J. Coat. Technol. Res., **20** (5) 1595–1609, 2023
https://doi.org/10.1007/s11998-023-00765-8

Traditional science in pigments and recipe of painting woodcarving in medieval Assam, India

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Received: 14 November 2022 / Revised: 11 January 2023 / Accepted: 14 January 2023

Abstract A painting tradition of medieval Assam, popularly known as Hengul-Hāitāl, has been studied with an aim of restoring and conserving centuries-old woodcarvings and Sāncipat manuscripts for preserving in ordinary open conditions at villages and Vaishnavite monasteries. The pigments, their combinations for producing various shades and the resulting colors have been characterized using various physicochemical techniques. The study unravels some interesting traditional science, such as, using red Hengul (cinnabar), yellow Hāitāl (yellow orpiment) and blue Nīl (Indigo or Prussian blue) as primary colors to produce any desired shade, inclusion of either or both of Hengul and Hāitāl in every shade to repel fungi and insects, applying Kharimāti (a clay) as a wood-primer for better painting effects, choosing of Bael gum as a robust non-staining natural adhesive and finally varnishing with Lā (a natural lac) to protect the pigments from natural erosion and protect the woodcarving from humidity and contaminating hands touching them. The findings provide clues to develop an appropriate method of restoration of partially worn-out woodcarvings for preserving them in ordinary open conditions, based on the traditional method of preparation.

Keywords Traditional pigments, Traditional painting, Woodcarvings, Sāncipat manuscripts, Hengul-Hāitāl, Color analysis

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Introduction

Traditional pigments and other materials used in paintings by our ancestors are of great importance in terms of art history and art conservation.[1–3] The various pigments used in ancient prehistoric fine mural paintings in caves like those in Ajanta and Ellora and on the walls of temples and other monuments have drawn a great deal of interest.[3,4] The history of mural painting shows that there were various painting methods such as encaustic painting, tempera painting, fresco painting, ceramics, oil painting, etc.[5] Iron containing earth minerals with different hues are said to be the first pigments used by the prehistoric artist in the cave paintings.[6] Evidence of use of different colored rocks, different types of animal blood, charcoal, etc., have also been found in ancient cave paintings.[7] There is evidence of use of different types of red, yellow, black, blue and green pigments as well as of using egg yolk as a binder in the paintings.[3] The art of woodcarvings, often painted with pigments, is also believed to have originated from the beginning of human creation.[8–11]

Black, red, purple and yellow were the main colors used in the cave paintings of India during the stone age of about fifteenth century BC, including Bhimbetka in Madhya Pradesh and the Indus valley civilization in the 4th millennium BC.[12] Hengul, a hard red crystalline mineral, and Lapis Lazuli, along with a combination of red, blue, yellow, and green, were used in the contemporary cave paintings at Ajanta and Elora, in addition to colored clay and herbal dyes.[13] Other mineral and natural dyes used in ancient and medieval paintings include Manganese Black, Red Ocher, Egyptian Blue, Greek White, Yellow Ochre, Tyrian Purple, Cinnabar, Vermilion, Minimum, Black Ink, Gold, Green Earth, Logwood Black, Lead White, Titan Blue, Mummy Brown, etc.[14] In medieval India, various painting schools, including Rajasthani, Mughal, Pahari, Madhubani, and Patachitra, used a combination of mineral and plant dyes, including Hengul, Hāitāl, Lapis Lazuli, Nīl, and Indian Yellow.[15–17] Hengul, also called vermilion and cinnabar, is a complex, red, crystalline mineral, chemically mercuric sulfide.[13] Although it is also somewhat present in the Indian mountains, it is most common in China. Hāitāl, chemically arsenic sulfide, is a hard yellow crystalline mineral known as yellow orpiment, found in northern Meghalaya and Arunachal in northeast India.[10] Lapis Lazuli, a deep blue metamorphic rock containing mainly lazurite, calcite, sodalite, and metallic pyrite mineral components is found in abundance in Badakhshan, Afghanistan and was very popular among painters in Asia and Europe since ancient times as the color blue.[18,19] Nīl, an herbal dye (indigo) produced in India and some other parts of Asia, was also used in medieval period for blue color. However, it was probably replaced with synthetic Prussian blue dye after it became easily available.[20–22] Indian yellow, another yellow dye, was made of clay and urine of cattle, fed with mango leaf.[14]

In Assam, a north-eastern state of India, where different types of woods are abundant, there was a great medieval tradition of woodcarvings painted with some mineral and natural dyes.[10] These woodcarvings included Vaishnavite mythological characters and different utility items[10,23–25] (Fig. 1). Mural painting for a drama, Cihna-yatra of 1497 AD, by Srimanta Sankardeva, a Vaishnavite saint, is considered to be the oldest recorded paintings in Assam using the Hengul and Hāitāl.[26,27] These mineral dyes were available in the hills around Assam.[10] Records also say, Sankardeva and his disciple, Mādhavadeva used Hengul-Hāitāl in paintings on pillars and walls of Namghar, a kind of Vaishnavite community prayer house.[26] Blue, white, green, brown and black colors were also used along with Hengul and Hāitāl in Assam.[28] The most widely used and developed style of painting in Assam is known as Satria painting style.[29] There are records about the use of the different mineral colors and herbal dyes in Tai-Ahom style or royal style of Assamese paintings of contemporary or even older sub genres in the period of the fifteenth to the nineteenth century.[12,30,31] Nīl, the blue natural dye, was cultivated in Assam towards the end of the sixteenth century AD.[31] A white clay, Kharimāti, was used for the white color. The green color was derived by mixing Hāitāl and Nīl. Hengul and Hāitāl are still applied on the handle of a traditional hand-fan of Auniati Satra, Majuli.[31] Various brown shades were obtained by mixing Hengul and Hāitāl at different ratios. The black color was either carbon black or was derived by mixing Hengul, Hāitāl and Nīl. Bael glue, obtained from the Bael fruit (stone apple, *Limonia acidissima*), Outenga glue, obtained from the Outenga fruit (elephant apple, *Dillenia indica*) and Dhekiya glue obtained from gum of the fiddlehead fern were used as natural glue in medieval Assam.[10] The tradition of painting using these mineral and natural dyes gained much popularity in medieval Assam. These mineral and natural dyes became popular for using in mural paintings as well as miniature illustration in Sāncipāt manuscripts, a special kind of manuscripts with folios made of bark of Sānci or Agaru tree (*Aquilaria malaccensis* syn. *A. agallocha*), another medieval tradition in Assam. The tradition became known as Hengul-Hāitāl probably due to their attractive colors or their high cost, though there were some other ingredients too. Even today, people in Assam refer to the old tradition of painting as 'Hengul-Hāitāl lagōwā', where 'lagōwā' means to apply or to fix in Assamese.

