



### RESEARCH ARTICLE

## METHODS FOR THE SCIENTIFIC TREATMENT AND PRESERVATION OF SURFACE OF ANCIENT COPPER OBJECTS: AN OVERVIEW

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#### Abstract

Metals objects have played such an important role to evaluate the information about the civilization and past culture in Archaeological Sciences. The ancient metal objects necessarily come from the archaeological record deliberately buried in the ground either for safe-keeping or as part of ritual offerings to the gods. As a result of their antiquity and the corrosion that affects most metals buried in soils, archaeological objects are both fragile and susceptible to accelerated deterioration once removed from the relative stability of the ground. This makes archaeological objects of any material, difficult to preserve and conserve. This paper focus to report the previously reported methods of cleaning and preservation of ancient copper objects for the new students of conservation field. Corrosion processes, signs and causes of active corrosion on the surface of copper objects with chemical, electrochemical and plasma methods for cleaning of the copper objects are discussed in this study. Plasma and electrochemical methods for cleaning of the objects were most desirable by conservator. Poly vinyl acetate (PVC) and Paraloid B-72 are most suitable for protective layer for the preservative treatment of on the exterior surface of copper objects.

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#### Introduction:-

Copper is a chemical element with the symbol Cu (from Latin: Cuprum), atomic number 29 and melting point 1084°C (1983°F). It is a soft, malleable and ductile metal with very high thermal and electrical conductivity. A freshly exposed surface of pure copper has a reddish-orange color. Copper tools and decorative items dating back as early as 9,000 BC have been discovered, archaeological evidence suggests that it was the early Mesopotamians who, around 5000 to 6000 years ago, were the first to fully harness the ability to extract and work with copper [1]. Researchers now believe that **the copper** came of regular use for a period - referred to as the 'Copper Age' - prior to its substitution by bronze. The substitution of copper for bronze occurred between 3500 to 2500 BC in West Asia and Europe, ushering in the Bronze Age [1]. The decorative copper objects have been discovered from the ancient civilizations of China, India, Peru and Rome such as ear-rings, rings, brooches, bracelets, combs and mirrors [2].

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Good properties of copper make it one of the most used metallic materials in various fields [3]. The gates of the Temple of Jerusalem used Corinthian bronze made by depletion gilding [4]. In ancient India, copper was used in the holistic medical science Ayurveda for surgical instruments and other medical equipment. Ancient Egyptians (~2400 BC) used copper for sterilizing wounds and drinking water, and later on used against headaches, burns, and itching. The Baghdad Battery, with copper cylinders soldered to lead, dates back to 248 BC to AD 226 and resembles a galvanic cell, leading people to believe this was the first battery; the claim has not been verified [5]. In the recent excavation in India reported the copper findings which indicated that the warrior class of people existed in the era from 2000 BC to 1800 BC [6].

The aim of this study intends to report the different methodologies for the scientific treatment and preservation of surface of ancient copper and copper-based objects, were used by the scientists and conservators which will help to give the directions to the new students of conservation research.

### Conservation Problems:-

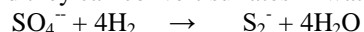
These are the several major conservation problems of ancient copper and copper based objects: 1. **Atmospheric** chlorides, react with the objects in the presence of moisture and oxygen which are extremely harmful and also responsible for the development of bronze disease [7]; 2. Sometimes object surface appearance transforming into greenish powder where stable degradation product can be also formed on the metal substrate as a passive protective layer known as patina  $[\text{Cu}_2(\text{OH})_3\text{Cl}]$ , Polymorphs and Cuprite[7]; 3. Sea object or artifacts suffer from cuprous chloride contamination as well as bacteria also [8]; 4. Formation of black and green layers of corrosion product such as bronchantite, antlerite, cuprite, admixtures of quartz and calcite. Ammonium copper sulphate  $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and copper formate  $\{(\text{HCOO})_2\text{Cu}\}$  can be formed as specific component in small quantity during the formation of crust, mainly in sheltered locations. 5. In aquamarine areas little pits can be observed on the surface of bronze sculpture; 6. Uneven corrosion along the grains can also be observe on the exposed surface of sculpture in highly polluted environments [9]; 7. Beeswax can be associated with severe copper corrosion [10], because bees wax ingredients are palmate and cerotic acids; 8. Untreated copper is exposed to air, it tarnished in a few weeks due to the formation of oxide film [11].

### Chemistry Behind The Corrosion Of Copper Objects: -

Copper is rarely found as a pure metal on archaeological sites; it is normally alloyed with tin, making bronze, or zinc, making brass. Chlorides, which, in the presence of moisture and oxygen are extremely harmful since are responsible for the bronze disease, based on an inexorable cycle copper corrosion process. Most frequently identified compounds in the patina of modern indoor and outdoor bronze sculptures are  $\text{Cu}_2(\text{OH})_3\text{Cl}$  polymorphs and cuprites [7]. Names and structure of compounds and degradation products are described in Table 1.

