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SODIUM TRIPOLYPHOSPHATE—A SAFE SEQUESTERING AGENT FOR THE TREATMENT OF EXCAVATED COPPER OBJECTS

V. C. Sharma and B. V. Kharbade

Abstract—The removal of calcareous accretions while protecting the green patina of excavated copper objects can be an important step in their conservation. Calgon®, a commonly used reagent, was found to affect the crust severely; therefore an alternative reagent, sodium tripolyphosphate (STPP), was evaluated. Basic copper carbonate was reacted with both Calgon and STPP solutions. Physical changes, such as effervescence, colour of the reaction products and their infrared spectra were recorded. Similarly, fragments from excavated copper objects were treated in both STPP and Calgon solutions and the colours of the fragments and infrared spectra of samples from the fragments were recorded before and after treatment. From the results, it is concluded that Calgon damages the crust of excavated copper objects whereas STPP proved to be an effective sequestering agent. To assess practical utility, several excavated bronze images with green corrosion crusts were treated with STPP. The results obtained were very satisfactory.

1 Introduction

Excavated copper objects are often found with a thin, uniform, bluish-green crust, principally composed of basic copper carbonate intermixed with either superficial or ingrained calcareous accretions. To protect the patina and remove the calcareous accretions is an important step in the conservation of such objects because the patina imparts an 'antique' appearance much admired by archaeologists, art historians and connoisseurs. Mechanical cleaning is advocated as a safe method but it is arduous, time-consuming and not suitable for deep-seated accretions in the interstitial spaces of the patina. The method of chemical treatment with Calgon®, sodium hexametaphosphate, has been in use for a long time. Calgon softens the tough accretions by forming soluble complexes with calcium and magnesium [1, 2]. However, long experience shows that Calgon treatment damages the bluish-green patina to a greater or lesser extent and sometimes removes it completely, exposing underneath an unsightly brown layer of copper(I) oxide. Similar observations were reported by Plenderleith [2]. To our knowledge, no scientific work has been carried out on how and in what way Calgon can affect the crust of basic copper carbonate. This study, therefore, aimed to assess the effect of Calgon on basic copper carbonate crusts and to evaluate suitable alternative chemical treatments to remove calcareous accretions without harming the patina.

Extensive information concerning the properties of chelating agents can be found in the literature of the detergent industry. Some detergent builders, for example citrates, sodium tripolyphosphate and EDTA (ethylene diamine tetracetic acid), have been used in conservation for surface cleaning. Sodium tripolyphosphate (STPP) was for many years the preferred builder for many detergent formulations. It is an excellent sequestrant for Ca^{2+}, Mg^{2+} and other metal ions. It provides and buffers alkaline conditions in the preferred range for optimum detergency (pH 9–10) [3].

STPP is very effective in defloculating, peptizing and dispersing finely divided solids, and this behaviour is utilized in many areas of technology [4]. It has also been established that STPP will dissolve calcium carbonate by forming water-soluble chelates with Ca^{2+} [5]. These properties of STPP favour its use in the treatment of excavated copper objects, whereas other polyphosphates are not suitable because of their acidic or alkaline nature. This paper describes the evaluation of sodium tripolyphosphate as a sequestering agent for the treatment of excavated copper objects with a patina of basic copper carbonate and compares the results with Calgon.

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2 Experimental

2.1 Reaction of aqueous Calgon and STPP solutions with basic copper carbonate

The pH of aqueous solutions of Calgon (Glaxo Laboratories, India) and STPP (Robert Johnson, India) of 10, 5, 2·5, 1·0 and 0·5% (w/v) was measured with a microprocessor ion analyzer and a flat combination pH electrode (Orion Research, USA) and 25ml of each solution were added to different reaction vessels containing 0·2g of basic copper carbonate (Glaxo Laboratories, India). The mixture was stirred while the solution was added and then kept at room temperature for eight hours. The reaction mixtures were then filtered; the solids were collected at a pump on a glass sinter, washed thoroughly with lukewarm distilled water, dried in an oven at 100°C for 24 hours and allowed to cool in a desiccator over silica gel.

