


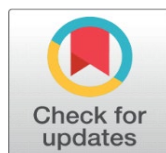


# THE BLUE GREEN PATINA ON SCULPTURES CAST IN COPPER AND ITS ALLOYS - THEIR CHEMISTRY AND AESTHETICS

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## ABSTRACT

Copper and its alloys have a tendency to naturally corrode and form a blue green finish over them. This blue green finish has been observed in everyday copper and bronze utensils and even in famous sculptures like statue of liberty. Artists have long taken advantage of this patina to achieve aesthetic of desolateness, age, and damage. This patina tends to change the luster of the metal from reflective to matt and color from pink (gold in case of brass and bronze) to bright blue or green. Artists are known to use this change to add to visual language of their sculptures. The current paper takes in account the whole spectrum of blue – green patinas, from bright blue azurites to dull green verdigris and also dark green copper chloride salts. The paper discusses the chemistry behind the formation of this patina, tests age old recipes and discusses aesthetics with respect to famous Indian sculptors.

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**Keywords:** Patina, Verdigris, Sculpture, Copper Rust, Aesthetics



## 1. INTRODUCTION

Corrosive properties of copper had been known to man ever since the discovery of copper. Copper and its alloys, if not protected, rust under environmental conditions. The conditions determine the compound formation on metal surface and these compounds occur in various brilliant colors and luster. Ancient sculptors took notice of this phenomenon and tried to experiment with it. Where ancient Egyptians focused on developing wax and polishes to avoid metal tarnishing, Ancient Greeks and Asians through trial and error introduced recipes to make even patina finishes

all over their works. A lot was talked about of the aesthetic of rust and corrosion in Japan and China as well. There have been many instances through ancient history where byproducts of corrosion or direct corroded copper have been employed as pigments or even medicine. This fascination with changes that occur through age and weathering was extensively studied and listed under an umbrella term of Patina.

Patina has been studied in various fields like chemistry, conservation sciences, environmental practices, and even aesthetics and fine arts. Even after extensive research, no comprehensive study on artificial patina on sculptures, discussing its chemistry, recipes and how it affects the aesthetics of the sculpture seems to have been worked upon. Separate efforts have been made to explain chemistry of corrosion in both scientific and conservation fields. Researchers like C. Leygraf, J. P. Franey, have extensively studied the compounds formed after corrosion that produce various colors on copper [Leygraf et al. \(2019\)](#), [Franey and Davis \(1987\)](#). Papers have also been written on age old recipes and processes of blue green patina by the likes of David Scott and Mary Virginia Orna (Mary Virginia Orna, 1980) [Scott et al. \(2001\)](#). Aesthetics of Patina have also been talked about in philosophical terms in books and papers by Manuel Ortega-Calvo, Koren, and Silva (Manuel Ortega-Calvo, 2014) [Koren \(2008\)](#) [Silva et al. \(2017\)](#). The present paper focuses on techniques, recipes, and aesthetics of natural and artificial blue green patina on contemporary sculptures made in copper and its alloys.

There were several issues in installing sculptures with virgin metal surfaces and letting the environment take its course with it. Firstly, there was no way of controlling the thickness, color, and texture of the patina. This created a risk of patina turning vile. Secondly, artists had limited options of patina that the specific environmental conditions could naturally produce. Natural patinas can be spatially heterogeneous, meaning they are neither uniform nor smooth. In addition to that, each sculptural surface with its crevices, nooks, cuts, bends, and folds will interact differently with the environment. Varying degrees of sunlight exposure is also a contributing factor of non-uniform patina [Graedel \(1987\)](#). Therefore, sculptors prefer to produce these surfaces artificially before letting nature take its course. Artificial patina produces an even layer; the artist can customize shadows and highlights according to his preference. In some cases, artists have been deliberately using artificial patina to form an uneven layer that adds to the language of the sculpture.

