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History and Characterization of Laundry Bluing-Derived Colorants

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History and Characterization of Laundry Bluing-Derived Colorants

A thesis submitted in partial satisfaction of the requirements for the degree Master of Arts in
Conservation of Cultural Heritage

by

Isabel Iris Schneider

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ABSTRACT OF THE THESIS

History and Characterization of Laundry Bluing-Derived Colorants

by

Isabel Iris Schneider

Master of Arts in Conservation of Cultural Heritage

University of California, Los Angeles, 2023

Professor Ellen J. Pearlstein, Chair

This research aimed to expand the scholarship of laundry bluing histories and technical considerations for analytical characterization. To illustrate the complexities of studying this material in cultural heritage collections, the author also analyzed blue colorants in a group of objects from the Michael C. Carlos Museum's African Art Collection. The use of laundry bluing as a source of pigments for artworks has been a relatively common practice worldwide, and was often closely tied to colonial enterprise. Bluing recipes varied, with the blue colorants ranging from smalt, indigo, Prussian blue, aniline blue, and synthetic ultramarine. The simplest recipes were often just pigments suspended in water, but other materials, such as binders or fillers, were often added to enhance the working properties of the product. The characterization methods for differentiating bluing recipes assessed included: X-ray fluorescence (XRF) spectroscopy, Multi-band Imaging (MBI), Fourier-transformed infrared (FTIR) spectroscopy, chemical testing, polarized light microscopy (PLM) and fiber optic reflectance spectroscopy (FORS).

The thesis of Isabel Iris Schneider is approved.

Thiago Sevilhano Puglieri

Allen F. Roberts

Ellen J. Pearlstein, Committee Chair

University of California, Los Angeles

2023

DEDICATION

This work is dedicated to my grandparents, Alfred and Tosia Schneider (A”H), for instilling their immense passions for learning in me, my mother, Cathy Moss Schneider, for instilling her passion for art, as well as the many family members and friends who have buoyed my spirits time and again. There are not enough poetic words to express my gratitude to Avrosh Kumar, whose love, patience, and support has been as infinite as the color blue itself.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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INTRODUCTION

Laundry bluing (LB), also commonly referred to as "Reckitt's Blue," “Robin Blue” or “Washing Blue”, has been used as a source of colorants since the 17th century and has been documented in Native American, Oceanic, Aboriginal Australian, Caribbean, Euro-American and African art and craftworks. Although LB products were designed to optically brighten yellowed textiles and papers, they have been used in various other ways, from treating bee stings in Australia to Voudon practice rituals in the American south. The use of LB as a source of pigments for artworks has been a relatively common practice, particularly in locations where access to commercially-produced artist-grade pigments may have been limited. LB recipes vary, with the core blue pigments ranging from smalt, indigo, Prussian blue (PB), aniline blue, and synthetic ultramarine. The simplest recipes were often just pigments suspended in water, but other materials, such as ammonia, biocides, sodium bicarbonate, carrageenan, starch, gum Arabic, or gum tragacanth, were often added to enhance the working properties of the product. Naturally, it follows that LB-derived pigments are not uniform in composition, although they are often lumped under one all-encompassing name in archival records. Understanding the origins of media can be beneficial for the study of cultural practices, tracing trade patterns, drawing conclusions about how it was prepared, applied, stored and/or manipulated, and understanding deterioration patterns induced by physical and chemical changes to a colorant over time.

This project aims to examine the nuances of LB-derived pigments, explore the history of LB production and the use of LB-derived pigments, and compare characterization methods for future researchers studying and caring for artworks made with these products. Practically, some of these characterization methods were applied to a group of objects from the Michael C. Carlos Museum's African Art Collection.

INTRODUCTION TO LAUNDRY BLUING

Worldwide, the Victorian era saw dramatic changes in demand for cleaning products, as both the standards of living and collective understandings of health and hygiene rose and technological advances made a wider range of products available at affordable rates[1].

Prior to industrialization, a typical Euro-American laundry process would entail the following: removing stains, washing (rubbing soap into a garment and rinsing it repeatedly), boiling, starching, and bluing. The last two steps, starching and bluing, were optional treatments that enhanced the optical and working properties of garments. Most textiles are rendered crisper, easier to iron, and more resistant to wrinkling and soiling by either dipping them in baths of starch solutions or applying liquid starches directly to their surfaces. Bluing, the process of applying a discrete layer of blue colorants to a textile by either painting dilute pastes of gums and pigments directly on them or placing them in a diluted colorant bath, optically brightened yellowed garments. Early records of LB practices date to Europe in the mid-16th century, and the practice commonplace enough in England to be included in the 1672 practical "cookbook" of Constance Hall [2]. Blue pigments could be added directly to a wash by themselves, but suppliers from the mid 19th century on often sold products as part of "All-in-one" bluing and starch composites. Although some purchasers may have preferred separate products in order to maintain more control over their laundering processes, composites helped cut down on the steps involved with laundering.

Across Europe and the US, market demographics for those purchasing LB were overwhelmingly women, often from lower or middle socio-economic status. When purchasing LB, buyers, often housewives, maids, or owners of laundry businesses would be looking for inexpensive products that were easily added to a bath, pleasant to handle, and unlikely to adversely affect the textiles being treated. Early recipes utilized smalt as a colorant, which is toxic when inhaled in large quantities and has an unpleasantly gritty texture, making it unpleasant if worn directly against the skin[3]. Early recipes focus discussion of bluing primarily to ruffs or lace, not whole garments. As smalt is insoluble in water, it would have to be applied as a dilute paste, which would have been time consuming. Indigo dyes are quite malodorous, and unless chemically altered are insoluble in water, so the only way to effectively "blue" a garment was to prepare a vat dye, another time-consuming process. Unfortunately many of the recipes in the 18th and 19th centuries for rendering indigo soluble quickly involved the use of strong, spewing acids that burned the arms of laundresses and/or dyers. Perhaps for these reasons, the records of indigo being used for LB do not begin until the late 19th century (although the significant expansion of high-quality indigo imports to Europe was also a likely influence) [4].

Water soluble colorants were preferred over insoluble ones, as they could be used to create simple baths. Once synthetic ultramarine, hexacyanoferrate pigments[1], and aniline dye products were available, they were generally preferred over smalt or most indigo-based products [5]. These colorants were also more vibrant in color than indigo. PB recipes could vary considerably, with some products being more pleasant to work with than others or having different tints, but the high iron content of PB could cause rust stains to form on treated fabrics over time. Nontoxic, vibrant ultramarine, first produced at scale in the mid 1830s, quickly found wide application in many industries and there are records of it being used for LB by at least the early 1850s. Aniline blue dyes, once available in the 1860s, also became popular bluing products. They were often sold in liquid forms, and although they were toxic and flammable, they produced vibrant blues at affordable rates. PB and ultramarine products could be prepared as liquids or in solid forms as sticks, cubes or balls, which were easy to transport, package, and store. Other synthetic blues synthesized in the early 19th century, such as cobalt blue and blue verditer (artificial azurite) were prohibitively expensive for laundering purposes. Ultimately however the individual choice of a laundry-doer of which pigment to use often came down to simply what was available to them. A comparison of bluing colorants can be found in Table 1.

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[1] As discussed further in this work, hexacyanoferrate(II) pigments have many associated names. Throughout this paper, the term “Prussian blue” (PB) is used synonymously with “hexacyanoferrate(II) blue pigments” for ease.

Table 1. Comparison of LB Colorants, Organized Chronologically

Pigment/ Dye	Availability Date	Advantages	Disadvantages
Indigo (Natural)	ca. 4200 BCE [6]	Nontoxic, widely available	Malodorous. Natural indigo comparatively expensive. Bonds directly to fabric, so not easily reversible with continued rinsing. Has to go through processing to be rendered soluble, and some treatments involved toxic, hazardous materials. Color not as vibrant as other blue colorants.
Smalt	ca. 900	Vibrant color	Gritty texture. Toxic. Moderately priced. Difficult working properties. Insoluble in water
Hexacyanoferrate (II) Pigments (Prussian Blue (PB))	Late 1720s	Water-soluble, could be sold as solid or liquid	Range of colors. Early recipes variable in solubility, optical properties, and additives. Sensitive to acids and anoxic treatments.
Ultramarine	1830	Water-soluble, inexpensive, vibrantly colored, nontoxic, could be sold as solid or liquid	Sensitive to acids.
Aniline	ca.1860s	Inexpensive, widely available	Toxic, flammable, variable light-fastness, often requires a mordant, binds directly to fabric. Very sensitive to light.
Indigo (Synthetic)	Beginning of 20th century	Inexpensive, widely available	Malodorous. Bonds directly to fabric, so not easily reversible with continued rinsing. Has to go through processing to be rendered soluble, and some treatments involved toxic, hazardous materials. Color not as vibrant as other blue colorants. Toxic.

The grade of pigments used for LB was often not significantly lower than those being marketed as an artist-grade colorant, however they were often cut with extenders to expand the volume or adjust the working properties. Starches were particularly common additives, as they could both increase the volume, starch the textiles being washed directly, and be hydrated during production to help bind the pigment into a ball or cube and then readily dehydrated. The same properties that made bluing a convenient product for use in laundering (i.e. water soluble, easily combined with binders, vibrantly colored), also made it easy for artists to use as paint. Although many discussions of LB as a pigment tend to see it primarily in “ethnographic” (i.e. non-Western) or folk art contexts, it is certainly not beyond the realm of possibility that it could have been broadly used by established Western artists as well.

The historic use of various starches, common additives to LB products, was often limited to product availability and ease of preparation, but with the rise of industrialization and expanded product availability in the 19th and 20th centuries launderers had more freedom to choose products based on their final effectiveness. The rapid expansion of the laundry and synthetic colorant industries, coupled with colonization and globalization of markets in the late 18th and 19th century led to broad international demand for LB products.

European Christian missionaries and colonial enterprises were likely responsible for initially introducing LB to many parts of Africa, the South Pacific, Australia, and Asia. Missionaries and European colonists had two major objectives in introducing European fashion and hygiene practices to colonized territories. The first was to spread conservative dress standards inspired by religious beliefs [7]. Figure 1 shows two advertisements from a British company that exemplify commonly held colonialist sentiments that directly link racially-motivated imperialism to hygiene products. The second was to advance the capitalist agendas of their countries; by expanding the demand for European-produced textile and hygiene goods, they created large new markets that economically benefitted their home countries[7].

Figure 1. Two advertisements for Pears Soap ca. 1890s that highlight the relationship between European hygiene products and colonialist missions. Credit: Public Domain

To illustrate an example of how LB could make its way into indigenous art and craft practices we can follow its use in Western Arnhem Land and other northern territories in Australia. LB first appeared in Australia in the mid-1800's, and Aboriginal people began using LB as a colorant outside of the washroom not long after, as evidenced by a shield collected in 1888, now housed in the Macleay Museum, with blue stripes painted across credited as being made with Reckitt's Blue[8]. English missionaries in that region first introduced LB [8]. For them the color white was associated with innocence, redemption and purity, thus the use of LB on introduced white cotton clothing to achieve bright white colors was more than just a nicety. It was a necessity for Australian colonial policy as missionaries symbolically “clothed the heathen souls” and sought to “redeem” them [6]. Early Australian LB consisted of variations of synthetic ultramarine with sodium bicarbonate, likely arriving first as Reckitt’s products imported by third-party merchants in the 1860s (Reckitt’s would later open an Australian branch in the 1880s and import directly)[9]. In Aboriginal culture and beliefs, color had multilayered symbolism and bright colors had direct connections to First People and Ancestral Beings[8]. But no mineral pigments in Australia could be used to produce as vibrant a blue as synthetic ultramarine, so it was swiftly adopted alongside other historic pigments, such as chalks and ochres. LB was used prominently in spiritually powerful worn material culture, rock art, and bark paintings. Folk practices in various cultural groups in Australia have also found use for LB washes as insect repellants[10], [11]

The presence of synthetic ultramarine in a work is often used to help date works with limited provenance. There is evidence of synthetic ultramarine being used in Ethiopian art from the mid 19th century; the first use of synthetic ultramarine in the wall paintings of Ethiopian churches is attributed to a German painter, Zander, in 1852[12]. Wooden sculptures, masks, and other cultural material objects from the Yoruba-Nago region in what is now Nigeria and the Republic of Benin have been found with synthetic ultramarine colorants dating from the late 1800s[13]. A conservator working for the University of Oslo’s Ethnographic Museum recorded the use of synthetic ultramarine in a mask collected from the Witu Islands, near Papua New Guinea ca. 1897, and suspected it was derived from LB [14].

In the Northern Plains of North America, the first record of indigenous people's use of aniline blue dyes dates to the 1870s, PB use to 1888, and the first recorded use of synthetic ultramarine ca. 1890, in objects made by Navajo, Sioux and Blackfoot creators, respectively[15], [16]. PB, along with other modern synthetic pigments, were available on the Plains from roughly 1880, brought and sold by Euro-American traders[15]. However, trade records do not list synthetic ultramarine as a traded pigment, and it is likely it entered Plains artists' hands through the trade of LB products[15]. LB has been recorded as a colorant in indigenous art and decorated objects across North and Central America in the 20th century. In the region of modern-day Labrador, Canada, the Naskapi adopted pigments made from repurposed LB in the early 21st century, and there are records of both PB and ultramarine being used for this purpose[17], [18] Prior to ultramarine and PB being traded, few inorganic blue pigments were available in North America. Natural azurite has been found in a few archaeological sites across the Southwest, but it was not widely available. Although not as vibrant and prone to fading over time, vivianite was relatively common in the Northwest[19].

In the Caribbean and Caribbean diaspora, Voudon traditions often involve LB, sometimes sold under the names LB or Mexican Añil Blue balls. Zora Neale Hurston recorded the use of LB for Voudon spiritual rituals in Haiti and Jamaica in her 1938 work *Tell My Horse*, and in the Caribbean and Caribbean diaspora LB still finds use in Voudon spells and rituals, but is often described as "Mexican Añil Blue balls"[10], [20]

PIGMENTS AND COLORANTS COMMONLY FOUND IN LAUNDRY BLUING

As described previously, colorants found in LB products include dyes (soluble colorants that chemically bind directly to substrates), such as aniline and indigo, as well as pigments (colorants that disperse to form emulsions when combined with liquid media and rest on the surface of substrates), such as smalt, synthetic ultramarine, and PB. When coloring a textile, dyes typically need to be combined with mordants, polyvalent metal ions which form coordination complexes that bind dye molecules to substrates. Organic dyes that have been mordanted and combined with binders to make paints are referred to as lake pigments. Expanded colorant histories can be found in the appendix.

ANILINE BLUE

The term "aniline blue" is colloquially used to refer to a number of toxic, organic, water-soluble dyes derived from aniline ($C_6H_5NH_2$), a simple aromatic amine typically derived from coal by-products. Most aniline blue dyes include triarylmethane backbones are readily soluble in water, and can be used with mordants to create color-fast dyes. Although most aniline blue dyes are quite light-sensitive, the light fastness varies by recipe[15].

INDIGO

Both a dye and a lake pigment, natural indigo is derived from the leaves of various plants in the Indigofera species, members of the Leguminosae family. Leguminosae plants are native to various parts of South and Central America, Eurasia, and Africa. Although not all plants in the Leguminosae family are used for dye production, some variants, such as *Indigofera tinctoria L.*

(common name: true indigo)*, Isatis tinctoria L.*(common name: woad) and *Lonchocarpus cyanescens* (common name: Yoruba indigo) have been used as colorants for millennia[18]. For most of human history, dyers typically used the species of indigo-producing plant most geographically convenient, but the expansion of international trade and new methods for drying and preparing materials allowed the more vibrant variants, such as the south Asian *indigofera tinctoria L.,* to dominate global markets. For example, woad, once ubiquitous in dyehouses across Europe, was widely replaced by imported *indigo tinctoria L* in the 17th century. In the 19th and 20th centuries, West African artists may have used dyes made from the indigenous plants *Philenoptera cyanescens* and *Lonchocarpus cyanescens*, as well as imported *I. tinctoria [13], [21].*

In order to be used as a dye, indigo-producing plants must undergo chemical changes in order to bind to substrates. The indigo molecule does not occur naturally; rather plants contain precursors, such as indican and isatan B, which can be reduced to free indoxyl molecules during a reduction process, which, in turn, combine to form indigo when the molecule is oxidized. After reduction, the indigo-precursors undergo molecular changes that renders them both water-soluble and a whitish-yellow color, known as a *leuco*-form. When removed from an indigo vat, the indoxyl forms bound to a substrate are oxidized, turning into the water-insoluble blue indigo[22]. There are several methods for reduction, and some species react more favorably to certain methods over others. Most historic methods involved macerating the leaves, fermenting the resulting pulp, and combining it with an alkaline solution[18], [22]. However, few dyers globally used natural indigo products after the turn of the 19th century, as the invention of inexpensive synthetic indigo dyes became commonplace.

During the industrial revolution, many novel methods for reducing and dyeing indigo arose, some of which involved combining ferrous sulphate with slaked lime or potash or zinc powder (or various combinations of the above) to form hydrogen reducing agents. Others utilized strong, fuming acids, such as sulfuric acid for reduction, followed by neutralization with an alkaline material, such as aluminum carbonate[22], [23]. However, by the end of the 19th century, the dominant agent for reduction was sodium dithionate ($Na_2S_2O_4$)[22].

HEXACYANOFERRATE(II) PIGMENTS

Oft-credited as the first modern synthetic pigment, hexacyanoferrate(II) blue pigments ($Fe_4[Fe(CN)_6]_3xH_20$, where X= 14-16) are relatively inexpensive blue pigments with strong tinting power. The general structure of the hexacyanoferrate compound contains a cubic network of Fe(III)–C–N–Fe(II) units and some vacancies, as well as water molecules that are contained within the structure [24]. Other transition metals, such as copper, zinc or cobalt, can be either substituted into the framework, replacing either iron(II) or iron(III) ions, or freely enter the structure without disrupting the iron ions[18], [25].

