A New Method for the Stabilisation of Archaeological Copper-Based Artefacts

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Abstract

A new method for stabilising difficult-to-stabilise copper-based artefacts is introduced. The method is based on the treatment of copper-based artefacts with neopentyl (diallyl) oxy tri(diocetyl)pyro-phosphato titanate. This chemical interacts with the surface active and hydrophilic groups of the corrosion products covering copper-based objects and converts them to hydrophobic and inactive groups. Flotation experiments and accelerated corrosion tests prove that the stability of the treated objects is exceedingly improved. No alteration of the appearance of the treated objects was observed.

Introduction

Copper and its alloys, mainly bronze and brass, were used in antiquity in the manufacture of art objects, coins, jewellery, cutting tools and various utilitarian items such as fasteners, cooking vessels and small tools.

When buried, these objects suffer from corrosion and deterioration due to the presence of various corrosive agents in the burial environment such as humidity, oxygen and soluble salts, mainly chlorides and sulphides. However, after a certain time, the rate of corrosion slows down and finally the objects can reach a state of thermodynamic equilibrium with their environment. This is mainly due to the formation of corrosion layers on the surface of the objects. These layers act as an inhibitor for further corrosion mainly by shielding these objects from the attack of the corrosive agents in their burial environment (Kalish, M. K., 1978; Thomson, G., 1978).
Upon excavation, objects are removed from their stable environment and exposed to completely different environmental conditions. This will initiate new cycles of destructive corrosion that might continue until the object is completely mineralised (Feitknecht, W., 1948; Stambolov, T., 1970).

During storage and display most copper-based artefacts, especially those excavated from environments of high chloride contents, suffer from the appearance of disfiguring, powdery efflorescence on their surfaces that gradually spread and coalesce eventually reducing the object to a highly mineralised state. This phenomenon is known as "bronze disease" (Goffer, Z., 1980; Gilberg, M., 1988).

While today this phenomenon is generally understood to be a manifestation of the chemical transformation which cuprous chloride undergoes in the presence of moisture and oxygen, for many years it was attributed to some sort of bacterial or fungal infection. Cuprous chloride reacts with water and oxygen to form basic cupric chlorides, Atacamite, Cu$_2$(OH)$_3$Cl, or the unstable Paratacamite, CuCl$_2$.3Cu(OH)$_2$, (known as "bronze disease") and hydrochloric acid. The generated hydrochloric acid can attack more of the metal in a repetitive sequence of reactions until the metal is completely mineralised (Evans, U. R., 1981; Goffer, Z., 1980).

The stabilisation of excavated copper-based artefacts is a subject that has attracted considerable attention. In the past few decades a number of treatments aiming at stabilising actively corroding copper-based artefacts have been developed. These methods tend to be based on four classes of treatments, these are: electrolytic reduction (Plenderlieith, H. J., 1962), stripping of the corrosion products using mechanical, chemical (Organ, R. M., 1977) and electrochemical (Organ, R. M., 1963a; 1963b; 1977) methods and stabilisation methods using chemical inhibitors such as sodium sesquicarbonate (Oddy, W., 1970) and benzotriazole (Madsen, B., 1967; Richey, W. D., 1972; Greene, V., 1975; Sease, C., 1978).

All treatment methods currently in use are totally or partially unsatisfactory in their theory of action, mode of application and/or the results they produce. Electrolytic reduction and stripping techniques are questionable as they can remove all evidence of an object's original shape. Inhibitive methods, although attractive in theory, are not successful in practise. It has been observed that, in most cases, these treatments fail to stop further corrosion. Furthermore, these treatments result in changes in the appearance of the treated objects that are aesthetically and ethically not accepted.
There is almost a consensus among conservation scientists, conservators and museum curators (Organ, R. M., 1977) that a new method for stabilisation actively corroding copper-based artefacts is badly needed. It is agreed that this treatment should fulfill the following requirements before being adopted for treating the irreplaceable artefacts: first, it should provide the maximum stability to the treated objects; second, it should effectively inhibit future corrosion for the maximum time; third, it should preserve the integrity of the treated objects with the minimal effect on their aesthetic value; and fourth, it should be relatively cheap, safe and easy to apply.

