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Analysis of the Paints Used to Decorate Northern Plains Hide Artifacts during the Nineteenth and Early Twentieth Centuries

Elizabeth A. Moffatt, P. Jane Sirois, and Judi Miller

Analytical Research Laboratory, Canadian Conservation Institute, Department of Canadian Heritage, 1030 Innes Road, Ottawa, Ontario, K1A 0M5, Canada.

An analytical study of the paints used to decorate selected Northern Plains hide artifacts in ethnographic collections is described. In addition to establishing a database for provenance studies, analysis of ethnographic paints provides useful information for the curator and conservator about individual artifacts that may assist in the selection of appropriate treatment or display conditions. Results are reported for 258 paint samples from 95 well-documented artifacts that date from the early nineteenth century to 1930. More than half the artifacts were from the Blackfoot Confederacy, i.e., the Blackfoot, Blood, and Piegan tribes. Paint samples were analyzed by Fourier transform infrared spectroscopy, x-ray diffraction, x-ray microanalysis, and polarized light microscopy. The pigments and binding media identified are compared to those described in the ethnographic literature. Traditional pigments identified include red, yellow, and brown iron-containing minerals and earth colours, and green copper-containing minerals and fatty acid salts. The most important trade pigments were vermilion, chrome yellow, and ultramarine blue. Both native and trade pigments were usually applied in a proteinaceous medium.

Une étude analytique des pigments utilisés pour décorer certains objets en peau provenant des plaines du Nord et faisant partie de collections ethnographiques est décrite. En plus de permettre d'établir une base de données pour des études de provenance, l'analyse des peintures ethnographiques fournit au conservateur et au restaurateur des informations utiles concernant des objets spécifiques qui peuvent aider à sélectionner un traitement ou des conditions d'exposition appropriés. Les résultats sont donnés pour 258 échantillons de peinture provenant de 95 objets bien documentés qui datent du début du XIX^e siècle à 1930. Plus de la moitié des objets proviennent de la Confédération des Pieds-noirs – les Pieds-noirs, les Gens-du-Sang et les Piégans. Les échantillons de peinture ont été analysés par spectroscopie infrarouge à transformée de Fourier, diffraction des rayons X, spectrométrie des rayons X couplée à la microscopie électronique à balayage et microscopie en lumière polarisée. Les pigments et les liants identifiés sont comparés à ceux décrits dans la littérature ethnographique. Les pigments traditionnels incluent des minéraux à base de fer et des terres de couleur rouge, jaune et brune, et des minéraux et des sels d'acides gras à base de cuivre de couleur verte. Les pigments du commerce les plus importants étaient le vermillon, le jaune de chrome et l'outremer. Les pigments indigènes et les pigments du commerce ont été souvent appliqués dans un liant protéique.

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Introduction

The Northern Plains region was inhabited by many aboriginal groups. While its exact geographical boundaries are difficult to define, it included an area of western Canada in present-day southern Alberta, Saskatchewan, and Manitoba, and parts of adjacent American states. A major aboriginal group of the Northern Plains was the Blackfoot Confederacy, which included three Algonkian-speaking tribes, the Blackfoot, Blood, and Piegan.¹ The Gros Ventre, allies of the Blackfoot, and their enemies, the Plains Cree and Plains Ojibwa, were also Algonkian-speaking. The Athapaskan Sarcee became part of the Blackfoot Confederacy while the Stoney (Siouan Assiniboin) were allied with the Plains Cree. The Dakota Sioux moved into Canada in the nineteenth century, before the end of the horse and bison days in the early 1880s. The Crow lived south of the Blackfoot.

The majority of Plains artifacts were fashioned from hides, primarily buffalo hides. Traditionally, many types of artifacts,

including both ceremonial and utilitarian objects, were decorated with paint. Some of the most impressive examples of these artifacts are robes made from buffalo hides that were painted with figures depicting battle scenes. Rawhide parfleches, shields, drum heads, robes, tipi linings, and men's clothing, such as shirts and leggings, were often decorated with paint.² As well as the figurative forms seen on robes, artifacts were often painted with geometric designs.

This paper describes an analytical study of the paints used on well-documented ethnographic artifacts of the Northern Plains cultures. This formed part of a larger study of the pigments and binding media found on historic native artifacts in museum collections, primarily in Canada.³ The project encompassed the paints of the Naskapi of the Quebec-Labrador peninsula,⁴ the native peoples of the Pacific Northwest coast, and various Northern Plains tribes.

The major goals of the project were to identify the pigments

used on ethnographic artifacts from 1800 to 1930 and to document the introduction of trade pigments. In addition to establishing a database for provenance studies, analysis of ethnographic paints provides useful information for the curator and conservator about individual artifacts that may assist in the selection of appropriate treatment or display conditions. Identification of the binding media that were used with native pigments and with trade pigments was another area of interest.

Before contact with Europeans in the mid eighteenth century, “native” pigments from a variety of mineral, vegetable, and animal sources were available on the Plains. These are described in detail in the ethnographic literature. During the nineteenth century, commercially-prepared trade pigments were often used instead of the traditional pigments. The introduction of trade pigments in various areas is not, in general, well documented in the literature. On a number of occasions, curators have approached the Analytical Research Laboratory requesting information concerning the earliest possible date for an artifact decorated with commercial pigments. The ethnographic literature was, in general, of limited use in addressing such questions. Published information on the patent date and history of the manufacture of commercial pigments was the major source of reference.

The following two analytical studies of Plains painted hide robes illustrate the problem of determining the date that an ethnographic artifact was painted. In one case, the vendor claimed that the robe in question was a Blackfoot robe that had been painted in 1896.³ Analysis showed the presence of three synthetic organic pigments, lithol red, benzidine yellow, and dianisidine orange. Lithol red, the earliest of these pigments, was patented in 1899.⁵ Benzidine yellow was not produced commercially until 1938.⁶ The robe clearly could not have been painted with these pigments in 1896 as had been claimed. A second study concerned another buffalo robe being considered for acquisition. The curator was interested in knowing whether or not the robe had been painted before 1900. Analysis of a red pigment on the robe revealed it to be para red, a synthetic azo pigment, patented in 1885.⁷ There was no published information, however, on when para red was first available on the Plains, so it could not be said with certainty that the robe had been painted prior to 1900.