There are a multitude of methods for producing hexacyanoferrate(II) blue pigments and, consequently, there are many names for such pigments, some of which are indicative of specific recipes. However the most broadly acceptable term in modern parlance for most blue hexacyanoferrate(II) pigments is Prussian blue (PB), the term used most consistently throughout this paper. Once an initial production method was published in 1724, many early chemists were eager to produce their own inexpensive blue pigments. Naturally, many variations in production methods emerged. There are records of over 100 different known manufacturing methods published between 1724 and 1904 [26]. The hexacyanoferrate pigments produced were often mixed with other ingredients, such as alumina, magnesia and zinc oxide, before being sold as paints. Differences in solubility, tinting strength, color, and working properties exist across different recipes. But the general synthesis principle behind hexacyanoferrate pigments involves combining a solution containing ferric (II) salts with ferrocyanide solution, and precipitating the mixture. The resulting precipitant is a deep blue mixed valence compound containing two oxidation states of iron.

PB was less expensive than indigo, natural ultramarine, smalt, or aniline and could be used as a dye or a pigment; production and use proliferated across Europe in the 18th and 19th centuries. By the first half of the 19th century, it had replaced indigo as the most common blue dye in Europe[4], [27]. Even after aniline dyes hit the markets, PB dyes were still preferred in most cases, as they were less light fugitive and nontoxic. Being water-soluble, PB could be added to laundry by creating a bath of a dilute emulsion of PB and dipping garments in. Garments could be dipped multiple times to achieve a darker blue or rinsed with clean water to remove bluing, making application much simpler than previous bluing products. However, if large amounts of PB were left on a garment for extended periods of time, iron could leach out and oxidize, leaving undesirable orange rust stains.

SMALT

Smalt pigments, widely available in Euroasia from at least the 17th century, consist of ground cobalt-containing, potassium silicate glass($CoO \bullet K \bullet Si$)[18]. The depth of color can depend on the amount of cobalt and potassium flux in the glass as well as how finely ground the pigment is. Higher grade smalt pigments were typically a vibrant blue-purple and lower grade products were paler blues. Coarser pigments, while more vibrant, yield less pliant paints.

Early smalt-based bluing recipes focus on applications for ruff collars and decorative laces, i.e. textiles that would likely not have been in direct contact with skin when worn. Smalt's texture would be unpleasant to have in direct contact with skin. Additionally, because it is insoluble in water, it needed to be mixed with binders and brushed directly on as paste, a time-consuming process.

SYNTHETIC ULTRAMARINE

Synthetic ultramarine blue is an aluminosilicate $Na_{6.8}[AlSiO_4]_6(S_3^-)_{0.8}$ comprised of AlO_4 and SiO_4 tetrahedra joined in a disorder arrangement to form a three-dimensional framework in which anions and cations are locked inside central cavities, or β-cages. Within the β-cages are two different sites that bind sulfur polyanions[28]. Different sulfur species can impact the color of molecule; disulfur (S_2^-) radicals shifting the color towards yellow, tetrasulfur (S_4^-) radicals shifting towards red, and trisulfur radicals (S_3^-) shifting towards blue[28]. Optimal ultramarine possesses primarily trisulfur radicals[28], [29].

Although recipes and methods can vary, generally, synthetic ultramarine is produced by heating a paste of kaolin clay, sodium carbonate, bitumen (or similar carbonaceous binding media), and sulfur at ~750 °C in reduction conditions for several hours, then cooling the mixture to ~500 °C in an oxidative environment, adding additional sulfur, then calcinating the mixture again at ~500

°C for a few hours[28]. The resulting pellets of ultramarine are then ground to create a viable pigment. The larger the final particle size, the more brilliant the color will be. Excess sulfides and other impurities can be removed by washing the ground pigment. Throughout much of the 19th century impurities, such as iron, lime, magnesia, potash and excessive amounts of sulfur, were common and the quality of commercially available pigments was not consistent [28]. Prior to a reproducible synthesis method for synthetic ultramarine being discovered in 1828, natural ultramarine pigments were prohibitively available and would have been reserved only for expensive works of art.

When dispersed in a colloidal solution, ultramarine creates a negatively charged colloidal system with highly reactive Brownian motions, which makes it ideal for laundering solutions[30]. As ultramarine can be easily precipitated out of hard water solutions containing free cations, trace amounts of sodium silicate or sodium bicarbonate were frequently added to LB products[30].

BINDERS AND ADDITIVES FOUND IN LAUNDRY BLUING

Paints typically consist of pigments, solvents, additives, and binding media that adhere the pigments and additives to the surfaces they are applied to in the form of a cohesive film. Polysaccharides, such as gums or starches, are common binding media for colorants.

GUMS

Gums are polysaccharide exudations from plants that are soluble in water and harden upon dehydration. The three gums explored in this research are all anionic and chosen because they were common binders for LB recipes. Gum Arabic is derived from an exudate of acacia trees (family: *Leguminosae*); gum tragacanth (a.k.a. gum dragon) derived from legumes in the genus *Astragalus* and carrageenan extracted from Rhodophyta (common name: red seaweed).

STARCHES

Starches are common forms of carbohydrates derived from plants comprised of two organic polymer chains, the soluble linear helical amylase and insoluble branched amylopectin[31]. Starches are used regularly in laundering and were common additives in LB recipes as they could both increase the volume, starch the textiles being washed directly, and be hydrated during production to help bind the pigment into a ball or cube and then readily dehydrated to make a shelf-stable product. The historic use of various starches in laundering was often limited to product availability and ease of preparation, but with the rise of industrialization and expanded product availability in the 19th and 20th centuries launderers had more freedom to choose products based on their final effectiveness. The use of smaller molecular grained starches, such as rice starch, for laundering yields more pliable products, whereas larger-grained starches, such as potato or corn starches, leave textiles much stiffer[5], [9]. A potato starch may have been preferable for those preparing formal collars or cuffs and a rice starch more appropriate for undergarments. Some starches are relatively inexpensive and simple to prepare from raw materials in home kitchens, such as potato starch, while others, such as wheat starch, were more difficult, making pre-rendered packaged starches more enticing for buyers. The advent of starch solutions that were readily dissolved in room-temperature water met an important market demand in the 19th century, making it easier to incorporate starching into regular home laundering processes. Many of these solutions were made with dextrins, products obtaining by depolymerizing (hydrolysing) and transglycosylation (molecular rearranging) starches through a process of heating and exposing to moisture to acid which are more water-soluble and produce less viscous solutions than parent starches[32], or glucose ($C_6H_{12}O_6$), a monosaccharide component of carbohydrates that could be further isolated from complex sugars in the late 19th century.

ADDITIVES

Many LB products also included nonreactive bulking agents, such as gypsum ($CaSO_4{\cdot}2H_2O$), that expanded the volume of a product, but offered few other advantages. Sodium bicarbonate ($NaHCO_3$) was a common additive which both bulked the product and enhanced the rheological properties of the LB powders when they were added to a bath. First synthesized in 1872, glycerol, a trihydric alcohol that forms a thick, viscous syrup that binds readily with water, was often added to starches as a plasticizer[33]

A COMMERCIAL HISTORY OF LAUNDRY BLUING

The early 19th century laundering product markets were relatively accessible for small manufacturers, as they were not heavily regulated and the technological and capital investment barriers for production were relatively low[1]

From the mid 19th century on, English companies dominated much of the world market for soap, starch, and other laundering products, among them the company which gave birth to many of synonyms now commonly associated with blue pigments. In 1840, the entrepreneurial Isaac Reckitt bought a small wheat starch works in Sutton Drain, England. The company began small, producing and selling wheat starch as well as buying and selling other common laundry products, including smalt pigments for bluing[9]. Over the next decade, the company expanded and Isaac's sons became increasingly involved in the management of the company[9]. Although, the company dabbled in sago[2] flour during the Irish potato famine of the late 1840s when the price of farina[3], as well as wheat skyrocketed, a water soluble wheat starch developed by Isaac Reckitt was their primary product, and Reckitt's Imperial Wheaten Starch was copyrighted in 1848 [1]. In 1874, the company built a rice starch plant.

Through the first three decades of the company's existence, bluing pigments were produced primarily in German factories and exported; Reckitt's serving as a distributor for smalt. The first introduction of ultramarine-based Reckitt's LB, sold first as a "ball blue" occurred in 1852, but by 1854, a published price list showed that their product lines had expanded[1], [9]. Along with a wider variety of starch products, washing paste, and black lead, they offered several blue materials including: Reckitt's Powder Blue, Thumb Blues, Ultramarines (purchased from Rawlins & Sons), Reckitt's Azure Ball Blue, and Liquid Blue. By 1857, black lead and blue pigments began to rival starch as the primary sources of revenue for the company[1].

Much of the company's success is credited to their diversification of products, which allowed them to maximize their advertising investments, and their distinctive, vibrant branding[1]. In

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[2] Sago flour is derived from the pith of tropical palms, but some historic records reserve the term "sago" for cassava-derived flours and starches.

[3] Farina is a starch product that can be derived from a variety of root vegetables, such as cassava or potatoes.

1850, the company spearheaded several novel marketing campaigns, purposefully selling to (or at least claiming in their advertising they were selling to) high-profile clients. The schemes were effective, and the company was given a booth at the 1850 Great Exhibition, which further amplified their marketing reach. They were the first company to package starch in "picture" boxes and use attractive wrappers for all of their products[1]. When Isaac Reckitt died in 1864, his three sons became equal partners and the company began its first exports – LB sold in Montreal, Canada. In 1873, the company began selling the recently introduced Paris Blue, a square of ultramarine-based LB in a wrapper, which was immensely popular and nearly doubled blue sales within a few years. By 1879, the company was converted to a private joint stock company and the name officially changed its name to Reckitt and Sons Ltd.

Until the 1880's all technological innovation was driven by Frederic Reckitt in trial and error experiments, but the hiring of trained chemists in the 1880s and 1890s brought forth significant changes in the product lines[1]. In 1883, the company convinced a German engineer, Johannes Eggerstoff, to come to England and open a small pigment factory under the management of A.W. Wilson. The first year, it produced 150 tons of synthetic ultramarine. By 1891, the factory was producing 500 tons and by 1904 650 tons were produced; all of which was initially sold as LB[9]

The same year a Reckitt and Sons Ltd. Factory first produced ultramarine, the company opened its first foreign office in Australia. Although Reckitt's products had been sold internationally through third party merchants, the company itself had not focused heavily on international markets and exportation prior to this event [9]. In 1888, the company became public and opened a second foreign office in South Africa. In 1890, they began selling a product called "Bag Blue," which was LB sold in a calico bag that could be dipped in a wash briefly to color the bath. In 1897, Reckitt and Sons Ltd. bought the patent "Mack's Double Starch" from the German inventor Heinrich Mack that included borax in the starch solution, which made irons glide more smoothly over linen during pressing. The chemists employed by Reckitt and Sons Ltd. improved upon the patent, eventually patenting the upgraded rice starch-based product under the names Robin Starch and Robin's Composite Starch in 1899. In some global markets, including India and Pakistan, the company sold a variety of their products, including bluing, under the brand name "Robin." In 1908, the company opened a manufacturing plant in New Brunswick, USA to sell their "Bluebird Bag Blue" and a new liquid bluing product, further expanding their global market[9].

By 1962, Reckitt's was responsible for producing nearly half of the world's ultramarine. By the mid 20th century, Reckitt's was selling ultramarine pigments in a variety of grades to many industries, including cosmetics, inks, paints, enamels, soaps and detergents, cellulose-based polymers, rubber products, epoxy resins, and a variety of plastics[30]. Ultramarine's low toxicity even made it a viable additive for food applications[30], [34]. Reckitt's ground their pigments in a range between <0.5 μ to 6.0 μ in diameter, reserving moderately coarser grades (~3 μ - 4 μ) for laundering purposes[30].

The U.S. was slow to compete with European producers of dyes and pigments; the first synthetic dye manufacturing plant, founded by British immigrant Thomas Holliday in Brooklyn, NY, did not open until 1864[35]. German immigrant Farbenfabriken Bayer began manufacturing dyes, including the ragingly popular new aniline dyes, in a plant in Albany, NY a year later. By this point, several recipes for aniline blue dyes were patented and products available on European and American markets. Although corrosive, toxic, and flammable, the water-soluble nature of aniline and its affordability made it a popular choice for liquid LB[5]. Ultramarine was not produced in the states until 1869, when Frederick Heller and Henry Merz opened a plant in Newark, New Jersey. A handful of other companies began producing dyes and pigments, but by the dawn of World War I there were only seven firms manufacturing dyes in the states – the largest being Schoellkopf Dye Works— and collectively they only dominated 10% of the dye market[35]. Trade restrictions with Germany, where many major dye plants were located, inspired rapid investment in dye research and manufacturing. Dow Chemical company, DuPont, and Allied Chemical and Dye Corporation expanded the market considerably over the next few decades and by the eve of World War II the US produced more dyes than any other country [35]. However, changes in tariff protections in the 1960s, oil shortages and nearly industry-wide fines for large-scale price fixing in the 1970s, increased regulation and oversight by the Environmental Protection Agency (EPA) in the 1980s and 1990s, and constant competition from overseas culminated in a substantial drop in US dye and pigment manufacturing in the latter half of the 20th century. By the turn of the millennium, the number of sources for dyes and pigments in US markets was less than half of what it had been just a decade earlier, and the majority of products were produced in China and India[35].

The major producers of LB products in the U.S. were Eastman and Heller & Merz, the latter known for distinctive packaging that often featured puzzles and games. Heller & Merz brought several prominent lawsuits against smaller companies attempting to copy their trademarked "American Laundry Blue Balls," before selling their company in 1930 [36], [37]. One of the most common brands of LB seen on American shelves since the 19th century was Mrs. Stewart's Bluing. In the 1870s, traveling salesman Al Stewart and his family produced a liquid bluing using a recipe likely modified from the patented Litchfield Blue recipe, which was printed in several widely available texts of household chemical products. In 1883, Stewart sold the rights to a wholesale businessman, Luther Ford, who, with his sons, expanded the business considerably in the early 1900s [38]. By1925, factories producing Mrs. Stewart's Bluing were operating in Portland, San Francisco, St. Louis, Pasadena and in Winnipeg, Manitoba and the product was sold widely across the US and Canada. Today, manufacturing is limited exclusively to Bloomington, Minnesota, but distribution is still widespread[38]

In the early and mid-19th century, many small manufacturers across the globe produced their own versions of LB, selling them in a variety of ways, from squares to balls to liquids. By the late nineteenth and early twentieth centuries heavy competition between rival companies existed; there are a number of records of civil court cases that highlight efforts to patent and protect brands and products. William Edge & Sons fought (and lost) two large cases in 1910 and 1911 in English courts to protect their unique "Dolly Blue" bag concept, which they had sold the rights to for a five-year period in 1890 to Reckitt's[39], [40]. The Dolly blue bag was a LB product made of a cube held in a custom bag attached to a distinctive stick which could be used to dip the bluing bag in and out of a bath without staining the hands of the laundress. The Reckitt's version, Reckitt's Bag Blue, was introduced to the Australian and British markets successfully prior to the case entering court dockets, and Reckitts and Sons Ltd. were able to legally oppose Edge's claim that the bag concept was trademarked[1]. The once vast number of 19th century companies producing and/or selling laundry products included: Cadbury's, Rowntree's, Lever's, Glenfield, Anderson, Orlando and Jones', Tordoff, Ripley's Oval Blue, Dolly Blue, Bandey's, Lancashire Ultramarine Company, and Griffith's. But few could hold their own against the growing monopolies of household products for long; William Edge and Sons merged with Reckitt and Sons Ltd., as did Lancashire Ultramarine Company[41].

The only company that truly rivaled Reckitt and Sons Ltd. was Colman's. Like Isaac Reckitt, Jeremiah Colman began as a flour miller in the early 1800s, but acquired a mustard mill in 1814 that grew into a successful business. Also like Reckitt, Colman had youthful and energetic family partners; his nephews operated the company together with Jeremiah as a partnership and added starch production into their portfolio in 1830[1]. They began selling washing blue supplied by a Bristol factory prior to Reckitt[2]. In fact, in the same year that Reckitt and Sons Ltd. created their first branded bluing product (made of imported synthetic ultramarine from Germany), Colman's began manufacturing their own blue. Both Colman's and Reckitt and Sons Ltd. were quick to patent innovations, swift to bring legal action against competitors, and eager to acquire smaller companies[1]. But Colman's made an unusual agreement with Reckitt and Sons Ltd. to not sell products with competing names in the late 1800s (Reckitt and Sons Ltd. using "Paris Blue" and Colman's sticking with "Azure"). J.J. Colman's combined with Reckitt's in 1933 to become Reckitt and Colman's[9]. Reckitts and Colman's maintained their individual brands and also sold in South America under the name Colrex Ltd., and later Atlantis Ltd. Other offices were eventually opened in India, Egypt, Russia, Belgium, Spain, and Brazil, and their products were sold nearly globally. In 1999, the Reckitt and Colman organization of companies merged with another corporate group, Benckiser N.V., to become Reckitt Benckiser plc, which rebranded in 2021 as Reckitt, which is to date the world's largest household cleaning product manufacture[42].

Ulysses Nigeria Ltd., a company founded in 1990, is the major producer of LB in present-day Nigeria; their "Sunshine Ultramarine Blue" product, available since 2004, features a picture of a robin on their packaging, a likely marketing nod to the once ubiquitous "Robin Bluing" sold by Reckitt's and Sons Ltd. The packaging also claims that the product is made in arrangement with Polypex Ltd. in England, however Polypex dissolved in 2021[43], [44].