The aim of this paper is to search for and propose a treatment that could meet the above requirements. For that purpose, a large number of chemical compounds that potentially could inhibit copper corrosion have been investigated. Among these, a titanate-based organic compound with the name neopentyl (diallyl) oxy tri(dioctyl)pyro-phosphato titanate has been selected for further investigations. This compound has been recently manufactured and used for various industrial purposes. It has been mainly used as a coupling agent in the production of various composite industrial products such as glass fiber and coated steel used in space shuttles (Monte, S. J., and Sugerman, G., 1985). It functions by bridging various inorganic substrates and organic polymer matrices. The main reason behind its selection for this study is that it has been found, besides its coupling function, to exceedingly enhance the hydrophobocity, corrosion and acid resistance of these manufactured products (Monte, S. J., and Sugerman, G., 1979; 1983; 1984). Titanate In this work the organotitanate compound was tried for stabilising actively corroding copper-based artefacts. A collection of different types of actively corroding copper-based artefacts and synthetic copper corrosion products usually found covering the surfaces of these objects were treated with this compound. The changes that the treatment caused to the chemistry of the surfaces of these objects, their hydrophobicity and corrosion resistance were measured and assessed.

Materials and experimental methods:

Materials:

Neopentyl (diallyl) oxy tri(dioctyl)pyro-phosphato titanate designated as LICA 38 was kindly supplied by Kenrich Petrochemicals, Inc., New Jersey, USA. This compound is a greenish brown liquid with a specific gravity (at 16 °C) of 1.13. It is soluble in toluene, xylene, mineral oil and isopropyl alcohol. Malachite and azurite
samples were obtained from the Geology Department, Yarmouk University. Two types of excavated copper-based objects were used in this work. The first type consists of ten brass bracelets and the second type consists of twenty bronze coins belonging to various periods. All these materials are from the collection of the Institute of Archaeology and Anthropology, Yarmouk University. All the selected samples have thick layers of corrosion but with a sound metal core left. Most of them have had bright spots of bronze disease indicating active corrosion.

_Treatment of samples of malachite and azurite with titanate:_

Samples of malachite and azurite were immersed in a 5% solution of the titanate in toluene for 12 hours. The temperature of the solution was kept at 35°C. The samples were then washed with toluene to remove the unreacted titanate and then left to dry at room temperature.

_Treatment of copper-based objects with the titanate:_

The surfaces of all the objects treated in this work were prepared before they were treated with the titanate. This was done by mechanically removing the concretions and extraneous soil adhered to the surfaces of the objects by using a scalpel. Also all the bright spots of bronze disease were mechanically removed. The objects were then immersed in 5% solution of the titanate compound in toluene for 24 hours. The solution temperature was kept during this period at around 35°C to enhance the reaction between the titanate and the copper objects' surfaces. The objects were then taken out and washed with excess toluene to remove unreacted titanate molecules and then left to dry at room temperature. Sixteen bronze coins and six brass bracelets were treated by this method. Four coins and two bracelets were left to be used as control for comparison purposes.

_Methods of testing the effectiveness of the proposed treatment:_

For evaluating the effectiveness of the titanate coupling agent in hydrophobing the surfaces of copper-based objects and in stabilising these objects against various corrosive agents, the following tests were carried out:

_(1)-Simple flotation experiment:_

This experiment is designed to evaluate the resilient of the deposited organic layer to water penetration and stability of the linkage formed between the titanate compound and the copper surfaces to hydrolysis.
To do so, samples of malachite and azurite (the usual outer layers of corrosion on most archaeological copper-based objects) were treated with the titanate coupling agent and then exposed to direct water attack for a long time. The hydrophobicity introduced by the treatment should prevent the treated samples from being wetted by water and therefore they should float on the water surface. However, if water molecules could penetrate the deposited organic layer and reach the interface of the deposited layer and the copper corrosion, cleavage of the Cu-Ti-O bonding will, to some degree, proceed by a hydrolysis reaction. If these bonds are not stable enough to withstand water attack, debonding will occur. If hydrolysis occurs to an extent to convert the surface from hydrophobic into hydrophilic, the sample will be wetted by water and sinks.

0.5 g samples of malachite and azurite treated with the titanate were placed in small glass vials. The vials were then half filled with distilled water by gently flowing the water down the side of the vial. The behaviour of the oxide samples was then monitored over a period of six months.

(2) Accelerated corrosion tests:

Accelerated corrosion tests are used to evaluate the long term resistance of treated samples to corrosion under certain environments. The only wholly reliable test for measuring the actual behaviour of the objects is by the actual exposure to the natural environments. The major disadvantage here is the length of testing time required to obtain useful data. To obtain data in a reasonable time, accelerated tests are specially designed to reproduce similar patterns of corrosion to those encountered in natural environments within a limited test period. To allow the interpretation from the tests to be made with a high degree of confidence, the tests were standardised and equally applied to the test objects as well as to a control sample (Carter, V. E., 1982).