There are several interesting things to note about the Hengul-Hāitāl painting tradition. Firstly, the tra-

Fig. 1: Traditional woodcarvings and other things painted with Hengul and Hāitāl. (a) Garud Pakhi deity at Auniati Satra, (b) Vaishnavite story in woodcarving on wall of Namghar, (c) pole of Namghar, (d) a Khōl (a lather musical instrument with lather at two ends of a hollow wood), (e) a folio of a Sāncipāt manuscript and (f) a box for preserving Sāncipāt manuscript

ditional knowledge of preparation of different shades of composite colors by mixing three primary colors, viz., red, yellow, and blue was known to them. Second, and perhaps more significantly, the choice of the antifungal and insect-repellent Hengul and Hāitāl for the red and yellow colors, respectively, and the inclusion of at least one of them for any shade of color, protected the woodcarvings from fungus and termites, which are common in a hot, humid climate like that of Assam.[11] Thirdly, the selection of a very robust and transparent adhesive of Bael (*Aegle marmelos*) gum which neither leaves any stain nor affects the color is important.[31] Fourthly, applying a primer coat is done in accordance with the custom of using inexpensive Kharimati as a primer coat before painting. Finally, ''Lā carōwā',' application of a final coating of Lā, a thin natural primer, protects the paints from natural erosion and also shields the hands of devotees of the idol woodcarvings or users of the utility materials with antifungal and insect-repellant Hengul and Hāitāl. We have observed heads of woodcarvings with hair painted with colors other than Hengul and Hāitāl, e.g., white using Kharimāti have been damaged by termites while those painted using composite colors containing Hengul or Hāitāl remain intact for centuries (Fig. 2).

With the passage of time, the tradition of Hengul and Hāitāl painting in Assam has become almost extinct due to increasing use of synthetic paints.[11] Nowadays, newly made Vaishnavite woodcarvings are often colored with synthetic paints. It is disappointing to note that hundreds of such heritage woodcarvings, some of them centuries-old, which were originally painted with the traditional pigments, are losing their original glaze due to natural weathering and dirt as they are always kept in open condition at Namghars, a community place of worship, and social and cultural activities in villages of Assam. Some of them are being destroyed slowly by fungus and termites as a passive air-conditioned environment is impractical in the rural set up of Namghars in villages and Satras, Vaishnavite monasteries in Assam. Unfortunately, many of such centuries-old heritage woodcarvings are often repainted by the Namghar authorities with synthetic paints destroying their antique look due to ignorance of the importance of heritage conservation or due to easy availability of synthetic paints, with the tradition of Hengul-Hāitāl painting at the verge of extinction.

The present work was aimed at studying the traditional science involved in the tradition of Hengul-Hāitāl painting including analysis of the ingredients, formulations, application, and effects of the paints which is expected to help in developing a suitable method for restoration of such partially damaged heritage woodcarvings reinstating their original look. The analysis of pigments in the present study was confined to samples locally available at stores of traditional items. Analysis of the pigments used in any piece of medieval woodcarving found in Assam was avoided as destructive sampling of pigments from heritage woodcarvings was not allowed and portable instruments required for non-destructive analysis on the spot were unavailable. We have also tried to characterize various formulations of the paints including synthetic and natural binder through physicochemical analyses including Hunter color analysis, zeta potential measurements, glossiness, and hiding power measurements.

Materials and methods

Materials

Three mineral pigments, viz., Hengul (HgS, cinnabar, vermillion), Hāitāl (As_2S_3, yellow orpiment) and Kharimāti ($Al_2Si_2O_{54}$, clay) and a natural dye, viz.,

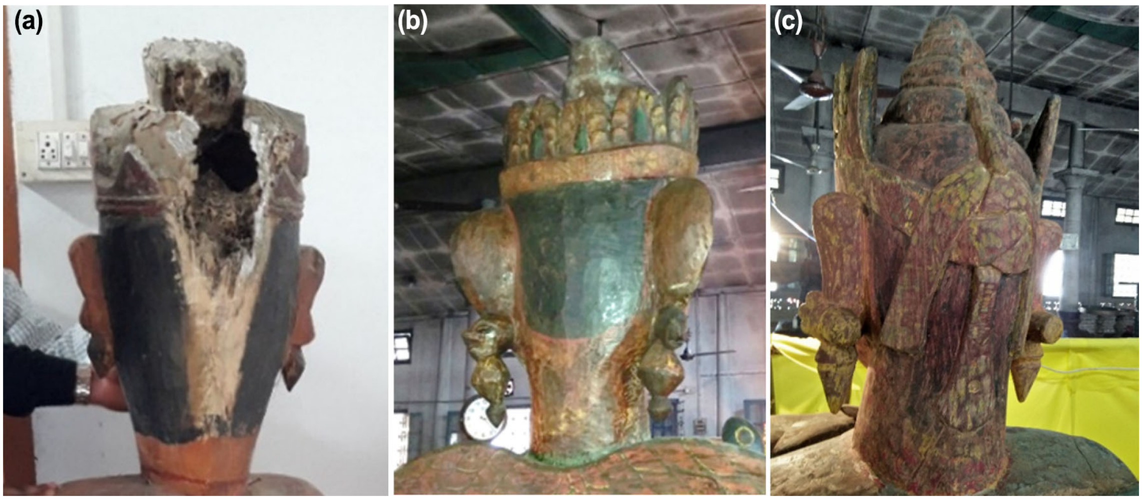


Fig. 2: Woodcarving at Boralimora Satra, Tezpur (≈1930AD, a) with head painted with Kharimāti damaged by termite while woodcarving at Bardowā Thān, Nagaon (1916AD, b) and (1833AD, c) painted with Hengul-Hāitāl remain intact

Nīl ($Fe_4[Fe(CN)_6]_3{\cdot}nH_2O$, Prussian blue) used in the present work were obtained from Kamakhya Bhandar, Nagaon (Fig. 3) though Indigo ($C_{16}H_{10}N_2O_2$) was used traditionally as Nīl. Stone mortar pestles were used to grind Hengul, Hāitāl, Nīl and Kharimāti. Bael gum was obtained from bael trees available in the Tezpur University campus. A synthetic adhesive, Fevicol, a polysaccharide-based glue, obtained from local market was also used for comparing with the natural gum. Distilled water was used in the study.

Instrumental analysis

Digital weight balance, model ME204, Mettler Toledo, was used for weighing. A Hegman grind gauge was used to measure how finely the pigments were ground (ASTM Test Method D-1210). Using a Perkin Elmer spectrophotometer model Frontier MIR FIR and the conventional KBr pellet method, FTIR spectra with a resolution of 4 cm^{-1} and in the range of 400–4000 cm^{-1} were captured. At room temperature, the powder X-ray diffraction (P-XRD) study was carried out using the D8 FOCUS, Bruker AXS, Germany (Software XRD COMMANDER 2, DIFFRAC.EVA.). Further analysis of the X-ray diffraction spectra recorded in the D8 Focus Spectroscope with XRD COMMANDER 2 and DIFFRAC.EVA software was performed using PCPDF-WIN software. A platinum crucible containing 3–4 mg of sample was heated to 600°C at a rate of 20°C per minute while being exposed to a dynamic nitrogen atmosphere flowing at a rate of 30 mL per minute using the Japanese company TGA 50 to record thermal curves (TG/DTG). The dyes' Raman-active vibrational modes have been measured using a Raman spectrophotometer model Renishaw basis series with 514 nm lasers (Software WIRE 3.4). Zeta potential and nano-particle size analyzer model Nanoplus-3 was used to measure the particle size and the zeta potential of the samples. The hiding power measurement was done using a Spectrophotometer, AGS, model X-Rite Ci200UV.