Today, LB products are scarce, and often marketed for applications other than laundering (e.g. Voudon rituals). In the mid twentieth century, bluing treatments for textiles and other cellulosic materials were phased out as the use of fluorescent brighteners (often referred to in literature as "optical brighteners"[4]) became commonplace. Fluorescent brighteners are molecules that cause a visible brightening of the substrates they are placed on by fluorescing, that is absorbing ultraviolet radiation and emitting visible light. Blue pigments on a substrate decrease the amount of light reflected by a substrate, but fluorescent brighteners can emit light creating a "whiter than white" effect. Fluorescent brighteners were developed for keratinous fibers, such as silk and wool, in the 1940s and in the 1960s products specific to synthetic fibers, such as viscose rayon, nylon, polyester, polyacrylonitrile, and cellulose acetate hit the market[45]. There are thousands

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[4] For the sake of clarity, the phrase "fluorescent brighteners" is the only term used in this paper to refer exclusively to fluorescent laundering products, as bluing materials are also often referred to as "optical brighteners."

of fluorescent brightener formulations in the world today used for textiles, some of which are incorporated into the original products themselves, others into laundry detergents.

EXPERIMENT GOALS AND DESIGN

Although there exist considerable resources for the discernment of blue colorants, this work sought to compare common analytical methods used in cultural heritage for their ability to discern between historic LB recipes, as well as provide insight into the properties and behaviors of these materials. To achieve this, a variety of recipes for LB were prepared. LB cubes or solutions could have been made at home, by commercial laundering facilities, or by pharmacists or alchemists to be sold in local shops. Of interest to this project are recipes that were often recorded being used in home maintenance manuals, as well as those that were likely sold by pharmacists or mass-produced in factories and sold to wider markets. Two historic recipes were adapted from the publication *Fortunes in Formulas* by Hiscox and Sloane, a compendium of recipes for both amateur and professional use that would have had broad influence[23]. A third was adapted from "Litchfield blue," a bluing recipe referenced often in a wide variety of 20th century literature. Combinations of different binders and additives were added to ultramarine (the most common colorant for LB) and indigo. Indigo that had not undergone any treatment was also compared against indigo that had been rendered soluble. Reference samples of binders and additives, as well as smalt and PB, created by combining powdered pigments with gum Arabic, were also assessed. The project also sought to understand the composition of several samples of common commercial LB.

SAMPLE PREPARATION

Two commercially available LB squares were purchased, one labeled as a Reckitt's Crown Blue and one labeled as Reckitt and Coleman's LB Squares, as well as two liquid bluing solutions. The squares acquired were purchased from third-party vendors, as Reckitt no longer directly sells bluing. They were mixed with deionized water and gum Arabic and applied on the substrate described below.

Powdered pigments were combined with a binder and deionized water on a glass slide and mixed with a spatula until a texture and viscosity was achieved deemed to be most appropriate for painting. The binders explored were gum Arabic, gum tragacanth, and carrageenan. Two additional samples were made using ultramarine powder, gum Arabic, and a starch – potato and wheat starch respectively.

Samples were prepared in the UCLA/ Getty lab and painted onto matt boards (both a white and a neutral gray board were used.) Table 2 lists all of the samples created, and

Table 3 shows the manufacturer and/or distributor of materials used. Descriptions of the three recipes adapted from historic chemical formularies follow.

Table 2. Sample List

Sample #	**Description**
1	Prussian Blue + Indigo Sulfate (Adapted from Litchfield’s Patented Laundry Bluing)
2	Ultramarine + Glucose + Sodium Carbonate (Adapted from Fortunes in Formulas)
3	Ultramarine + Dextrin Mucilage + Glycerol (Adapted from Fortunes in Formulas)
4	Ultramarine + Gum Arabic
5	Ultramarine + Gum Arabic + Wheat Starch
6	Ultramarine + Gum Arabic + Potato Starch
7	Ultramarine + Gum Tragacanth
8	Ultramarine + Carrageenan
9	Prussian Blue + Gum Arabic
10	Indigo (Insoluble) + Gum Arabic
11	Indigo (Insoluble) + Gum Arabic + Wheat Starch
12	Indigo Sulfate (soluble) +Gum Arabic
13	Smalt + Gum Arabic
14	Gum Arabic
15	Gum Tragacanth
16	Carrageenan
17	Gum Arabic + Wheat Starch
18	Gum Arabic + Potato Starch
19	Commercial Product. Square Of Reckitt’s Crown Blue
20	Commercial Product. Square Of Reckitt's And Coleman
21	Commercial Product. Meadowblossom Aniline Laundry Bluing
22	Commercial Product. Mrs. Stewart's Patented Laundry Bluing

Table 3. Origin of materials used in experiment

Material	Manufacturer/ Distributor
Carrageenan powder	Talas
Gum tragacanth powder	Talas
Gum Arabic powder	Kremer
Ultramarine dry pigment	Kremer
Indigo (insoluble) dry pigment	Kremer
Prussian Blue dry pigment	Kremer
Smalt dry pigment	Kremer
Mrs. Stewart's Concentrated Laundry Bluing	Mrs. Stewart's
Aniline blue liquid concentrate	Meadowblossom Goods
Reckitt's Crown Blue commercial laundry cube	Amazon
Reckitt and Coleman Blue commercial laundry cube	Amazon
Glucose	Aldon Corporation
Dextrin (yellow)	Eisen-golden laboratories
Glycerol	Unknown
Potato Starch	Made in-house by author using Russet potatoes
Wheat Starch	Unknown

"Litchfield's Patented Laundry Bluing"

This formula was adapted from a recipe patented by Litchfield. Although Litchfield recommends using a combination of "Turnbull and Chinese blue," the decision was made to use a pre-formulated PB pigment instead. Both Turnbull and Chinese blue are hexacyanoferrate pigments; they are chemically identical to PB, but formulated with slightly different synthesis methods. In his published recipes, Litchfield recommends using substitutions when necessary[46].

The pH-neutral indigo sulfate mixture was prepared first. Natural indigo derived from the *Indigofera Tinctoria L.* plant, was chosen as it is the most widely used species for the production of natural indigo dye and pigment, and would have been for much of the 19th and 20th centuries. 10.0 g of indigo powder was added to 40.0g of sulfuric acid (H_2SO_4), mixed thoroughly and then allowed to rest for one hour. 50.0 g of ammonia carbonate ($(NH_4)_2CO_3$) was then added to the mixture, along with slight quantities of deionized water to aid in the reactions. The resulting mixture was tested using MQuant pH Universal Indicator Strips and found to have a neutral pH of 7. Next, 35 g of PB powder was added to 7g of oxalic acid ($C_2H_2O_4$). 50mL of boiling deionized water was combined with the PB/ oxalic acid mixture to dissolve the powder. 7g of the indigo sulfate mixture was then added to the solution. Half of the mixture was kept in a sealed glass jar, and half was spread on a glass dish to air dry, but after 48 hours there were no notable differences in the behaviors of the mixtures. It is worth noting that although this recipe may have produced a final product with a favorable color, it would have been have been very unpleasant to manufacture in the 19th or 20th century kitchens, washrooms, or labs, and the final products may even have been dangerous to use if not mixed properly. Sulfuric acid is a strong acid that can cause severe burns and other health issues if not handled appropriately, and many early recipes recommended using a formulation known to spew excessively.

“Laundry Sour and Bluing”[23]

6.0 g of ultramarine blue powder, and 4.0 g of sodium carbonate, and 1.0 g of 90% glucose ($C_6H_{12}O_6$) in deionized water solution (w/v) were combined to form a paste, and then spread on a glass tray sheet to dry. Sections were then cut into cubes. When applying the material to substrates, the media was rehydrated with deionized water and then painted out.

“Leaf Bluing for Laundry[23]”

5.0 g of dextrin ($C_6H_{10}O_5$) was added to 9.0 mL of deionized water to make a syrup. 5.2 g of glycerol ($C_3H_8O_3$) was then added to the mixture, followed by 9.1 g of ultramarine powder. The mixture was combined and then spread on a glass dish and left to air dry for 48 hours.

ANALYTICAL METHODS USED

POLARIZED LIGHT MICROSCOPY (PLM)

Samples of commercially available LB products as well as reference samples of blue pigments and common binders and additives were assessed using an Olympus BX51 Polarized Light Microscope (PLM) to determine whether pigments made from different LB preparations could be differentiated using microscopic samples required by the technique. Reference slides were prepared for smalt, PB, wheat starch, potato starch, synthetic ultramarine, indigo powder and sodium carbonate.

MICROCHEMICAL TESTING

Chemical testing for starch and different ionic species were performed on samples from the two commercial LB squares to determine whether such testing could assist in distinguishing between different LB recipes and possibly contribute to provenance studies.

Starch Test

A common chemical test used to identify the presence of starches includes iodine and potassium iodide[47]. When in contact with a starch a potassium (I_2) in potassium iodide (KI) solution will undergo a noticeable color change, turning a dark blue. The mechanism is described below:

$$I_2(s) + I^-(aq) \rightarrow \underset{\text{Triiodide ion}}{I_3^-(aq)}$$

$$2I_3^-(aq) + \text{starch} \rightarrow \underset{\text{(blue)}}{[\text{starch-}I_5]^-} + I^-(aq)$$

The potassium/ potassium iodide (KI_3) solution was prepared by adding 0.9g of potassium iodide (KI) to 5mL deionized (DI) water and then combining them with 0.04g of iodine (I_2). Once the iodine was completely dissolved in the potassium iodide solution, the solution was diluted to 35mL with DI water. Several drops of the triiodide reagent solution was then added to small amounts of powders from the commercial samples and positive and negative references.

Salt Tests

Samples were taken from the Reckitt Crown and Reckitt and Coleman commercial LB products to better understand the presence of additives to these products and assess whether recipes were consistent. All samples were compared alongside known positive and negative references. The samples were tested for their ability to dissolve readily in deionized water. Then Merck indicator strips were used to explore the presence of chlorides, nitrates, and sulfates in solutions of the sample. To confirm the presence of carbonates ($CO_3{}^{2-}$), a few drops of nitric acid were added to commercial samples and positive and negative references. Nitric acid reacts exothermically with carbonate compounds to form carbon dioxide gases and nitrate salts, as seen in the reaction below:

$$RCO_3(s) + 2HNO_3(g) \rightarrow R(NO_3)_2(s) + CO_2(g) + H_2O(g)$$

Sodium (Na^+) and potassium (K^+) were tested by reacting the sample with a bismuth sulfate reagent solution prepared by combining bismuth (III) nitrate ($Bi(NO_3)_3$) with sulfuric acid (H_2SO_4), deionized water, and 2M nitric acid (HNO_3)[48]. Sodium reacts at room temperature with the reagent solution to form rod-shaped crystals of sodium bismuth sulfate ($3Na_2SO_4 *2Bi_2(SO_4)_3*2H_2O$), while potassium reacts with the reagent under heat to form iridescent hexagonal platelets of potassium bismuth sulfate ($K_2SO_4 * Bi_2(SO_4)_3*2H_2O$). Calcium ($Ca^{2+}$) was tested by adding 1M sulfuric acid (H_2SO_4) to a solution of the material being sampled, and then warming the mixture on a hotplate and observing the reaction under the microscope. If calcium is present, acicular calcium sulfate crystals will precipitate on the edges of the droplet, as well as hydrogen gas, as seen in the following reaction:

$$Ca + H_2SO_4^{-}{}_{(l)} \rightarrow CaSO_{4(s)} + H_{2(g)}$$

Magnesium (Mg2+) presence was tested by combining a solution of the material being sampled with a drop of dilute (5-10%) hydrochloric acid, Titan yellow solution, and 2M sodium hydroxide (NaOH) solution and agitated. Magnesium, if present, combines with the reagents to form a red precipitate[48]. However, results can be disrupted by the presence of calcium ions, which can also react with the solution to form orange-red precipitates.

PORTABLE X-RAY FLUORESCENCE (XRF) SPECTROSCOPY

Analysis was performed using a Tracer 5 portable X-ray fluorescence spectrometer run under the following acquisition conditions: voltage 40kV; current5.5μA; no filter; no vacuum; collection time 120 seconds. XRF provides elemental identification of materials.

FOURIER-TRANSFORMED INFRARED SPECTROSCOPY (FTIR)

Although FTIR requires a small sample, it is a valuable tool for material investigation as it provides information on molecular structure that can be used for the identification of an unknown material. Fourier-transformed infrared(FTIR) spectroscopy was performed with a Thermo Scientific Smart iTR Nicolet iS10 instrument using Attenuated Total Reflectance (ATR) parameters. The spectra was collected in the range of 4,000-650 cm^{-1} using 64 accumulated scans at a spectral resolution of 4 cm^{-1} and results compared using OMNIC software and a variety of reference libraries. Pigment samples were prepared by removing material from the matt board where samples had been painted out. Gums and starches were rehydrated on a piece of silica-release mylar and then dried to create films that were placed in the instrument.

MULTIBAND IMAGING (MBI)

Multiband imaging (MBI) is a nondestructive, noninvasive analytical method used to identify specific colorants and media using modified cameras capable of capturing a wide spectrum of reflectance radiation, including the ultraviolet and infrared sections of the electromagnetic spectrum, and further uses a series of filters, radiation sources, and post-processing software to capture image data within narrow spectral wavelengths.

FIBER-OPTIC REFLECTANCE SPECTROSCOPY (FORS)

FORS is a nondestructive, noninvasive technique for collecting spectra in the VIS and IR range that can be used for material characterization. Readings of the samples painted out on the matt board were taken with a FieldSpec 3 portable spectroradiometer in the spectral range of 350 nm to 2500 nm, held at 45° angle to the sample. At least three readings were taken of each sample and data processed with ViewSpecPro software.

RESULTS

PLM

Table 4 details microscopic characteristics of the materials sampled.

Differentiation of PB, indigo, and ultramarine is difficult with polarized light microscopy. All are often very fine-grained, prone to forming heterogeneously-sized aggregates, and blue-colored under plane-polarized light (although indigo is often a darker blue)[18]. Both ultramarine and PB are isotropic, and indigo is only weakly anisotropic[18]. While indigo has a low birefringence in cross-polarized light (XPL), it can easily be obscured by its dark coloration [18]. When viewed with a Chelsea filter, ultramarine exhibits a strong red color, while both indigo and PB appear dark black[18]. Smalt particles are readily distinguished from the other blue pigments studied, as they have a unique morphology consisting of angular shards that often contain conchoidal fractures or visible gas bubbles and are usually much coarser than the other pigment particles[18]. The colors of smalt particles are variable; ranging from transparent pale blue to deep purple, with color intensity increasing commiserate with particle size.

Both of the commercial samples of LB squares contained ultramarine, identified based on color, morphology, isotropism, and behavior under a Chelsea filter. The sample of Reckitt's crown blue had starch inclusions. Characteristic starch grain features include: birefringence, the presence and/or shape of central hilum, the visibility of lamellae, the position and shape of an extinction cross in XPL, the size and morphology of individual granules, and the type of granules[31]. The starch grains seen in the sample were circular, approximately ~5µ in diameter with a small, central hilum and extinction crosses visible in XPL. Although those characteristics are consistent with those found in wheat starch, there are other starch grains with similar characteristics (e.g. arrowroot), making a definitive identification without further study not possible. However, these characteristics are inconsistent with potato starch, as potato grains are larger, irregularly shaped, and have prominent lamellae[31]. The second commercial sample, Reckitt's and Coleman, had transparent, birefringent, medium-sized crystals mixed with the blue particles A definitive identification of the crystal species was not made, but it was evident that the two commercial samples had different additives and inclusions.

Table 4. Characteristics Under Polarized Light Microscopy (PLM)

Sample	Color	Morphology	Particle Size	Isotropic (no light transmitted in XPL regardless of	Pleochroism yes or no	Birefringence none, low, medium, or high	Effect Under Chelsea Filter	Expected Refractive Index[14]	Notes
Ultramarine	blue	Crumb-like aggregates. Irregular. Ragged.	heterogeneous. Fine to coarse (1 - 32 um)	yes	no	none	strong red	1.5	
Natural indigo	dark blue	dispersed, fine round particles	very fine to fine	no	no	low	appears black, but has high red transmission, however most only visible in near-infrared range	>1.662	
Prussian Blue	blue	aggregates of fine particles with variable translucency. Aggregates often angular with some rounded surfaces.	extremely fine	yes	no	none	black	1.56	In literature reviews, Prussian blue has been noted to occasionally have bronze undertones.
Smalt	transparent pale blue to deep purple, particularly dependent on particle size	Angular shards, sometimes with conchoidal fractures or visible gas bubbles.	medium to very coarse	yes	no	none	weak red	1.46-1.55	Presence of additional crystallites or quartz common, and may affect readings (e.g. quartz is anisotropic and birefringent).
Potato Starch	white/clear	Irregular ovoid. Lamellae visible under high magnification. Small hilum off-center, typically in narrower end. Extinction cross visible in XPL.	heterogeneous. Large to very coarse	no	yes	medium		<<1.622	
Wheat Starch	white/ clear	Circular with small central hilum	heterogeneous. Medium to coarse	no	yes	medium to high		<<1.622	
Sodium carbonate	white/ clear	Crystalline	variable	no	yes	yes		1.415, 1.535, 1.546	Birefringence identified, but level not identified at time of analysis
Reckitt's and Coleman	Blue	Blue crumb-like particles are very fine and evenly dispersed. Rounded	very fine to fine	yes	no	none			Birefringent, transparent crystals also identified.
Reckitt's Crown Blue	Blue	Blue crumb-like particles are very fine and evenly dispersed. Rounded	very fine to fine	yes	no	none			Blue particles mixed with starch grains
Starch in Reckitt's Crown Blue	white/clear	circular with central hilum and cross	~5um	no	yes	yes			Birefringence identified, but level not identified at time of analysis

Particle Size Classification System[18]	
Absolute particle size (µm)	**Relative Particle size**
> 40	very coarse
10- 40	coarse
10 - 3	large
3 - 1	medium
1.0 - 0.3	fine
< 0.3	very fine

MICROCHEMICAL TESTING

Both samples of the commercial laundry products readily dissolved in water and had a variety of inclusions present (see Table 5), but not necessarily the same ones or in the same concentrates, indicating different recipes used. Both had high concentrations of sodium, which is expected for ultramarine, but may also be attributable to common bulking agents for commercial products, such as sodium carbonate. Although both had carbonates present, the Reckitt and Coleman sample had a much stronger reaction with the nitric acid than the Reckitt Crown sample, suggesting it had a higher concentration of carbonates present. The Reckitt Crown sample had sulfate and magnesium ions present, unlike the Reckitt and Coleman sample. The Reckitt Crown sample also had calcium ions present, while calcium could not be definitively confirmed to be present in the Reckitt and Coleman sample.