Ethnographic Literature

Native Pigments

Indigenous pigments of the Plains have been documented in the ethnographic literature. One of the earliest reports describes the face painting pigments of the Piegan. This information, originally recorded by Alexander Henry, a fur trader, is found in articles by Wissler⁸ and Ewers.^{2,9} It is quoted in the paper by Wissler as follows:

“The ten different colors of earth and clay they use in painting and daubing their garments, bodies and faces are: a dark red, nearly a Spanish brown; a red, inclining to pale vermillion [sic]; a deep yellow; a light yellow; a dark blue; a light or sky-colored blue; a shining and glossy lead color; a green; a white; and charcoal.”

Wissler also provides the following list of native pigments: yellow earth, yellow from buffalo gallstones, red earth prepared by burning yellow earth, “red earth (as found),” “Rock paint (a yellowish red),” “Many-times-baked-paint (a yellow earth made red by exposure to the sun),” “Red many-times-baked,” “Seventh paint (a peculiar ghastly red-purple),” a dark blue mud, a white earth, and charcoal black.

McClintock reports the following pigments, quoting paint gatherers:¹⁰

“Onesta said he obtained some paints from the ground — a white earth, a red earth, also a red from burned yellow earth. Most of the yellow came from a place on the Yellowstone River near some warm springs, but there was also a yellow from buffalo gall-stones. Yellow and black were both found along the Marias River; but there was also a black from charred wood, blue from a dark-blue mud, and a green was once procured from the scum of a lake northeast of the Katoyisix (Sweet Pine Hills).”

Information on the pigments used in the Plains region, before and after European contact, was reported by Ewers in his book *Plains Indian Painting*.⁹ Before contact, the major pigments were clays coloured with iron oxides, which gave a range of yellows, reds, and browns. Red was sometimes prepared by heating yellow ochre. Blacks included black earth and charcoal. A blue earth may have been available to the natives before European contact. Regarding green pigments, Ewers states:

“. . . Lewis and Clark found a green earth pigment in use among the Indians near the Rocky Mountains at the beginning of the nineteenth century, and the Blackfoot Indians are known to have made green paint from the vegetable coloring in certain dried water plants.”

Other colorants included pussy willow buds for red, yellow earth from beside the Yellowstone River, yellow from buffalo gallstones, dried duck manure for blue, and white earth.² Possible sources of green pigments were a coloured mud, plants growing near lakes, and a native blue and yellow mixture. Red was the most frequently used colour and “Red earth was applied liberally to the surfaces of sacred objects used in ceremonials.”² Sacred objects in Blackfoot ceremonial bundles could be completely covered with red paint.

Trade Pigments

According to Ewers:⁹

“Commercial colors were traded to the Plains tribes at an early date. We know that gifts of vermilion were made to the Assiniboin before 1776, and that vermilion is frequently listed as a favorite article of trade in the accounts of fur traders who bartered with the Plains Indians in the early years of the nineteenth century.”

The following trade pigments were reported to have been used by the Plains Indians around 1880: “. . . vermilion, red lead, chromate of lead (yellow), Prussian blue, chrome green, ivory black and lamp black, Chinese white, and oxide of zinc. All these are in the form of powder or in crude masses.”⁹ Feder also reported the availability of vermilion during the late eighteenth century.¹¹ A 1936 article on parfleches mentions the use of commercial pigments obtained from traders.¹² This article indicated that it was likely that many of the painted hides in museum collections at that time were painted with commercial pigments.

Binding Media

The traditional binding medium of the Plains tribes was proteinaceous. It was made from hide scrapings or beaver tails that were boiled to prepare a glue that was mixed with powdered pigments.⁹ In addition to adhering the pigment to hide, the glue medium increased the luminosity of the paint. The paint was sometimes mixed only with water before application to the hide with subsequent application of the glue to hold the paint in place. It has also been reported that, some time after contact with Europeans, the Blackfoot obtained rice from which they prepared a glue, presumably starch-based.²

Tools

Before being mixed with the binding medium, the pigments were stored in skin bags. Prepared paints were placed in containers such as hollow stones, clam shells or turtle shells during painting, with each colour in a separate container.⁹ The most popular painting tool was the cancellous part of a buffalo bone.^{2,11} A different paint bone was used for each colour. A number of paint bones, collected after 1900, were available for analysis as part of this study.

Artifacts to be Discussed

The composition of 258 paint samples from 95 Northern Plains objects with well-documented dates will be discussed. Several dates can be associated with an ethnographic artifact: the date it was acquired by the museum where it is presently held, the date it was collected in the field, and a date attributed to it based on historical documentation or curatorial research. This information is presented in the **Appendices 1 to 3**.

The artifacts to be discussed belong mainly to museums in Canada – the Canadian Museum of Civilization, the Royal Ontario Museum, the Manitoba Museum of Man and Nature, and the Provincial Museum of Alberta. In addition, there were a limited number of samples from the Peabody Museum of Archaeology and Ethnology, the National Museum of Denmark, the Ethnographical Museum of Sweden (Etnografiska Museet), and the Royal Scottish Museum.

More than half the artifacts (54, accounting for 147 of the 258 samples) were from the Blackfoot Confederacy, *i.e.*, the Blackfoot, Blood, and Piegan tribes. Considerably fewer, 39 samples in all, were from Sioux objects, with the remainder including artifacts of the Mandan, Sarcee, Cree, Stoney, and Crow.

Experimental

Minute samples were taken from unobtrusive areas of the artifacts for analysis of the pigments and binding media. Samples were chosen that were representative and were not from areas where artifacts had been repainted. Care was taken to separate the paint from any hide fibres in the sample to avoid interferences in the analysis of the binding medium. Results obtained from the various analytical techniques described below were considered together in determining the composition of a paint sample.

A portion of each sample was mounted in a diamond anvil micro-sample cell and analyzed by Fourier transform infrared spectroscopy (FTIR), using either a Bomem Michelson MB-120 or a Nicolet 5DX spectrometer, in the range of 4000 to 400 cm^{-1} . All organic constituents, *i.e.*, binding media and organic pigments, reported here were identified by FTIR. Certain inorganic pigments (*e.g.*, Prussian blue, ultramarine blue, and hematite), and extenders or accessory minerals (*e.g.*, barium sulfate, quartz, and kaolin) could also be identified by this technique. Pigments, such as vermilion, that absorb below 400 cm^{-1} , could not be identified by FTIR.