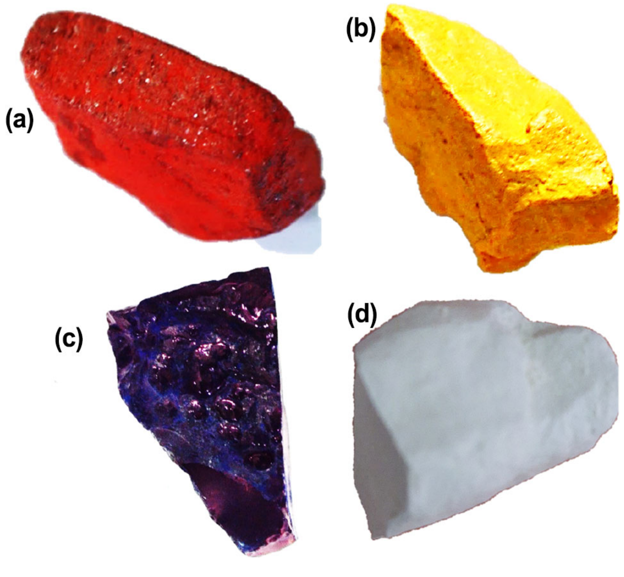


Fig. 3: Pieces of (a) Hāitāl, (b) Hengul, (c) Nīl and (d) Kharimāti

Preparation of shades of pigments with binders

A recipe of preparation of Hengul, Hāitāl, Kharimāti and Nīl as per the traditional method is briefed here. About 30 g of each of Hengul or Hāitāl is ground in a hard granite mortar manually into fine powder. About 50 mL of water is added to the natural dye powder and ground again for about half an hour. Then the mixture is allowed to settle down for about 10 min. The highly insoluble powdered dye settles down with scum appearing at the surface. The scum is removed by decanting to get cleaner powder. The pigment is ground again after replenishing the water. The process of removing scum is repeated until the scum disappears on grinding and the particle size is reduced to approximately 5–10 and 27–32 μm. For Kharimāti and Nīl, the grinding is simple, and the scum removal only needs to be done once. About 40 fresh and matured wood apples were cut cross-sectionally into two halves with a knife and the glue was squeezed out from around the seeds and collected in a ceramic bowl. About 20 mL of distilled water is added to 80 mL of pure glue obtained from Bael fruit and thoroughly mixed to get 100 mL of the natural glue, Bael gum. Various shades have been prepared by mixing the dyes in varying ratios together with a certain quantity of Bel gum as a natural binder (NB) and water as shown in Table 1. A wheat-based synthetic polysaccharide glue is also used as a synthetic binder (SB) in the place of the natural binder for comparison.

Hunter color analysis method

Colorimeter method or CIELAB system (UltraScan VIS, HunterLab, USA) was used to characterize the colors imparted by various compositions of the paints used in the study in terms of L^*, a^* and b^* scales.[32–34] Relative brightness is indicated on L^* scale. The range of 0–50 on the L scale reveals the darkness of the sample and the range of 51–100 on the L^* scale means lightness of the sample. a^* scale indicates redness vs greenness. The color and chroma of the object are represented by the (a^*, b^*) pair, also known as the yellow-blue x-axis and the red/green y-axis. The value of a^* can be either positive or negative. The positive value of a^* means redness and the negative value means greenness of the sample. Yellowness vs blueness is indicated on the b^* scale. The value of b^* can be either positive or negative. Here, yellowness is indicated by positive value and blueness indicated by negative value. The color characteristics of various

Table 1: Ratio of volumes of the pigments, binder, and water in mL mixed to prepare paints of various shades with their average (of at least four measurements) particle size measured in Hegman scale

Color	Hengul	Hāitāl	Nīl	Kharimāti	Bael gum	Water	Particle size (μm)
Red	1	–	–	–	1	–	7
Yellow	–	1	–	–	1	–	10
Blue	–	1	2	–	6	–	4
White	–	–	–	4	1	8	5
Brown	1	8	–	–	12	–	22
Green	–	6	1	–	9	–	32
Black	4	–	1	–	12	–	31

(–) indicates absence of the respective component in a particular shade

paints have been prepared separately using both Bael gum and the same amounts of the commercial starch-based gum for comparison. The h indicates hue angle, and it is given by

$$h = \tan^{-1}(b^*/a^*)$$

C^* is for chroma/saturation and a positive C^* indicates brightness while a negative C^* indicates dullness. C^* is given by

$$C^* = [(a^{*\wedge}2) + (b^{*\wedge}2)]^{1/2}$$

Measurement of hiding power

The hiding power or opacity of the paint formulations has been measured by contrast-ratio method using black and white opacity chart. The contrast ratio is calculated as the difference between the reflectance of paint backed by a completely non-absorbing white surface (R_w) and the reflectance of paint backed by a perfectly absorbing black surface (R_b). Opacity in percentage is defined as

$$\text{Opacity}(\%) = (R_b/R_w) \times 100$$

Results and discussions

A physicochemical characterization of the natural pigments used in the study has been presented here.

Morphological and elemental analysis

SEM images of Hengul, Hāitāl, Nīl and Kharimāti (Fig. 4) show the morphological structures of the pigments. The particles of Hengul, Hāitāl and Nīl have been found to be distinctly distributed while that of the particles of Kharimāti have been found to be spread smoothly and due to its cohesiveness and agglomeration, accurate particle size determination was not possible.[35] This is evidenced by the surface plot of all the samples obtained using ImageJ software. The particles of Hāitāl and Hengul are spread out almost equally. On the other hand, the size of the particle is the clearest and largest in Nīl. Figure 4 also includes the histogram of particle size distribution obtained using ImageJ software. The mean length of the particles of Hāitāl, Hengul and Nīl, estimated from ImageJ software, were 12.50 μm, 11.58 μm and 19.26 μm, respectively.

The atomic percentage of different elemental composition in different pigment can be seen in the EDX analysis results presented in Fig. 5. The EDX spectra shows the presence of 32.04:23.04 atomic percentage ratio of As to S in the sample of Hāitāl which is higher than the ideal atomic percentage ratio of 2:3 of the two elements in As_2S_3. The atomic percentages of Si, O and C present in atomic percentages of 0.89%, 7.25% and 36.78% in the sample of Hāitāl suggest presence of considerable amounts of impurities containing these elements. This correlates with the moderate crystallinity of Hāitāl obtained from XRD. Similarly, EDX of Hengul (Fig. 5b) shows 11.77:35.75 atomic percentage ratio of Hg to S in the sample of Hengul which is lower than the ideal 1:1 atomic percentage ratio in HgS. Here, the presence of elements C, O in atomic percentages 41.92 and 9.55, respectively, and also the presence of trace amount of Fe and As in atomic percentages of 0.03 and 0.98, respectively, again indicate presence of considerable impurities containing these elements in the sample of Hengul. The presence of the impurities is also reflected in the XRD data of Hengul. The atomic percentages of different elements present in Nīl found from the EDX spectra (Fig. 5c) are C (53.28%), N (6.50%), O (15.30%), Fe (24.91%). The observed atomic ratio of C:N:O of 52.28:6.50:15.30 in the sample of Nīl is far from the ideal atomic ratio of C:N:O of 8:2:1 to match with the molecular formula of Indigo ($C_{16}H_{10}N_2O_2$), which was traditionally used as Nīl. The ratio, however, is closer to Prussian blue of ($Fe_4[Fe\ (CN)_6]_3.\ nH_2O$) with some impurities of iron oxide. Kharimāti has shown the presence of C, O, Al, and Si in the atomic percentages of 28.58, 59.35, 5.40

