

# SSCR JOURNAL MAY 1998 VOL 9 No 2

## COLOUR CHANGES INDUCED WHEN TREATING COPPER AND COPPER ALLOY ARCHAEOLOGICAL ARTEFACTS WITH THE CORROSION INHIBITORS BENZOTRIAZOLE AND AMINO-MERCAPTO-THIADIAZOLE

by

*Robert Faltermeier*

### Introduction

Archaeological copper and copper alloys are often prized for their patina. A patina is developed as a result of deterioration process involving copper, its alloying constituents and the surrounding environment. A colourful corrosion layer is formed covering, in most cases, a metallic core. Copper and copper alloy archaeological artefacts are frequently treated with corrosion inhibiting compounds such as Benzotriazole (BTA) and amino-mercapto-thiadiazole (AMT), to prevent further corrosion. Previous experimental work undertaken identified the darkening of mineralised surfaces on copper alloy artefacts treated with BTA (1:17). This alteration in surface appearance after treatment has not been accounted for. There are several reasons for this. Photographic records taken before and after a conservation treatment have often been in black and white and, even when comparing colour photographs, it is still difficult to determine slight colour changes. Another problem is that a colour picture is rarely taken with a colour reference card (supplied by most colour film producing companies). This attitude towards photographic record keeping, in private and public collections, has resulted in a generally low quality of colour recording for copper and copper alloy artefacts.

The colour changes due to BTA treatment have not been accurately assessed by qualitative or quantitative means. Describing slight alterations in colour poses many difficulties when evaluating corrosion surfaces after a conservation treatment. In the following investigations, an attempt was made to qualify and quantify colour changes induced by corrosion inhibitors for copper and copper alloy archaeological artefacts in the most precise manner possible. The two inhibitors evaluated were BTA and AMT.

### Measuring Colour

Every observer perceives colour differently. A major obstacle encountered when comparing colours is the choice of descriptive words. Colour also varies in its appearance due to changes in the light source and the distance of the light source. The Munsell Colour System <sup>(2)</sup> is used to name and describe colours of soil and ceramic shreds from archaeological contexts. The colour change is qualified by comparing archaeological specimens with a set of Munsell colour reference chips, but these have been found to cover only a small range of colours, a range too narrow for the evaluation of colour changes in copper minerals. Another drawback with this type of colour matching is the inaccuracy introduced when visually comparing colour chips with test samples. This is largely dependent on the observers colour perception and changes in light source. One should also take into account the possibility that some people might suffer from a degree of colour blindness.

The drawbacks encountered with visual assessment of colour changes led to the application of a colorimeter. Schilling used such an instrument to evaluate conservation treatments in the tomb of Nefertari in Egypt <sup>(3)</sup>. A colour-measuring device, such as this colorimeter assigns a numerical value

## SSCR JOURNAL MAY 1998 VOL 9 No 2

to colour. This avoids individual colour perception and results in a higher accuracy and reproducibility of colour values. The Minolta Chroma Meter CR-200 was used for colour matching in the following work and expresses colours in precise numerical values. The instrument relies on modern optoelectronic technology completely avoiding the subjective variations of individual observers. This tool was ideal for measuring the small variations in colour observed on copper minerals treated with corrosion inhibitors.

The Minolta Chroma Meter CR-200 enables accurate measurements to be made of chromaticity (colour and its saturation) and illuminance (lightness or darkness of a colour) of the surface analysed. It provides the means of a quick objective comparison of samples based on individual numerical values. The colorimeter uses a diffused illumination and measures the sample in a 0° angle. The consistent illumination is achieved with a pulsed xenon arc lamp inside a mixing chamber, resulting in a diffused lighting over the sample area. Three photocells read the colour over an area of Ø 8mm [4:3] Calibration is carried out with a standardised white ceramic tile provided by Minolta.

The colour can be expressed as L\*a\*b\* (Table 1), as L\*C\*H\* or using the older Munsell notations colour system. L\*a\*b\*, the CIELAB system is a uniform colour 'space' recommended in 1976 by CIE (Commission Internationale de l'Eclairage or International Commission on Illumination). This is the most widely applied colour standard used in industry today. The CIE colour system closely represents perceived colour and colour differences. Its main advantage is the use of a standard observer and a standardised light source [5:34]. Colour values change under different light sources, due to a difference in the wavelength of each light source.

H*	Hue value, describing type of colour	L*	Lightness
+a*	Red hue	+b*	Yellow hue
-a*	Green hue	-b*	Blue hue
E*	Overall calmer		

**Table 1: symbols for colour evaluation**

This system attributes a numerical value to every colour. A positive L\* defines the brightness and a negative value defines the darkness of a specimen. Hue value (H\*) defines the quality of a colour usually described by words such as red, yellow, green, blue, etc. Positive values of a\* represent a red hue and negative values of a\*, a green hue, positive b\* values are yellows and negative b\* values are blue.