Ideally, these tests are carried out in specially designed climatic chambers where different environmental conditions could be simulated and highly controlled. Due to the unavailability of such a device, accelerated corrosion tests were done using an air tight desiccator that contains a dish of saturated calcium carbonate solution. In theory this produces a relative humidity of 87%. This value is considered to be realistic for an accelerated aggressive atmosphere. In some of the tests, chloride ions will be introduced to observe their effect on the treated samples.
The treated objects were divided into two groups based on their condition. The first group consists of the objects that show signs of active corrosion and the second group consists of the objects with no clear active corrosion spots. Each group of the treated objects with untreated control sample was placed in an air tight vacuum desiccator at a high relative humidity. Relative humidity and temperature inside the desiccator were monitored throughout the test period. The condition of the objects was monitored over a period of 12 weeks and observations were recorded. In another test the treated samples were brushed with 4% solution of sodium chloride and then exposed to the high humidity test for the same period.

**Results and discussion:**

The main reason behind the failure of the existing stabilisation methods of copper-based objects lies in their inability in preventing corrosive agents, especially moisture and oxygen from reaching the underlying cuprous chloride layer. This is mainly because most of these methods did not pay attention to the active role played by the corrosion products covering the surfaces of copper objects in interacting with and transporting these corrosive agents.

Copper-based objects are usually covered with layers of basic copper carbonate mainly malachite (\(\text{Cu}_2\text{CO}_3\text{(OH)}_2\)) and azurite (\(\text{Cu}_3\text{(CO}_3\text{)}_2\text{(OH)}_2\)). These have hydrophilic hydroxyl groups that cover the outer surface of the objects. These hydroxyl groups have a strong reactivity toward various corrosive agents and act as transporting media for these agents into the inner layers and the metal core of the objects.

It is now agreed that stripping these layers of corrosion is not acceptable due to the invaluable information preserved in them. Also, stripping is not ethically or aesthetically accepted. Therefore, permanent and sustainable stability of copper-based objects could only be achieved if the surface active groups could be converted into inert groups toward the corrosive agents. Ideally, this could be achieved if the active and hydrophilic hydroxyl groups could be chemically exchanged with inactive and hydrophobic groups. Organic groups are water repellent and are inert toward atmospheric corrosive agents. This replacement can hopefully result in stopping the corrosive agents from reaching the inner cuprous chloride layer and the metal core and consequently stabilising the object.
In this work, the modification of the surfaces of copper-based artefacts has been achieved by treating these objects with a titanate-based coupling agent. This coupling agent is neopentyl (diallyl) oxy tri(dioctyl)pyro-phosphato titanate (Monte, S. J., and Sugerman, G., 1985) which has the following chemical structure:

\[
\begin{align*}
\text{CH}_2=&\text{CH-CH}_2\text{O-CH}_2 \\
\text{CH}_3\text{CH}_2\text{C-CH}_2\text{O-Ti(O-P-O-P(O}_\text{C}_8\text{H}_{17})_2}_3 \\
\text{CH}_2=&\text{CH-CH}_2\text{O-CH}_2
\end{align*}
\]

This compound has two ends: a reactive end and an organic end. The neopentyl (diallyl) oxy group is the reactive end that could chemically react with the protons of the surface hydroxyl groups by an alcoholsysis (sovolysis) mechanism. This results in the formation of a Cu-O-Ti linkage and alcohol as shown in the following general reaction:

\[
\text{MOH + RO-Ti(O-P-O-P(O}_\text{C}_8\text{H}_{17})_2)_3} \rightarrow \text{M-O-Ti(O-P-O-P(O}_\text{C}_8\text{H}_{17})_2)_3 + \text{ROH}
\]

Where M is the inorganic substrate (Copper carbonate in this case) and RO is the neopentyl (diallyl) oxo group.

Along with this chemical interaction, the oxygen atoms of the pyrophosphate part of the titanate could form strong hydrogen bonds with the surface hydroxyl groups. As a result of these chemical interactions, the organic part of the titanate coupling agent is chemically attached through covalent linkages and hydrogen bonds to the outer surface of the corrosion products. This means that the surfaces of the copper-based objects are converted from hydrophilic and active toward various corrosive agents to hydrophobic and inactive. Consequently this should improve the stability and survival chances of these objects in display and storage.