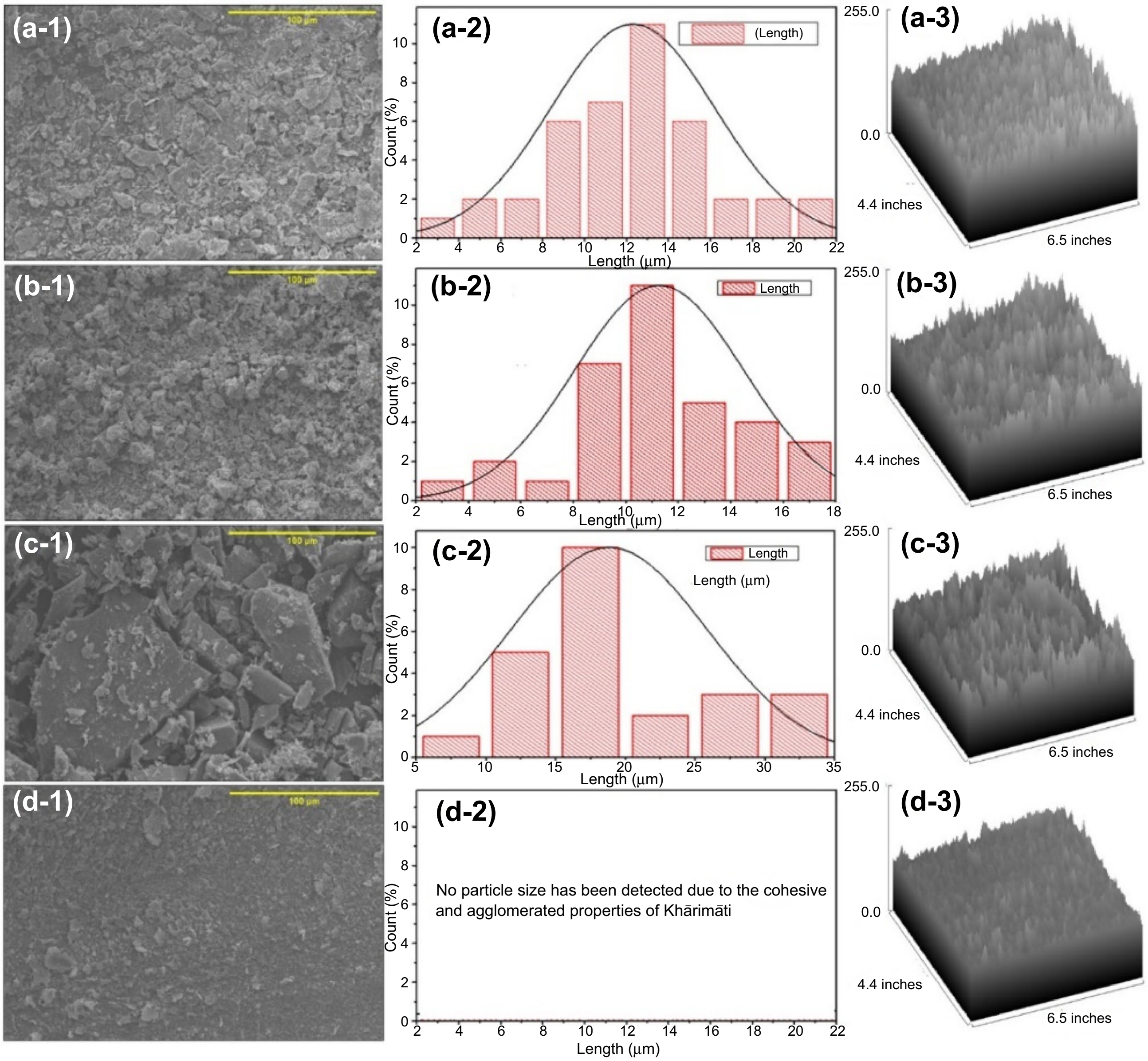
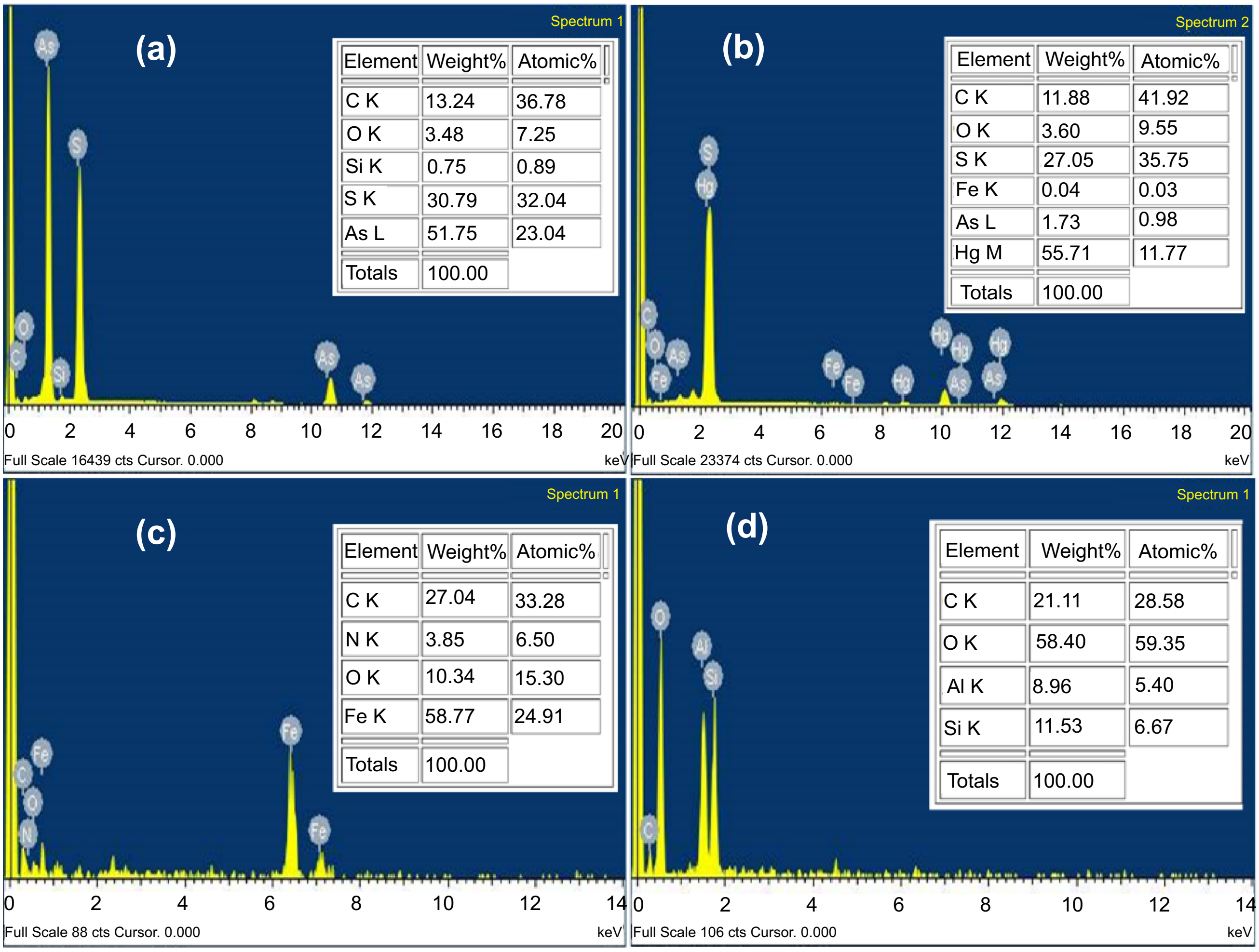


Fig. 4: SEM images of (A-1) Hāitāl, (B-1) Hengul, (C-1) Nīl and (D-1) Kharimāti at 100 μm scale; Histogram diagram of particle size distribution of (A-2) Hāitāl, (B-2) Hengul, (C-2) Nīl and (D-2) Kharimāti; surface plot of (A-3) Hāitāl, (B-3) Hengul, (C-3) Nīl and (D-1) Kharimāti

and 6.67 which is commensurate with the clay containing aluminosilicate with metal carbonates and oxides.