Copper and its alloys, brass and bronze have been the prime choice of medium for sculpting since ancient times. The choice is attributed to its malleability and ductility, low melting point and strength. Another important choosing factor especially for modern sculptors and architects is its ability to form patina [Graedel \(1987\)](#). Post modern and contemporary eras saw artificial recipes being developed to produce these corroded surfaces in colors other than the usual, brown, green, and black. However, it was observed that most environmental conditions lead copper to inevitably turn into the iconic blue green patina. The blue green patina once established is relatively stable. When studied under spectroscopy the patina was known to be a mixture of oxides, sulfates and carbonates and had many variants in compositions discussed under section 2 of the paper.

Different colorful effects had been applied to bronze sculptures since early classical times, but it was not until the eighteenth century that green corrosion products began to be of value. According to the Oxford Dictionary of the English Language, the earliest reference to the use of green patina dates from 1797 [Koren \(2008\)](#). Blue green patina also became popular when ancient artists and sculptors

found out that exposure to acetic acid makes copper turn green relatively quickly. A blanket term for this acetic acid produced blue-green patinas is known as verdigris – Vert de Grece roughly translated to Green of Greece, or the French spelling Vert de gris translated to green of grey. Verdigris is known as both the patina as well as the pigment that is scraped off the copper to be later used in paintings [Scott \(2002\)](#). The accessibility of materials and ease of the process with which this patina can be achieved made it popular amongst the masses.

Another aspect of popularity is familiarity with the color, since this color is naturally achieved on copper objects around in everyday life like utensils, vessels, bathroom amenities, pipes and tools if left without care. This made verdigris come to be associated with old, desolated things and antiques. Soon artists discovered ways to recreate this finish artificially, taking advantage of the familiarity and the color's association with the age. Artists found philosophical references with the ever-changing patina which is in artistic terms referred to as a live patina. It becomes imperative to discuss how this alteration affects the language of the sculpture.

### 1.1. OBJECTIVE

The current paper aims to understand the chemistry of the compounds and environmental conditions that cause copper and its alloys to acquire a blue green finish. It also discusses the methods of recreating the same finishes on sculptures artificially. Lastly it aims to observe and analyze various modern sculptures in which artists have employed this patina finish to their advantage.

## 2. CHEMISTRY FOR PATINATION

In terms of metal cast sculptures (especially those cast in copper and its alloys), the environment where they are installed affects the composition of the patina on them. In most cases, virgin copper first interacts with oxygen, creating copper oxides which are reddish brown to dark brown in colour. In presence of sulfur or sulfur dioxide, and humidity in the environment, Oxides turn to sulfate minerals that give the copper its iconic blue green colour. Depending on the actual environment and exposure time, the sulfate minerals that form on copper surface can be posnjakite ( $\text{Cu}_4\text{SO}_4(\text{OH})_6\cdot\text{H}_2\text{O}$ ), brochantite ( $\text{Cu}_4\text{SO}_4(\text{OH})_6$ ), antlerite ( $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ ), atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) or combinations thereof (C. Leygraf, 2019). Antlerite, brochantite, and chalcantite are the dominant corrosion products formed during the extended atmospheric exposure of copper and copper alloys [Noli et al. \(2003\)](#).

Copper sulphate is popularly known as blue vitriol. Ninth century Indian physician and writer Vagbhata is known to have used the term Sasyaka in Sanskrit for the same. It is one among the Maharasa (group of minerals) in Ayurveda and finds a huge significance in Ancient Indian medicine. Naturally occurring copper sulphate is called Sasyaka while the artificially made is termed Tuttha. Chemically the formulas differ, Sasyaka is  $\text{Cu}_5\text{FeS}_4$  and Tuttha is  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ . Tuttha is known as copper (II) sulphate, (chalcantite), blue vitrol and blue stone and it is obtained through processing the sulphuric acid over the copper. Sasyaka is known as naturally occurring copper iron sulphide, which reflects the colour similar to the neck of a peacock and is heavy in weight [Shankar \(2019\)](#).

Brochantite is the most stable and most often occurring patina of copper alloys in the environment and has a greener finish than the blue of chalcantite. Antlerite is another commonly occurring copper sulphate mineral and has a similar vitreous

green finish. These kinds of patinas were found to occur naturally on both Lorenzo Ghiberti's Gates of Paradise and Rodin's Thinker [Scott \(2002\)](#).

