Known and New Corrosion Products on Bronzes: their identification and assessment, particularly in relation to organic protective coatings.

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Abstract: *Extensive investigations on outdoor bronzes in Augsburg and Nürnburg (both in West Germany) have shown that the methodical starting point for the determination of corrosion products on this type of bronze must be improved. X-ray diffractometric analyses provide an extensive spectrum of inorganic copper, lead and calcium compounds some of which are already known and others which have not until now been described. Additionally, investigations using gas chromatography/ mass spectrometry allow the identification of various metal soaps and other purely organic products. With the help of these results it is possible to identify both older and younger protective coatings. A warning can be derived from the presence of copper soaps (i.e., copper salts of fatty acids) against the use of waxes and oils which are not acid-free.*

Introduction

Analogous to the development of instrumental analysis, investigations of outdoor bronzes show recent improvements in their accuracy, width and quality. Particular examples of this are the investigations on the horses of San Marco in Venice (Marchesini *et al.* 1979; Rosetti *et al.* 1979), and on the Braunschweiger Burglöwe (Lion of Braunschweig) (Matteini *et al.* 1983).

This contribution attempts to extend the spectrum of analytically-detectable corrosion products. The problem of damage by environmental factors is pursued, as is the ever-recurring question of whether or not the bronzes were covered with organic coatings. In regard to this, the question must be raised of whether these coatings were then protective or harmful. Bearing in mind the focal point of this conference, it must be stressed that the results presented here are valid not only for outdoor bronzes, but also for archaeological bronzes.

Investigated Objects and Analytical Starting Point

This contribution is based on completed studies of the Augsburg Cathedral doors (dating from the second half of the 11th century) (Fig. 1), and on the St. Georgsbrunnen (St. George's Fountain) in Augsburg (Fig. 2). The results of the former have already been published (Burmester and Koller 1985). Furthermore, similar investigations are currently being carried out on the Nürnburger Tugendbrunnen (Fountain of Virtue) which is dated to 1589. The Cathedral doors were last conserved in 1975, and in 1979 the Tugendbrunnen was completely restored and conserved.

Our attempts at analytical determination contain a greater number of new aspects than those of other study groups:

1. Crystalline corrosion products are identified with the help of automatic powder diffractometry (X-ray Powder Diffraction Analysis). The quality of these measurements on the powder samples is greatly increased thanks to the use of a sample holder made of a silicon monocrystal, which allows virtually background-free measurements. The computer-supported evaluation of the diffractograms was carried out using a commercial software package and in comparison with the JCPDS Powder Diffraction File. In this way it is possible to identify even complex
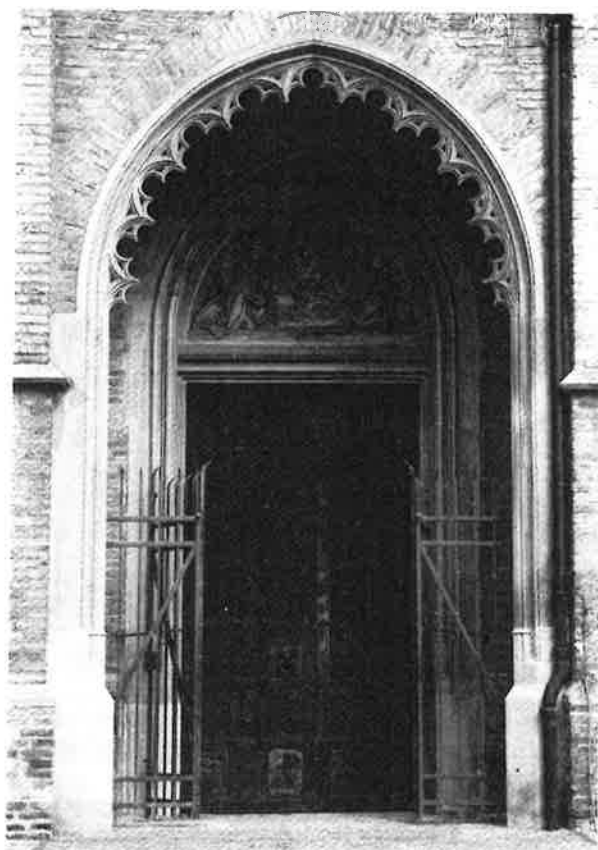

Fig. 1. The Romanesque bronze doors of the Augsburg Cathedral, Neo-Gothic portal.
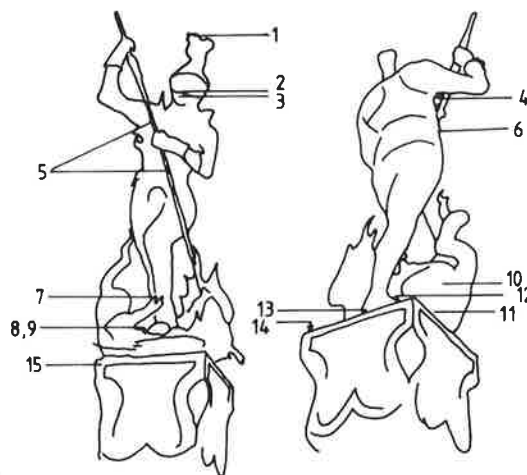
mixtures. Figure 3 shows as an example the comparison between a diffractogram and the positively identified phases.

The following equipment was used: Philips PW 1700 Automatic Powder Diffraction, Cu-FF-Tube 40 kV/30mA; vertical goniometer with monochromator, range: 2 to 80 2θ, scan-speed: 0.02 2θ/sec, fixed divergence slit: 1 mm, proportional counter; DEC PDP 11/23 computing device with Philips APD software and JCPDS Powder Diffraction File.