Although the starch test was relatively simple to perform, its usefulness for the identification of starches in LB samples was found to be limited. The triiodide reagent solution turns a dark blue in the presence of starches, but because a LB sample contains blue pigment the results may be easily misinterpreted.

Table 5. Microchemical Test Results

	Sample	
Test	**Reckitt Crown**	**Reckitt and Coleman**
Starch	**Not definitive**	**Not definitive**
Dissolution	+	+
Chloride Cl^- (Merck)	+	-
Nitrate NO_3^-(Merck)	-	-
Sulfate SO_4^{2-} (Merck)	+	-
Carbonate $(CO_3)^{2-}$	**Slight**	+
Ca^{2+} calcium	+	**Not definitive (formed crystals with sulfuric acid, but no orange crystals with Mg^{2+} test)**
Mg^{2+} magnesium	+	-
Na^+ sodium	+	+
K^+ potassium	-	-

XRF

The readings were taken of samples painted out onto a white matt board supported by Ethafoam above an MDF table. Spectra were compared against a reference of the matt board and peaks associated with the matboard and/or atmospheric conditions were subtracted from results. The findings from XRF analysis can be seen in Table 6 and spectra can be seen in the appendix.

Table 6. XRF Results of Experimental Samples

Sample	All peaks (including those likely from substrate or instrument interference)	Major Peaks	Minor Peaks	Trace Elements
Aniline Blue	S, Rh, Ar, Ca, Ti, Fe, Ni, Cu, Rh, Pd	S		
Ultramarine and Gum Arabic	S, Si, K, Fe, Rh, Ar, Ca, Ti, Ni, Cu, Rh, Pd	S, Si, K, Fe		
Indigo	S, Si, K, Fe, Rh, Ar, Ca, Ti, Ni, Cu, Rh, Pd	Fe	Si, S, K	
Litchfield Blue	S, Si, K, Fe, Rh, Ar, Ca, Ti, Ni, Cu, Rh, Pd	Fe		S, Si, K
Mrs. Stewarts	Fe, Sr, Rh, Ar, Ca, Ti, Ni, Cu, Rh, Pd	Fe		Sr
Prussian Blue	Rh, Ar, Ca, Ti, Ni, Cu, Rh, Pd	Fe		
Reckitt's and Coleman	Si, S, K, Fe, Rh, Ar, Ca, Ti, Ni, Cu, Rh, Pd		Si, S, K, Fe	
Reckitt's Crown Blue	Si, S, K, Fe, Rh, Ar, Ca, Ti, Ni, Cu, Rh, Pd	Fe, K, S	Si	
Smalt	Co, Si, K, Fe, Cu, Rh, Ar, Ca, Ti, Ni, Cu, Rh, Pd	Co	Si, K, Fe, Cu	
Matt board Reference	Rh, Ar, Ca, Ti, Fe, Ni, Cu, Rh, Pd			

XRF can be an excellent tool for distinguishing some blues. Smalt, or any other cobalt-based blue, would exhibit peaks consistent with cobalt, as well as other elements common in glass matrixes, such as silica, potassium, lead, calcium, or sodium, or those that may be added to glass as metal oxides to finetune the color. However, cobalt would not generally be expected in other known blue pigments. As an organic dye containing primarily low Z elements not discernible in XRF spectra, indigo would be unlikely to display many discerning characteristics, however, sulfur found in some synthetic indigos and aniline dyes may be detected with appropriate instrument settings. Some reduction methods for indigo processing may introduce other trace elements, such as iron, sodium, sulfur, and other elements that may be introduced in dyes that were processed in alkaline baths[22], [49]. Like indigo, the core elements of synthetic ultramarine-- sodium, silicon, aluminum, and sulfur— are not always readily detectable in XRF, unless the instrument has been calibrated for lower Z elements, and appropriate voltages and filters are implemented. However, trace amounts of iron and copper are not uncommon in ultramarine. Spectra for iron-hexacyanoferrates should naturally be expected to display strong characteristic peaks for iron. Although not seen in these spectra, PB may also contain other metals, such as cobalt or copper, in addition to iron[25], [26].

The spectra collected were not calibrated for quantitative analysis. Classification as “major,” “minor,” or “trace” is based on relative comparisons of peak intensities, but spectral interferences, such as those caused by bremsstrahlung radiation (common when low ($Z<26$ elements) are present), the impact of beam angles, instrument-specific deviations, and the thickness of samples were not corrected for in these readings, all of which can inhibit definitive quantitative analysis. The data collected here is appropriate for qualitative analysis. Minor or trace peaks found ubiquitously in all samples, including the matt board reference, were attributed either to the atmosphere or reference and were not considered as diagnostic.

In the spectra collected for aniline, the only peak assignment seen in the spectrum not assignable to the matt board reference correlated with sulfur. PB displayed clear lines for iron. Mrs. Stewart’s, a Prussian-blue-based commercial product, also had clear lines for iron, but showed additional trace elements of strontium. The smalt displayed characteristic lines for cobalt, as well as other elements commonly found in colored glass.

All ultramarine-based samples had indistinguishable spectra, with the major peaks identifiable as iron, silicon, sulfur, and potassium. Interestingly, these were the same peaks found in the indigo sample and Litchfield Blue, a combination of water-soluble indigo and PB. Although aluminum is found in ultramarine and not expected in pure samples of indigo or PB, its common use in additives and its regular presence as an impurity does not render it sufficient evidence for distinguishing between these pigments on the basis of XRF alone.

FTIR

The spectra of all samples are included in the appendix, and

Table 7 shows the results compiled.

Ultramarine, regardless of what binders or fillers accompanied it, displayed distinctive peaks at ~980 cm^{-1} that corresponded to Si-O-Si and Si-O-Al stretching vibration modes[13]. When ultramarine was mixed with gum Arabic, an additional peak around 690 cm^{-1}arose, but this peak was not identified in the samples of pure gum Arabic, suggesting it correlates to either a physical or chemical interaction between ultramarine and gum Arabic or to a chemical product resulting from the mixture. The peak may relate to either bending from Si-O bonds or vibrational C-H bonds commonly found in complex organic molecules in this region, but due to limited time, no literature reviews or experiments were undertaken to confirm this hypothesis. PB has distinctive strong bands around 2070 cm^{-1} caused by the C≡N bond stretching of the cyanide group[13]. The main peaks of the FTIR spectra of the mixture of indigo and PB were consistent only with the characteristic peaks of PB; those of indigo may have been either masked or only present in low concentrations. This phenomena has been relatively recently identified in other research, including that of Biron et al [50].

The saccharides had broad bands in the 3250 – 3460 range corresponding to deformation and elongation of O-H bonds. While the binders were distinguishable in spectra taken of just the binders, when mixed with pigments the distinct signals were often masked or diluted.

Table 7. FTIR Results of Experimental Samples

Description	**Band wavenumber/ Cm-1 and relative intensity**	**Assignments**	**References**
PB + Indigo + GA (Litchfield)	983m, 1412m, 1611m, 2070s, 3253m	Prussian Blue: 2070 intense absorption band corresponds to CN triple bond stretching of cyanide group; 1611 and 3253 - characteristic bands corresponding to vibration and deformation of OH group; 1412 CH2 symmetric scissoring; 983 C-O stretching or C=C bending	[13]
Ultramarine + Glucose + Sodium bicarbonate	848m, 978s, 1456m, 1682m, 3455br	Ultramarine: 978 stretching vibration bonds of Si-O-Si and Si-O-Al tetrahedra; Glucose: 3455 broad band caused by deformation and elongation vibrations of OH bonds; 848 C-O stretching or C=C stretching; 1456 CH2 symmetric deformation	[13],[51]
Ultramarine + Glycerol + dextrin	977s, 3320br	Ultramarine: 977 stretching vibration bonds of Si-O-Si and Si-O-Al tetrahedra; Glycerol: 3320 broad band caused by deformation and elongation vibrations of OH bonds	[13]
Ultramarine + GA	691m, 977s	Ultramarine: 977 stretching vibration bonds of Si-O-Si and Si-O-Al tetrahedra; Gum Arabic bonded to ultramarine: 691 C-H bending and/or Si-O bonds	[13]
Ultramarine + GA + wheat starch	690m, 980s, 3318br	Ultramarine: 980 stretching vibration bonds of Si-O-Si and Si-O-Al tetrahedra; Gum Arabic bonded to ultramarine: 690 C-H bending and/or Si-O bonds Wheat Starch: 3318 broad band caused by deformation and elongation vibrations of OH bonds	[13]
Ultramarine + GA + potato starch	690m, 981s, 3354br	Ultramarine: 981 stretching vibration bonds of Si-O-Si and Si-O-Al tetrahedra; Gum Arabic bonded to ultramarine: 690 C-H bending and/or Si-O bonds; Potato Starch: 3354 broad band caused by deformation and elongation vibrations of OH bonds	[13]
Ultramarine + gum tragacanth	657m, 691m, 796w, 977s, 3693vw	Ultramarine: 977 stretching vibration bonds of Si-O-Si and Si-O-Al tetrahedra; Gum Tragacanth: 3693 broad band caused by deformation and elongation vibrations of OH bonds; 796 C-O bonds; 660 and 691 C-H bending and/or Si-O bonds	[13]
Ultramarine + carrageenan	691m, 980s	Ultramarine: 980 stretching vibration bonds of Si-O-Si and Si-O-Al tetrahedra, Carrageenan: 690 C-H bending and/or Si-O bonds	[13]
Prussian Blue + GA	1038m, 1412m, 1611m, 2067s, 3254m	Prussian Blue: 2067 intense absorption band corresponds to CN triple bond stretching of cyanide group; 1611 and 3254 characteristic bands corresponding to vibration, stretching and deformation of OH group, 1412 CH2 symmetric stretching; 1038 C-O stretching	[13], [52]
Indigo (insoluble) + GA	696m, 710s, 765m, 789m, 859m, 877m, 1009m, 1062s, 1095m, 1122m, 1168m, 1296m, 1316m, 1389m, 1459m, 1481m, 1583m, 1606m, 1622s, 3246br	Indigo: 1583, 1622, 1389 stretching vibrations of conjugated system C=C, C=O, and N=H groups; 1481, 1459 C-C and C-H rocking; 1606, 1296, 1316, 1009, 859, 877, 789, 765, 710, 696 C-H ring vibrations; 3246 broad, intense band corresponds to OH group, likely carboxylic acid functional group	[53]

Indigo (insoluble) + GA + wheat starch	~650s, ~850m, ~1000s, ~1050s, ~1120m, ~1300dm, ~1380m, ~1440m, ~1450m, ~1620m, ~2900m, ~3250mbr	Indigo: 3250 - broad, intense band corresponds to OH group; ~1620, ~1380 stretching vibrations of conjugated system C=C, C=O, and N=H groups; ~1450, ~1440 C-C and C-H rocking; ~1300, ~1050, ~1000, ~850, ~650 C-H ring vibrations; 3250 broad, intense band corresponds to OH group, likely carboxylic acid functional group	[53]
indigo (soluble, using Litchfield process) +GA	747m, 1027s, 1064s, 1403s, 1620m, 3030brs	Indigo: 1027 ascribed to glycosidic linkages; 1064, 747 C-H ring vibrations; 1620, 1403 stretching vibrations of conjugated system C=C, C=O, and N=H groups; 3030 broad, intense band corresponds to OH group, likely carboxylic acid functional group, but the nonuniformity of the band is likely related to the N-H bond.	[53]
Smalt + GA	693m, 774m, 997s, 3252brw	Smalt: 3252 Si-OH stretching. 997 Si-O-metal Gum Arabic: 693 and 774 C-H bending;	[54]
GA	1023s, 1417m, 1601m, 3262sbr	3262 and 1601 O-H stretching; 1023 C-O stretching of glycosidic linkages; 1417 COO asymmetric stretching	[55]
Gum tragacanth	1019s, 1369m, 1424m, 1624m, 2918sh, 3334sbr	3334 and 1624 O-H stretching; 1019 C-O stretching; 1369, 1424, 2918 C-H stretching	[55]
Carrageenan	699m, 771m, 843m, 927m, 1027s, 1125m, 1154m, 1221s, 1455m, 1623m, 3358br	1221 S=O bond of sulfate esters; 1027 ascribed to glycosidic linkages; 843 galactose-4-sulfate; 1623 and 3358 O-H stretching; 1455 CH2 symmetric deformation	[56]
Wheat Starch	860m, 996s, 1076m, 1150m, 1336m, 1636m, 2927sh, 3285br	3285 O-H stretching; 2927 C-H stretching; 1636 C-O bending associated with OH group; 1336 C-H symmetric bending; 1150 C-O-C asymmetric stretching; 1076 C-O stretching; 860, 996 C-O-C ring vibration	[47]
Potato Starch	928m, 1000s, 1078m, 1149m, 1358m, 1640m, 3269br	3269 O-H stretching; 1640 C-O bending associated with OH group; 1358 C-H symmetric bending; 1149 C-O-C asymmetric stretching; 1078 C-O stretching; 1000, 928 C-O-C ring vibration	[47]
Commercial Product. Square of Reckitt's Crown Blue	664m, 981s, 1417m, 3333br	Ultramarine: 981 stretching vibration bonds of Si-O-Si and Si-O-Al tetrahedra; Unknown organic binder (likely natural gum, possibly gum Arabic): 3333 - Broad band caused by deformation and elongation vibrations of OH bonds; 1417 asymmetric CH_2 scissoring; 664 C-H bending	[13]
Commercial Product. Square of Reckitt's and Coleman	657m, 689s, 832m, 988s, 1031msh, 1045msh, 1282m, 1451m, 1614m, 1916m, 2454br	Ultramarine: 988 stretching vibration bonds of Si-O-Si and Si-O-Al tetrahedra; Unknown organic binder (likely natural gum, possibly gum Arabic) bonded to ultramarine: 689 C-H bending and/or Si-O bonds; Unknown/ other:1451 CH_2 symmetric deformation; 832, 1031, 1045, 1282 C-O stretching; 657 C-H bending; 1916 C=C stretching ; 2454 pi bonds	[13]
Mrs. Stewarts	850m, 970m, 1130m, 1410s, 1610m, 2060s, ~3250mbr	Prussian blue: 2060 intense absorption band corresponds to CN triple bond stretching of cyanide group; 1610 and 3250 characteristic bands corresponding to vibration and deformation of OH group; 1410 CH2 symmetric scissoring; 850, 970, 1130 C-O stretching	[13]
s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad; d, doublet[5]			

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[5] These assignments are subjective. At the time of analysis, the author was unaware of best practices and did not clarify the percentages for each assignment. Software access was later limited, so the data could not be clarified prior to publication.

MBI

MBI was completed on samples that had been painted out on a white matboard using a modified Nikon D90 DSLR camera, capable of capturing electromagnetic emissions in the wavelength range of 350 to 1100 nanometers. A Labsphere reflectance standard and XRITE Color Checker Passport were included in all captures. A variety of filters and radiation emission sources were used to capture specific wavelengths, as detailed in Table 8.

Table 8. Multiband Imaging Capture and Post-Processing Techniques

Capture Technique	Abbreviation	Lighting Source	Filters	Post-Processing
Ultraviolet Luminescence (Shortwave UV)	UVL	Analytikjena, handheld UV source. Shortwave (254 nm)	B+W 486	
Ultraviolet Luminescence (Longwave UV)	UVL	Analytikjena, handheld UV source. Longwave (365 nm)	B+W 486	
Ultraviolet Reflectance	UVR	Analytikjena, handheld UV source. Longwave (365 nm)	XNITE 330 and XNITE BP1	Reduced saturation to -100
Visible Light	VIS	Halogen bulb	B+W 486	Color corrected using X-rite color checker passport.
Narrow Wavelength-Induced Luminescence	VIL	Crimescope (white light)	XNITE 830 + orange filter	Reduced saturation to -100
Infrared Reflectance	IRR	Halogen bulb	XNITE 830	Reduced saturation to -100
Infrared Luminescence	IRL	LED	PECA 902 (#89B)	Reduced saturation to -100
Multiband Reflectance Image Subtractions	MBIR	Halogen	Midopt 660	Subtracted absolute value of desaturated images shot with Midopt 660 and Midopt 735 filters
Multiband Reflectance Image Subtractions	MBIR	Halogen	Midopt 735	Subtracted absolute value of desaturated images shot with Midopt 660 and Midopt 735 filters
False-Color UVR	FCUV	n/a	n/a	VIS and UVR images combined and RGB channels mixed to render derivate image
False-Color Infrared	FCIR	n/a	n/a	VIS and IRR images combined and RGB channels mixed to render derivate image

All MBI interpretation results can be found in Table 9 and images can be seen in the appendix.

In some instances, samples had been painted out with variation in thickness and this often had impact on MBI interpretation. For example, the indigo samples reduced using the Litchfield reduction process and mixed with GA were brighter in thin applications in IRR and VIL. The indigo itself was neither reflective in IR nor luminescent with narrow-band visible light illumination, but the GA had contrasting properties. In thinner application, the GA shone through stronger, and it was harder to distinguish thin applications of indigo from ultramarine in IRR.

Binders and additives can also impact MBI interpretation. In UVR, it was evident that the use of different binders impacted the reflectance levels of the pigments, particularly noticeable with ultramarine. Wheat and potato starch were highly reflective, and their inclusion in a sample brightened the results. In short-wave UVL, wheat starch and indigo fluoresced a bright white color, however, indigo, both when unbound and when bound with GA, was much darker. In VIL, GA, gum tragacanth, carrageenan, wheat and potato starch fluoresced, unlike the known samples of ultramarine, PB, and most indigo samples. Interestingly, the two commercial Reckitt samples had very different properties. The Reckitt's and Crown sample fluoresced, unlike the Reckitt's and Coleman sample.