If copper objects are exposed to air at high temperatures, a thin coating of interference colors will form and traces of sulfides or hydrogen sulfide are present in the atmosphere, copper becomes dark. The principal constituents of beeswax are palmitic and cerotic acids which are also responsible for degradation [12]. On surface of the copper alloy objects these acids can produce metal soaps containing copper ions [13] and these copper soaps are chemically unstable and surface active, and may transport copper cations. Their presence can increase the rate and degree of corrosion on copper alloys. Copper ions serve as a catalyst in the production of low molecular weight fatty acids and dicarboxylic acids which are chemically active, attack metallic copper and dissolve oxide and carbonate corrosion layers [13].

The atmospheric sulfur dioxide being dissolved in rain, oxidized and react with the copper to form sulfates. The atmospheric Carbon dioxide also dissolves in rain, dew or moist soil to give carbonic acid which attacks on the copper surface. Green malachite  $[\text{CuCO}_3\text{Cu}(\text{OH})_2]$ [11, 12] is the more abundant formation, but blue azurite  $[2\text{CuCO}_3\text{-Cu}(\text{OH})_2]$  also occurs described by the Walker 1980. Collins has observed botryoidal malachite up to 1.2 cm thick with crystals of cuprite and a crust of azurite on Chinese bronzes that have corroded underground [14, 15]. Walker 1980 also described the presence of hydrogen sulfide in polluted atmospheres, copper may form chalcocite ( $\text{Cu}_2\text{S}$ ), or covellite ( $\text{CuS}$ ) [11, 12]. The sulfate-reducing bacteria (*Desulphouibrio*) are found in the decaying the copper and bronze with wood and they can convert sulfates in water to sulfides according to the equation.

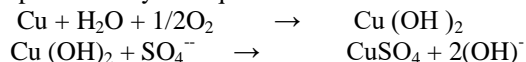


These bacteria also survive underground so that buried structures may show similar corrosion products. As already mentioned, certain bronzes contain high concentrations of iron. Iron compounds are found in some soils, so in these

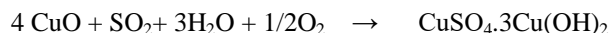
copper iron sulfides can form underground. Dauhree has studied Roman bronze medals and coins, and he identified chalcopyrite  $\text{CuFeS}_2$ , hornite  $\text{Cu}_2\text{FeS}_4$ , and tetrahedrite  $(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$  [18].

The presence of sulfur dioxide in air can result in the conversion of copper oxides to a mixed salt,  $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$ , which is gradually changed to brochantite  $[\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2]$ .

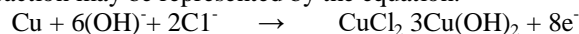
The reactions may be represented by the equations:



or

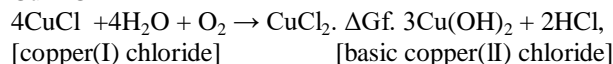
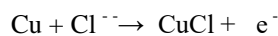


the Statue of Liberty (New York), although surrounded by the sea atmosphere where the high chloride concentration present in the air, is covered with mainly brochantite with basic copper chloride as only a minor constituent [17]. Long contact with sodium chloride in saline soils or desert sands can give basic cupric chloride, atacamite  $[\text{Cu} \cdot \text{Cl}_2 \cdot 3\text{Cu}(\text{OH})_2]$  [12]. This is reaction may be represented by the equation:

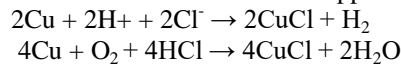


Atacamite is dark green and non-protective so bronzes with it are usually fissured and distorted. Another aggressive chloride is cuprous chloride, nantokite  $\text{CuCl}$  which is unstable, has the appearance of wax and is the cause of bronze disease.

Tel Nami is located near the Mediterranean Sea; the bronze artifacts suffer from cuprous chloride contamination. The standard electrochemical reaction for copper in seawater occurs in a series of steps as described by the Oddy 1970 [8, 19]



The value of  $\Delta G_f = 360.9 \text{KJ/mole}$ . Hamilton 1976 also describes that the copper (I) Chlorides, combines with the oxygen and seawater, will hydrolyze to form hydrochloric acid and basic copper (II) chloride. The hydrochloric acid then attacks the uncorroded copper to form more copper(I) chlorides [65].