Colour matching with the colorimeter allows the plotting of the different L\*a\*b\* values in the format of a chart, so that the colour changes of particular regions can be pinpointed more clearly and accurately. To enable the overall evaluation of colour changes between specimens, mathematical equations can be applied (see below). The CIELAB colour difference equation is mainly used for colorants in paints, plastics and textiles, and defines E\* (overall colour change).

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad [5:103]$$

Calculation of  $\Delta E^*$  has the drawback that some detailed information is no longer reported such as  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$ . In the work presented here,  $\Delta E^*$  documents the entire change of surface appearance due to a corrosion inhibitor treatment. After this initial evaluation, more detailed quantification of changes in colour can be made.

## SSCR JOURNAL MAY 1998 VOL 9 No 2

Modern colour measuring devices are able to calculate colour differences to one or two decimal places of CIELAB units, whereas observers cannot detect colour differences beyond the first decimal point. This fact should be considered when the data for colour changes of conservation treatments is evaluated. This significant point was raised by Billmeyer and Saltzman [5:105]. However, Minolta Ltd revealed that a professional can detect differences in  $\Delta E^*$  to 0.3 and a normal viewer  $\Delta E^*$  to 0.65 [6].

When copper minerals were treated with corrosion inhibitors, it was expected that BTA and AMT would induce a colour change in copper corrosion products. It is recognised that all industrial inhibitors react with either copper 1 or copper 11 species or, in some cases, both. The formation, of an inhibitor-copper polymer suggests a colour change following treatment with inhibitors. However, the extent of such colour changes could not be readily predicted and the colour variations may often be hardly detectable to an observer.

### Experimental Work

To evaluate the colour changes induced by BTA and AMT treatments, the inhibitors were individually dissolved in 50ml of reagent-grade ethanol and exposed to 0.005M dry weight of reagent-grade cuprite, malachite and nantokite. These are the three main copper corrosion products found on archaeological copper and copper alloys. The mineral weight was chosen arbitrarily, BTA was applied in a 0.25M (equal to 3% as recommended by Madsen (171)) and ANT in a 0.01M (recommended by Ganokar et al (81)) solution.

The mineral powders were immersed for 24 hours in the inhibitor-ethanol solution, the standard duration for a corrosion inhibitor treatment on artefacts containing copper chlorides within their corrosion crust. This was repeated until the object was stabilised and no further active chloride corrosion was detectable.

The inhibitor solutions were filtered with filter paper (grade one) and dried in an oven at 50°C for 24 hours. The oven-drying should prevent further corrosion as a result of water present in the mineral slurry. The powder was then placed in a desiccator filled with silica gel, prior to measurement with the colorimeter.

An attempt was made to produce pellets of the treated powder in a hydraulic press. Compact pellets were thought to have a more even surface texture, resembling more closely an archaeological patina. This also might have improved the accuracy of the colour measurements. In practice, it was extremely difficult to produce the pellets, because they crumbled when any attempt was made to remove them from the press. A binder could not be used since this would introduced morphological changes, which would interfere with the colour.

To measure the colour differences, the treated mineral powders were spread over filter paper as an oven covering and analysed with the colorimeter. This was repeated three times to ensure an accurate reading of the surface and to obtain an average measurement. Table 2 indicates the colour differences in  $\Delta L^*$   $\Delta a^*$   $\Delta b^*$   $\Delta E^*$ . The table is divided into the three main minerals found on chloride-infested copper objects: cuprite, malachite and nantokite.

# SSCR JOURNAL MAY 1998 VOL 9 No 2

## Experimental Results and Discussion

After 24 hours in the BTA and AMT ethanol solutions, cuprite, malachite and nantokite changed in colour. Generally, it was observed that cuprite exhibited greater colour change than malachite, and nantokite was affected most by colour changes due to the corrosion inhibitor treatments. The various minerals are discussed separately in more detail and the individual data is presented below in Table 2.

Cuprite	L*	a*	b*	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E^*$
Blank	41.8	39.9	20.7				
BTA	38.8	36.9	21.8	-3	-3	1.1	4.4
AMT	38	33.8	21	-3.8	-6.1	0.3	7.2
Malachite							
Blank	55.3	-34.6	4.9				
BTA	53.2	-33.1	5.3	-2.1	1.5	0.5	2.6
AMT	53.1	-31.7	6.5	-2.2	2.9	1.7	4.0
Nantokite							
Blank	65.0	-25.3	19.5				
BTA	49.3	-11.9	22.1	-16.5	13.5	2.6	21.5
AMT	61.1	-22	30.3	-4.7	3.3	10.8	12.2

Table 2: Individual numerical colour values

### Cuprite

The resulting data shows that cuprite changes colour when treated with AMT and BTA. AMT ( $7.2\Delta E^*$ ) discoloured cuprite more than BTA ( $4.4\Delta E^*$ ). This was mainly due to ( $-6.1\Delta a^*$ ) when measuring AMT pointing towards a slight green hue. A slight darkening of the mineral can be expected when treating with AMT ( $-3.8\Delta L^*$ ), and BTA ( $-3\Delta L^*$ ). The changes in  $\Delta L^*$  are more extreme than those found in malachite.