Aniline blue had the most divergent behaviors from the rest of the samples, and could be readily distinguished from true indigo using MBI. In both long- and short-wave UV, aniline blue fluoresced a bright white color, much brighter than the other blues samples. In VIL, aniline blue exhibited a bright fluorescence, noticeably brighter than any other sample on the board. Aniline had a bright reflectance in IRR, but there was little impact in IRL.

The indigo samples did not have consistent results across the all MBI techniques, some of which is attributable to the inclusion of fillers, but some may be related to the different structures of indigo. Substitutions at different ring positions as well as transformations to leuco forms can results in shifts in the long-wavelength visible and UV bands[57]. As mentioned previously, the inclusion of wheat starch impacted the UV fluorescence properties of indigo. In IRR, the soluble forms of indigo were slightly less reflective than the insoluble forms. Generally, indigo and PB had very similar behaviors in most MBI techniques, with the exception being MBR. Indigo, like ultramarine and smalt, was bright white in MBR, but Prussian blue was a medium grey. However, recent research by Salas in 2020 suggests that MBR is not consistently reliable for identifying indigo from other blue colorants, as the bandwidth being examined is too broad for clear distinction [58]. Litchfield blue, a mixture of PB and indigo, behaved more like PB in MBR. Mrs. Stewart's properties were consistent with the sample of PB; under infrared illumination, PB and Mrs. Stewart's did not reflect at all, unlike all other samples. They also did not exhibit any visible light-induced luminescence in the IR range.

Both FCUV and FCIR are useful in identifying ultramarine from the other blue samples; in both images ultramarine had a distinctive color from the other blues. The starches and gums had noticeably different behaviors from each other in FCUV and FCIR.

Table 9. Multiband Imaging Results

	Technique									
Sample	**UVL Short-wave**	**UVL Long-wave**	**UVR**	**VIL**	**IRR**	**IRL**	**MBR**	**FCUV**	**FCIR**	**Vis**
PB + Indigo + GA (Litchfield)	NT	NT	LT	NT	LT	NT	LT	Blue	Grey	Purple-blue
Ultramarine + Glycerol + dextrin	NT	ST	ST	NT	ST	LT	BT	Teal	Pink	Vibrant Blue
Ultramarine + Glucose + Sodium bicarbonate	NT	LT	ST	NT	ST	LT	BT	Teal	Pink	Vibrant Blue
Ultramarine + GA	LT	ST	HT	NT	ST	ST	BT	Teal	Pink	Vibrant Blue
Ultramarine + GA+ Wheat Starch	LT	ST	HT	NT	ST	ST	BT	Teal	Pink	Vibrant Blue
Ultramarine + GA + Potato Starch	LT	ST	HT	NT	ST	ST	BT	Teal	Pink	Vibrant Blue
Ultramarine + Gum Tragacanth	LT	ST	HT	NT	ST	ST	BT	Teal	Pink	Vibrant Blue
Ultramarine + Carrageenan	LT	ST	HT	NT	ST	ST	BT	Teal	Pink	Vibrant Blue
Prussian Blue +GA	NT	NT	LT	NT	NT	NT	ST	Blue	Dark Blue	Blue-grey
Indigo Sulfate + GA	NT	NT	LT	LT	LT	LT	BT	Blue-grey	Light Purple	Purple-blue-grey
Indigo (insoluble) + GA	NT	NT	LT	LT	ST	LT	BT	Blue-grey	Light Purple	Purple-blue-grey
Indigo (insoluble) + GA + Wheat Starch	BT	ST	NT	NT	ST	LT	BT	Blue-grey	Light Purple	Purple-blue-grey
Smalt + GA	NT	LT	ST	NT	LT	LT	BT	Light blue	Purple	Dark blue
GA	BT	BT	ST	HT	HT	HT	NT	Medium Grey	Light Grey	Clear
Gum Tragacanth	BT	BT	ST	HT	BT	BT	NT	Medium Grey	Light Grey	Clear
Carrageenan	BT	BT	HT	HT	BT	BT	NT	Light Grey	Light Grey	Clear
Wheat Starch + GA	HT	BT	HT	HT	BT	BT	NT	White	White	White
Potato Starch + GA	BT	BT	HT	HT	BT	BT	NT	White	white	White
Reckitt Crown	LT	LT	HT	HT	ST	ST	BT	Teal	Pink	Vibrant Blue
Reckitt's and Coleman	LT	ST	ST	NT	ST	ST	BT	Teal	Pink	Vibrant Blue
Aniline	BT	BT	ST	BT	BT	ST	LT	Teal	Light Pink	Light blue-purple
Mrs. Stewart's	NT	LT	LT	NT	NT	NT	ST	Dark Teal	Dark Blue	Dark Purple-blue

Key:

UVL – Ultraviolet Luminescence
UVR – Ultraviolet Reflectance
VIL – Visible-induced Luminescence
IRR – Infrared Reflectance
IRL – Infrared Luminescence
MBR – Multiband Image Retraction
FCUV – False Color Ultraviolet Reflectance
FCIR – False Color Infrared Reflectance
VIS – Visible Light Image

NT – No transmittance (i.e. black in image)
LT – Little transmittance
ST – Some transmittance
HT – High Transmittance
BT – Bright Transmittance (i.e. white in image)

Descriptions based on color seen in image.

FORS

Notes on the spectra can be found in Table 10 and the spectra can be seen in the appendix. FORS is a valuable tool for comparing colorants, but may not be discerning for distinguishing binders and additives or instances of colorant combination. The sample of Litchfield Blue showed that the PB effectively masked the peaks associated with indigo.

The two commercial samples Reckitt's Crown and Reckitt's and Coleman had noticeable differences; the spectrum of the Reckitt's and Coleman sample was similar to the samples of ultramarine that had been mixed with gum Arabic and starches and the absorbance bands in the VIS range were shifted to slightly higher wavelengths than the Reckitt Crown sample. The dextrin mucilage sample had a lower overall reflectance, indicating it was darker in color, than the other ultramarine-based samples.

Results in general were slightly hard to discern from the interference of the matt board. Most of the binders and starches were very similar to each other, as well as to the matt board. It is possible the matt board itself was sized with a starch or binder when made, or that the matt board was causing general interference. Although some samples were painted out in various thicknesses, only one section, Litchfield Blue, was tested in thick and thin applications with FORS, but the results showed notable differences between those readings. The thinner application had much higher reflectance levels in the 400-600 nm VIS range and in NIR than their thicker counterparts, likely due to the matt board's interference.

Table 10. FORS Results

Samples	Notes:
PB + Indigo + GA (Litchfield)	Generally darker overall (low reflectance). Slight reflectance peak around ~420 nm. No reflectance in NIR. Slight gradual rise beginning around ~1250, absorption bands around 1920, 2100, 2270, 2370, 2410, 2490
Ultramarine + Glycerol + dextrin	Mid-range reflectance in UV. Broad absorbance from ~480- 650. High reflectance in IR. Wide absorbance bands ~1410. Strong absorbance bands ~1920, 2090, 2280, 2320
Ultramarine + Glucose + Sodium bicarbonate	Mid-range reflectance in UV. Broad absorbance from ~480- 650. High reflectance in IR. Wide absorbance bands ~1410. Narrow absorbance bands ~1920. Slight peak ~2200
Ultramarine + gum	Mid-range reflectance in UV. Broad absorbance from ~480- 650. High reflectance in IR. Wide absorbance bands ~1410. Strong absorbance bands ~1920, 2200
Ultramarine + gum + wheat	Mid-range reflectance in UV. Broad absorbance from ~480- 650. High reflectance in IR. Wide absorbance bands ~1410. Strong absorbance bands ~1920, 2200
Ultramarine + GA + Potato Starch	Mid-range reflectance in UV. Broad absorbance from ~480- 650. High reflectance in IR. Wide absorbance bands ~1410. Strong absorbance bands ~1920, 2200
Ultramarine + Gum Tragacanth	Mid-range reflectance in UV. Broad absorbance from ~480- 650. High reflectance in IR. Wide absorbance bands ~1410. Strong absorbance bands ~1920, 2200
Ultramarine + Carrageenan	Mid-range reflectance in UV. Broad absorbance from ~480- 650. High reflectance in IR. Wide absorbance bands ~1410. Strong absorbance bands ~1920, 2200
Prussian Blue + GA	Low reflectance in UV. Slight reflectance peak around 420, then low absorbance levels until 1400. Absorbance bands ~1910, 2020, 2090, 2140, 2270, 2370, 2410, 2480
Indigo Sulfate (soluble) + GA	Low reflectance in UV. Low reflectance in VIS. Reflectance peaks up a lot ~720nm. High reflectance in NIR. Broad absorbance ~1420. Narrow absorbance bands ~1930, 2100, 2270, 2340
Indigo (insoluble) + GA + Wheat Starch	Low reflectance in UV. Low reflectance in VIS. Reflectance peaks up a lot ~720nm. High reflectance in NIR. Broad absorbance ~1420. Narrow absorbance bands ~1930, 2150, 2270, 2340
Indigo (insoluble) + GA	Low reflectance in UV. Low reflectance in VIS. Reflectance peaks up a lot ~720nm. High reflectance in NIR. Narrow absorbance bands ~1570, 2020, 2120
Smalt + GA	Smalt had highest variation in reflectance, likely because of its coarseness and naturally reflective nature. Mid-range reflectance in UV. Broad absorbance from ~500- 690. High reflectance from 900-1150, but general absorbance from 1200 to 1900. Reflective in FIR (1900-2490)
GA	Generally reflective in VIS. Low reflectance in UV. Slight absorbance between 400 and 450 nm. Reflective in NIR. Absorbance bands around ~1210, 1460, 1770, 1930, 2100
Gum Tragacanth	Generally reflective in VIS. Low reflectance in UV. Slight absorbance ~1210. Absorbance bands~1480, 1780, 1920, 2100, 2280, 2340, 2490
Carrageenan	Generally reflective in VIS. Low reflectance in UV. slight absorbance between 400 and 450 nm. Reflective in NIR. Broad absorbance bands between ~1420 and 1480. Narrow absorbance bands ~1920, 2100, 2270, 2490
Wheat + GA	High reflectance in VIS range. Slight absorbance between ~450 and 470. High reflectance in NIR. Broad absorption bands from ~1475 to 1600 nm. Narrow absorption bands around ~1940 and 2100, 2270, and 2340 and 2480
Potato + GA	Generally reflective in VIS. Low reflectance in UV. Shoulder of slight absorbance from 410-460. Slight absorbance ~1210. Absorbance bands ~1480, 1780, 1920, 2100, 2280, 2340, 2490
Reckitt's Crown (unbound)	Mid-range reflectance in UV. Broad absorbance from ~500-700. Slight absorbance peak ~1430. Strong peak ~1920. Slight absorbance around 2110, 2280, 2340
Reckitt's and Coleman (Unbound)	Mid-range reflectance in UV. Broad absorbance from ~480- 650. High reflectance in IR. Very slight absorbance bands ~1410, 1950, and 2230.
Meadowblossom Aniline	Broad absorbance between ~550 and 675. High reflectance in IR. Broad absorbance bands ~1580, narrow bands around ~1930, 2110, 2270, 2345, 2490
Mrs. Stewart's	Low reflectance in UV. Slight reflectance peak around 420, then low absorbance levels until 1100. Absorbance bands ~1440, 1480, 1760, 1910, 2100, 2270, 2370, 2490
Matt Board Reference	Low reflectance in UV. Shoulder of slight absorbance from 410-460. Slight absorbance ~1210 Stronger peaks around 1490, 1940, 2150, 2280, 2340, 2490. Similar to starches. Possibly sized?

BLUE COLORANTS IN COLLECTIONS: A CASE STUDY OF OBJECTS FROM THE CARLOS MUSEUM

BACKGROUND

In 2020, Michael C. Carlos Museum at Emory University decided to launch investigations into blue pigments in their African Art collection. Eleven polychrome wooden objects were chosen for study, described in Table 11, originating from four different cultural groups across central and west Africa. The objects were sampled as part of an initial 2020 undergraduate research project by Markaila Farnham under the supervision of Renée A. Stein, Director of Conservation and Chief Conservator. Farnham performed XRF readings by sampling the objects directly with a Bruker AXS portable XRF spectrometer and analyzing them with Viewspec software and FTIR spectroscopy by removing colorant samples and analyzing them with Thermoscientific Nicolet iN10 Infrared Microscope FTIR spectrometer and OMNIC Pecta software[59]. In 2022, I continued this examination by conducting polarized-light microscopy and reviewing the data collected by Farnham.

RESULTS AND DISCUSSION

The analysis results are in Table 11.

The choice of colors in most of these works was influenced by culturally-specific color symbolism. As Moyo Okediji writes on Yoruba chromacy: “Color is approached as disjunctive phenomena separate from other cultural apparatuses, but is regarded as an intrinsic expression of potent cosmic forces which permeate the whole of Yoruba culture”[60]. However, in many central and west African cultures, the symbolic importance of a color is determined by the optical properties of the color, not the material origin of the colorants (although the rarity of historic media influence the perceived value of a color)[60]. The primary blue colorants identified in this area prior to colonial contact are primarily species of indigo and other plant-derived dyes, such as *Rothmannia Longiflora* and *Cremaspora Triflora[60].* These could be used to create deep, dark blues or mixed with chalk or kaolin to create light blues. Colorants may have been applied by sculptors, but were more likely applied by ritual practitioners or spiritual leaders[60]. Colonialist powers operating in West and Central Africa had strong active trade operations with Europe in the 19th and 20th century, and synthetic colorants such as PB and ultramarine would have been available in regions with strong trade operations in the late 19th century. The cultural significance of LB to colonial missions was discussed previously, and the market for LB on the African continent was powerful and Reckitt's opened offices in South Africa and Nigeria in the late 1800s.

A complication for study often seen in ritual objects from central and west Africa arises from the cultural practices of continuously re-painting and surface treating objects as part of traditional care and maintenance practices. Objects associated with ritual use may also have had various other materials applied to their surfaces as part of their life-use. Another complication arises from the broad use of pesticides. Copper acetoarsenate, zinc phosphide, zinc hexafloursilicate, and various sulfur compounds were relatively common pesticides used in museums in the 19th and 20th centuries[61]. Potassium, chlorine and calcium peaks, also often seen in XRF, are likely from additives that may have been mixed directly with colorants or contaminants from other colorants.

Kaolins are clays consisting of layered alumino-silicate minerals found commonly in central and west Africa. They were used as both white pigments (which could be mixed with blue colorants to brighten them), fillers for paints, and ritual application materials. In IR spectra they present O-H stretching peaks indicative of hydroxyl groups between 3500 and 4000 cm-1, O-H deformations about 1636 cm-1, and hydroxyl stretches around 910 and 930[62]. They also present Si-O stretching peaks between 980 and 1115 cm-1 and between 690 to 730cm-1[62]. Titanium, manganese, iron, calcium, and potassium are common trace elements in kaolin [62]. These peaks may be easily confused with those of ultramarine or smalt, particularly if they are mixed together.

Table 11. Analysis of Blue Colorants Sampled from Michael C. Carlos African Art Collection

Catalog Number	2016.036.004	1999.003.056	1994.004.607
Object Title	Male Mask	Mask	Mask
Origin	Central Africa, Democratic Republic of the Congo	Central Africa, Democratic Republic of the Congo	West Africa, Liberia
Culture	Kongo	Pende	We
Period/ Date	Unknown	Unknown	20th Century
Area Sampled	Proper Right Eye	Blue Pigment	Ear/ Horn
XRF Major Peaks	K, Ca, Mn, Fe	Ti, Fe, Zn, As, Kr, Ca, Cu, Sr	Ca
XRF Minor Peaks	S, Cu, Cl, Co	S, K	S, Fe, Cu
XRF Discussion	Cu likely from pesticide treatment, but may be associated with PB. Co, may be related to PB. Mixtures of chalks, gypsum and clays likely present.	As, Cu, Zn likely correlated with pesticide. Fe associated with PB. Other elements likely traces from clay.	S and Fe likely associated with ultramarine. Ca may be associated with chalk or gypsum. Cu may be pesticide residue.
FTIR Bands	687m, 697m, 783m, 912m, 1007s, 1030s, 2080w	1069m, ~1330m,~1410m, ~1620m, 2084vs, ~3350vwbr	671m, 697w, 757w, 806w, 1000s, 1109m
FTIR Discussion	Database had no reliable matches. Likely a mixture of materials. The ~2080 peak is suggestive of CN triple bonds, so Prussian blue likely present. The bands seen at 1007 may relate to Si-O-Si or Si-O-Al bonds found in ultramarine or kaolin.	Strong band at 2084, correlated with PB in database. 1069 Si-O stretching, ~1330, ~1410 and 3350 associated with O-H hydroxyl groups. Kaolin likely present.	80% match in database to ultramarine. Bands assignable to Si-O-Si or Si-O-Al bonds found in ultramarine or kaolin.
PLM Discussion	In PPL, blue particles are very fine-sized, vibrantly colored, with a crumb-like texture. Particles form aggregates. Isotropic in XPL. Large-grained, birefringent, ovoidal starch grain identified, as well as translucent crystalline inclusions of heterogenous size.	In PPL, blue particles are very fine-sized, brightly colored, with a crumb-like texture. Particles form angular aggregates/ Isotropic in XPL.	In PPL, blue particles are very fine-sized, vibrantly colored, with a crumb-like texture. Particles form aggregates/ Isotropic in XPL. Inclusions of fine to medium-fine sized, triangular particles with rounded edges that have 1st-order birefringence.
Tentative Blue Colorant Assignments	Mixture of ultramarine, PB, clay, and large-grained starch	Prussian Blue, Kaolin	Ultramarine with unknown additives.