FTIR and Raman spectra

The FTIR spectra of Hāitāl, Hengul, Nīl and Kharimāti are shown in Fig. 6. The FTIR spectra of Hāitāl (Fig. 6A) show small peaks in the 1100–500 cm^{-1} range, which point to an arsenic-containing compound like As_2S_3.[36] The peak at 1098 in Fig. 6A indicates the presence of strong S=O stretching frequency[37] while the peak at 650–950 cm^{-1} range indicate the presence of As-O stretching frequency possibly due to aerial oxidation of surface molecules of As_2S_3.[36,38–40] On the other hand, cinnabar of HgS is not expected to show any major characteristic IR absorption.[40] However, some absorption bands have been observed due to the presence of moisture and other impurities. The small peak at 1406 cm^{-1} in Fig. 6B indicates the presence strong S=O stretching frequency of some sulfate groups associated with mercury containing compounds[38,41] caused by ariel oxidation of HgS. Similarly, the peak at 1030 cm^{-1} in Fig. 6B indicates the presence of Si–O stretching frequency.[42] In Fig. 6B, an absorption at 1639 cm^{-1} indicates the presence of some metal impurities in the form of a carbonate lattice related to calcite.[42] The FTIR spectra of Nīl (Fig. 6C) have one



(a)

Element	Weight%	Atomic%
C K	13.24	36.78
O K	3.48	7.25
Si K	0.75	0.89
S K	30.79	32.04
As L	51.75	23.04
Totals	100.00	

(b)

Element	Weight%	Atomic%
C K	11.88	41.92
O K	3.60	9.55
S K	27.05	35.75
Fe K	0.04	0.03
As L	1.73	0.98
Hg M	55.71	11.77
Totals	100.00	

(c)

Element	Weight%	Atomic%
C K	27.04	33.28
N K	3.85	6.50
O K	10.34	15.30
Fe K	58.77	24.91
Totals	100.00	

(d)

Element	Weight%	Atomic%
C K	21.11	28.58
O K	58.40	59.35
Al K	8.96	5.40
Si K	11.53	6.67
Totals	100.00	

Fig. 5: EDX analysis of (a) Hāitāl, (b) Hengul, (c) Nīl and (d) Khārimāti

sharp and broad peak in the 3100–3500 cm^{-1} range which indicates the presence of N–H stretching of secondary amines. Similarly, the peak at 1586 cm^{-1} indicates the presence of C=C stretching frequency. The peak at 1350–1000 cm^{-1} indicates the presence of C–N stretching. The presence of some C–H stretching frequencies of some aromatic compounds is indicated by the presence of a peak at 900–700 cm^{-1}.[43] Thus, the FTIR spectra suggest the substance, obtained from the local market as Nīl to be Prussian blue instead of Indigo. It indicates that though Indigo had been traditionally used for blue color as Nīl earlier, it was likely replaced by low-cost synthetic Prussian blue after the latter became easily available. Two medium sharp peaks at 3688 and 3622 cm^{-1} seen in the FTIR spectra of Kharimāti (Fig. 6D) indicate the presence of alcoholic O–H stretching and the peak found in 1629 cm^{-1} may be attributed to the presence of medium physiosorbed H–O–H stretching frequency.[44,45] The peaks in the range of 1112 cm^{-1} to 779 cm^{-1} as shown in Fig. 6D may be attributed to strong mono substituted Si–O stretching frequency.[44,46]

Raman spectroscopy has been used to obtain information about the IR-inactive vibrational modes of the constituents of Hāitāl, Hengul and Nīl.[47] For all these samples, the excitation was at 514 nm with the same laser power of 10 mW and different exposure time. Figure 7A shows four strong Raman bands in the range of 400–100 cm^{-1}[48,49] for Hāitāl. The peaks at 191 cm^{-1} and 145 cm^{-1} indicate the lattice vibrations of the compound and proves the presence of some arsenic containing sulphide compound (Fig. 7A).[48–50] Some strong and broad peaks are observed in the range of 500–100 cm^{-1} in Fig. 7B. The peak at 337 cm^{-1} indicates the presence of Hg-S stretching frequency which clearly gives the evidence that mercuric sulphide, commonly known as Cinnabar is present.[42,48,49,51,52] On the other hand, the peak observed at 493 cm^{-1} indicates the presence of v(S–S), v(S–O–S) and v(Hg-O) stretching frequency.[42,48,49,51,52] In Fig. 7C, we have seen many characteristic peaks of Prussian blue within 1000–100 cm^{-1}. The position of the broad peak we see in the 949 cm^{-1} range refers to v (C–O–O). The Raman shift seen in the 727 cm^{-1}–534 cm^{-1} range indicates the presence of aliphatic v(C-S) and v(C–Br),

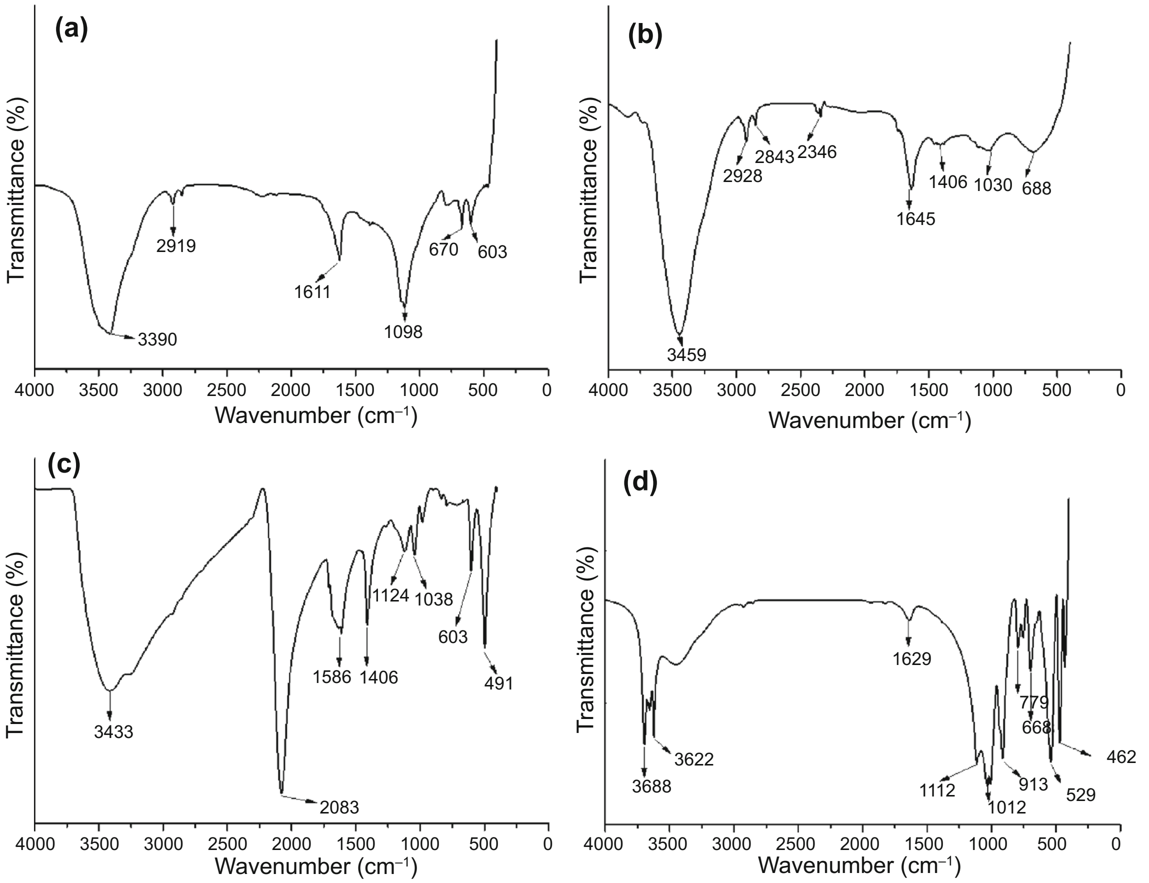


Fig. 6: FTIR spectra of Hāitāl (A), Hengul (B), Nīl (C) and Kharimāti (D)