X-ray microanalysis was performed on all samples using an Hitachi S-530 scanning electron microscope integrated with a Tracor Xray, Inc. x-ray detector and a Noran Instruments Voyager II x-ray microanalysis system (or, in earlier work, with a Tracor Northern TN-2010 spectrometer). Elemental analysis of small volumes, down to a few cubic micrometers, is obtained by this technique for elements from sodium to uranium with a sensitivity of about 1%.

X-ray diffraction (XRD) was undertaken using either a 12 kW Rigaku RTP 300 RC rotating anode generator with a cobalt target or a Phillips PW1130 x-ray generator and a cobalt tube in order to identify crystalline components, *i.e.*, most inorganic pigments. Samples were mounted on glass fibres using silicone grease and then placed in a 114 mm diameter Gandolfi camera. Selected paint samples were dispersed in Aroclor 1260

(in earlier work) or Cargille Meltmount for examination by polarized light microscopy.

Results

The objects have been divided into three time periods: 19 objects that date from before 1850, 39 from 1851-1900, and 37 from 1901-1930. A listing of the pigments, binding media, and accessory minerals or extenders identified on each artifact is presented in the **Appendices** and the results will be discussed here.

Artifacts Dating from before 1850

Fifty-three paint samples were obtained from 19 artifacts that date from before 1850 (**Appendix 1**). The samples were primarily from hide robes and clothing, such as shirts and leggings. The Blackfoot, Sioux, and Mandan tribes were represented. The paints were primarily earth colours: brown, red, orange, and yellow.

Two of the earliest hide artifacts included in the study are in the collection of the Peabody Museum of Archaeology and Ethnology.¹³ One was a Mandan painted hide robe, collected by Lewis and Clark in 1805, which has been described as the earliest known Plains buffalo robe recording an event.¹⁴ It depicts a battle between the Mandan and enemy tribesmen in about 1797. This robe was painted with vermilion (mercuric sulfide), hematite, an iron-containing yellow pigment, and a green copper-containing pigment. The infrared spectrum of the green pigment, which displayed a major peak at 1588 cm⁻¹, was characteristic of copper salts of fatty acids.¹⁵ It was probably produced by the reaction of a fatty material with a source of copper. The samples usually contained quartz and/or silicates. All pigments were applied in a proteinaceous medium. The second artifact, a Sioux little girl's hide robe, acquired by the Peabody c 1850 and thought to date from the early 1800s, was painted with the same pigments – hematite, an iron-containing yellow, and vermilion (and quartz). Protein was positively identified as the medium in two samples.

These two sets of results are typical for the pre-1850 Northern Plains painted hide artifacts that were analyzed. Fifteen of the red, orange, and brown pigments were identified as hematite, often mixed with quartz and/or silicates. Hematite was found on articles of clothing (*e.g.*, leggings and shirts) and ceremonial objects (*e.g.*, several robes and a rattle). Some of the brown colorants were not identified more precisely than as iron-containing pigments. Yellow pigments were also iron-containing pigments, such as goethite, a naturally occurring iron oxyhydroxide. For example, goethite was identified on a Northern Plains hide shirt collected between 1846 and 1848 by Paul Kane.¹⁶ Quartz, silicates, and gypsum were usually mixed with the iron oxides.

Six green paints and one green-blue paint were analyzed. Green copper-containing compounds were identified on several early objects. The green pigments of the Mandan hide robe described above, Sioux hide leggings collected before 1836 and a Sioux hide robe collected between 1842 and 1844 were all composed of copper salts of fatty acids.¹⁷ The hide shirt collected by Paul Kane between 1846 and 1848 described above¹⁶ was painted with a green earth pigment that had a green-blue colouration. The shirt was also painted with another green pigment, identified by XRD as a mixture of copper silicate hydrate and copper silicate hydroxide. Azurite (a blue basic copper carbonate) was identified on a hide shirt that was worn by the Yanktonai Sioux chief Wonatak who died in 1837.¹⁸

Chrome yellow (lead chromate) was identified on a Blackfoot man's hide shirt collected in 1840.¹⁹ This was the only occurrence of chrome yellow in the group of objects dated before 1850. Barium sulfate was present on Sioux hide leggings, collected before 1836.²⁰ The barium sulfate was mixed with calcium carbonate and quartz in an orange-brown paint.

Protein was confirmed as the medium in 30 samples and tentatively identified in 4 others by infrared spectroscopy.²¹ In many samples the paint was quite powdery and contained a low concentration of medium. No type of medium other than protein was identified in the artifacts dated before 1850.

Artifacts Dating from 1850 to 1900

This group consisted of 107 paint samples from 39 objects dated from 1850 to 1900 (**Appendix 2**). The artifacts included clothing (particularly shirts and leggings), painted hides, a hide robe, and 14 bags (including 4 paint bags). Other samples were taken from shields, a war club, a drum, a rattle, and a model tipi.

The earth pigments that were identified in these samples were: hematite, which was identified in 12 samples, goethite found in two, and other, less precisely characterized iron compounds in 3 samples. A number of green copper-containing compounds were also identified. Green copper salts of fatty acids were detected on 3 artifacts, including a painted hide acquired by the National Museum of Denmark in 1870. The green pigment on a Dakota winter hide, acquired by the same museum in 1861, was composed of copper salts of fatty acids and chalcopyrite, a copper iron sulfide mineral.²²

Vermilion was detected in samples from 10 artifacts. Red lead was identified on 7, all collected during the last decade of the nineteenth century. Two synthetic blue pigments were identified, ultramarine blue on 12 artifacts and Prussian blue on two. Ultramarine blue, a complex sulfur-containing sodium aluminum silicate, was present on several artifacts collected c 1890, for example, a Sioux hide robe and a Blackfoot bag.²³ It

was also identified on a number of artifacts collected in the twentieth century that are thought to date from between 1870 and 1890. The earliest occurrence of Prussian blue (ferric ferrocyanide) on a painted hide artifact was on a Blood drum acquired by the Royal Ontario Museum in 1888.²⁴

Chrome pigments became very popular on the Plains during the last half of the nineteenth century. There were 27 occurrences of chrome yellow and 5 of chrome green, a mixture of chrome yellow and Prussian blue, among the samples. The chrome yellow was often mixed with barium sulfate or gypsum. Chrome red was identified on 2 artifacts from the 1880s.