2.2 Treatment of fragments from excavated copper objects having bluish-green patina

In order to compare the results of the synthetic studies with those obtained from the treatment of copper art objects, a number of fragments of excavated copper objects obtained from the Ramayana excavation site (Sringverpura, Allahabad, India) were dipped into aqueous solutions of Calgon and STPP, as described in section 2.1, and kept at room temperature for eight hours. The fragments were taken out and brushed gently with a soft nylon toothbrush, washed thoroughly with distilled water, dried in an oven at 100°C for

Table 1 Physical changes[a] *in basic copper carbonate and crust of excavated copper object after treatment with aqueous solutions of Calgon and STPP at different concentrations*

Solution, % (w/v)	*pH*	*Changes in basic copper carbonate (pastel green)*		*Changes in crust (bluish-green) of fragment*	
		Effervescence	*Colour*[b]	*Effervescence*	*Colour*[b]
Calgon					
10	5·4	brisk	light turquoise	very slow	light turquoise
5	5·7	brisk	light turquoise	very slow	pale turquoise
2·5	5·8	less brisk	pale turquoise	very slow	pale turquoise
1	5·9	less brisk	pale green	no	greyish green
0·5	6·0	less brisk	pale green	no	greyish green
STPP					
10	8·4	no	pastel green	no	bluish green
5	8·6	no	pastel green	no	bluish green
2·5	8·7	no	pastel green	no	bluish green
1	8·9	no	pastel green	no	bluish green
0·5	9·0	no	pastel green	no	bluish green

(a) These changes were observed in aqueous solutions at room temperature (35°C) for eight hours.
(b) Identified and specified according to *Methuen Handbook of Colour* [6].

24 hours and stored in a desiccator over silica gel.

2.3 Methods of evaluation

The solid samples of basic copper carbonate and the reaction products with Calgon and STPP, and samples isolated by mechanical scraping with a fine-edged razor from the fragments before and after treatment with Calgon and STPP, were analyzed by infrared spectrometry using a Perkin-Elmer 783 spectrophotometer. The colours of the solid samples were examined and specified according to the *Methuen Handbook of Colour* [6]. For infrared analysis, the solid samples were finely ground in an agate pestle and mortar, and mixed in a few drops of Nujol oil (DD 057, Perkin-Elmer) to form a paste. The IR spectra of the samples were recorded using the Mull technique; infrared spectrophotometer parameters were: slit width 3, scan time 12 minutes.

3 Results and discussion

The sequestering agents Calgon and STPP were assessed on the basis of the criteria that they should not alter the composition of the patina, basic copper carbonate, while effectively removing calcareous accretions, and that they should not leave any residue on the surface. To understand the alteration of basic copper carbonate on treatment with Calgon and STPP, physical changes such as effervescence, colour of the reacted products and chemical changes were recorded (Table 1). All the changes were observed after eight hours, which was determined to be the optimum time for completion of the reaction, after a series of experiments in which basic copper carbonate reacted with Calgon and STPP for two, four, six, eight and 36 hours. It was observed that no further reaction occurred after eight hours.

Calgon solutions gave effervescence on addition to basic copper carbonate. The pH of these solutions also indicated their acidic character (Table 1). Generally the pH range from 5·5 to 8·5 is preferred for surface cleaning, though mild alkaline solutions are often selected for their enhanced detergency [3]. Pollard *et al.* have mentioned that alkaline treatment of copper objects can lead to the alteration of cuprite to tenorite which gives undesirable black spots on some copper objects [8]. The colour of basic copper carbonate in Calgon treatment changed to a light turquoise or pale green whereas effervescence and colour change were not observed during STPP treatment.