### Signs Of Active Corrosion:-

On the surface of copper objects light green, powdery and voluminous deposits are normally a sign of active corrosion (occasionally referred to as 'bronze disease'), but not all bright green corrosion layers are unstable. Mediterranean and Near Eastern bronzes are most likely to suffer from active corrosion, due to high chloride levels, and monitoring of these objects is highly recommended. Active copper corrosion can commence within hours of excavation as the object is exposed to oxygen. It can also occur on objects that have been apparently stable for long periods of time, if the corrosion layers are disrupted by cleaning or handling as described by the Cronyn 1990 [18]. The voluminous corrosion products that form physically disrupt the overlying layers and force them apart. This damages the shape of the object and its associated corrosion patina. Remaining metal in the object will also be attacked by active corrosion, causing an ongoing problem [18]. Allowing copper alloy corrosion to proceed unchecked will result in serious disruption of the corrosion layers and underlying metal. This results in disfigurement of the visual appearance of the object, loss of object shape and coherence. In extreme instances the object can be rendered to powder.

### Causes Of Active Corrosion:-

Copper alloy objects can develop a corrosion layer of cuprous chloride during burial, located at the metal surface under the patina (Table 2). When this is exposed to damp and oxygenated conditions, it reacts rapidly to form powdery corrosion and disrupt the otherwise stable patina [20]. Relative Humidity (RH) is a key factor in whether cuprous chloride reacts to cause active corrosion. There is some dispute about the exact threshold humidity at which active copper corrosion begins to occur. Different studies have produced different threshold limits for the commencement of the reaction: 42–46% RH [21]; 40–50% RH [22]; and 63% RH [23]. Empirical data from the British Museum and English Heritage on the appearance of bronze disease in continuously monitored environmental conditions show that there is certainly a risk above 42% RH. Above 68% RH, the point at which cuprous chloride

attracts enough water to form liquid, corrosion occurs very rapidly. Between these two points, the exact risk is difficult to evaluate and further research is required.

The cuprous chloride reaction is self-perpetuating, and therefore once exposed to higher RH the reaction may take a period of time to cease when the RH is reduced [21]. High levels of acetic acid are known to cause corrosion of copper above 85% RH [24, 25]. Unfortunately there is no published research on the effect of organic acids on archaeological copper alloys. Their effect on archaeological iron is different in its detail and risk than that of historical iron and it is possible the effect on historical copper alloys is not the same for archaeological material. Copper corrosion rates are also increased by sulfur dioxide and nitrogen dioxide, particularly when these gases are present together at high RH [26]. The composition of the burial environment or prior conservation treatments may also be responsible for causing active copper corrosion. If corrosion products different from those described are forming on copper alloys, it is best to seek the advice of a conservator in identifying the products and their cause.

#### Storage And Display Conditions:-

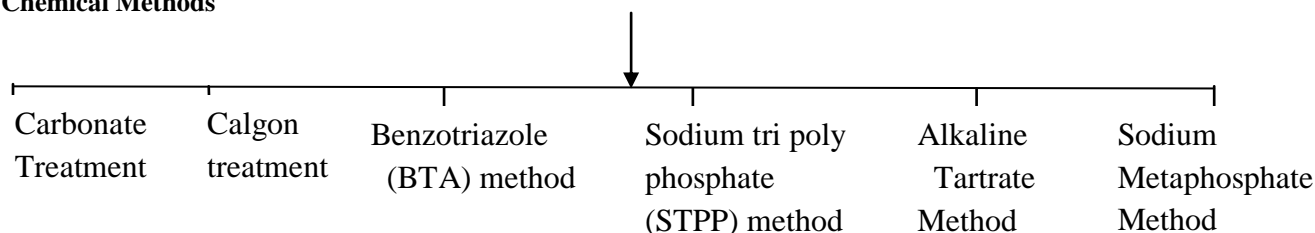
The varying results from studies of bronze disease mean that evaluating risk is difficult (Table 3), but all the studies suggest that below RH of 42% active corrosion is unlikely. Until the risks above this RH can be more fully evaluated, this remains the recommended threshold. Above 68% RH the risk of outbreaks of bronze disease is very high; exposing archaeological copper alloys to RH above this level should certainly be avoided. An acetic acid free environment is also recommended, although the effect of low amounts of acetic acid at 42% RH cannot be quantified based on current evidence. Once an object is experiencing active copper corrosion, reducing RH to below 42% should help to prevent further problems. RH above 42% should still be avoided for treated objects [27-31].