Black pigments were difficult to characterize precisely. They were frequently composed of both black and brown particles. Their microscopical characteristics were indicative of brown and black materials ranging from brown earths similar to the pigment van Dyke brown²⁵ to sub-bituminous coal to charcoal black.

The pigments in 4 paint bags were analyzed.²⁶ A Blood paint bag, acquired in 1888, contained a mixture of chrome red and vermilion. A mixture of chrome yellow and gypsum was found in a Blackfoot paint bag, collected in 1890 and thought to date from c 1870. Two other Plains paint bags, thought to date from 1897, contained red and brown pigments, identified as vermilion, and a mixture of hematite and quartz, respectively.

A number of accessory minerals, extenders, and white pigments were also identified. Barium sulfate, in a variety of pigment mixtures, was in widespread use with 27 occurrences. Kaolin, other silicates, quartz, gypsum, and calcium carbonate were also frequently identified. There was one occurrence of lead white in this group; it was mixed with red lead on a Blackfoot bag collected c 1890 and acquired by the Royal Ontario Museum in 1944.²⁷

In all samples dating from 1850 to 1900 where a binding medium was detected, *i.e.*, 72 of the 107 samples, it was identified as protein.

Artifacts Dating from 1901 to 1930

Eighty-seven samples from 26 painted hide artifacts, dated between 1901 and 1930, were analyzed (**Appendix 3**). The ceremonial artifacts included 4 painted bison robes, a painted hide, rattles, drums, a necklace, and a war medicine bundle. Utilitarian objects were mainly parfleches and blankets with one example each of a pouch, shirt, leggings, and doll. The predominant colours were red, green, yellow, and blue, with limited use of black and brown.

Fourteen of 15 yellow pigment samples were identified as chrome yellow, and the remaining one as iron oxide yellow.

Chrome green was identified in 8 green paint samples, and Prussian blue (one of the constituents of chrome green) was identified in 4 other greens. There was one occurrence of emerald green, a synthetic, copper acetoarsenite pigment.²⁸ Red and red-brown pigments were distributed as follows: 11 hematite, 11 red lead, and 4 vermilion. There were 12 occurrences of ultramarine and 7 of Prussian blue. Bone black, a pigment prepared by calcining bones, was identified in 3 samples. Barium sulfate was in widespread use; it was present in mixtures in 30 samples. Other accessory minerals or inert fillers in the paints were quartz, calcium carbonate, and gypsum. One occurrence of zinc white was noted, on a Piegan bison robe collected in 1909.²⁹

The binding medium of 52 samples was identified as protein. A drying oil medium was indicated in only 4 samples. Even during early decades of the twentieth century, dry pigments were usually mixed with a proteinaceous medium.

In addition to the 87 samples from painted hide artifacts described above, 11 samples from Blackfoot paint bones and paint bags, collected during the twentieth century, were analyzed. Two paint bones, containing residues of red and blue paint, were collected during the period 1907 to 1910 and belong to the Royal Ontario Museum.³⁰ The red paint was a mixture of hematite, quartz, and protein. The blue paint consisted of ultramarine, calcium carbonate, and a calcium soap (probably a reaction product between a calcium-containing material and an oil or fat). The other 7 paint bones, which belong to the Canadian Museum of Civilization, were collected in 1928 and 1929.³¹ The blue paint on 2 bones was composed of ultramarine. Two other paints contained a mixture of chrome yellow and barium sulfate. The remaining 3 bones had iron oxide, para red, and a mixture of Prussian blue, gypsum, and calcium carbonate, respectively. A Sarcee paint bag acquired in 1922 contained hematite and quartz, a typical pigment mixture. A Blackfoot paint bag collected in 1922 contained a grey pigment in which only calcium carbonate and quartz were identified.³²

Discussion

Naturally-occurring Pigments

The naturally-occurring colorants identified on the Northern Plains artifacts were likely “native” pigments from locally available sources. These include pigments of mineral origin, such as iron oxide pigments, as well as calcite (CaCO₃), gypsum (CaSO₄·2H₂O), quartz (α-SiO₂), and clays. A number of green pigments including copper-containing compounds and green earth, were also likely of local origin. Black pigments in this category include charcoal and earth blacks, both mentioned by Ewers.⁹

Iron oxide pigments provide various shades of red, brown, and yellow. The major iron oxides are the red-brown hematite (Fe_2O_3) and the yellow goethite ($\alpha\text{-FeOOH}$). The brown was frequently identified as an iron-containing earth pigment. The ethnographic literature indicates that these pigments were abundant locally and that the use of red pigment often had symbolic importance. Iron oxide pigments were found on all types of artifacts. They continued to be used frequently in the twentieth century.

Azurite, a blue copper-containing mineral with the formula $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ was found on one artifact. The green pigments that were likely of local origin were copper salts of fatty acids, chalcopyrite, copper silicate hydrate with copper silicate hydroxide, and green earth. A blue-green sample of a green earth pigment was identified on a Northern Plains hide shirt collected between 1846 and 1848. Green earth is composed of either of two silicate minerals, celadonite or glauconite, and can range in colour from a pale green to an intense blue green. The use of green earth by North American native peoples is noted in the article by Grissom³³ with two possible sources suggested, large glauconite deposits in the Missouri River basin and the Blue Earth River in Minnesota. Ewers also mentions that, at the beginning of the nineteenth century, Lewis and Clark found a green earth pigment in use by native people near the Rocky Mountains.⁹ The green earth on the hide shirt may therefore have been from a local source.

Green copper salts of fatty acids were detected on 5 artifacts, including a Mandan hide robe collected in 1805 and a Dakota winter hide acquired in 1861. These salts may have been prepared locally by the reaction of a fatty material with a source of copper. In the case of the Dakota winter hide, the green also contained chalcopyrite, a copper iron sulfide mineral (CuFeS_2).