Basic copper carbonate has principal infrared bands at 1100, 1050 and 875cm^{-1}. These were missing in the IR spectra of Calgon-treated basic copper carbonate whereas there was no distortion in these bands in the STPP-treated carbonate (see Figures 1, 2a and 2b). These infrared results confirmed that Calgon alters the basic copper carbonate chemically, whereas STPP solutions do not give any signs of alteration. Earlier IR study of the mineral malachite (basic copper carbonate) describes bands at 1045 and 875cm^{-1} as due to the hydroxy group while the carbonate group gives bands at 1500, 1400, 1095, 820, 803, 748 and 710cm^{-1} [9, 10].

The disappearance of the bands at 1045 and 875cm^{-1} in Figure 2a indicates that the hydroxy group of basic copper carbonate might react with Calgon. Infrared measurements are diagnostic for such changes.

In order to compare the studies on synthetic minerals with those obtained from the treatment of excavated copper objects, a number of fragments were treated with both Calgon and STPP solutions at the same concentrations used in the above study. Before and after treatment, colour and infrared spectra of the patina were recorded (Table 1). It was observed that the fragments treated with Calgon showed a colour change from

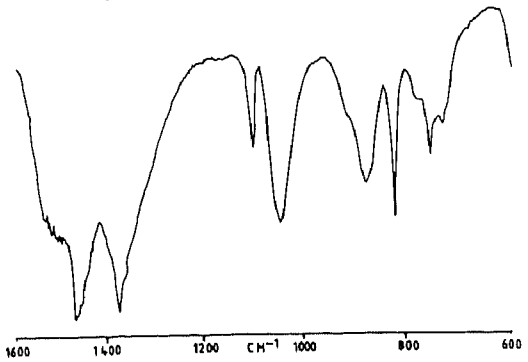

Figure 1 Infrared spectrum of basic copper carbonate.

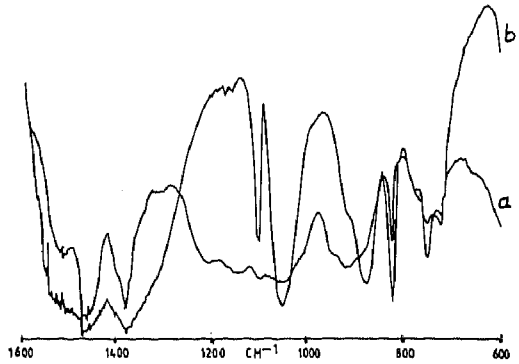

Figure 2 Infrared spectra of (a) basic copper carbonate treated with Calgon, showing disappearance of bands at 1045 and 875cm⁻¹; (b) basic copper carbonate treated with STPP, showing no alteration in bands.

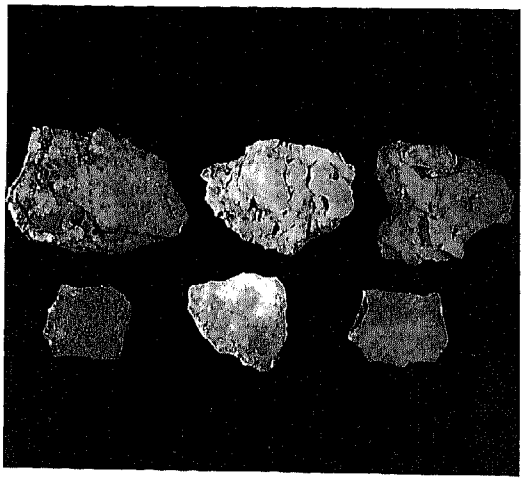

Figure 3 Photograph of representative fragments: those on the left, untreated, have a uniform bluish-green crust; those in the centre, treated with Calgon (5% aqueous solution), show damage to the crust; in those on the right, treated with STPP (5% aqueous solution), no damage was found and accretions were removed.

bluish green to pale green and the patina was etched, creating an uneven surface at several places, whereas such changes were not observed in the fragments treated with STPP solutions (Figure 3). An infrared spectrum of the sample from an untreated fragment shows the presence of basic copper carbonate and some unidentified extraneous matter, revealed by extra peaks at 940 and 986cm^{-1} (Figure 4a). All the important IR bands of basic copper carbonate appeared unimpaired after the STPP treatment but were distinctly distorted after Calgon treatment. The additional peaks mentioned above were eliminated in STPP treatment, which shows that some of the accretions were removed in this treatment (Figure 4b and c).