Copper is known to form salts in reaction with various organic acids like acetic acid, formic acid, tartaric acid, and citric acid. These acids can be sourced from plants, fruits, resins, urine etc. As discussed above in Section 1, these patinas form verdigris and a bundle of ancient recipes from all around the world can be found to produce these. Since medieval times, a patina pit was a common occurrence in metal foundries, where cast sculptures were buried with products that are known to produce acetic acid. Lemons, grapes, pineapple, vinegar and wine, salt and honey and ammonia from urine are known to be used in producing verdigris. This experiment has been conducted under section 3.2. Verdigris ranges from pale blue through turquoise till green and is extremely difficult to consistently produce the exact same results every time. The recipes rely on naturally occurring products which makes it difficult to control external factors and compounds that seep in along with the desired acetic acid. As a pigment, verdigris is typically greenish blue

when it is first applied and develops its full green hue after a month following application [Roy \(1986\)](#).

Excess carbon in the air or dissolved carbon in waters around copper result in basic copper carbonate. More accurately known as copper carbonate hydroxide  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ . It occurs in nature most readily as Malachite and is often found in areas with copper deposits near limestones ( $\text{CaCO}_3$ ) or other carbonic sources. Another similar mineral is Azurite, it can form readily in natural environments if very dilute  $\text{CuSO}_4$  solutions react with  $\text{Ca}(\text{HCO}_3)_2$  solutions, which usually result from the dissolution of limestone by  $\text{CO}_2$ -rich waters. Where Azurite is deep blue in colour, Malachite is bright green to blackish green. Both exist in forms of crystals on top of the surface of copper and are very rarely vile. Widely used as the green pigment, colouring agent in glazes and glass making, it occurs often as a corrosion product on **buried** bronzes. Small crystals of azurite can be produced by rapidly stirring a few drops of copper sulfate solution into a saturated solution of sodium carbonate and allowing the solution to stand overnight [Scott et al. \(2001\)](#)

Darker green patina is formed due to copper chloride compounds. Atacamite and its polymorphs  $\text{Cu}_2(\text{OH})_3\text{Cl}$ , nantokite  $\text{CuCl}$ , antlerite  $\text{Cu}_3(\text{OH})_4\text{SO}_4$  form green, and it can be lightened by lead carbonate  $\text{PbCO}_3$  or tin oxide  $\text{SnO}_2$  (G.Di Carlo, 2017). Chloride patinas are usually found in artifacts that are discovered from underwater areas or areas with very moist air. Artists usually stay away from chloride as cupric chloride has a tendency to turn vile. Commonly referred to the 'Bronze Disease', chloride corrosion on copper-based artifacts is highly contagious and eats away the metal. To preserve sculptures with bronze disease, they are to be kept away from oxygen, water, and chlorides. Differentiation of verdigris from bronze disease can be made using two pointers. Verdigris is pale green where chloride compounds are bright to dark green. Verdigris, as mentioned above, is highly stable, where bronze disease can be scraped off using a wooden stick or nail thus making the sculpture's layer weaker with its action [Turner-Walker \(2008\)](#).

### 3. METHODOLOGY

3 by 4 inches and 4 mm thick copper and brass slides were taken for experimentation. The slides were washed and sanded off with first a soft steel wool and then 620 grit sandpaper. This was done to remove a layer of oxidation on top and bring the virgin metal forward.

**Hot Process:** A heat gun was aimed at the slide, to achieve a temperature of 125-130 degrees. Chemicals were then sprayed on the slide. The moisture in the chemicals evaporates immediately on hitting the slide and chemicals start to act on the virgin metal. The spray has to be even and thin in order to achieve a long-lasting patina. In case of increase in temperature of the heat gun held too close to the slide, the patina will burn to form splotchy black spots.

**Cold Process:** The slide was either submerged in or painted upon with chemicals at room temperature for the given duration in the recipe. The chemicals work relatively slower than the hot process and the patina is often uneven. A relatively closed environment was achieved where impurities like dust, pollution etc. were kept to minimum.