No pigments of vegetable or animal origin were identified. This could be due to several reasons, an important one being the relatively recent origin of most of the artifacts sampled. It is also possible that organic colorants may have been present at a level below the detection limit of the infrared spectroscopic technique or that they may have been fugitive and would no longer be detected. Lack of suitable reference materials may account for a few unusual pigments not being identified; however, there was no evidence to suggest that pigments of animal origin, such as the blue from duck droppings or the yellow from buffalo gallstones suggested by Ewers² (see earlier discussion), were present in the samples analyzed.

Synthetic Pigments Acquired through Trade

The list of trade pigments used on the Plains around 1880, found in the 1939 book by Ewers, proved to be quite accurate. Ewers noted the following: “. . .vermilion, red lead, chromate of lead (yellow), Prussian blue, chrome green, ivory black and lamp black, Chinese white, and oxide of zinc.”⁹ Analytical results

support this list, but one important pigment, ultramarine blue, is missing from it. The occurrences of each pigment will be summarized.

The pigment vermilion is synthetically produced mercuric sulfide (HgS), an analogue of the mineral cinnabar. Cinnabar, and vermilion made by sublimation, have been in use since classical times in Europe and Asia while the production of wet process vermilion in Europe dates from 1687.³⁴ Vermilion was present on the earliest artifacts in the study, dating from the beginning of the nineteenth century. They include a Mandan hide robe collected in 1805, a Sioux little girl's robe thought to date from the early 1800s (collected in 1850), and a Sioux hide shirt thought to date from before 1837. These occurrences are consistent with ethnographic reports, such as that of Ewers,⁹ on the early availability of vermilion on the Plains, *i.e.*, it was available to the Assiniboin before 1776.

Both synthetic red lead and the mineral minium are composed of Pb_3O_4 . Red lead has been prepared as a pigment since ancient times and is currently an important industrial pigment.³⁵ Red lead has been available to the Plains tribes at least since the late nineteenth century. There were 6 occurrences in the second group of artifacts – a Blackfoot rattle collected in 1898 (thought to date from *c* 1870), a Blackfoot bag collected *c* 1890, and 3 artifacts collected in 1900 and thought to date from *c* 1890: a Blackfoot hair fall, a Blood rattle, and a Blood model tipi.

The pigment chrome yellow is composed of lead chromate (PbCrO_4). Lead chromate occurs naturally as the rare mineral crocoite; this mineral is unlikely to have been found or used for pigment. The first synthetic chrome yellow was made in 1809, with commercial production beginning in Europe around 1815.³⁶ During the second half of the nineteenth century, chrome yellow became the yellow pigment of choice in the Plains region. There were 42 occurrences on painted hide artifacts and 2 on paint bones (where it was mixed with barium sulfate). The earliest occurrences of chrome yellow were on a Blackfoot man's hide shirt collected in 1840 and a Dakota winter hide acquired in 1861. The most common extenders identified with chrome yellow on Plains artifacts were barium sulfate and gypsum.

Prussian blue is a synthetic pigment that was first produced in 1704.²⁵ It consists of ferric ferrocyanide ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$). Prussian blue was in limited use on late nineteenth century artifacts; for example, it was identified on a Blood drum acquired in 1888. Prussian blue is used in combination with chrome yellow to produce chrome green. Chrome green, which has been available since about 1825,³⁷ was identified on several Blackfoot and Sioux objects with attributed dates in the late nineteenth century – a parfleche, a shield, and shirt.

Ewers refers to the use of ivory black on the Plains by about 1880.⁹ Ivory black is often used as a synonym for bone black, a

pigment produced by charring animal bones.²⁵ Bone black was identified on several objects collected in the late nineteenth and early twentieth centuries. There was very limited use of zinc white (ZnO) and lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) as extenders in these samples. The only occurrence of zinc white was on a Piegan robe collected in 1909. The term “Chinese white” usually refers to zinc white;²⁵ however, it is not clear which pigment was meant by this term in the list of trade pigments available on the Plains.

Ultramarine blue is an important pigment that was not mentioned in Ewers' list. Synthetic ultramarine is a complex sodium aluminum sulfosilicate that became commercially available in 1830.³⁸ Ultramarine blue was used extensively on the Plains by the Blackfoot and Sioux. It is not possible to give a precise date for the introduction of ultramarine blue to the Northern Plains region based on the results of this study. It was found on 12 artifacts attributed to the late nineteenth century and on 12 artifacts dating from 1901 to 1930. The commercial laundry bluing Reckitt's blue was a source of ultramarine blue for the Naskapi of Labrador;⁴ however, it is not known if this product was available in the Northern Plains region. The use of various types of laundry bluing as colorants by a number of other aboriginal cultures has been described by Odegaard and Crawford.³⁹

The mineral barite is widely distributed geographically and is often associated with fluorite, quartz, and calcite.⁴⁰ Precipitated barium sulfate or synthetic barium sulfate (BaSO_4), often referred to as blanc fixe, was introduced during the period 1810 to 1820. Barium sulfate was present, combined with other pigments, in 61 samples. In half of these samples it was mixed with chrome yellow or chrome green. It was also used as an extender with Prussian blue, red lead, vermilion, and iron oxides, where it may have been an accessory mineral. The earliest occurrence was in an orange-brown paint on Sioux hide leggings, collected before 1836, where it was mixed with calcite and quartz. This was the only occurrence of barium sulfate in the first group of artifacts and it is most likely barite, present as an accessory mineral. The next occurrence of barium sulfate was as a mixture with chrome yellow on a Plains painted hide acquired in 1870.

Chrome red is a basic lead chromate having the formula $\text{PbO} \cdot \text{PbCrO}_4$. It was first prepared in 1809 but its use commercially and as an artists' pigment during the nineteenth century is not well documented.³⁶ Chrome red was found, mixed with vermilion, in a Blood paint bag acquired in 1888.

No synthetic organic pigments were identified on hide artifacts dated before 1929. The only organic pigment identified was para red, which was present on a bone paint brush acquired in 1929. Para red, the first synthetic organic azo red pigment, was patented in 1885.⁷

Binding Media

Protein was identified as the binding medium in 30 of 53 samples from artifacts dating from before 1850, 72 of 107 samples from the artifacts dating from 1850 to 1900, and 52 of 87 samples from the early twentieth century painted hide artifacts. A drying oil medium was indicated in 4 of the twentieth century samples. The identification of the binding medium as a protein is consistent with reports in the ethnographic literature.⁹

In the remainder of the samples, the nature of the binding medium was not determined. There are several reasons for this: the medium may have been present at a concentration below the detection limit of the infrared spectroscopic analysis, absorptions in the infrared spectrum due to certain pigments or fillers may have overlapped the protein absorptions, or no medium may have been present.