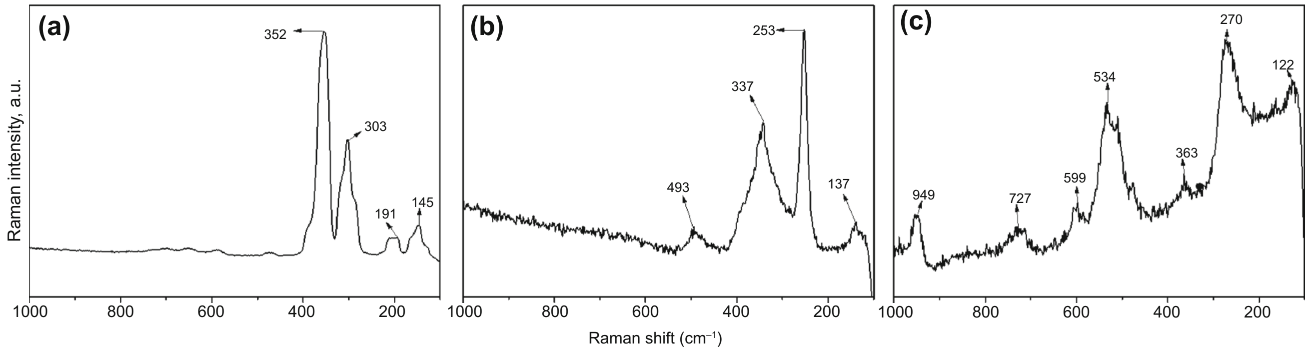


Fig. 7: Raman spectra for (A) Hāitāl (Excitation was at 514 nm exposure time = 1 s and laser power = 10 mW), (B) Hengul (Excitation was at 514 nm exposure time = 2 s and laser power = 10 mW) and (C) Nīl (Excitation was at 514 nm exposure time = 4 s and laser power = 10 mW)

respectively.[49] Due to the presence of cohesive and agglomeration properties in khārimāti, Raman peaks could not be detected.

XRD analysis

The XRD spectra of the pigments of Hāitāl, Hengul and Nīl and the p-XRD peak interpretation from Pcpdwin Software have been shown in Fig. 8. The moderate crystallinity of the three pigments, estimated to be 38%, 28% and 32%, respectively, may be attributed to impurities in the natural pigments (Figs. 8A, 8B, 8C). Two sharp peaks at 18.51°, 52.36° observed for Hāitāl (Figs. 8A, 8D) can be assigned to (020) and (051) reflections, respectively. The dense peak observed between 28.26° and 43.75° ranges correspond to the monoclinic crystal system of

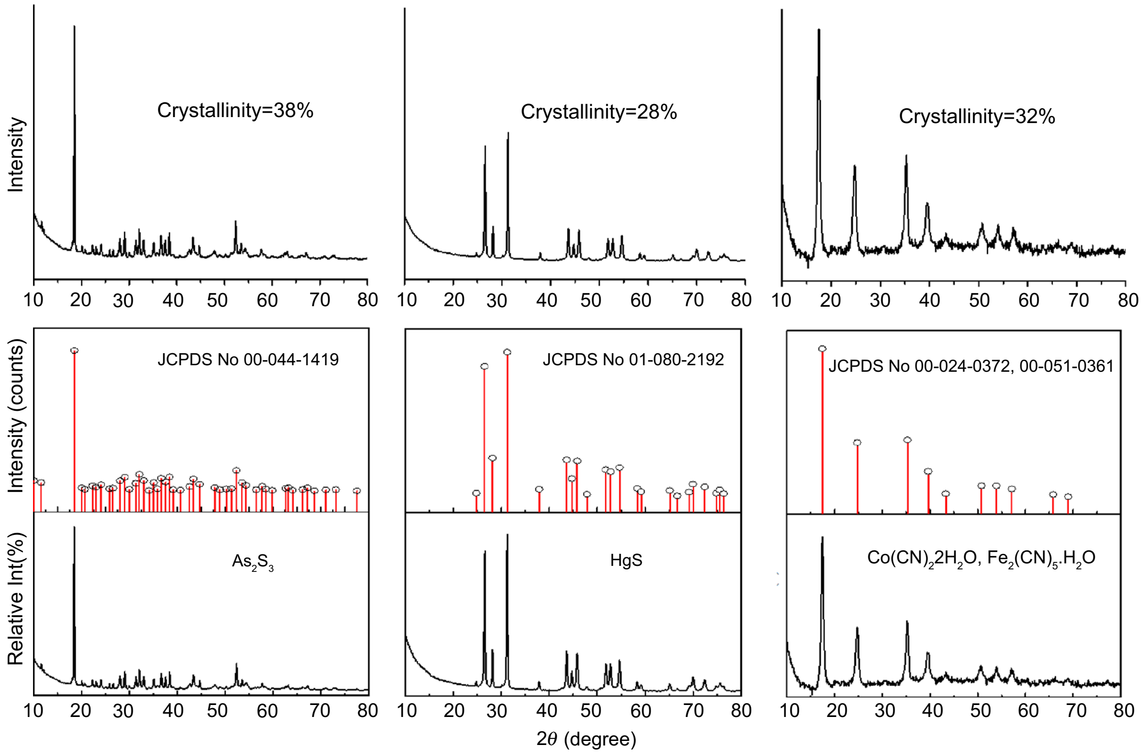


Fig. 8: p-XRD graphs of Hāitāl (A), Hengul (B) and Nīl (C) and p-XRD peak interpretation from Pcpdwin Software of Hāitāl (D), Hengul (E) and Nīl (F)

Hāitāl[53–55] (Figs. 8A, 8D). The d-spacing of the highest peak is 4.79 Å, whereas for the smallest one, it is found to be 1.74 Å. A comparison with JCPDS Card 00-044-1419 shows that the sample corresponds to As_2S_3.[53,55,56] Similarly, we found two very sharp peaks at 26.46° and 31.43° for Hengul (Figs. 8B, 8E). These two peaks correspond to (101) and (012) reflection and 3.35 Å and 2.86 Å d-spacing. In addition to these, some comparatively sharp peaks were observed at 28.13°, 43.96°, 44.72°, 46.09°, 51.75°, 52.69°, and 54.82° angles which correspond to (003), (110), (104), (111), (021), (113) and (015) reflections. When compared with JCPDS card 00-080-2192, the sample corresponded to the hexagonal crystal system of HgS, i.e., cinnabar.[57,58] Four major peaks were observed in the XRD spectra for Nīl, as shown in Figs. 8C and 8F, corresponding to the angles of 17.73°, 24.81°, 35.21°, and 39.71°. These sharp peaks are associated with the (200), (220), (400) and (420) reflections and 5.06 Å, 3.59 Å, 2.54 Å, and 2.27 Å d-spacing. After comparing this data with the JCPDS card 00–051-0361, we found that the sample corresponded to a cubic crystal of iron cyanide hydrate.[59] More peaks were observed at different angles, viz., 40.51°, 43.71°, 50.81°, 54.11°, 57.43°, 66.21° and 69.45°. The angles 43.71° and 40.51° are associated with 2.09 Å (422) and 2.22 Å (421) d-spacing, which indicates the presence of cubic crystalline compound known as cobalt cyanide dihydrate ($Co(CN)_2 2H_2O$) [JCPDS card 00-024-0327].[60] The remaining angles were associated with 1.84 Å (024), 1.69 Å (116), 1.60 Å (122), 1.41 Å (125), and 1.34 Å (208) d-spacing with reflections. After comparing these data with the JCPDS card 00-033-0664, we may say that the compound is also associated with rhombohedral crystal known as iron oxide (Fe_2O_3), which is commonly known as hematite mineral.[61,62]

Thermal analysis

The thermal analysis revealed that the pigments Hengul and Hāitāl are highly stable even at higher temperatures. The SI-1 contains all the information reached through thermal analysis.