#### Treatment And Preservation Methods:-

The copper artifacts were first gently brushed for removing the dust and dirt. Appearance of the surface and its features should be documented digitally. Different levels of corrosion removal was adopted, artifacts with less corrosion have given minimal cleaning, while those with heavy calcareous deposit and encrustations were cleaned with utmost care. The objects were cleaned with soft brush to remove the dirt and dust. To expose the surface details, it was found necessary to remove the heavy siliceous and calcareous encrustations. Ethanol is applied on the surface to moisten and soften the calcareous and siliceous encrustations so as to facilitate their easy removal. The fine tools such as fiber brushes, paint brushes, dental picks, metallic scalpels, points, needles, tools fashioned in wood or sticks etc. were used. This treatment was applied to objects like knives, blades, nails, daggers, rods and rings. There are several other scientific methods as follows .

1. Chemical Methods
2. Plasma Methods
3. Electrolytic Reduction Method.

#### Chemical Methods



#### Chemical Methods:

##### Carbonate treatment:

The cuprous chloride components of copper and its alloys are insoluble and cannot be removed by washing with water alone. When bronzes or other alloys of copper are placed in a 5 % solution of sodium sesquicarbonate (Fig. 1), the hydroxyl ions of the alkaline solution react chemically with the insoluble cuprous chlorides to form cuprous oxide and neutralize any hydrochloric acid by-product formed by hydrolysis to produce soluble sodium chlorides [36, 48]. The chlorides are removed each time the solution is changed. Successive rinses continue until the chlorides are removed. The object is then rinsed in several baths of de-ionized water until the pH of the last bath is neutral. Initially, the baths are changed weekly; as the duration of treatment progresses, the interval between bath changes is extended. Monitoring the chloride level by the quantitative mercuric nitrate test enables the conservator to determine

precisely how often to change the solution. In lieu of a quantitative chloride test, the qualitative silver nitrate test can be used to determine when the solution is free of chlorides.

**Calgon treatment:**

One to five percent of sodium hexa meta phosphate (Fig. 2) (calgon) solution as per the condition of the objects, can be used for removal of calcareous encrustations by applying the solution-soaked cotton on it. After the removal of deposits object should be cleaned with distilled water for several time until the pH of the object reach up to neutral [32, 33].

**Benzotriazole (BTA) method:**

Bronze disease has been investigated since 1894 [35, 36, 37]. Sharmanand et al 1994 [32] also described the treatment of active corrosion areas with separately and carefully stabilization of active corrosion. They described that the active corrosion areas of the objects were cleaned minutely and treated with corrosion inhibitor Benzotriazole (Fig. 3) (1-3% solution is prepared with isopropanol). A bath of BTA solution is specially prepared in a glass trough for the copper vessel and is kept in the bath overnight so as to allow its all bent/curved inner areas get stabilized where bronze disease was severely affected. The object was removed from the bath and BTA solution was applied on it at preferential areas where severe bronze disease was observed. The application of BTA with cotton was done at every half an hour during the day time repeatedly for three days. White powdery deposit of BTA was cleaned by using isopropanol and cotton swab. BTA works by forming a thin, insoluble and invisible film, and the effectiveness of BTA depends on how well the film can form. It is observed in the copper vessel at some local spots due to acidity, BTA film forming is not occurred properly and demanded preferential stabilization treatments [37, 38]. The active areas can also be treated with a silver salt (such as silver oxide), which can seal the active area with a coating of silver chloride (hornsilver) [11, 39, 48].

**Sodium tri poly phosphate (STPP) method:**

To reduce the damage of the patina, (basic copper carbonate) sodium tripolyphosphate (STPP) (Fig.4) which is less reactive with patina was used for cleaning the calcareous encrustation further. On an area approximately 10cm<sup>2</sup>, Cotton pads soaked with solution (5% STPP solution were applied for the thicker accretions, whilst 2-5% and 1% solutions were used for thinner areas of accretion) of sodium tri poly phosphate were left in contact with the object for half an hour followed by mechanical cleaning of the surface accretions with the help of sharp scalpel and blunt knife, needle etc. For removing the ingrained accretions freshly prepared carboxyl methyl cellulose (CMC) paste with 2.5% STTP in distilled water was applied on the affected part and left to dry for a day. The dried CMC film was then removed carefully with forceps. After removal of incrustations from the surface, the deposits of STTP were removed from the cracks, depressions and uneven areas. The object was cleaned with hot distilled water and dried in an oven [32].