Conclusion

By the late nineteenth century, the Plains tribes were using commercial pigments for many colours. These pigments added variety to their traditional palettes, which were composed of red, yellow, and brown iron-containing minerals and earth colours, charcoal and earth blacks, green copper-containing minerals and fatty acid salts, green earth, and natural organic materials. Both native pigments and trade pigments were usually applied in a proteinaceous medium.

Trade pigments, in combination with mineral pigments, provided more permanent and effective colouration than previously possible. Trade pigments would have required less preparation and would have been faster and easier to use. The data indicate that vermilion was the earliest trade pigment, found on artifacts dating from the beginning of the nineteenth century. Particularly important trade pigments in the Plains region were vermilion, chrome yellow, ultramarine blue, Prussian blue, red lead, and chrome green. Barium sulfate was a common extender. Synthetic organic pigments, which became commercially available in the late nineteenth century, were not found on any artifacts dated before 1929.

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17. Sioux hide leggings – Canadian Museum of Civilization (CMC), accession number V-E-280; Sioux hide robe – Ethnographical Museum of Sweden, accession number 1854.2.27.
18. Sioux hide shirt – Royal Scottish Museum, accession number 1942.1.
19. Blackfoot man's hide shirt – CMC V-B-413.
20. Sioux hide leggings – CMC V-E-280. Barium sulfate was identified by XRD. The complex composition of the sample precluded characterization of the pigment morphology by polarized light microscopy. This examination may have allowed a distinction to be made between a mineral source and precipitated barium sulfate.
21. When the infrared spectrum of the paint sample was free from overlapping absorptions due to inorganic components, a collagen-type protein was indicated. The specific source of the protein, such as an animal hide glue or bone glue, cannot be determined by the FTIR analysis. Since the presence of hide fibre fragments in the sample would also result in collagen absorptions in the infrared spectrum, care was taken in the sample preparation to minimize this source of interference.
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27. Blackfoot bag – ROM 944.7.147.
28. Emerald green ($\text{Cu}[\text{C}_2\text{H}_3\text{O}_2]_2 \cdot 3\text{Cu}[\text{AsO}_2]_2$) was mixed with Prussian blue on a Blackfoot blanket acquired 1928 – CMC V-B-132.
29. Piegan bison robe – ROM HK.461.
30. Red paint on paint bone ROM HK.418; blue on paint bone ROM HK.420.
31. Blackfoot paint bones: CMC V-B-122, V-B-123, V-B-225, V-B-257, V-B-258.
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Appendices - Summary of Analytical Results

Appendix 1. Hide Artifacts with Documented Dates Before 1850

Object	Tribe	Dates*	Owner Acc. No.	Pigments and Media	Accessory Minerals/Extenders
hide robe	Mandan	col: 1805 acq: 1899	PMAE ¹ 53121	copper salts of fatty acids, vermilion, hematite, yellow iron-containing pigment, protein	quartz, silicates
little girl's robe	Sioux	att: early 1800s acq: c 1850	PMAE 53124	hematite, vermilion, yellow iron-containing pigment, protein	quartz
man's hide shirt	Mandan	col: 1832 acq: 1973	CMC ² V-H-2	unidentified brown	quartz, silicate
hide leggings	Mandan	col: 1833 acq: 1973	CMC V-H-4	unidentified red-brown and black	quartz
child's mantle	Blackfoot	col: pre 1833 acq: 1973	CMC V-B-280	black of natural origin (possibly a charcoal-type pigment)	quartz, kaolin
hide leggings	Sioux	col: pre 1836 acq: 1973	CMC V-E-280	copper salts of fatty acids, hematite, unidentified brown, protein	calcium carbonate, quartz, barium sulfate, gypsum, kaolin
hide leggings	Sioux	att: pre 1837 acq: 1942	RSM ³ 1942.1A,B	probably bone black, protein	kaolin, quartz, gypsum
hide shirt	Sioux	att: pre 1837 acq: 1942	RSM 1942.1	azurite, vermilion, unidentified brown and yellow, protein	gypsum, quartz, kaolin,
hide dress	Plains Cree	col: 1840 acq: 1973	CMC V-A-439	unidentified orange, protein	kaolin
man's hide shirt	Blackfoot	col: 1840 acq: 1973	CMC V-B-413	chrome yellow, unidentified brown, protein	kaolin, quartz
hide shirt	Blackfoot	col: c 1841 acq: 1969	CMC V-B-345	hematite, iron-containing brown pigment, protein	quartz, gypsum
skin shirt	Blackfoot	col: 1842-4 acq: 1854	EMS ⁴ 1854.2.1	hematite, protein	kaolin, quartz
skin robe	Sioux	col: 1842-4 acq: 1854	EMS 1854.2.27	copper salt, hematite in orange and brown, protein	kaolin, quartz
hide shirt	Northern Plains	col: 1846-8	MMM ⁵ H4-4-4	green: copper silicate hydrate and copper silicate hydroxide; green blue: green earth, hematite, goethite, unidentified brown, protein	quartz, kaolin, calcium carbonate, gypsum
rattle	Northern Plains	col: 1846-8	MMM H4-4-11	hematite	kaolin, quartz
shirt	Northern Plains	col: 1846-8	MMM H4-4-2	hematite, iron-containing brown pigment, protein	kaolin, quartz, gypsum
legging	Northern Plains	col: 1846-9	MMM H4-4-3a	iron oxides in red and dark brown	kaolin
shirt	Northern Plains	col: c 1848	MMM H4-43-1	hematite in orange and brown, natural charcoal-type pigment, protein	kaolin, quartz
legging	Northern Plains	col: 1848	MMM H4-43-2A	hematite, iron-containing browns	quartz, kaolin, gypsum, anhydrite

*Dates: acq - date acquired by the present owner; col - date collected in field if known to be different from the acquisition date; att - attributed date based on historical documentation or curatorial research