### 3.1. EXPERIMENT WITH APPLE CIDER VINEGAR AND TABLE SALT

Two plates of copper and brass were left submerged in a solution of 90 mL apple cider vinegar and 30 grams of iodized salt. The observations are as follows.

- **Day 1-** Slight brightness on the metal, copper is in its original pink color and brass is its original yellow. The slight oxidization and impurities seem to get removed [Figure 1](#).

**Figure 1**



**Figure 1** Copper (Left) And Brass (Right) Submerged In A Solution Of Apple Cider Vinegar And Salt

- **Day 7-** No change
- **Day 14-** Start to see slight browning in both copper and brass.
- **Day 21-** Green crystals start to form at the edge of the tray and on the edges of the plates.
- **Day 28-** Crystallization process starts rapidly. The plates turn bright green, with crystals forming on the edges as the vinegar volume starts to decrease [Figure 2](#).

**Figure 2**



**Figure 2** Copper (Left) And Brass (Right) Copper Acetate (Verdigris) Crystals Form as Vinegar Solution Gets Absorbed Off Completely

- **Day 32-** The plates have been covered with verdigris crystals; vinegar solution has completely evaporated leaving behind the whole tray with dark green to green crystals [Figure 3](#) [Figure 4](#).

**Figure 3**



**Figure 3** Brass Plate with Dark Green Verdigris Crystal Formation

**Figure 4**



**Figure 4** Details of Scraped Off Crystals of Verdigris

### 3.2. COPPER NITRATE EXPERIMENTS

Hot process was opted to execute this patina. A spray of a water diluted solution of copper nitrate was sprayed evenly on the brass slide. The composition of the chemical should depend on the patina artist and how opaque the color needs to be. Sky blue color appears after 2-3 sprays. This patina is highly sensitive to fire and often gets burnt. The recipe works on all copper alloys.

Figure 5

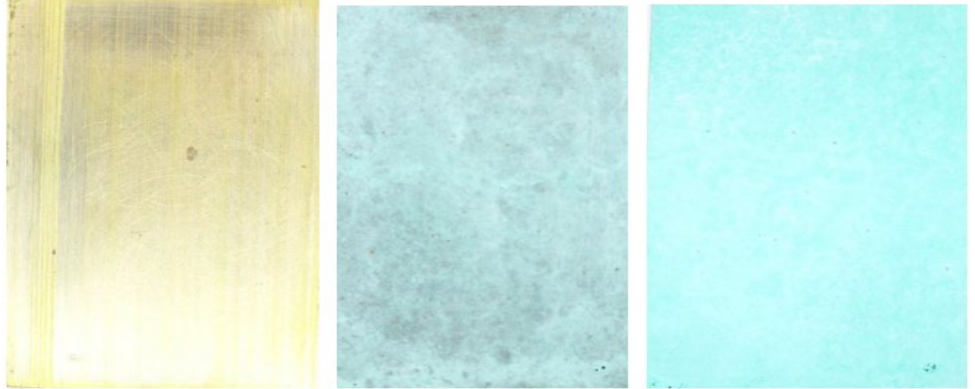


Figure 5

- a) Brass Plate Washed and Lightly Abrade to Remove Any Oxidation.
- b) Brass Plate With 3-4 Light Sprays Of 3:7 Ratio of Copper Nitrate and Water. (Hot Process)
- c) Brass Plate With 6-8 Light Sprays Of 4:6 Ratio of Copper Nitrate and Water. (Hot Process)

### 3.3. COMBINATION OF COPPER SULFATE AND FERRIC NITRATE

Dull sea green to yellow sap green can be produced by mixing the two solutions: Copper Nitrate and Ferric Nitrate. Hot process of patination is used to spray thin coats of the solution. Experimentation with ratios of chemicals will result in various tones of green.