**Alkaline TartrateMethod:**

A 10 per cent solution of Rochelle salt containing the same proportion of caustic soda can also be employed, but the former solution is much quicker and is, therefore, to be preferred. Treatment with the alkaline tartrate solution results in the decomposition of basic copper carbonate and chloride and leaves the object covered with the red oxide of copper (cuprite). If the elimination of basic copper chloride has been complete and green corrosion-product is no longer found sticking to the object, the chemical treatment may be considered to be successful; the object should then be subjected to thorough washing in the usual way. A very fragile object should be treated with a 10 per cent solution of sodium sesquicarbonate solution for a period of ten to fifteen days, by which time the desired cleaning would be complete; the object should then be washed in plain water, dried and preserved. Where an object has undergone deep corrosion, it should be treated with a solution of 1 part caustic soda, 1 part tartaric acid and 10 parts water. A very fragile object should be treated with a 10 per cent solution of sodium sesquicarbonate solution for a period of ten to fifteen days, by which time the desired cleaning would be complete; the object should then be washed in plain water, dried and preserved. [33]

**Sodium Metaphosphate Method:**

It is occasionally found that some objects which are covered with a calcareous or argillaceous incrustation do not respond to the alkaline tartrate treatment. In such cases, a 10 per cent solution of sodium metaphosphate should be employed at the first stage of chemical treatment and the object transferred to the alkaline tartaric acid bath after the calcareous incrustations have been removed by sodium metaphosphate; this may in itself result in complete

elimination of corrosion-products and removal of deleterious materials of secondary origin. In such a case no further treatment is necessary and the object may be washed, dried and preserved.[33]

#### **Plasma Treatment:-**

- a. Novakovic et al 2009 [39] has reported the application of hydrogen plasma in the conservation and restoration of metallic archaeological objects has been under research and development for the last 20 years [40-41]. This method is based on the reduction of the corrosion products on the metal-excavated objects by reactive reducing species such as hydrogen atoms in a H<sub>2</sub> glow discharge plasma of low pressure and temperature. In the glow discharge plasma, electrons accelerated by an external electrical field have enough energy among many other interactions to dissociate hydrogen molecules H<sub>2</sub> to hydrogen atoms at low pressure and temperature. The reduced layer becomes brittle and can be easily removed by conservators. In addition, the phases containing chloride ions can be destabilized and the chlorides can be removed to the gaseous phase of the discharge. A radio frequency (RF) glow discharge plasma apparatus was used, similar to the Veprek prototype apparatus [40].
- b. A method to prevent copper oxidation prior to Cu-to-Cu bonding was described by Seo et al 2019[42] using two-step plasma treatment. The first plasma step was to remove copper oxide and to clean any contaminants by Ar plasma, and then the second plasma step was to form copper nitride with N<sub>2</sub> plasma. The formed copper nitride on the Cu surface was expected to decompose into metallic Cu and nitrogen. The copper nitride formation was carried out in a conventional direct current sputtering technique because it is a simple and highly cost-efficient method. Although a decomposition of copper nitride depends on various deposition and growth techniques, it typically occurs at 300 °C[43, 44], which can potentially lower the Cu-to-Cu bonding temperature. Previously the Ar plasma effect in two-step plasma treatment process using sputtered Cu thin film has been studied [45].
- c. Mozetic, et al 2006 described in their patent about the cleaning of organic and inorganic impurities deposited on the copper objects. The present methods used the object exposed successively to an oxygen plasma and a hydrogen plasma, in order to eliminate organic impurities first and then oxidative impurities. Between the two plasma-treatment steps, specific conditions are maintained with regard to the pressure in the treatment chamber (10 to 50 mbar), to the type of excitation of the plasma in the chamber (by a high-frequency generator having a frequency of greater than approximately 1 MHz) and to the intensity of the action of oxygen radicals on the components (the flux of radicals on the component surface exceeds approximately 10 radicals per square meter). Hereby further processing is favored, by the fact in particular that the subsequent adhesion of cement or soldering metal on the surface is improved and the resistance of connection points is lowered. As regards the environment, this method is a favorable alternative to industrial cleaning processes, which currently use wet-chemical cleaning. Their team also described the removal of inorganic impurities (mainly copper or nickel oxides) which are removed by introducing hydrogen or a mixture of argon and hydrogen into the vacuum chamber. Argon can be replaced by any noble gas. A plasma is generated by a high-frequency discharge. Hydrogen radicals formed in the discharge interact with the inorganic surface impurities and reduce them to water and other simple molecules such as HCl (Hydrochloric Acid), HS (Hydrogen Sulfide), HF (Hydrogen Fluoride), etc., which are desorbed from the surface and pumped out. Following the hydrogen treatment, the surface is truly free of any kind of impurities. A special aspect of the present method is to be seen in the fact that, by virtue of the specific conditions during the treatment, little or no bombardment of the surface with high-energy ions takes place, and this is regarded as particularly favorable [46].
- d. Grigoreva et al 2017 also described the laser-cleaned cleaning method on the surfaces of copper and copper-alloy objects using a Smart Clean 2 (El. En., Italy) pulsed YAG:Nd laser and a commercial MiniMarker2 M20 ytterbium pulsed fiber-optic laser, both with emission wavelengths of 1064 nm. They also showed that discoloration of the copper surface can be mitigated by performing the laser treatment in a nitrogen atmosphere [45].