¹PMAE - Peabody Museum of Archaeology and Ethnology, ²CMC - Canadian Museum of Civilization,

³RSM - Royal Scottish Museum, ⁴EMS - Ethnographical Museum of Sweden, ⁵MMM - Manitoba Museum of Man and Nature

Appendix 2. Hide Artifacts and Paint Bags with Documented Dates from 1850-1900

Object	Tribe	Dates*	Owner Acc. No.	Pigments and Media	Accessory Minerals/Extenders
hide shirt	Eastern Sioux	col: pre 1852 acq: 1973	CMC V-E-279	hematite, black of natural origin (probably charcoal-type pigment), protein	kaolin, quartz
shirt	Teton Sioux	col: c 1860 acq: 1973	CMC V-E-306	hematite, brown iron earth pigment, protein	gypsum
winter hide	Dakota	acq: 1861	NMD ¹ Hc477	vermilion, chrome yellow, chalcopyrite and copper salts of fatty acids, iron-containing brown pigment, protein	quartz, silicates, calcium carbonate
chief's summer hide	Blackfoot-type	acq: 1861	NMD Hc478	hematite in red and brown, goethite, protein	kaolin, quartz, calcium carbonate
painted hide	Plains	acq: 1870	NMD Hd60	hematite in red and brown, copper salts of fatty acids, chrome yellow, protein	silicates, quartz, barium sulfate, calcium carbonate
painted hide	Sioux	att: pre 1870 acq: 1971	CMC V-E-259	chrome yellow, ultramarine, probably charcoal black, unidentified green, red and orange-red, protein	calcium carbonate, barium sulfate, quartz
war club	Northern Plains	att: 1870s or poss. 1846-8 acq: 1941	MMM H4-4-15	unidentified red-brown, protein	
hide leggings	Sioux	att: c 1870 acq: 1971	CMC V-E-258a,b	unidentified blue-green	barium sulfate
drum	Blood	att: c 1870 acq: 1888	ROM ² 5510	Prussian blue, gypsum in white	kaolin
paint bag	Blood	att: c 1870 acq: 1888	ROM 5512	chrome red and vermilion	
pipe bag	Northern Plains	att: 1870s-1880s	MMM H4-0-144	chrome yellow, iron-containing brown and red pigments, protein	quartz
shirt	Northern Plains	att: 1870s-1880s	MMM H4-0-153A	hematite, naturally occurring black (likely a charcoal-type pigment), chrome yellow with unidentified red, protein	quartz, calcium carbonate, silicates, kaolin
legging	Northern Plains	att: 1870s-1880s acq: 1978	MMM H4-0-153C	hematite, chrome yellow with unidentified red, protein	
paint bag	Blackfoot	att: c 1870 col: 1890 acq: 1944	ROM 944.7.3	chrome yellow	gypsum
painted deer hide	Blackfoot	att: c 1870 col: 1890	ROM 975x73.6	unidentified brown, red lead, chrome yellow, protein	quartz, barium sulfate
rattle	Blackfoot	att: c 1870 col: 1898	ROM HK.1809	red lead, chrome yellow, protein	gypsum, barium sulfate
parfleche	Blackfoot	att: 1867-72 acq: 1964	PMA ³ H64.7.2	ultramarine, lead chromate-sulfate, chrome green, unidentified red, protein	barium sulfate
shield	Blackfoot	att: c 1880 acq: 1968	PMA H68.117.2	ultramarine, chrome green, chrome yellow, protein	gypsum, barium sulfate
painted raw hide	Blood	col: 1888	ROM 17810	bone black, protein	
painted hide	Blackfoot	col: 1880s acq: 1975	CMC V-B-536	blue-green copper salt, green copper salt, hematite, chrome red, protein	kaolin, quartz, barium sulfate
hide robe	Sioux	col: pre 1890 acq: 1973	CMC V-E-271	chrome yellow, vermilion, ultramarine, protein	kaolin, quartz, barium sulfate
moccasins	Cree	col: 1875-90 acq: 1910	CMC V-A-26	Prussian blue, vermilion, chrome yellow, protein	calcium carbonate, kaolin, quartz, barium sulfate

Object	Tribe	Dates*	Owner Acc. No.	Pigments and Media	Accessory Minerals/Extenders
bag	Blackfoot	col: c 1890 acq: 1944	ROM 944.7.147	ultramarine, red lead with lead white, chrome yellow, protein	gypsum
leggings	possibly Blackfoot	col: c 1890 acq: 1944	ROM 944.7.97B	chrome yellow, protein	
leggings	Blackfoot	col: c 1890 acq: 1944	ROM 944.7.96B	unidentified yellow, protein	quartz, silicate
leggings	Cree	col: 1890 acq: 1944	ROM HD.5479A	chrome yellow with unidentified red, protein	
bag	Blackfoot	col: 1897	CMC V-B-30	ultramarine, chrome yellow, vermilion	gypsum
bag	Sioux	att: pre 1900 acq: 1915	ROM HD.7257	vermilion, ultramarine, protein	
man's shirt	Sioux	att: 1890s	MMM H4-45-3	chrome yellow, ultramarine, chrome green	calcium carbonate, gypsum, barium sulfate
two paint bags	Plains	att: 1897	CMC V-X-16	hematite, vermilion	quartz
war shield	Blackfoot	att: c1815? col: c 1897 acq: 1914	CMC V-B-39	vermilion, chrome green, unidentified brown, protein	barium sulfate, kaolin, quartz
parfleche	Crow	col: c 1900 acq: 1954	CMC V-L-2	iron oxide, Prussian blue, chrome yellow, red lead, protein	quartz, gypsum, barium sulfate, kaolin
parfleche	Crow	col: c 1900 acq: 1954	CMC V-L-3	ultramarine, vermilion, protein	
parfleche	Crow	col: c 1900 acq: 1954	CMC V-L-16	ultramarine, chrome yellow, vermilion, protein	gypsum, barium sulfate, silicates
parfleche	Crow	col: c 1900 acq: 1954	CMC V-L-35	chrome green, ultramarine, chrome yellow, red lead, protein	barium sulfate, silicates
pouch	Plains	col: 1900 acq: 1954	CMC V-X-338	goethite	kaolin, quartz, barium sulfate
rattle	Blood	att: c 1870 col: 1900	ROM HD.5652	chrome yellow, red lead, protein	gypsum, barium sulfate, silicates
dance wand	Blackfoot	att: c 1890 col: 1900	ROM HD.5656	chrome yellow, ultramarine, hematite	gypsum, kaolin
model tipi	Blood	att: c 1890 col: 1900	ROM HD.6862	ultramarine, chrome yellow, red lead, protein	quartz, gypsum, calcium phosphate