Figure 6



Figure 6

- a) Brass Plate Washed and Lightly Abrade to Remove Any Oxidation.
- b) Brass Plate First Sprayed 3-4 Times with Copper Sulfate Solution in Water In 3:7 Ratio. Then Ferric Nitrate Solution with Water of Ratio 2:8 Is Sprayed on Thinly Twice.
- c) Brass Plate First Sprayed 3-4 Times with Copper Sulfate Solution in Water In 3:7 Ratio. Then Ferric Nitrate Solution with Water of Ratio 2:8 Is Sprayed on Thinly 4-5 Times.

### 3.4. AMMONIA EXPERIMENTS

This experiment was conducted using two different methods, cold fuming, and cold submerging process. Ammonia in itself produces a light green color, but during literature review it was found that salt is used to encourage better stability of the ammonia layer.

Slides were sprinkled with water and then drops of ammonia were poured on the slide. The patina thus formed was thicker and opaque. Could be used to add extra texture to the metal but might not be feasible for sculptures with no flat surfaces.

Figure 7

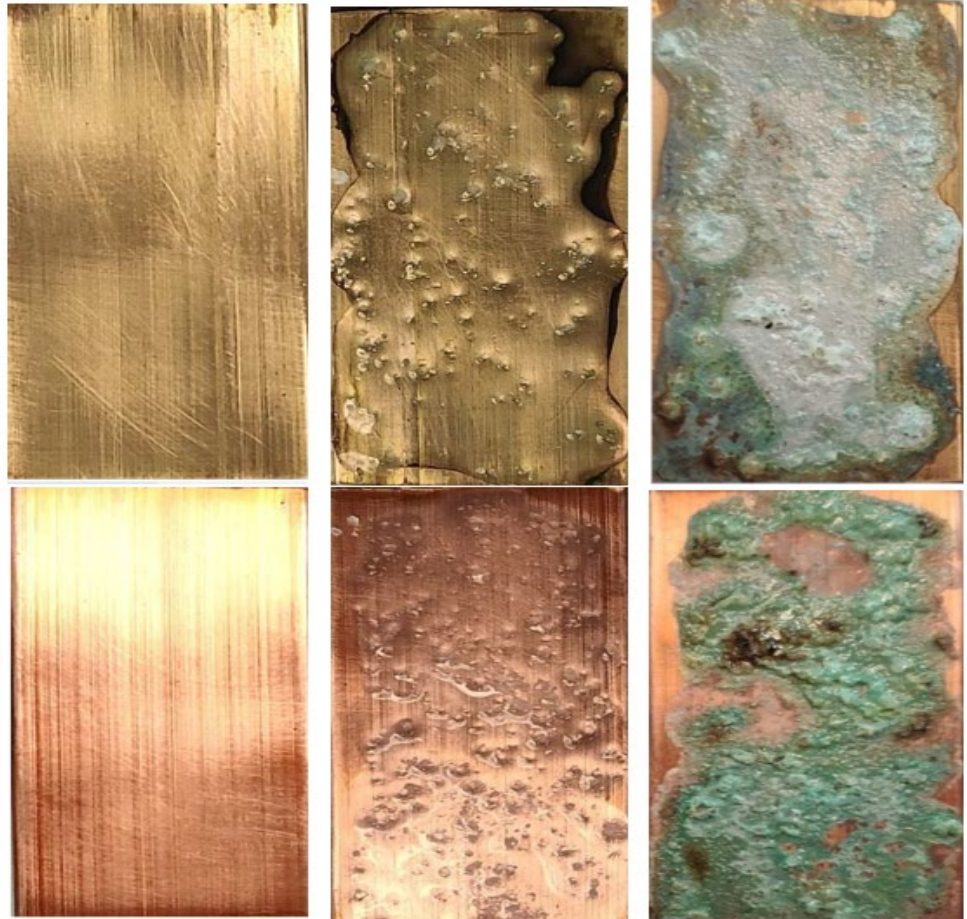


Figure 7

- a) Brass Plate. Washed And Slightly Abrade to Remove Oxidation.
- b) Pure Ammonia Is Pooled Over the Slide and Crystals of Salt Are Sprinkled Over.
- c) Formation Of Whitish Blue Patina with Edges Turning Green.
- d) Copper Plate. Washed And Slightly Abrade to Remove Oxidation.
- e) Pure Ammonia Is Pooled Over and Salt Crystals Are Sprinkled on Top.
- f) Green Patina Is Seen to Develop with Some Areas Are Observed to Be Greenish Brown.