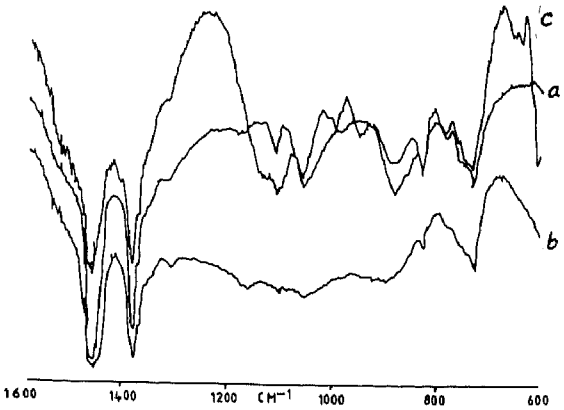

Figure 4 Infrared spectra of (a) untreated bluish-green crust from excavated copper object with extra peak at 940 and 985cm⁻¹; (b) crust of fragment treated with Calgon, showing band missing at 1095, 1045 and 875cm⁻¹; (c) crust of fragment treated with STPP, showing all the identifying peaks of basic copper carbonate intact.

It can be concluded from these observations that Calgon severely damages the crust of basic copper carbonate patinas, while STPP proved to be an effective sequestering agent for the removal of calcareous accretions without disturbing the patina.

4 Treatment with STPP

In order to evaluate the practical utility of STPP in the treatment of excavated copper objects, 20 treasure-trove bronze images, solid cast, mainly for the Chola period (ninth-thirteenth century A.D.), retrieved over the last 50 years by the Thanjavur Art Gallery from different places in the district of Thanjavur, South India, were treated with STPP. All these images had tough whitish accretions of variable thickness covering the objects and obscuring their finer details. X-ray diffraction patterns confirmed the presence of calcareous

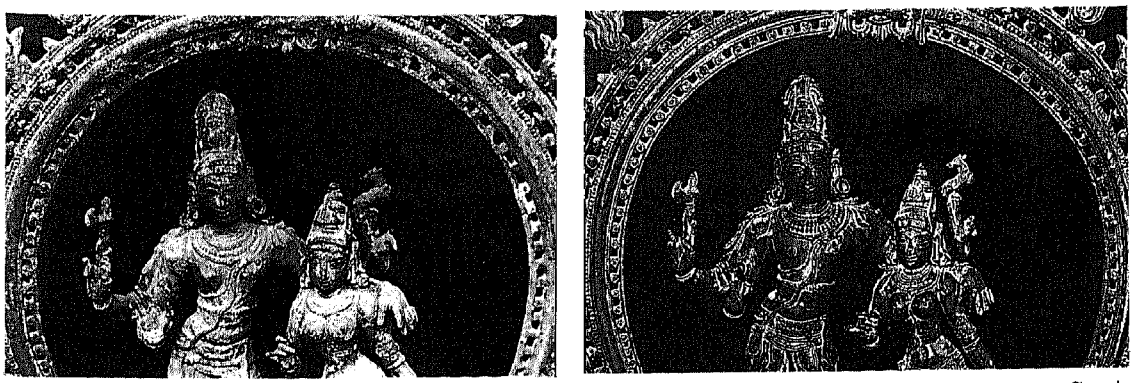

Figure 5 Treasure-trove bronze image from the Chola period (eleventh century A.D.), Thanjavur, South India: (left) tough whitish accretions hiding the finer details; (right) after treatment with STPP.