Impurities in the pigments

The above physicochemical analyses suggest the samples of Hāitāl, Hengul, Nīl and Kharimāti, available locally as traditional dyes, contain mainly As_2O_3, HgS, Prussian blue and aluminosilicate clay, respectively, with some impurities. Both Hāitāl and Hengul to contain oxide and carbonate impurities of the respective metals. The sample of Hengul also contains traces of iron and arsenic impurities. The sample of Nīl (Prussian blue) contains hematite iron impurity, probably added to increase its weight. The presence of some oxide or other mineral impurities is natural in the mineral pigments and is not expected to have any serious implication on the paints. However, the impurities and their levels may differ in the mineral pigment samples depending upon the source.

Analysis of paints of different shades prepared from the pigments

Zeta potential

The polarity changes and zeta potential of the pigments, prepared as per Table 1, were measured for dilute suspensions of the pigments using a Nanotrack wave machine. The zeta potentials of Hengul and Hāitāl and Nīl have been found to be 2.6, 2.0 and − 3.0 μm, respectively. Observed positive polarity values of Hengul and Hāitāl indicate positive surface charges as expected for mineral oxides and sulfides of the mineral pigments. On the other hand, an observed negative polarity of Nīl indicates a negative surface charge which may be due to the presence of iron cyanide impurity in Nīl. All the three pigments have low value of zeta potential which indicates the attracting forces exceeding the repulsive forces leading to agglomeration of the particles, decreasing the stability. The agglomeration and low stabilities of the pigments have been in fact observed with the pigments after if the paint mixture is kept for more than 2–3 h. This may be the reason for which the paints, once prepared, should be used up completely as quickly as possible.

Particle size analysis

We calculate the fineness of the final particle of all paints, prepared as per Table 1, with the help of Hegman scale. The fineness of Hengul and Hāitāl particles is 7 microns and 10 microns. Similarly, the fineness of Nīl is 4 microns and that of Kharimāti is 5 microns. The average particle sizes for composite brown, green, and black colors were measured to be 22, 32 and 31 microns, respectively, which are close to that of Hāitāl, an ingredient of the colors. It may be noted that the particle size of Hāitāl is large compared to the others despite a much greater effort made for grinding it. Traditionally, a much greater effort is made for grinding Hāitāl as it is difficult to grind it to smaller size particles due to its flake-like shape. Interestingly, there is a saying among the traditional practitioners of Hengul-Hāitāl about Hāitāl that though it is very difficult to grind Hāitāl, the intensity of the color of this pigment continues to increase on grinding.

Hunter color analysis

The results of Hunter color lab analysis on paints of all compositions as described in Table 1 are shown in Table 2. Hunter color analysis was done also for compositions where the natural Bael gum was replaced with a commercial synthetic gum binder based on polysaccharides to examine the possibility of replacement of somewhat scarce and seasonal Bael gum with the commercial gum.

Among the different shades prepared with Bael glue, only red and green paint samples, with L^* less than 50, showed slight darkness property while all others showed lightness property with the maximum lightness for the yellow sample. The blue and green paint samples, with negative a^* values, showed greenness property while all the other paint samples showed redness properties with the maximum redness for red and brown samples. The black and blue samples, with negative b^* values, showed blueness property while all other samples showed yellowness property with the maximum yellowness for the yellow and the brown samples as expected. It was interesting to note that all paint samples were estimated to be bright (positive C^*) with the blue and black with minimum brightness. That the highest estimated brightness was obtained with the yellow followed by brown and then red paint samples is commensurate with a very bright color observed with woodcarvings with the yellow, brown and red paints. The yellow sample also showed highest hue angle, h.

There was hardly any change in the color properties of the red and yellow samples on changing the gum (SI-2). A small decrease in lightness of the white sample and an increase in the redness of the brown sample were observed on changing the gum from Bael to commercial starch-based gum. There was a marked increase in the yellowness and brightness of the white sample with some decrease in both brown samples with Bael gum and commercial gum. There was a notable decrease in the hue of the blue sample followed by black with the commercial gum. The observed variations in the color properties may be associated with some differences between the interactions of the components of the blue and the white paints samples with the two gums.

Hiding power of the paint formulations

The hiding power of different color formulations prepared as per Table 1 has been measured as contrast ratio (CR), which is the ratio of light reflection from black to that from white after coating of respective colored paint on different colored panels (Fig. 9). The CR of the different color paints has been found to be 99.98 for red (Hengul), 92.85 for white (Kharimāti), 100 for blue (Nīl), 100 for yellow (Hāitāl), 100 for green (6:1 Hāitāl and Nīl) and 100 for brown (1:8 Hāitāl and Hengul). The results indicate that all the primary colors as well as the composite color formulations have very good hiding power. However, the blue (Nīl) and the yellow have shown CR of 100. The hiding power of white has been found to be slightly lower. On the other hand, a CR of approximately 100 has been observed for all color formulations containing the mineral pigments of Hāitāl and Hengul.

Table 2: Results of Hunter color analysis of the compositions as described in Table 1 except for the binder gum which here includes both Bael gum and a starch-based commercial gum with same proportions

Sample color	*L**		*a**		*b**		*C**		*h*	
	Bael	Comm	Bael	Comm	Bael	Comm	Bael	Comm	Bael	Comm
Red	44.61	42.31	17.84	20.34	13.62	7.12	22.47	21.45	0.65	0.33
Yellow	79.91	69.33	3.94	6.29	55.27	49.30	55.42	49.70	1.50	1.44
Blue	54.41	35.58	– 2.71	0.04	– 4.04	– 2.48	4.87	2.48	0.98	– 1.55
White	51.72	69.33	4.44	6.29	14.08	49.30	14.76	49.70	1.24	1.44
Brown	64.69	48.15	19.45	5.70	37.54	8.96	42.20	10.62	1.09	1.00
Green	45.84	42.23	– 12.30	– 6.54	15.14	3.08	19.50	7.22	– 0.89	– 0.44
Black	54.94	35.58	0.53	0.04	– 0.21	– 2.48	0.57	2.48	– 0.37	– 1.55