### 4. AESTHETICS

Aesthetics in sculpture can be divided into two broad categories, beauty of sight and beauty of touch. We do not appreciate sculpture by touching them but rather by seeing them. Modern sculptures are usually kept under protection of museums or even if displayed in public places are not accessible to touch. Therefore,



aestheticians coined the term imaginative touch, sense of sight as guided by touch or as a substitute for touch. This is why sculptors pay very careful attention to the textures of their forms. A rough texture of a cement sculpture evokes a different response from the observer than a highly polished aluminum even if the form is exactly the same. Patina is used as a brilliant tool to add texture over a metal sculpture as well as play with the luster of the metal. Patina can be used to enhance the form of the sculpture, i.e., darken the depth in the sculpture or add a lighter tone to the highlights. Sculptors use multiple colors of patina to create tonal variation on a monotonous surface. Artificial patina can also help to create harmony in an artwork. Artist Laxma Gaud almost extensively uses a blue green patina on a base of brown for the purpose of highlighting the desired area. The shades of green in his work enhance the simulated and real textures of the form. It also harmonizes all the different forms and textures into a one holistic visual.

**Figure 8**



**Figure 8** Untitled by Laxma Gaud, Bronze, 7" X 5" X 5"

Source : <http://thefarawaytree.com/artist/Laxma-Gaud>

In the Stanford encyclopedia of philosophy, under the section of Japanese aesthetics, the word 'Sabi' refers to rustic patina Zalta et al. (1995). Earlier the interpretation of the term was associated with the feelings of dejection, loneliness, and neglect Helmenstine (2020). There was a connotation of desolateness attached to this concept. One of the prime reasons for the patina being formed on a sculpture is neglect. If the sculpture is kept untouched and unmaintained for an extended period of time, it develops a patina that might turn vile. In terms of visual language, this kind of patina will add a sense of gloom and detachment. As in the case of 'Gandhi's three monkeys' by Subodh Gupta where the artist uses blue green patina over a grey, brown background. The blue green patina makes the soldiers look like they have been stationed here for a long time at one place. Thus, a patina could be a great way to make the sculpture look like it is a part of the selected landscape it is to be installed in. The patina can make it look like the sculpture has been in the position for an extended period of time. This gives the sculptor the opportunity to establish a unique connection with the environment.

**Figure 9**



**Figure 9** 'Gandhi's Three Monkeys' by Subodh Gupta, Bronze, Steel and Old Utencils, Doha, Qatar.

**Source :** <https://qm.org.qa/en/visit/public-art/subodh-gupta-gandhis-three-monkeys/>

Later the definition of Sabi was changed to something that has aged well. A sense of beauty was associated with the effect of aging. Patina meant ripe with experience and insight. Thus, patina on sculptures started to be associated with not only peace and tranquility but also wisdom [Koren \(2008\)](#). The person watching a sculpture with a blue green patina (even artificial) is tricked to believe that the sculpture is older than him. This psychological trick can be played to advantage when artists want to produce an image of a knowledgeable public figure like Buddha or Gandhi. Ram Kinker Baij created a bust of his guru Rabindranath Tagore and used blue green patina over matt black. The viewer is used to seeing blue green patina as a highlight, but Ram Kinker Baij uses green in the depth making the wrinkles and imperfections of the skin of his old model come to focus. This ages the sculpture and its muse with insight.

**Figure 10**



**Figure 10** 'Bust of Rabindranath Tagore' By Ram Kinker Baij. Bronze

**Source:** NGMA, Delhi

Raghav Kaneria's 1984 sculpture titled 'Nandi' has an even green patina with brown undertones. The sculpture exhibits an earthy and dated quality that imbibes within a personal and intuitive approach of the artist. Patina is used here to negate the romanticization of technology that comes with a brightly polished bronze surface. The aesthetic of blue green patina is in many ways antithesis of what classical antiquity sculptures are known to exhibit. The concept of perfection gets countered by the rustic simplicity. Soetsu believes that perfection in an artwork can be limiting. In his book 'Unknown Craftsman', he writes that we in our human imperfection are repelled by the perfect since everything is apparent from the start and there is no suggestion of the infinite Yanagi et al. (1989).