Catalog Number	1994.004.113	2017.032.128	1994.004.423
Object Title	Mask	Male Shrine Figure	Post with Figures
Origin	West Africa, Liberia	West Africa, Nigeria, Ilobu	West Africa, Nigeria
Culture	We	Yoruba	Yoruba
Period/ Date	Late 19th-Early 20th Century	20th century	Unknown
Area Sampled	Proper Right Eyebrow	Coiffure/ Hat	Blue Pigment
XRF Major Peaks	Fe	Fe	Fe
XRF Minor Peaks	S, K, Ca, Cu, Cl, Co	Ca, Cu	S, Ca, Co, Ru, Cl, K, Cu, Zn, Sr
XRF Discussion	Fe and S likely associated with ultramarine. Co, Cl, and K may indicate smalt. Ca likely relates to gypsum or chalk inclusions.	Fe likely correlates with ultramarine. Ca with gypsum or chalk. Cu possibly pesticide residue.	Fe, S likely associated with indigo. K, Ca, Si likely associated with chalk or kaolin. Cu, S, and Zn may be pesticide residue.
FTIR Bands	983s	665m, 684m, 703m, 730m, 765m, 918m, 1011s, 1456w, 1540m, 1635m, 2920w, 3292wbr	698m, 749m, 878m, 1003s, 1065s, 1612m, 1625m, 3300w
FTIR Discussion	The band seen at 983 likely relates to Si-O-Si or Si-O-Al bonds found in ultramarine.	Database had no reliable matches. Likely a mixture of materials, including ultramarine and kaolins.	The database found matches up to 76% with natural indigo. Bands consistent with Si-O bonds and hydroxyl groups suggest kaolin inclusions.
PLM Discussion	In PPL, most blue particles are very fine-sized, vibrantly colored, with a crumb-like texture. Some particles are very fine-sized, but appear more angular. All particles form aggregates. Isotropic in XPL. Inclusions of course-grained, triangular particles visible that may be smalt, but the blue particles (likely ultramarine) bind to the surface, obscuring features.	In PPL, blue particles are very fine-sized, vibrantly colored, with a crumb-like texture. Isotropic in XPL.	Very fine, medium blue particles with crumb-like texture in PPL. Center of particles has bronze coloration. Particles often form aggregates. In high magnification, particles seen to be somewhat angular. Isotropic in XPL.
Tentative Blue Colorant Assignments	Ultramarine with unknown additives. Possibly smalt, as well.	Ultramarine with unknown additives.	Indigo with unknown inclusions (possibly kaolinite?)

Catalog Number	2017.032.059	1994.004.718	1993.003.024
Object Title	Male Twin Memorial Figure (Ere Ibeji)	Twin Memorial Figure (Ere Ibeji)	Shango Wand (Oshe Shango)
Origin	Unknown	West Africa, Nigeria, Egbado, Ilaro vicinity	West Africa, Nigeria, Ekiti Region, Odo Owa
Culture	Yoruba	Yoruba	Yoruba
Period/ Date	Unknown	Late 19th century	Unknown
Area Sampled	Coiffure	Coiffure	Blue Pigment
XRF Major Peaks	Fe	Fe	Fe, K, Ca
XRF Minor Peaks	K, Ca, Si, S, Cu, Zn	K, Ca, Cu	
XRF Discussion	Indigo with unknown inclusions (possibly kaolinite?)	Potassium and calcium likely from clays or carbonates.	The minimal amount of minor and trace elements suggests this pigment may have less clay components.
FTIR Bands	698m, 749m, 878m, 1003s, 1065s, 1612m, 1625m, 3300w	690s, 713m, 731m, 745m, 778m, 798m, 811m, 849m, 865m, 917m, 957m, 988m, 1005s, 1036s, 1057s, 1078m, 2076m	659m, 678m, 690m, 916m, 1004s, 2070m, 3300vwbr
FTIR Discussion	The database found matches up to 76% with natural indigo. Bands consistent with Si-O bonds and hydroxyl groups suggest kaolin inclusions.	Database had no reliable matches. Likely a mixture of materials. The 2070 peak is suggestive of CN triple bonds, so Prussian blue likely present. The band seen at 988 and 1005 may relate to Si-O-Si or Si-O-Al bonds found in ultramarine or kaolin.	Database had no reliable matches. Likely a mixture of materials. The 2070 band is suggestive of CN triple bonds, so Prussian blue may be present. The band seen at 1004 may relate to Si-O-Si or Si-O-Al bonds found in ultramarine or kaolin.
PLM Discussion	Very fine, medium blue particles with crumb-like texture in PPL. Center of particles has bronze coloration. Particles often form aggregates. In high magnification, particles seen to be somewhat angular. Isotropic in XPL.	Blue particles are fine-grained with crumb-like texture, often adhered to a medium-grained, translucent, white crystalline particle that is not birefringent. Inclusions of medium-sized, spherical particles identified as likely starch grains.	In PPL, vibrant blue particles are very fine-sized, vibrantly colored, with a crumb-like texture. Particles form aggregates. Isotropic in XPL.
Tentative Blue Colorant Assignments	Indigo with unknown inclusions (possibly kaolinite?)	Mix of PB and other blue colorants, including ultramarine, and medium-grained starch inclusions.	Mixture, may include ultramarine and PB.

Catalog Number	1994.004.776	1994.004.723
Object Title	Efe/Gelede Headdress, Apasa	Male Twin Memorial Figure (Ere Ibeji)
Origin	West Africa, Nigeria	West Africa, Nigeria, Illobu
Culture	Yoruba, Ohori	Yoruba, Oyo, Ogbomoso or Ilobu
Period/ Date	Late 19th-Early 20th Century	Early 20th century
Area Sampled	Hair (XRF), Proper left cheek (PLM)	Coiffure
XRF Major Peaks	Ca, Fe	Fe, K, Ca
XRF Minor Peaks	K, Ti, Zn, Si	S, Si, Ti, Cu, Zn
XRF Discussion	Zn may be related to pesticide treatment, but may also be an inclusion of PB. Si, Ti, Ca likely from kaolin, gypsum, and/or chalk.	Cu Zn, and S likely related to pesticides. Fe, S, and Si relate to ultramarine. Other peaks likely relate to chalk and kaolin.
FTIR Bands	664s, 718m, 765m, 917m, 956m, 1015m, 1048m, 1083m, 2080w, ~3300wbr	983s
FTIR Discussion	Database had no reliable matches. Likely a mixture of materials. The 2070 peak is suggestive of CN triple bonds, so PB may be present. The weak band around 3300 may relate to N-H bonds of indigo.	71% match rate with ultramarine. Major band consistent with Si-O-Si and Si-O-Al bonds of ultramarine.
PLM Discussion	In PPL, dark blue, very fine-sized particles that form medium-sized aggregates. Difficult to distinguish individual particles. Isotropic in XPL.	In PPL, blue particles are very fine-sized, vibrantly colored, with a crumb-like texture. Particles form aggregates. Isotropic in XPL.
Tentative Blue Colorant Assignments	PB and possibly indigo	Ultramarine
Key: *XRF – X-Ray Fluorescence Spectroscopy* *FTIR- Fourier-Transformed Infrared Spectroscopy* *PLM- Polarized Light Microscopy* *strong; m, medium; w, weak; v, very; sh, shoulder; br, broad; d, doublet*[6]		

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[6] These assignments are subjective. At the time of analysis, the author was unaware of best practices and did not clarify the percentages for each assignment. Software access was later limited, so the data could not be clarified prior to publication.

DISCUSSION AND CONCLUSION

Although it is a relatively common practice for conservators or curators working with African collections to label ultramarine as "laundry bluing," bluing products were not uniform in composition, and did not always include ultramarine. The small sample of commercial products purchased for this research had significantly different make-ups, and inclusions identified included starches, carbonates, and salts, all products that may have been found in paints sold in other contexts. Further, many LB commercial products available in the latter half of the 19th century were made with recipes often identical to or only negligibly different from products marketed to European or American artists. As a practice, it is recommended to identify blue colorants by the pigments used, as that information will be more relevant for the care and study of materials. The immediate assignment of the "laundry bluing" designation to any late 19th or 20th century ultramarine pigments in works should be avoided, unless there is appropriate context to support that claim. Scientific investigation alone cannot readily distinguish laundry bluing derived-pigments from other blue pigments; historical documentation must be consulted to conclude a work was made with laundry bluing-derived pigments.

This study sought to understand the composition and dissemination of commercial and homemade LB products. Results comparing methods for identifying different recipes using noninvasive and invasive analytical techniques indicate the extent to which characterization is possible and demonstrates some of the complexities of analyzing unknown blue colorants. PLM and XRF alone are not sufficient techniques for distinguishing between all of the blue colorants explored in this paper. The morphology of indigo, ultramarine, and PB are similar at the micro scale, and have the same major elemental peaks in XRF spectra. FTIR was valuable for distinguishing colorants, but required invasive sampling. With the suite of MBI techniques, all blue colorants could be readily distinguished from each other, but binders/ additives/ and mixtures of colorants were not distinguishable . In the case of the historic recipe Litchfield blue, no technique used was reliable for consistently identifying both indigo and PB in combination without careful analysis; the characteristics of PB shielding those of indigo. However, it is not unexpected that African objects would have both blue colorants and this possibility should be considered when studying works. For example, Yoruba masks and ritual objects, such as those studied from the Carlos Museum African collections, are often re-painted as part of their life use, and the colorants of each successive coating may not be identical. The common presence of starches in LB may obfuscate efforts to analyze other starches associated with an object's use or life history.

Understanding the nuances of the working properties of materials is useful for art historians and artists, and is best achieved through experimental approaches. The potato starch was noted to be stiffer to handler, making it more difficult to integrate into the paint, and it is likely that any LB recipes that used large molecular-grained starches would have been less preferable than those made with finer-grained starches. Gum tragacanth does not bind as well as gum Arabic when dry, so the resulting products have more of a pastel-like, chalky texture. The samples made with glycerol reacted with atmospheric moisture, and appeared glossy and wet for long periods.

NEXT STEPS

It is well known that artists all over the world experiment with newly introduced colorants. In many cultures, color carries significance and meaning and it may be of interest to study the impact of new colorant technologies on the symbolism and meaning of color in cultural heritage works.

The identification of binders and additives in cultural heritage works is important for the study of provenance, authenticity, and preservation strategies. Future research into LB-derived pigments may include a deeper exploration into the variations in commercial products. Continued exploration of the colorants found in the Carlos Museum samples may include further analysis using additional analytical methods.

APPENDIX

Abbreviated Colorant Histories

ANILINE

In 1856, then-aspiring English chemist William Perkin, and student of the organic chemist responsible for understanding the structure of many dyes, August W. Hofmann, transformed the coal-derivative aniline into a mauve dye, heralded as the first true synthetic dye. Organic chemists of the industrial revolution scrambled to create higher-yield, lower-cost aniline dyes in other colors, and the first blue aniline-dyed fabrics began appearing in Paris and London just a few years later[24]. Dye manufactures in Europe dominated most of the commercial markets through the late 19th and early 20th century, and their products quickly spread across much of the world[35].

HEXACYANOFERRATE PIGMENTS

The story of Prussian blue (PB)'s invention has taken on a mythical mystique, but the most likely story involves a fortuitous accident in the Berlin laboratory of the alchemist Johann Konrad Dippel ca. 1706 CE [26]. Chemist Joh. Jacob Diesbach, was preparing a lake pigment with contaminated ingredients and noticed the resulting mixture produced a blue precipitate[26] Diesbach and another partner, Johann Leonhard Frisch, improved the method in the following years and began selling the pigment to artists as early as 1709. Although Diesbach and Frisch were zealous in keeping the production method a secret for roughly 20 years, John Woodward published a procedure for manufacturing Prussian blue in 1724 [26], prompting broad PB production by both professional and amateur chemists using a variety of production methods.

SYNTHETIC INDIGO

In 1870, German chemists Adolf Van Baeyer and Adolph Emmerling developed a synthetic approach to producing indigo from isatin. Baeyer expanded his work to produce a synthetic indigo from phenylglycine-o-carboxylic acid, and sold the patent to German chemical manufacturer Badische Anilin- und Soda-Fabrik (BASF), which began production in 1897 [63]. Further work by Swiss chemist Karl Heumann that utilized sodium hydroxide in the process made the process more affordable[22], [63] Improvements in the process developed in 1901 by Johannes Pfleger, who worked for BASF rival Hoeschst, allowed for large-scale, low-cost production of synthetic indigo the following year[63].

SMALT

Pliny the Elder recorded the presence of brilliant blue glass in his first century text, and there is evidence of cobalt blue glass in Germany in the 10th century CE and Persia in the 12th century CE, but it was not likely wide-spread until the 16th and 17th centuries [18], [64].

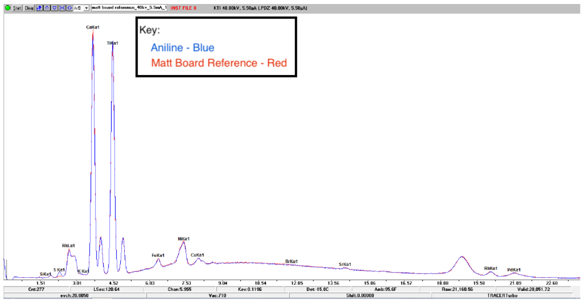
ULTRAMARINE

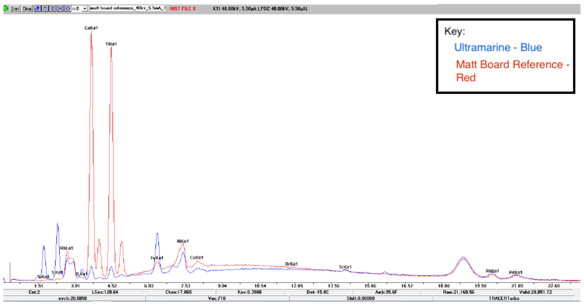
Prior to the early 19th century, the most stable blue mineral pigment with a consistent deep blue color was derived from lapis lazuli, a complex, metamorphic rock characterized as a mineralized limestone that contains various silicate minerals and a significant amount (>25%) of the blue, cubic mineral lazurite, a complex sulfur-containing aluminum silicate ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$) [65] Lapis lazuli was principally mined in a desolate province of modern-day Afghanistan, and was exported across Asia, Europe, and Africa for millennia to be used as a precious stone for ornamentation. Although lapis was traded as a gem since antiquity, the earliest documented used of lapis lazuli as a pigment dates to the 6th century C.E. in Afghanistan. However, the extensive transport and complexity of the processing needed to create a stable paint from the raw material made natural ultramarine one of the most expensive pigments in the world.

Although there are observations of accidental ultramarine by-products created during the manufacture of lime in Palermo, Italy being used for decorative work as early as 1787 the idea that ultramarine could be intentionally manufactured did not capture imaginations until 1824, when the chemist Vauquelin published confirmations that by-products from another soda kiln in Saint Gobin, France were extremely similar to natural ultramarine[18]. The Société d'Encouragement pour l'Industrie Nationale in France offered a prize for a reproducible recipe for synthetic ultramarine, and on February 4, 1828 the society awarded the prize to Jean Baptiste Guimet. A month after Guimet received the award, Christian Gottlob Gmelin, published a slightly different synthesis method[28]. In 1828, the Meissen porcelain works in Germany, under the direction of the chemist F.A. Köttig, who had published his own ultramarine synthesis method in 1829, began manufacturing the pigment using Gmelin's method and in 1830 Guimet began production at a factory in Fleurieu-sur-Sâone, France. Although early recipes and production methods were zealously guarded, Gmelin's recipe was eventually published in a pharmaceutical guide by Robiquet in 1833[28], [66]. A year later, the pigment was on the palette of prominent British painter J.W. Turner. Within a decade, other factories in France, Germany, England, Belgium, Austria, and the U.S.A. were churning out affordable batches of a colorant once thought inaccessible to all but the wealthiest in the world.

However, the tinting strength of artificial ultramarine was notably greater than natural ultramarine and price difference significant, making natural ultramarine demand drop sharply.