#### **Electrolytic Reduction Methods:-**

- a. Electro chemical treatment: Plenderleith and Werner (1971) and Hamilton 2011 were described about the electrochemical cleaning of archaeological objects on the basis of current supply, current density and chloride monitoring. The state that the moderate current density (0.005 to 0.05 amp/cm<sup>2</sup>) should be permitted to prevent the deposition of a salmon-pink film of copper on the objects [48,49]. Keel (1963) also describe that a current density above 0.01 amp/cm<sup>2</sup> will damage cupreous objects. Along these same lines [50], Pearson (1974) properly observes that care must be taken when electrolytically cleaning of marine-recovered mineralized bronze in order to prevent damage to the artifact surface by the evolution of hydrogen gas. Current densities, both within and in excess of the given ranges above, are commonly applied to different cupreous objects [ 52].

North (1987) also recommends using the hydrogen evolution voltage techniques described for the treatment of iron. In general, the same procedures regarding current density that are described for the treatment of iron apply to the treatment of cupreous artifacts also. The main variations in treatment involve the fact that the duration of electrolysis for chloride- contaminated cupreous objects is significantly shorter than that for comparable iron objects. Small cupreous artifacts, such as coins, require only a couple of hours in electrolysis, while larger cupreous specimens, such as cannons, may require several months [51].

- b. Gavano static cathodic treatment: Giovannelle et al 2010 reported a novel approach to the electrochemical treatment of bronze disease, based on the use of room-temperature ionic liquids (RTIL). In particular, his team employed 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide (Fig. 5) as the electrolyte for the galvanostatic cathodic treatment of a late bronze-age artifact that had been exposed to marine environment during its history, dating back to ca. 1100 B.C. [53]

#### Preventive Coatings And Consolidation:-

Several researchers and conservators are using different type cleaning methods and preservative to prevent the exterior surface of copper objects. As per the requirement of the Archaeologist and Museum curator preservative materials should be reversible in nature. In the review of the literature Polyvinyl acetate (PVA), Acryloid B72, Polyvinyl acetate (PVA) emulsions, Cellulose nitrate, also called nitro-celluloid, Polyvinyl butyral, Various polymethacrylates in an organic solvent, e.g., Elvacite 20/3; Polymethacrylate emulsions, e.g., Bedacryl, Polyvinyl alcohol, Elmer's Glue and Epoxy resins were using as consolidants [66]. Polyvinyl acetate (PVA) (Fig. 6) is the most commonly used thermoplastic polymer resin for organic material recovered from archaeological excavations [66]. It comes in a range of viscosities (V) ranging from V1.5 to V60. The lower the number, the less viscous the solution. The Paraloid B72 (Fig. 7), popularly known as Acryloid B72, is a co-polymer of ethyl methacrylate and methyl methacrylate has also been extensively used in bronze conservation work both as adhesive and also as preservative coating. Selwyn et al 1993 and Patel et al 2014 were disclosed in their study that 4-3% of the Acryloid B72 was used for coating so as to avoid shining appearance of the surface of the copper artifact [54, 65]

**Table 1:-** Details of composition of corrosion layers, chemical formula causes of formation and colour of patina.

Entry	Surface layers /minerals	Chemical Formula	Causes of Formation	Colour of patinas	Ref.
1	Antlerite	$\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$	Condensed air humidity	Blue and green	[9]
2	Brochantite	$\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$	Direct impact of rain, snow and dew and also depends on the concentration of $\text{SO}_2$ in the atmosphere	Blue and green	[9, 54]
3	Posnjakite	$\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_6 \cdot \text{H}_2\text{O}$	Presence of air humidity and oxygen with aggressive gaseous and solid components of atmospheric pollution	Green	[55,56]
4	Cuprite	$\text{Cu}_2\text{O}$	Presence of air humidity and oxygen, with aggressive gaseous and solid components of atmospheric pollution	Brown red, sub metallic red	[57]
5	Tenorite	$\text{CuO}$	Presence of air humidity and oxygen with aggressive gaseous and solid components of atmospheric pollution	Metallic gray black	[9,58]
6	Atacamite	$\text{Cu}_2(\text{OH})_3\text{Cl}$	Develop in Maritime environments (presence of chlorides)	Vitreous green	[59]
7	Paratacamite	$\text{Cu}_2(\text{OH})_3\text{Cl}$	Develop in Maritime environments (presence of	Pale green	[60]