### Malachite

The  $\Delta E^*$  indicates that this copper carbonate mineral is less affected by AMT ( $4\Delta E^*$ ) and BTA ( $2.6\Delta E^*$ ) than is cuprite. However, it was observed that AMT causes more colour changes than BTA. AMT gives the green malachite more of a red ( $2.9\Delta a^*$ ), yellow ( $1.7\Delta b^*$ ) hue. Both inhibitor treatments show a negative  $\Delta L^*$  value, due to a darkening of the malachite (BTA  $-2.1\Delta L^*$ , AMT  $-2.2\Delta L^*$ ). The change to a negative  $\Delta L^*$  in the BTA treatment is the main cause for the overall colour change ( $2.6\Delta E^*$ ) in malachite.

### Nantokite

This copper chloride mineral was severely affected when treated with both corrosion inhibitors. BTA ( $21.5\Delta E^*$ ) caused the greatest amount of colour change to nantokite in comparison with AMT

## SSCR JOURNAL MAY 1998 VOL 9 No 2

(12.2 $\Delta E^*$ ). BTA caused a darkening (-16.5 $\Delta L^*$ ) of nantokite and a shift to a red hue (13.5 $\Delta a^*$ ). AMT caused a smaller amount of darkening (-4.7 $\Delta L^*$ ), but demonstrated the largest colour change as a result of a yellowing (10.8 $\Delta b^*$ ) of the nantokite. The yellowing can probably be attributed to the sulphur in AMT (C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>S<sub>2</sub>).

These distinct colour variations after corrosion inhibitor treatments suggest that artefacts containing large amounts of nantokite will undergo a dramatic colour change. However, most objects contain more malachite and cuprite on their surface so the alteration in the colour of nantokite will not be as apparent. Artefacts with a surface comprising mainly cuprite will change colour more than an object containing more malachite in its surface. An artefact consisting mainly of cuprite and malachite will be more altered in colour during a treatment with AMT than by a BTA treatment.

### Conclusion

If archaeological copper and copper alloys are treated with corrosion inhibitors such as BTA and AMT, the induced colour changes should be born in mind. The data presented here highlights the importance of the qualitative and quantitative assessment of conservation treatments and their effects on the visual appearance of an artefact. Both corrosion inhibitors will darken a mineralised surface containing cuprite, malachite and nantokite. This evidence suggests that chloride-free copper and copper alloys should not be treated with BTA or AMT since this results in colour changes. If the artefact must be treated because of active copper chloride corrosion present in the corrosion surface, a drastic colour change of the nantokite can be expected. BTA causes almost double the amount of colour change in the nantokite than AMT. BTA darken the nantokite and AMT will yellow it.

Consequently, it is recommended that copper and copper alloy archaeological artefacts with highly-prized mineralised surfaces should not be treated with these inhibitors because of the colour changes induced. If the artefact contains chlorides, it should be stored in a desiccated environment and its condition monitored at regular intervals. However, one can argue that the surface exposed after a conservation treatment is not the original surface finish and that any interventive treatment will alter the appearance of the outer corrosion layer. A corrosion inhibitor treatment might, in some cases, be of benefit to the long-term stability of an artefact and the colour changes might be negligible. However, this point cannot be discussed here and the decision to carry out an inhibitor treatment must be made by looking at each object on an individual case.

# SSCR JOURNAL MAY 1998 VOL 9 No 2

## ACKNOWLEDGMENTS

The author wishes to thank R Gibbs, Dr A Lim and Dr J F Merkel for their encouragement, constructive dialogue and revision of the English. This research was financially supported by the Institute of Archaeology, University College London and Novartis Corp. Basel, Switzerland.

## REFERENCES

1. *Faltermeier, R. B., AMT, Unpublished BSc Thesis, University College London. Institute of Archaeology, ION*
2. *Munsell Soil Colour Charts, revised edition. Macbeth New York a992*
3. *Schilling. M., 'The color measurement Program in 00 tomb of Nefertari', In, Corzo, M. A. and Afshar All and Eternity (The Nefertari Wall Paintings Conservation Project 19W 1992), The Getty Trust. 1993*
4. *A Minolta Lid, Chrome meters ION*
5. *Billmeyer F W. mid Saltzman, M.. Principles Of Colour Technology, 2nd ad. New York 1061*
6. *Minolta Ltd, Personal communication 1995*
7. *Madsen, H. B.. 'Further remarks on the use Of benzotriazole for stabilising bronze objects Studies in Conservation. 16 1971.120-122*
8. *Ganorkar M.C., Pandit Rao V., Gayathri P. and Sreenivase Rao T A.. 'A novel method for conservation of copper and copper-based artifacts'. Studies In Conservation, 33. 190. 97-101*