of Art and Oxford University Press), 1997.

C. Gettens, Rutherford J. and George L. Stout. *Painting Materials: A Short Encyclopedia*. New York: Dover Publications, 1966.

D. Herbst, Willy and Klaus Hunger, *Industrial Organic Pigments*. Weinheim: Wiley-VCH, 2004.

E. Keijzer, de Matthijs, "The History of Modern Synthetic Inorganic and Organic Artists Pigments," *Contributions to Conservation, Research in Conservation at the Netherlands ICN*, ed. Mosk J. and Tennant N., London: James & James, pp 42–54, 2002.

F. Lomax, Suzanne Quillen and Tom Learner. "A Review of the Classes, Structures, and Methods of Analysis of Synthetic Organic Pigments." *Journal of the American Institute for Conservation,* 45, pp 107–125, 2006.

G. Mayer, Ralph and Steven Sheehan. *Artist's Handbook of Materials and Techniques*. Viking, 1991.

H. Patton, Temple C. Pigment Handbook, *Properties and Economics*. Vol. 1. New York: Wiley, 1973.