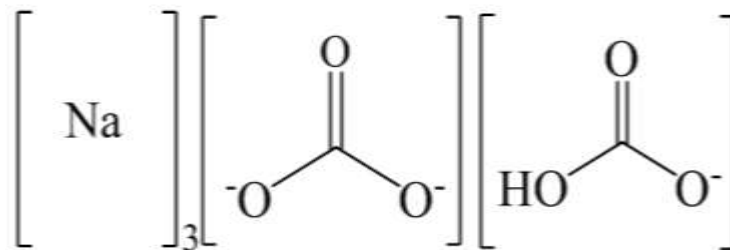
			chlorides)		
8	Botallackite	$\text{Cu}_2(\text{OH})_3\text{Cl}$	Heavy marine environments which change into basic copper chloride	Pale Bluish green	[59]
9	Moolooite	$\text{C}_2\text{CuO}_4 \cdot n\text{H}_2\text{O}$	Effect of bird excrement on the metal surface(direct impact of precipitation)	Varies from blue to green but most typically is Turquoise Green	[61]
10	Ammonium copper sulphate	$(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	Affected by anthropogenic influences(in the crust)	Deep blue	[9, 62]
11	Chalcanthite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Highly polluted environments (a part of soffit crusts)	Berlin blue to sky-blue	[9]
12	Gerhardite	$\text{Cu}_2(\text{OH})_3\text{NO}_3$	Formed in atmospheres polluted by anthropogenous and biological effects	Turquoise-blue& green	[9, 63]
13	Melanothallite	$\text{Cu}_2\text{OCl}_2$ $\beta\text{-Cu}_2\text{S}$ $\text{Cu}_2\text{S}$	formed in atmospheres polluted by anthropogenous and biological effects	Black to bluish-black	[9]

**Table 2:-**Types of Copper Alloy Corrosion.

SN	Composition	Colour	Minerals	Conditions
1	Oxides	Red	Cuprite	Forms on damp, aerated sites
2	Oxides	Black	Tenorite	Usually found in water logged conditions
3	carbonates	Green/blue	Malachite/ azurite	Can form in a variety of burial environments and may appear wax smooth or grainy / crystalline. Mixes blue and green are often found together.
4	Bronze disease	Green / blue	Cuprite	Pitting, powdery and voluminous deposits

**Table 3:-** Risk profile for corrosion of copper alloy objects.

Relative Humidity (%)	Below 42	42–68%	Above 68%
Corrosion Risk factor	Corrosion risk is low	Some risk, but exact level of risk unknown	Very high risk of corrosion

**Fig. 1:-**Structural formula of Sodium Sesqui Carbonate.



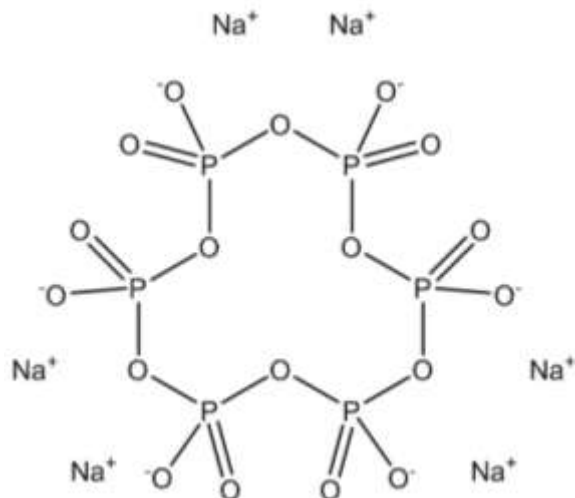


Fig. 2:-Structural formula of sodium hexa meta phosphate.

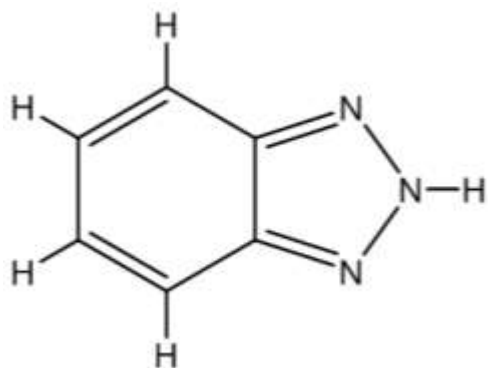


Fig. 3:-Structural formula of 1,2,3-benzotriazole (BTA).