material cementing the accretions. The method used in the treatment was as follows. On an area approximately 10cm², cotton-wool poultices soaked in 5% STPP solution were applied for the thicker accretions, whilst 2·5% and 1% solutions were used for thinner areas of accretion. Each poultice was left in place for about 30 minutes and it took seven, eight or more applications before the softened accretions were completely removed, aided mechanically with a sharp scalpel and a pointed needle. For the removal of ingrained deposits an STPP gel was used. The gels were made by dispersing carboxymethyl cellulose in a 0·5–2·0% solution of STPP. The gel was applied with a soft brush and allowed to dry, which took about 40 hours. The dried film was then peeled off. The image was washed in a boiling water-bath several times to remove STPP residues and then heated in an oven just above 100°C for about eight hours. On cooling, the object was coated with 2% polyvinyl acetate in ethanol as a preservative. The whitish tough accretions obscuring the bronze images were removed successfully using the STPP treatment, as is evident in Figure 5.

5 Conclusion

The results obtained confirm that sodium tripolyphosphate (STPP) is an effective sequestering agent for the treatment of excavated copper artifacts with green patinas of basic copper carbonate, while Calgon severely damages the green patina of basic copper carbonate and is not recommended for the treatment of these objects. The bronze images treated with STPP show that all the white accretions can be removed without affecting the green patina and that sculptural detail on the surface can be revealed safely, preserved in the patina layer.

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Résumé—L'enlèvement des concrétions calcaires qui recouvrent la patine verte des objects en cuivre provenant de fouilles est une étape importante de leur conservation. Il est prouvé que le Calgon, un réactif couramment employé, peut affecter dangereusement la croûte, et c'est pourquoi un autre réactif, le tripolyphosphate de sodium, a été étudié. Pour cela, on a fait réagir du carbonate basique de cuivre avec du Calgon et des solutions de tripolyphosphate de Na. Les changements physiques, tels que l'effervescence, la couleur des produits de réaction, ainsi que leurs spectres IR, ont été enregistrés. De même on a traité des fragments d'objets de cuivre provenant de fouilles à la fois dans des solutions de tripolyphosphate de Na et de Calgon. Les couleurs des fragments et les spectres IR des échantillons ont été enregistrés avant et après traitement. On conclut d'après ces résultats que, contrairement au Calgon qui altère la croûte de ces objets de cuivre, le tripolyphosphate de Na se révèle comme un agent efficace de conservation. Pour confirmer son utilité, plusieurs sculptures de bronze provenant de fouilles et présentant une croûte de corrosion verte ont été traitées avec des résultats très satisfaisants.

Zusammenfassung—Die Entfernung kalkhaltiger Ablagerungen bei gleichzeitiger Beibehaltung der grünen Patina auf archäologischen Kupferobjekten ist bei ihrer Konservierung ein bedeutender Schritt. Calgon, ein gängigerweise eingesetztes Mittel zur Entkalkung, beeinträchtigt die Patina nachhaltig; der Beitrag setzt sich deshalb mit der Alternative Natriumtripolyphosphat (NTPP) auseinander. Die Autoren setzten zunächst basisches Kupferkarbonat sowohl dem Einfluß von Calgon als auch von NTPP aus. Dabei wurden die physikalischen Vorgänge wie etwa Schaumbildung, die Farbe der Reaktionsprodukte und ihre Infrarotspektren aufgezeichnet. Gleichermaßen erfolgte die Behandlung von Fragmenten geborgener Kupferobjekte sowohl mit Calgon- als auch mit NTPP-Lösung, wobei man auch hier die Farbe der Probenstücke wie auch ihre Infrarotspektren vor und nach der Behandlung registrierte. Aus den Untersuchungsergebnissen läßt sich schließen, daß Calgon an der Patina geborgenen Kupfers Schäden verursacht während NTPP sich als effektives Trennmittel anbietet. Die praktische Anwendbarkeit dieser Methode wird an mehreren ausgegrabenen Bronzefiguren mit grünen Korrosionsschichten nachgewiesen, wo die erzielten Ergebnisse sehr befriedigend waren.