The stability of the deposited titanate layer over the corrosion layer is very crucial for the efficacy of the titanate treatment in introducing long term stability of the treated objects. This stability is governed by the ability of the deposited layer to
resist attack and penetration of the corrosive agents especially water. This was tested by comparing the behaviour of treated and untreated samples of malachite and azurite toward direct and constant water attack for a long time by the flotation experiment. The results of this experiment show a striking difference in the behaviour of the treated and the untreated samples. The untreated malachite and azurite particles became instantaneously wetted by water and sank. This is because the surfaces of untreated malachite and azurite are hydrophilic enough to be readily wetted by water due to the association of the surface hydroxyl groups and the water molecules. Observation of the treated samples that had been kept in direct contact with water for six months showed that these particles are still floating over the water surface with no noticed sinking particles. This demonstrates the outstanding resistance of the deposited titanate layer against water attack and penetration. This resilience to water attack could be attributed to a combination of water repellency of the deposited layer and the stability of the formed chemical linkages toward hydrolysates.

Accelerated corrosion tests were used to assess the effectiveness of the treatment in stabilising archaeological copper-based objects. Two types of corrosion tests were used: the first is the simple humidity test where the samples to be evaluated were exposed to high and constant levels of relative humidity. In the second type, chloride ions were combined with the high humidity levels. The first test is simple and considered to be a mild test, however sufficient to initiate corrosion of copper-based objects in a short time. The second test is considered more severe since humidity and chloride are the most corrosive agents for copper. A simple nominal scale with two divisions was used to measure the stability of the treated objects and the control samples. Objects were classified as "fail" or "pass". An object was classified as "fail" if the slightest sign of active corrosion was observed at any time during the test period.

At the end of the tests the treated and control objects were microscopically investigated for any spots of active corrosion. Observation of the objects tested by the simple humidity test showed that all the treated coins and bracelets were in very good condition with no spots of active corrosion. However, The surfaces of the control coins and the bracelet were extensively covered with pale green powdery spots of paratacamite indicating "bronze disease" and corrosion in process.

In the case of the combined humidity-chloride test, two small spots of active corrosion were detected on the surface of one of the treated coins. The other seven coins and the bracelets are all in sound condition with no sign of active corrosion or
instability. The control samples were very badly deteriorated and their surfaces were almost completely covered with cuprous chloride.

Causing the minimum alteration of the appearance of the treated objects is considered one of the most important criteria that a successful stabilising treatment of copper-based artefacts should meet. A large number of the existing stabilisation methods have been rejected on that ground. Therefore, the effect of titanate treatment on the treated objects was carefully observed and assessed. The visual and microscopic examinations of the treated objects before and after the treatment show no alteration of the colour of the surface patina or obstruction of the surface details of the treated objects. It is very hard to notice any difference in that regard between treated and untreated objects.

This treatment has many other advantages in addition to its effectiveness for hydrophobing and stabilisation of copper-based artefacts. Compared to other stabilisation treatments, the titanate treatment is easy and straightforward. No special equipment or skills are needed to perform this treatment. The objects to be stabilised are simply immersed in a dilute solution of the titanate for a relatively short time. Furthermore, the treatment is relatively safe. The titanate compound has a moderate toxicity and skin irritation potential. No other hazards are known to be associated with this compound (Monte, S. J., and Sugerman, G., 1985). Even though and for preventing any possibility of direct contact with the skin, wearing protective gloves and clothing during the treatment is recommended. Taking in consideration that dilute solution of the titanate is only needed, the cost of treatment is reasonable and cheaper than most of the other treatments. The cost of a pound of LICA 38 (prices of 1989) was $ 3.92. Even lower prices could be obtained when buying large quantities. The price of a 55 Gal. drum of this material from Kenrich Petrochemicals Inc. was $ 482 (Monte, S. J., and Sugerman, G., 1985). This quantity is sufficient to treat hundreds if not thousands of copper-based artefacts.

Conclusion:
At the present time there is no treatment that could satisfactorily stabilise copper-based artefacts especially those excavated from high chloride environments. Simple treatment with an organotitanate compound proved to be effective in exceedingly improving the stability of actively corroding copper-based artefacts. The treatment has no ethical or aesthetical problems. It causes no observable alteration of the appearance or texture of the treated objects. Compared to other treatments it
could be considered easy to apply, safe and cheap. However, further experiments and evaluation of this treatment using larger samples of copper artefacts excavated from various environments should be done before this treatment is recommended without any reservation. This is the aim of a research project that has been conducted for sometime at Yarmouk University using large amounts of copper-based artefacts turned out from different excavations. Spectroscopic techniques such as Fourier Transform Infra-red Spectroscopy and X-Ray Photoelectron Spectroscopy will be used in the future to study the nature of distribution of the deposited titanate layers on the surfaces of the corrosion products.

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