XRF Spectra


Key:
Aniline - Blue
Matt Board Reference - Red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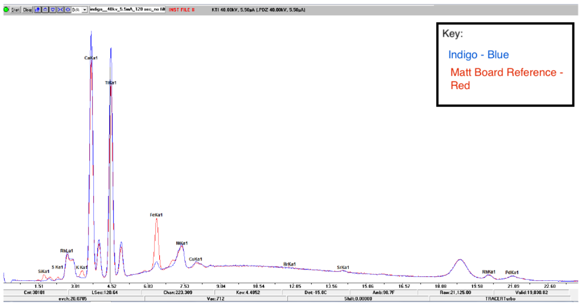
Matt Board Reference - Red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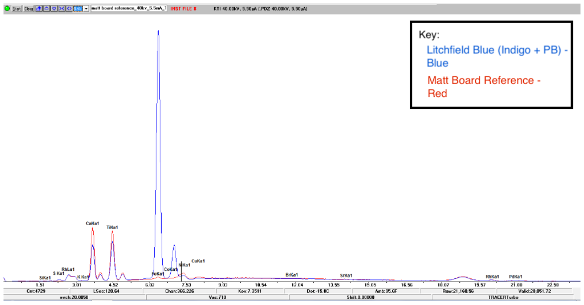
Matt Board Reference - Red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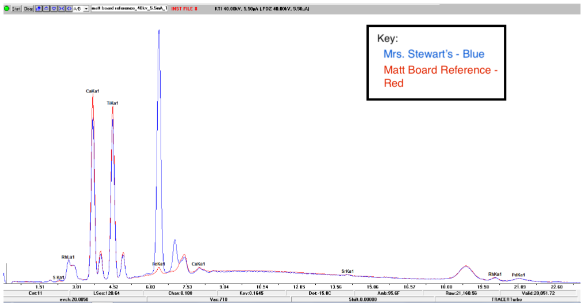
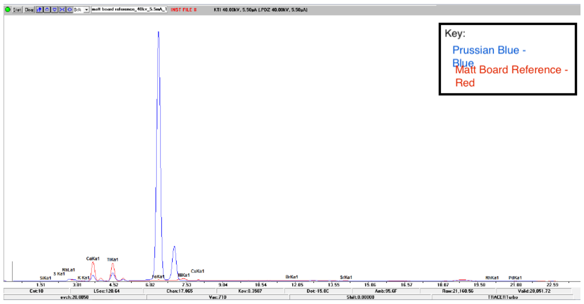
Litchfield Blue (Indigo + PB) - Blue
Matt Board Reference - Red


Key:
Mrs. Stewart's - Blue
Matt Board Reference - Red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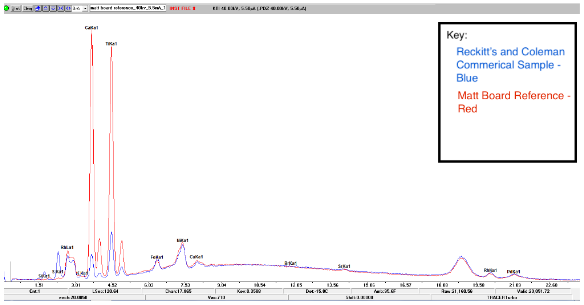
Matt Board Reference - Red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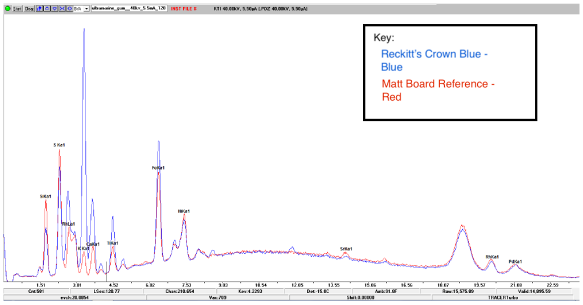
Reckitt's and Coleman Commerical Sample - Blue
Matt Board Reference - Red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Reckitt's Crown Blue - Blue
Matt Board Reference - Red

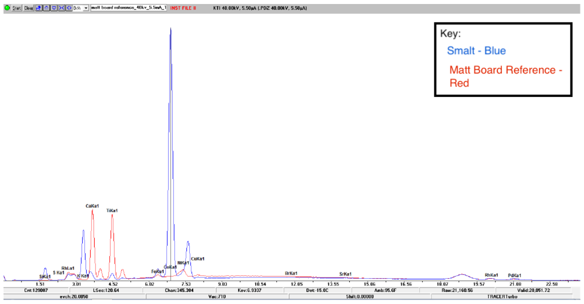

Figure 2. XRF Spectra of Samples

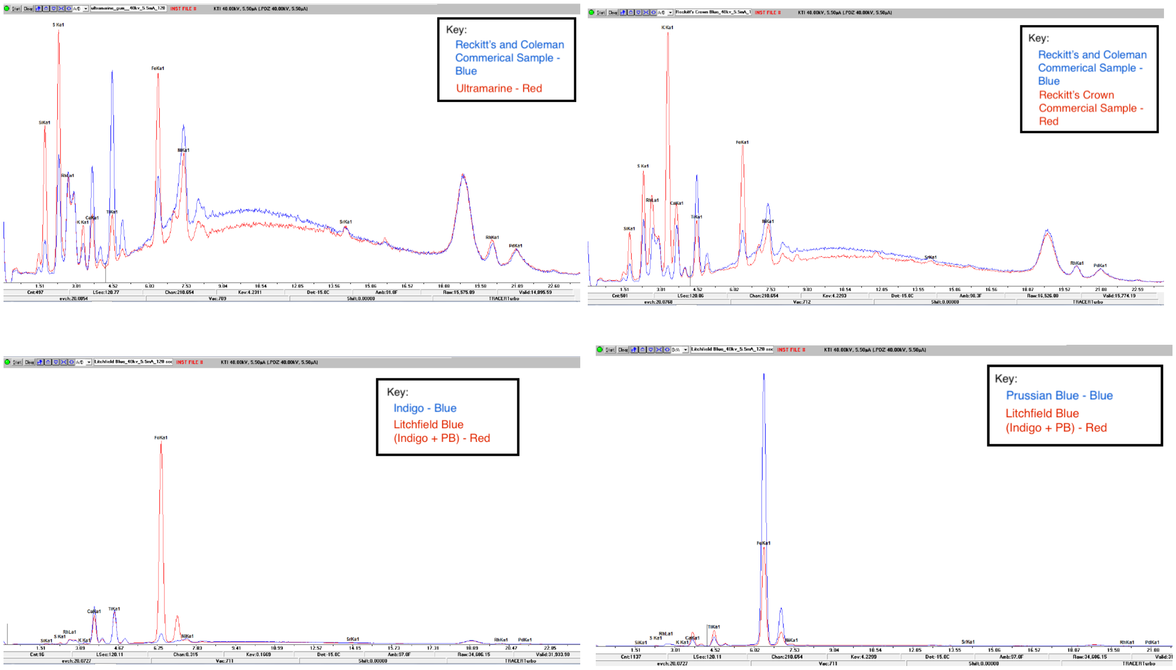

Figure 3. Comparative XRF Spectra

FTIR Spectra[7]

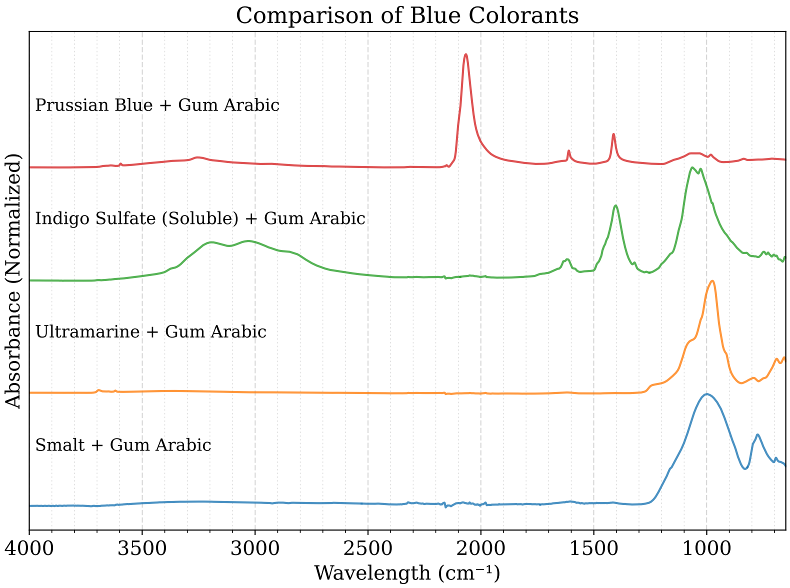

Figure 4. Comparison of FTIR Spectra of Blue Colorants

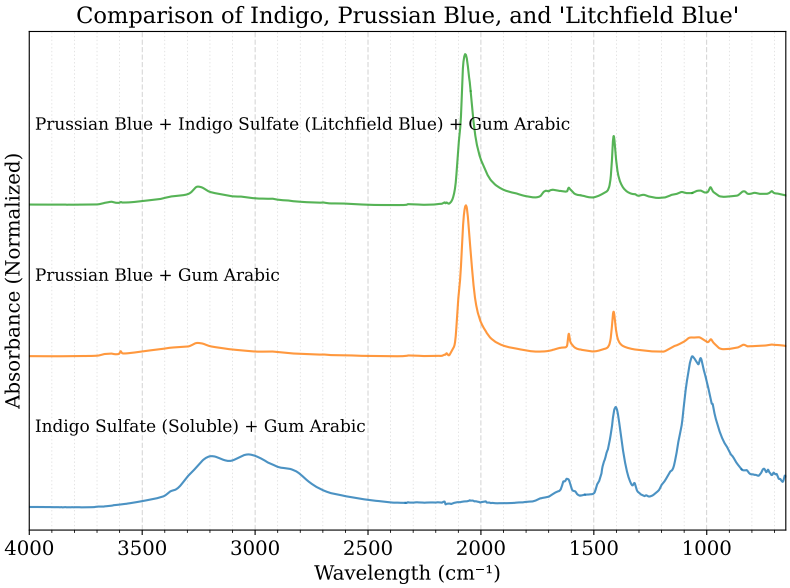

Figure 5. Comparison of FTIR Spectra of Indigo, Prussian Blue, and "Litchfield Blue" (Mixture of Indigo and Prussian Blue)

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[7] The FTIR spectra captured for the aniline, insoluble indigo, and Mrs. Stewart's could not be displayed.

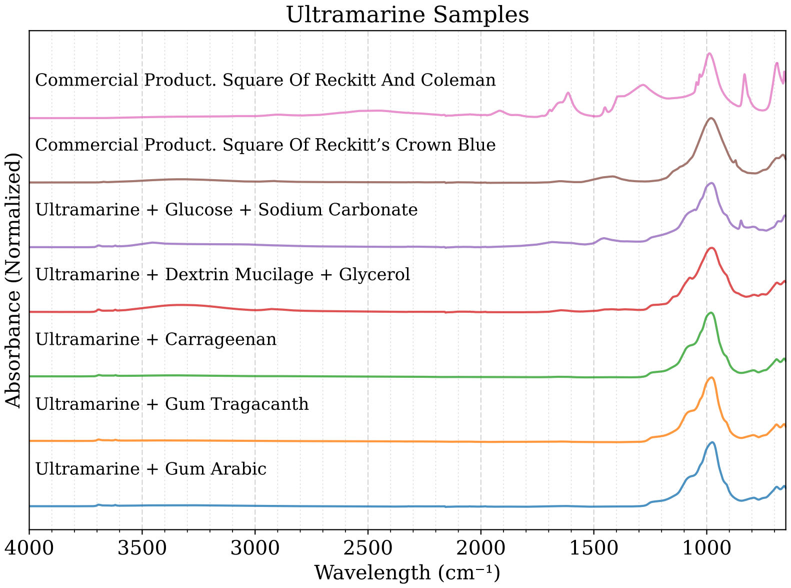


Figure 6. Comparison of FTIR spectra of Ultramarine-based Samples and Commercial Products

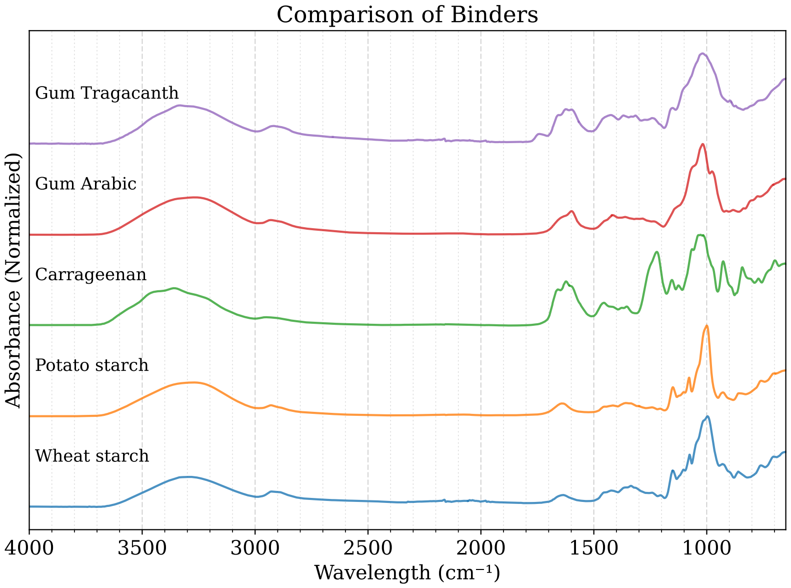


Figure 7. Comparison of FTIR Spectra of Binders

MBI Images

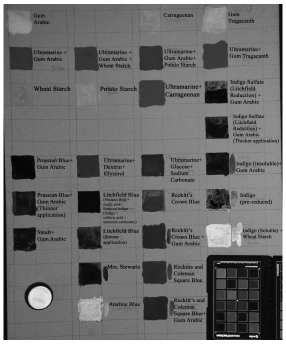
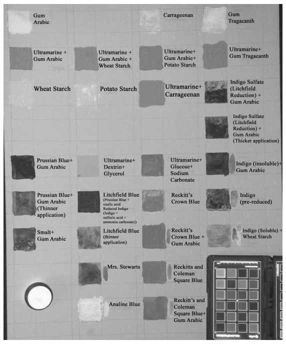
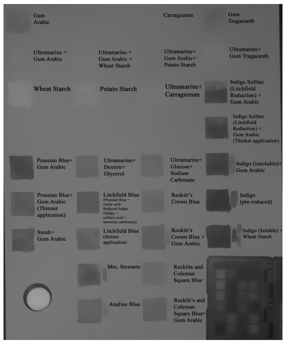




Figure 8. Ultraviolet-Induced Luminescence Short-wave (UVL SW), Figure 9. Ultraviolet-Induced Luminescence Long-wave (UVL LW), Figure 10. Ultraviolet Reflectance (UVR)

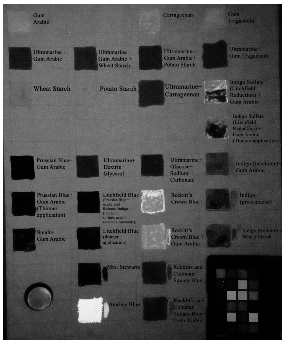
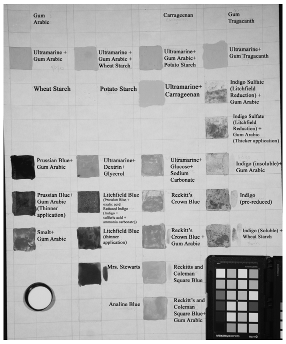




Figure 11. Visible Light (VIS), Figure 12. Visible-Induced Luminescence (VIL),Figure 13. Infrared Reflectance (IRR),

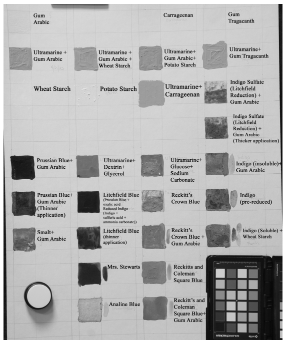
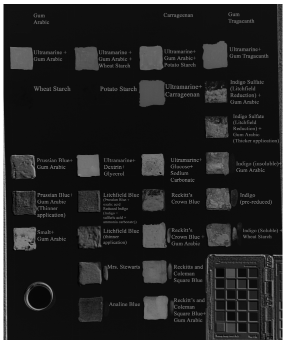
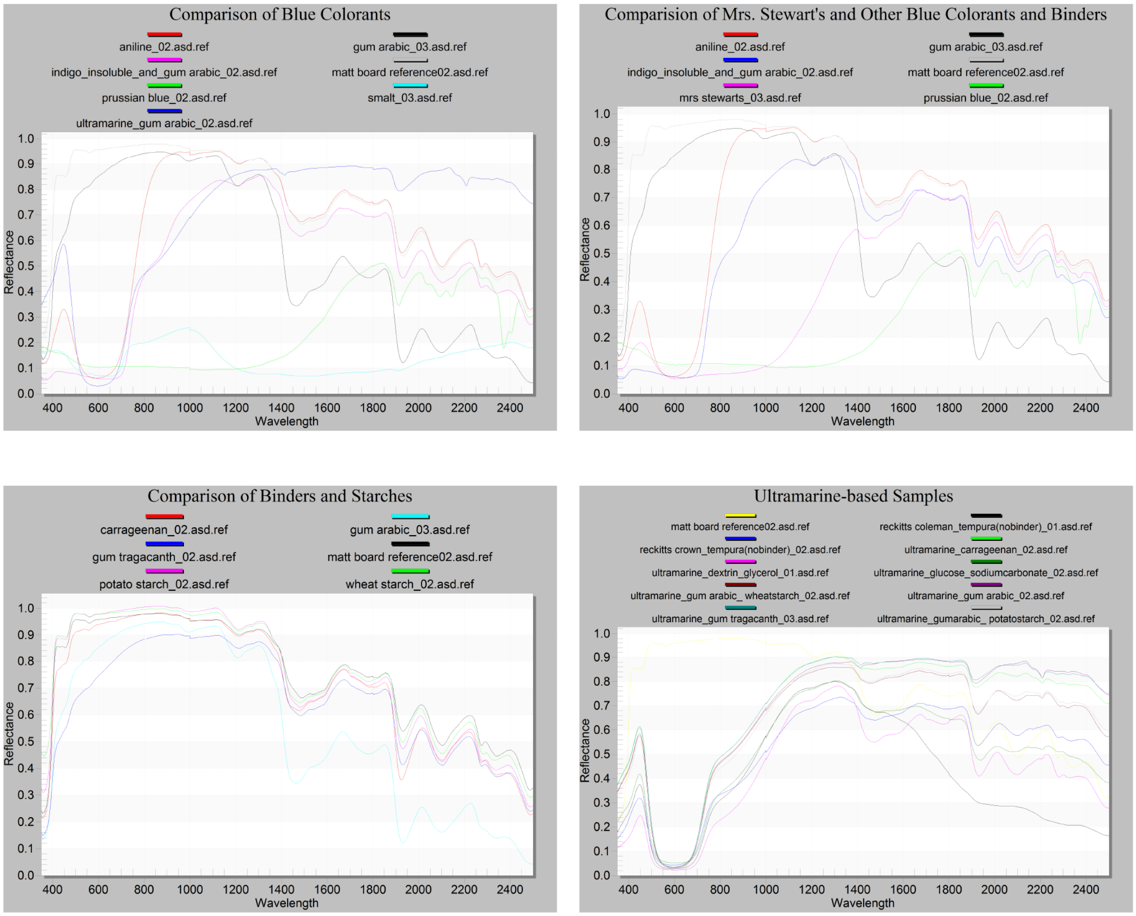



Figure 14. Infrared Luminescence (IRL), Figure 15. Multiband Reflectance Image Subtractions (MBIR)

Figure 16. False Color Ultraviolet Reflectance (FCUV), Figure 17. False Color Infrared Reflectance (FCIR)