*Dates: acq - date acquired by the present owner; col - date collected in field if known to be different from the acquisition date; att - attributed date based on historical documentation or curatorial research

¹NMD - National Museum of Denmark, ²ROM - Royal Ontario Museum, ³PMA - Provincial Museum of Alberta

Appendix 3. Hide Artifacts, Paint Bags, and Paint Bones with Documented Dates from 1901 to 1929

Object	Tribe	Dates*	Owner Acc. No.	Pigments and Media	Accessory Minerals/Extenders
drum	Stoney	col: 1907 acq: 1928	CMC V-C-71	red lead, goethite, iron-containing brown, protein	kaolin, gypsum
doll	Piegan	att: 1880 col: 1907 acq: 1978	ROM 978.x46.134	hematite, ultramarine, protein	calcium carbonate, silica
drum	Stoney	att: 1890 col: 1907	ROM HD.6853	chrome yellow, chrome green, red lead, carbon black, protein	gypsum, calcium carbonate, barium sulfate
rattle	Cree	att: 1905 col: 1907	ROM HK.277	Prussian blue, protein	barium sulfate
leggings	Blood	att: 1875 col 1907-10	ROM HK.468	chrome yellow, Prussian blue, red lead, protein	barium sulfate, quartz
parfleche	Blackfoot	att: 1885 col: 1907-10	ROM HK.496	ultramarine, red lead, protein	
bison robe	Sarcee	col: 1908	ROM HK.459	red lead, chrome green, ultramarine, unidentified black, drying oil, protein	calcium carbonate, barium sulfate, quartz
bison robe	Blackfoot	col: 1909	ROM HK.460	chrome yellow, chrome green, unidentified brown, protein	
bison robe	Piegan	col: 1909	ROM HK.461	hematite, chrome green, ultramarine, unidentified blue, red, purple and black, protein	silicates, quartz, zinc white, barium sulfate
bison robe	Blackfoot	col: 1909	ROM HD.6541	hematite, bone black, Prussian blue, chrome yellow, protein	calcium carbonate, barium sulfate, kaolin, quartz
painted hide	Blackfoot	col: 1910	ROM HK.457	ultramarine, chrome yellow, red lead, hematite in red and brown, protein, ester	barium sulfate, gypsum, calcium carbonate, quartz
pouch	Sioux	col: 1914	CMC V-E-165	chrome yellow, chrome green, vermilion, ultramarine and Prussian blue, protein	barium sulfate
shirt	Sarcee	col: 1921	CMC V-D-94	hematite, protein	silicates
hide blanket	Sarcee	acq: 1921	CMC V-D-103	ultramarine, unidentified red, protein	gypsum, barium sulfate, calcium carbonate
parfleche	Sarcee	acq: 1921	CMC V-D-106	Prussian blue, red lead, chrome yellow, bone black, protein	barium sulfate, quartz
war medicine bundle	Crow	att: 1850 col: 1922 acq: 1956	ROM 956.42.6	chrome yellow, vermilion, ultramarine, chrome green, protein	barium sulfate, quartz
parfleche	Sarcee	acq: 1922	CMC V-D-149	chrome yellow, ultramarine, chrome green, red lead, protein	gypsum, barium sulfate
parfleche	Sarcee	acq: 1922	CMC V-D-151	ultramarine, unidentified green, chrome yellow, protein	quartz, barium sulfate, calcium carbonate, gypsum
saddle blanket	Sarcee	acq: 1922	CMC V-D-327	chrome green	gypsum
rattle	Sarcee	acq: 1922	CMC V-D-342	hematite, protein	quartz
necklace	Blackfoot	acq: 1928	CMC V-B-53	hematite	quartz
parfleche	Blackfoot	acq: 1928	CMC V-B-68	red lead, chrome yellow, ultramarine, unidentified black, protein	calcium carbonate, quartz, barium sulfate

Object	Tribe	Dates*	Owner Acc. No.	Pigments and Media	Accessory Minerals/Extenders
parfleche	Blackfoot	acq: 1928	CMC V-B-72	red lead, Prussian blue, naturally occurring black (likely a charcoal-type pigment), chrome yellow, hematite, protein	calcium carbonate, quartz, barium sulfate, silicates, zinc stearate
blanket	Blackfoot	acq: 1928	CMC V-B-131	vermilion, unidentified green and brown, protein	quartz, silicate, gypsum, calcium carbonate
blanket	Blackfoot	acq: 1928	CMC V-B-132	Prussian blue and copper acetoarsenite, vermilion, chrome yellow, unidentified black, protein	barium sulfate, calcium carbonate, quartz, gypsum
skin drum	Blackfoot	acq: 1929	CMC V-B-185	hematite, bone black, unidentified green, protein	quartz, barium sulfate
paint bone	Blackfoot	att: 1900 col 1907-10	ROM HK.418	hematite, protein	quartz
paint bone	Blackfoot	att: 1900 col 1907-10	ROM HK.420	ultramarine	calcium carbonate, calcium salts of fatty acids
paint bag	Sarcee	acq: 1922	CMC V-D-240	hematite	quartz
paint bag	Blackfoot	acq: 1922	CMC V-B-343	unidentified grey	calcium carbonate, quartz
bone paint brush	Blackfoot	acq: 1928	CMC V-B-122	ultramarine	
bone paint brush	Blackfoot	acq: 1928	CMC V-B-123	ultramarine	
three bone paint brushes	Blackfoot	acq: 1929	CMC V-B-225	chrome yellow chrome yellow Prussian blue	barium sulfate barium sulfate gypsum, calcium carbonate
bone paint brush	Blackfoot	acq: 1929	CMC V-B-257	iron oxide	
bone paint brush	Blackfoot	acq: 1929	CMC V-B-258	para red	barium sulfate

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