**Figure 11**



**Figure 11** Nandi, Raghav Kaneria, Bronze, 14" X 10" X 8"

**Source:** Scanned from Exhibition Catalogue, 'Exhibition of Raghav Kaneria', 2015

Natural patina therefore was extensively observed and studied to be recreated in studios artificially. Although nature will always be the benchmark, artists started to play around with colors and textures to often achieve effects that nature could never create. Artists realized that if the aesthetic of patina needs to be preserved and celebrated there is a demand for guideposts and scientific reasoning backing the craft for future generations to follow. Himmat Shah's 2006 Untitled work has a blue green patina over all in the sculpture giving it an earthy, grounding quality. He buffs out the nose of the head, adding to a visual contrast of luster. The sculpture creates a visual play of bright and dull, reflective, and matt, polished, and rough.

**Figure 12**



**Figure 12** Untitled by Himmat Shah, Bronze, 12.5" X 7" X 6" Sanchit Art Gallery, New Delhi

**Source :** [https://www.sanchitart.in/Himmat-Shah\\_621.html](https://www.sanchitart.in/Himmat-Shah_621.html)

The aesthetic of the blue green patina is unique compared to the other patinas for copper and its alloys. The blue green patina is the inevitable truth of any copper-based object. It is the truth that time brings and that is why blue green patina can be effective in showing that time has caught on with the sculpture and has brought the metal to a state it is meant to be in a state of rest and balance. Even though it is still changing, and time will still continue to create its magic on the surface, this patina is relatively stable and slow to change. Statue of liberty acts as a perfect example of how blue green patina even though highly stable is relatively slower to establish. When one observes the stages of evolution of its patina one realises the concept of now, the statue was installed with shiny brown patina in 1886. In 1906 it had completely transformed to the iconic blue green color we have known to recognize it with. Presumably, it will not be the same in 50 more years. Other than the fascination with the never-ending process, this also makes the viewer appreciate the cosmic order and accept the inevitable [Helmenstine \(2020\)](#). The wabi sabi philosophy of 'devolving towards and evolving from nothingness' comes to play here [Koren \(2008\)](#).

Figure 13



Figure 13 Creative Visualization of Patina Changing Over the Years on Statue of Liberty, New York  
Source: <https://jtroofing.co.uk/news/why-does-copper-turn-green/>

## 5. CONCLUSION

It can be safely concluded that the blue green patina has made its way from rust on household items into a unique aesthetic in fine arts. Through experimentation on the naturally occurring patina on copper, scientists found out that various environmental factors act on copper to corrode it. Sulfur in the atmosphere makes copper turn to copper sulfate salts, brochantite is most stable and has a greener color where chalcantite gives out a bright blue hue. Copper acetate salts are made with exposure to acetic acid and are referred to as verdigris and have a dull green-grey finish. Exposure to chlorine is considered dangerous for copper and bronze sculptures, as copper chloride spreads quickly, eating away the metal surface. This is darker green in color.

Artificially, these patinas can be achieved using copper sulfate and ferric sulfate solutions and a hot process. For cold processes, the sculpture surface needs to be saturated with acetic acid from grapes, vinegar, wine etc. over time to produce bright verdigris color. Another method is to pool ammonia and table salt over the sculpture's surface to form an uneven and interesting blue green patina.

Observation of this patina in nature helped artists recreate the feelings of imperfection, dejection, and add a rustic charm to their sculpture artificially. When artists produce this patina artificially on their sculptures it helps them achieve the effect of nature taking its course over the sculpture, it tricks the viewer to believe the artwork has been aged over centuries. This patina also helps artists enhance textures of their works and add highlights. It was also seen that this patina creates a great contrast against the original color and shine of the metal.

### **CONFLICT OF INTERESTS**

None .

### **ACKNOWLEDGMENTS**

None .

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