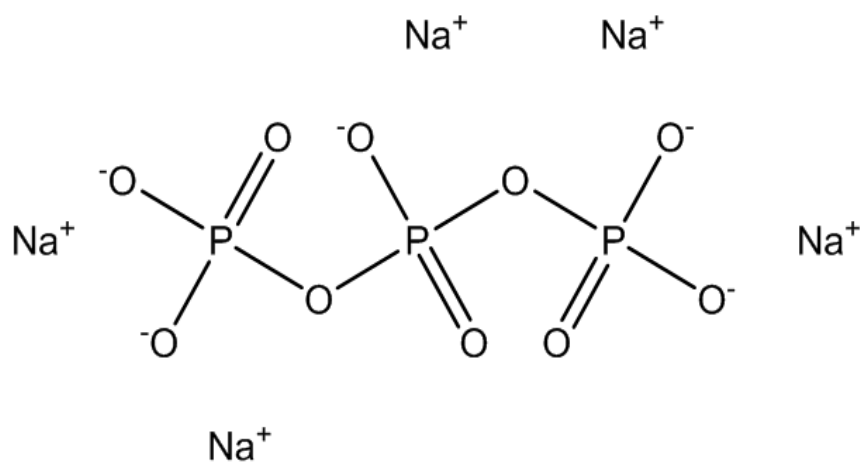


Fig. 4:-Structural formula of sodium tripolysulphate.

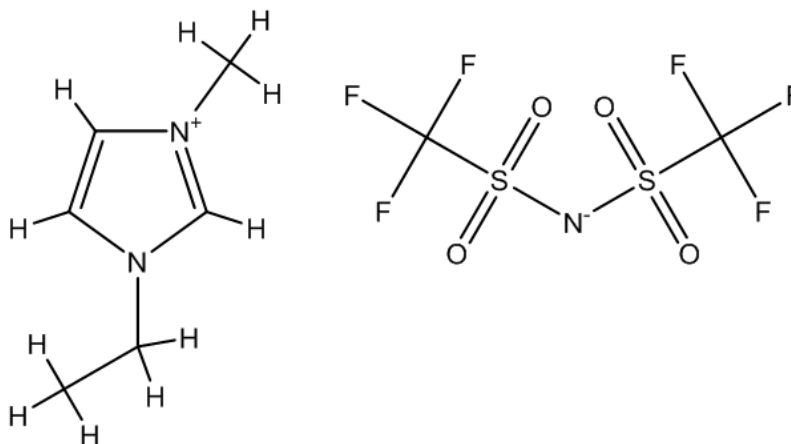


Fig. 5:-Structural formula of 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide.

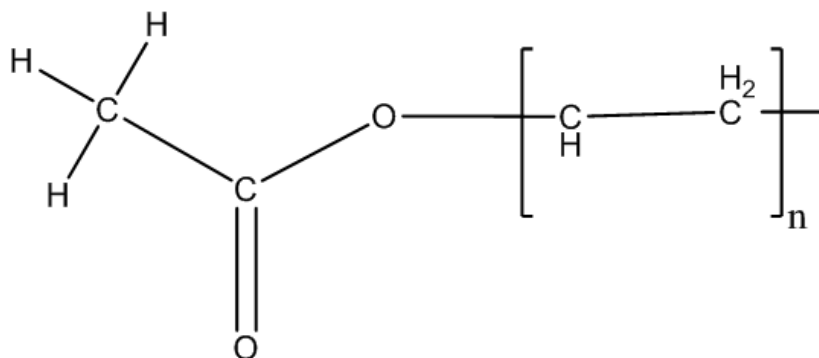


Fig.6:- Structural formula of Polyvinyl acetate (PVA).

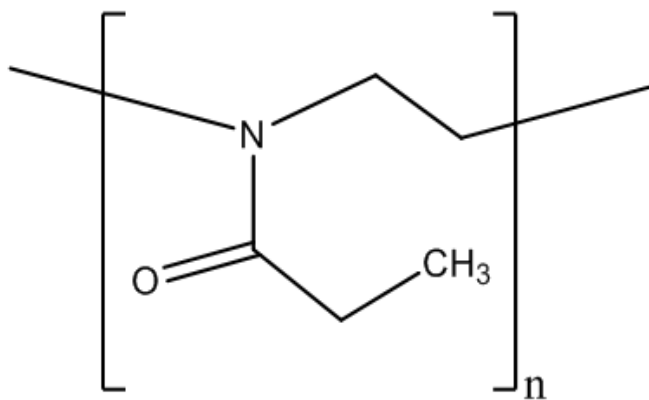


Fig. 7:-Structural formula of Paraloid B72.

### Conclusion:-

This study describes the methods for the scientific treatment and preservation of copper objects according to the experiences of the researchers and conservators. The study also suggested that the plasma and electrochemical methods for cleaning of the objects were most preferable by conservator. Poly vinyl acetate (PVC) and Paraloid B-72 are most operational for protective layer for the preservative treatment of on the exterior surface of copper objects. Forty Two percent Relative Humidity should be standard maximum limit for display the copper objects in the museum environment.

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