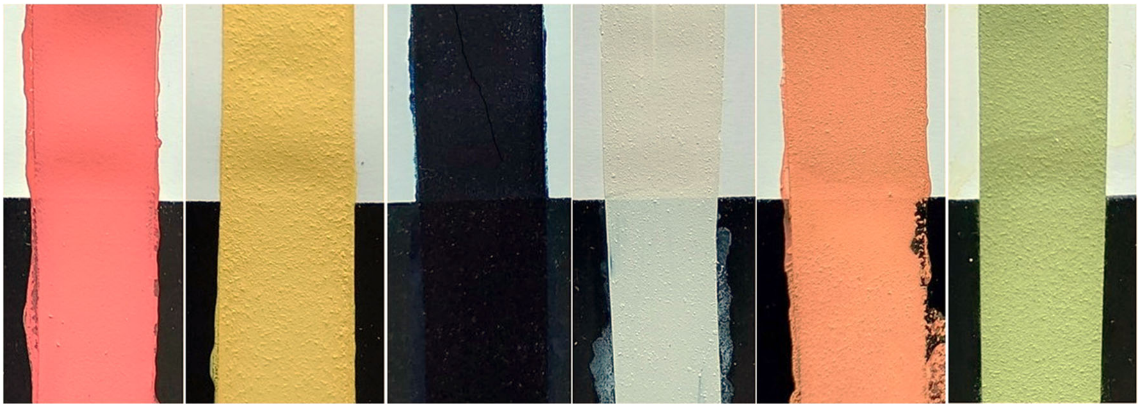


Fig. 9: Photographs of red, yellow, blue, white, brown and green colored panels prepared for contrast ratio measurement

Traditional science in the painting tradition

The Hengul-Hāitāl painting tradition involved some interesting traditional knowledge, such as selecting primary color pigments that guard woodcarvings against termites and fungus and applying a thin coat of traditional varnish after painting to shield the dyes from natural erosive processes.

Selection of primary color pigments

Red, yellow, and blue or green are considered as three primary colors. Centuries ago, the artists of Assam knew how to prepare any other colors or shades, including black, by mixing these three pigments of three primary colors, namely red, yellow, and blue, in varying proportions. There is no record of use of any pigments of any other color, mineral or herbal.

Antifungal and insect-repellant component in paint formulations

Woodcarvings can be easily damaged by cellulose-eating fungi and termites which are abundant in hot and humid climate of Assam. The artists of the Hengul-Hāitāl painting tradition probably knew about antifungal and insect repellant properties of Hengul or Hāitāl, and this might have been one of the reasons for choosing these two pigments.[11] These pigments were used throughout history in various artistic techniques and were very much loved for their color purity and intensity. However, using these pigments might impede the appearance of fungi or insects.[11] It is also interesting to note that the artists usually did not use Nīl alone for blue color and instead mixed a little of Hāitāl with Nīl, to protect the woodcarving from fungi and termites, which imparted a slight greenish tinge to the blue color. Figure 10 shows how termites damaged portions of woodcarvings with white paint whereas the portions with paints containing either Hengul or Hāitāl or even black remain unaffected for a much longer time. It is usually noticed that pure blue color was not applied on the woodcarvings which have survived for centuries (Fig. 10). A small amount of tutia was also traditionally mixed with Kharimāti which was used for white color.

Fig. 10: Woodcarvings of 1916 AD at Bardowā Thān, Nagaon, Assam, containing green color made by mixing Nīl with Hāitāl but without blue color of Nīl alone (a, b, c). The left (a) and the middle pictures (b) are of the same woodcarving before and after cleaning

Avoiding natural erosion and contact by Lā-coating

Though Hengul and Hāitāl are traditionally used as Sindur by married Hindu women, as a make-up ingredient by Kathakali dancer in India, for lightening of dark skin, etc., contamination of antifungal and insect-repellant pigments may have some toxic effects on human health.[63] Users of utility wooden items painted with Hengul-Hāitāl naturally come into contact with the users. On the other hand, Vaishnavite woodcarvings are usually placed open in Namghars where the devotees often touch them. The contamination of the pigments as well as natural erosion of the paints from the woodcarvings were avoided by applying a thin coating of wood sap on the woodcarvings after completion of the painting.

Selection of a non-staining natural gum

There are some more natural gums available in Assam, namely, gum of Outenga or elephant apple and the gum of fiddlehead fern in addition to the gum of stone apple or Bael gum. Bael gum is a very good adhesive and at the same time it does not leave any stain on the object. This gum is also available locally in all seasons of the year which are conducive for painting except the rainy season during which painting is usually not done.

Use of primer coating

It was traditional procedure to fill any gaps in the surface of woodcarving with a coat of Kharimāti primer followed by soft rubbing to smoothen it. The aluminosilicate Kharimāti primer coat also increases the hiding power of the paint. As Kharimāti does not have antifungal or insect-repellant properties, it was customary to mix a small quantity of tutia with Kharimāti in order to make the primer antifungal and insect-repellant.[11] It may also be noted that a small quantity of tutia was added to Kharimāti for preparing white paint.

Conclusions

The present scientific study of the ingredients, the properties and application of traditional Hengul-Hāitāl paints has revealed some interesting traditional knowledge related to the pigments and their application. Mineral pigments of Hengul (mercuric sulfide, HgS), Hāitāl (arsenic sulfide, As_2S_3) and Kharimāti (calcium aluminum silicate clay) were used for red, yellow, and white, respectively. However, though a natural dye, Indigo, was traditionally used as blue color, it is now replaced by synthetic Prussian blue. The physicochemical analyses of the pigments have shown that Hengul and Hāitāl samples showed some natural oxide and carbonate impurities. On the other hand, the sample of Nīl (Prussian blue) was found to be adulterated with hematite. The sample of Hāitāl showed 38% crystallinity, which was higher than 28% observed for Hengul. The particles of Hengul, Hāitāl and Nīl, after grinding, have been found to be distinctly distributed while that of the particles of Kharimāti have been found to be spread smoothly. The average particle sizes of the pigments were between 4 and 10 μm. Measured low zeta potentials of the pigments indicated rapid agglomeration which was in fact observed in practice requiring complete use of the paints within 4–5 h of preparation.

The use of three primary colors, viz., red, yellow, and blue in the tradition for preparing any desired shades is noteworthy. It was also interesting to note the selection of a non-staining robust natural gum, viz., Bael gum, to prepare the paints. However, there was hardly any change in the color properties of paint samples of different colors on replacing the Bael gum with a starch-based commercial gum. While all shades obtained from Hengul, Hāitāl and Nīl have shown very good hiding power, all shades containing Hengul and Hāitāl have shown high brightness. It is also interesting to note the use of either Hengul or Hāitāl or both for preparation of any of the shades except white probably to repel termites and fungi. It was also a practice to mix a little of antifungal and insecticide tutia with Kharimāti for white color. Application of a primer coat of Kharimāti mixed with tutia is indicative of the traditional knowledge of use of primer as well as preservation of woodcarvings from fungi and insects. On the other hand, application of Lā coating finally is indicative of traditional knowledge of stopping natural erosion of the paints and avoiding toxic Hāitāl by devotees of idols and utility items by users upon touching. The unraveled traditional knowledge pertaining to glaze and durability applied in the preparation of woodcarvings and Hengul- Hāitāl painting tradition of Assam will be helpful in developing a customized method for restoration of worn-out woodcarvings for preservation in open ordinary environment in villages and Satras.

Acknowledgments Authors thank INSA, New Delhi for a financial assistance (HS/RC568) under its history of science research program. AAA thanks Tezpur University for an Innovation Research Grant and an Institutional fellowship.

Author contributions All the authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, and writing and there are no conflicts to declare. All authors read and approved the final manuscript.

Funding This work was supported by Tezpur University. Author Asadulla Asraf Ali has received research support from Tezpur University and thanks Tezpur University for an Innovation Research Grant (No. DoRD/RIG/10-73/1544-A) and an Institutional fellowship (No. F.14-5/3/2003(Acad)/375-A). The authors also thank SAIC, Tezpur University for providing instrumentation facilities.

Availability of data and materials On request, data is made available.

Competing interests The authors have no relevant financial or non-financial interests to disclose.

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