FORS Spectra

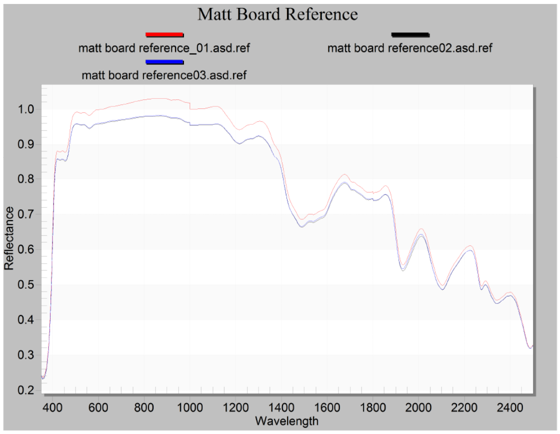

Comparison of Blue Colorants

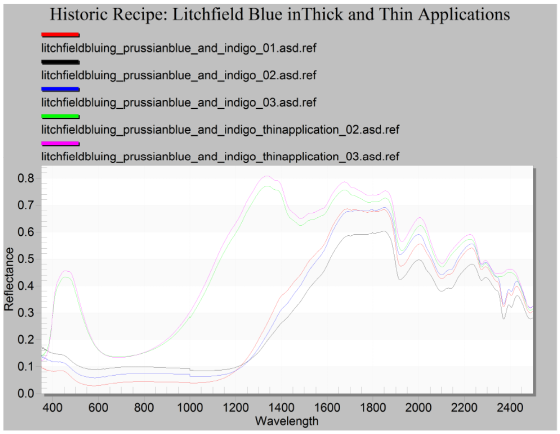
Comparision of Mrs. Stewart's and Other Blue Colorants and Binders

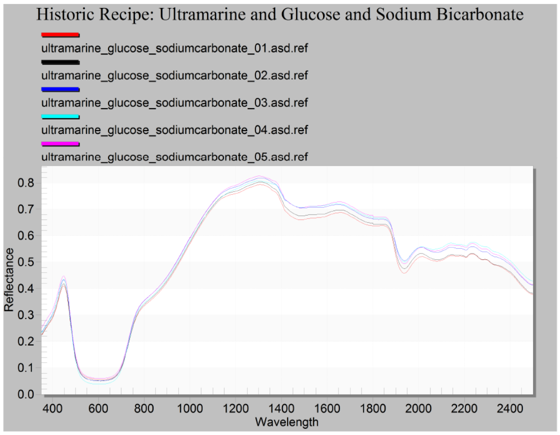
Comparison of Binders and Starches

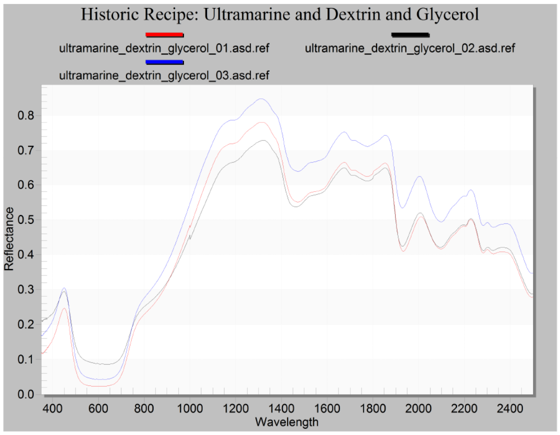
Ultramarine-based Samples

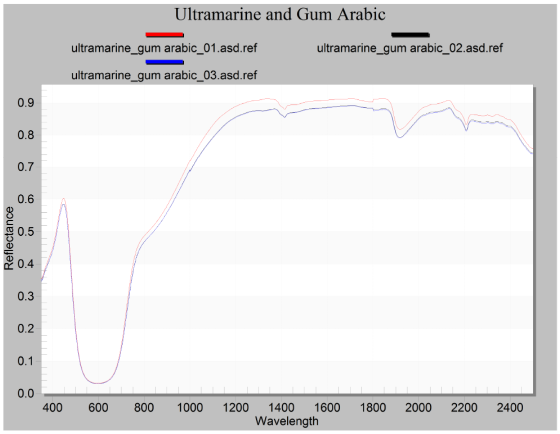
Figure 18. Comparative FORS Spectra

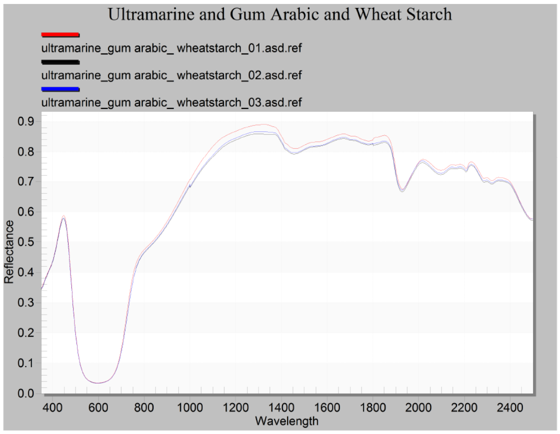

Matt Board Reference

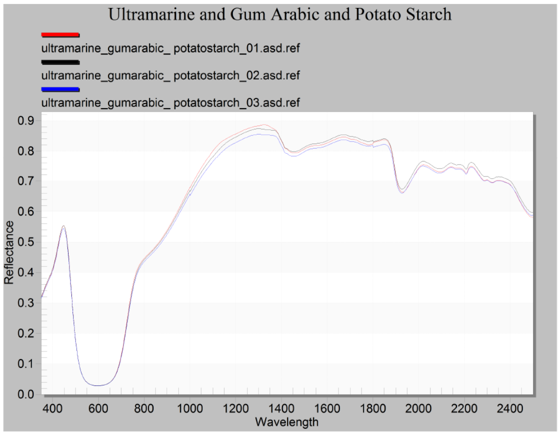

Historic Recipe: Litchfield Blue inThick and Thin Applications

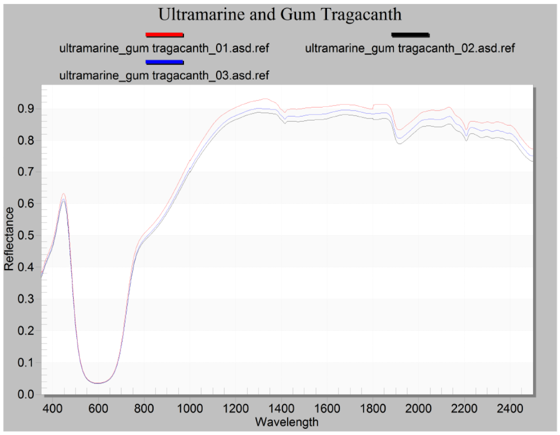

Historic Recipe: Ultramarine and Glucose and Sodium Bicarbonate

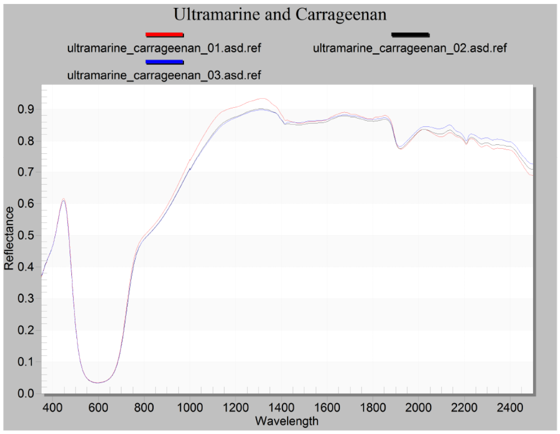

Historic Recipe: Ultramarine and Dextrin and Glycerol

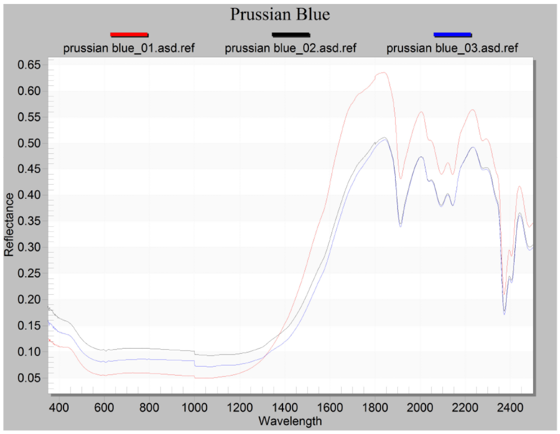

Ultramarine and Gum Arabic

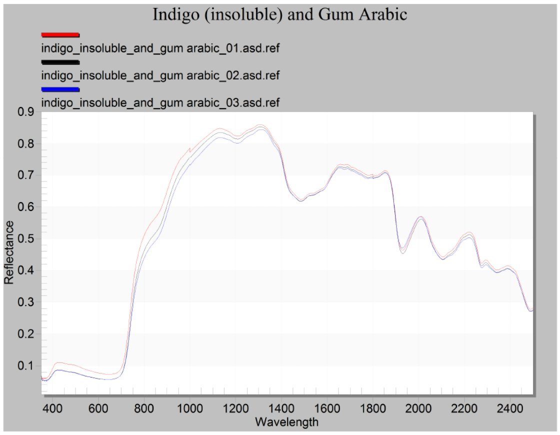

Ultramarine and Gum Arabic and Wheat Starch

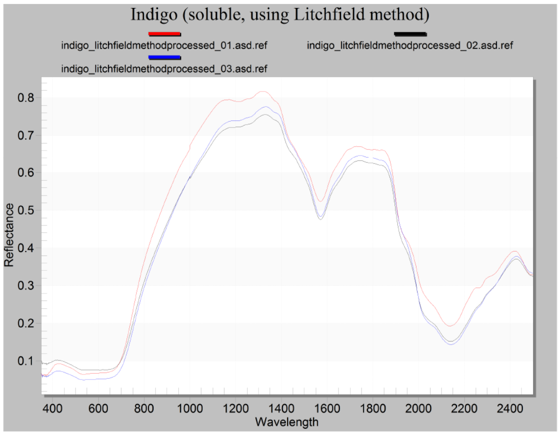

Ultramarine and Gum Arabic and Potato Starch

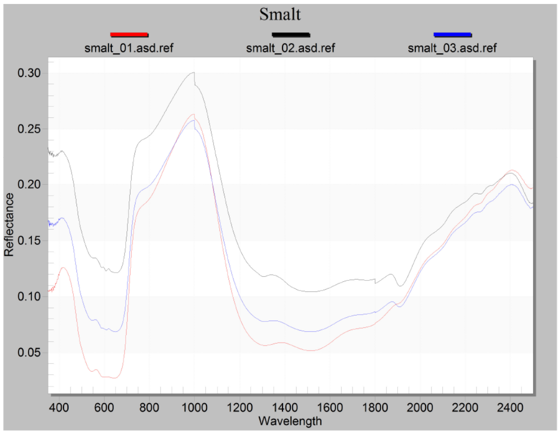

Ultramarine and Gum Tragacanth

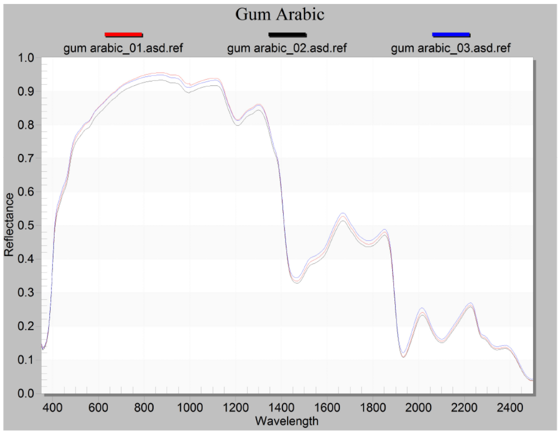

Ultramarine and Carrageenan
ultramarine_carrageenan_01.asd.ref
ultramarine_carrageenan_02.asd.ref
ultramarine_carrageenan_03.asd.ref
Reflectance
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Wavelength

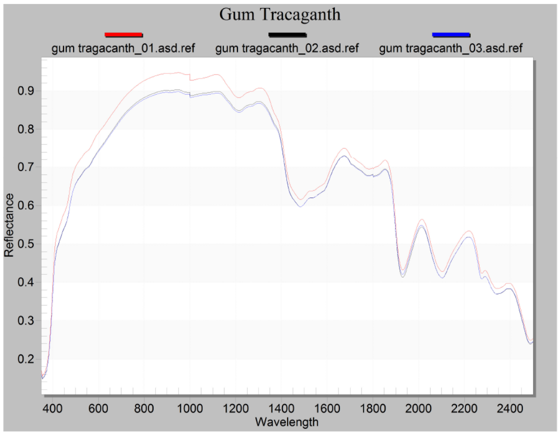

Prussian Blue
prussian blue_01.asd.ref
prussian blue_02.asd.ref
prussian blue_03.asd.ref
Reflectance
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Wavelength

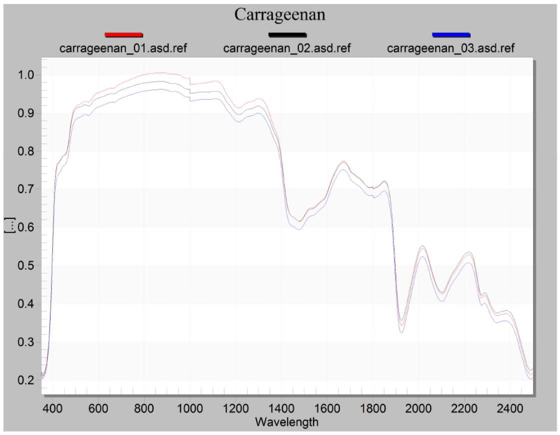

Indigo (insoluble) and Gum Arabic
indigo_insoluble_and_gum arabic_01.asd.ref
indigo_insoluble_and_gum arabic_02.asd.ref
indigo_insoluble_and_gum arabic_03.asd.ref
Reflectance
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Wavelength


Indigo (soluble, using Litchfield method)
indigo_litchfieldmethodprocessed_01.asd.ref
indigo_litchfieldmethodprocessed_02.asd.ref
indigo_litchfieldmethodprocessed_03.asd.ref
Reflectance
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Wavelength


Smalt
smalt_01.asd.ref
smalt_02.asd.ref
smalt_03.asd.ref
Reflectance
0.30
0.25
0.20
0.15
0.10
0.05
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Wavelength


Gum Arabic
gum arabic_01.asd.ref
gum arabic_02.asd.ref
gum arabic_03.asd.ref
Reflectance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Wavelength


Gum Tracaganth
gum tragacanth_01.asd.ref
gum tragacanth_02.asd.ref
gum tragacanth_03.asd.ref
Reflectance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Wavelength


Carrageenan
carrageenan_01.asd.ref
carrageenan_02.asd.ref
carrageenan_03.asd.ref
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Wavelength

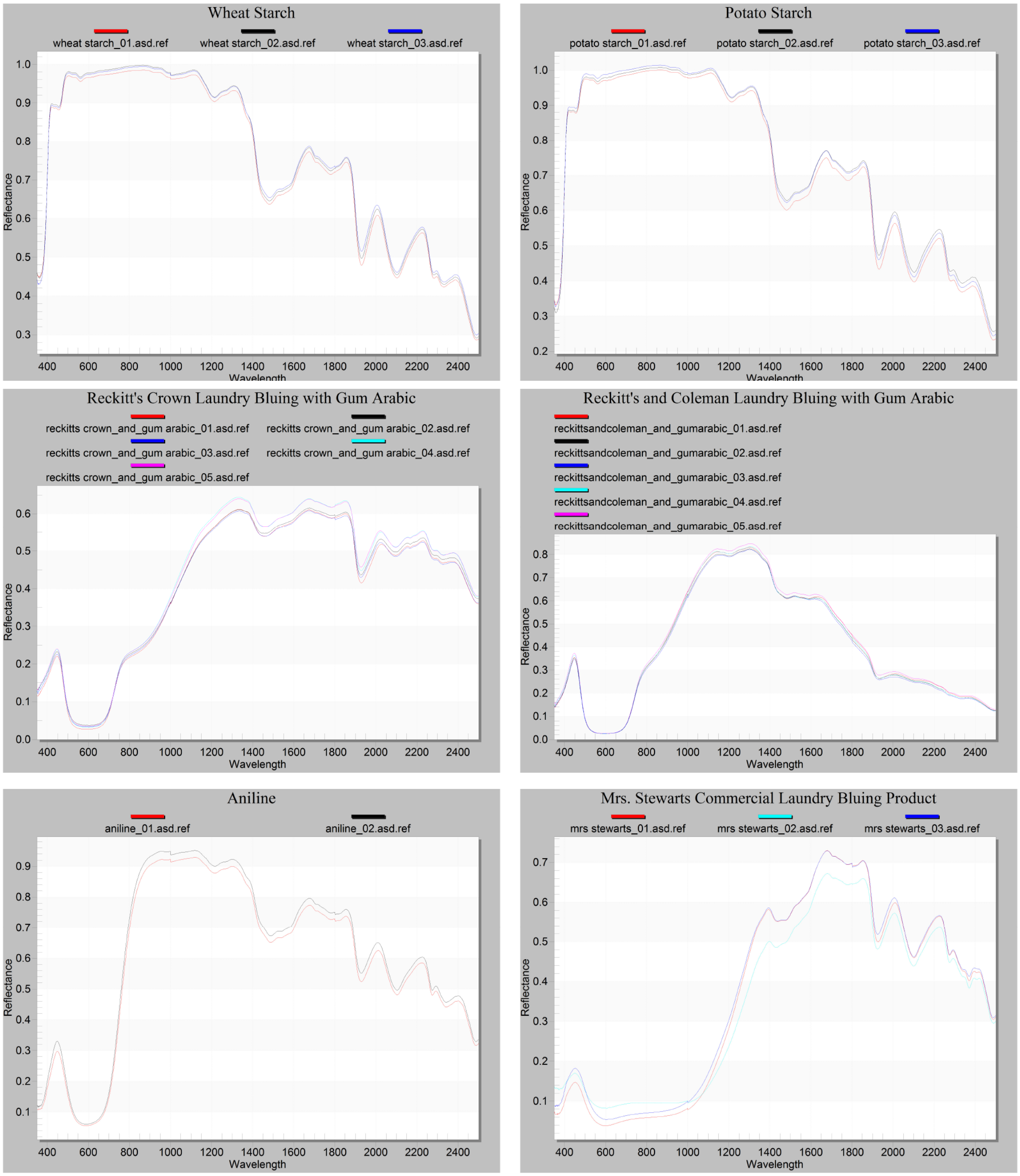


Figure 19. FORS Spectra of All Experimental Samples

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