2. Although the interaction between the bronzes and the organic protective coatings is often discussed, as far as we know the resulting products have never been precisely described. For example, the presence of an older linseed oil coating on the Braunschweiger Burglöwe has been discussed using data from infra-red spectroscopy, but without any concrete results (Matteini *et al.* 1983). In the case of our studies, the determination of the characteristic components using gas chromatography/ mass spectrometry (GC/MS) leads to a definite designation of older as well as younger coatings with which the objects investigated were coated. However, their determination is much more complex than in the Braunschweig case: the samples have to be prepared in several steps (Figure 4), separated by gas chromatography and then identified using mass spectrometry (see also Burmester and Koller 1985). The identification relies on the NBS-Spectral

a

b.

Fig. 2. St. Georgsbrunnen, Augsburg (a-above) and plan of our sampling areas (b-above right).

Libraries as well as on the reference collection of our Institute. Figure 5 shows a typical GC/MS-ion chromatogram; the identified peaks are marked.

The following equipment was used: Quadrupole mass spectrometer: Hewlett Packard 5985B GC/MS system; gas chromatograph: Hewlett Packard 5840 GC; inlet system: split mode; capillary column: 10m (or 25m) fused silica, 0.2 mm inner diameter, coated with 0.11 micrometer methyl silicon [OV 101 (or UB1)]; carrier gas: He 6.0; column pressure = 0.7 bar (or 1.4 bar); injection temperature = 250° C (or 260° C); T1 = 180° C (or 120° C), t1 = 1 min, heating rate = 7° C/min (or 10° C/min), T2 = 260° C (or 290° C); attenuation = 2^{4}; detector: FID, in case of GC/MS: quadrupole mass spectrometer; GC/MS coupling: open split connection (SGE).

3. In addition to those procedures named above, the powder samples are described microscopically and also the qualitative pattern of elements determined with the help of optical emission spectral analysis. Both facilitate the interpretation of the results from the analyses from points 1 and 2 above. Furthermore, the chloride content of the samples was determined photometrically by the usual methods.

Results and remarks on the method

Tables 1 to 4 attempt to summarise the variety of results from the investigations; the results from the Augsburg Cathedral doors are abridged because they have already been published in detail.

Regarding Table 1, it should be mentioned that non-crystalline products cannot be identified by X-ray diffraction analysis. Infra-red spectrometry looked promising for this problem (Matteini *et al.* 1984). However, it turned out that this method wa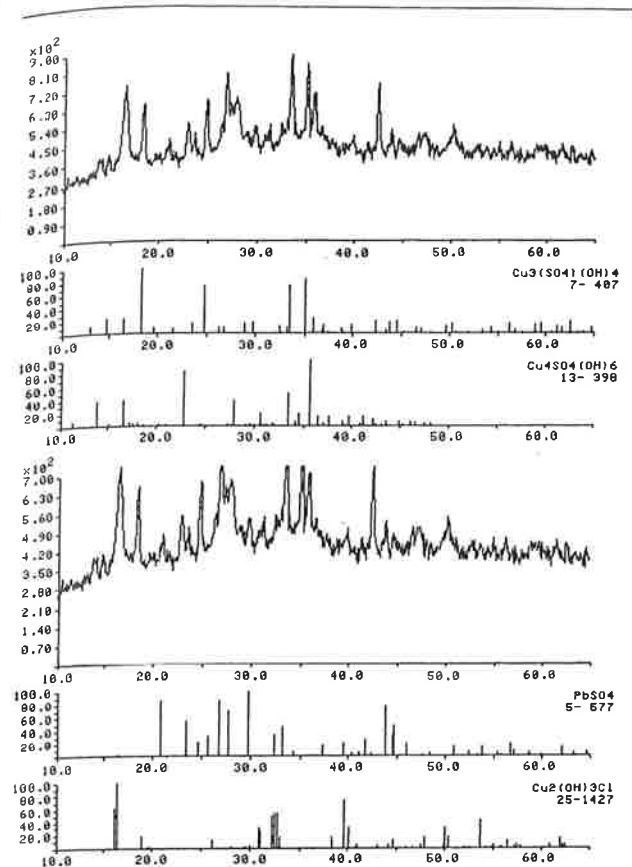s suitable for confirming those phases already determined by diffractometry, but did not help in the identification of new substances. This is understandable in view of the fact that the wide range of identified crystalline components are embedded in a matrix of organic compounds (Table 4), and these dominate the infra-red spectra.

The spectral analyses (Table 2) provide a qualitative impression of elements present in the samples. Here the elements are listed in the order of their frequency which was found by the estimated intensity of their lines. By experience these semi-quantitative investigations overestimate the magnesium content but otherwise the high amounts of copper, calcium and silicon usually correlate with results from X-ray diffractometry. However, the Tugendbrunnen, Nürnberg seems to be an exception, the results from diffractometry show fewer copper salts, whereas the spectral analyses show a higher copper content. The reason for this could be either the indistinct crystallinity of the identified or suspected copper chloride in the five samples, or the presence of the amorphous copper soaps which are dealt with in detail below.

A quantitative elemental analysis of the corrosion samples as well as of the alloy was left out on purpose. In our experience, the semi-quantitative estimation of the spectral analyses, along with X-ray diffraction, is sufficient. Furthermore, we have observed that in bronzes the heterogenous composition of the alloys does not necessarily influence the nature, variety and quantitative composition of the corrosion products. For example, in the case of the Augsburg Cathedral doors, it is known that the composition of the alloy varies a great deal (Riederer 1985): the nature, variety and composition of the corrosion products is, however, homogenous and really rather monotonous (see Table 1, Burmester and Koller 1985). Exactly the same conclusions can be drawn from the investigations on the Braunschweiger Burglöwe and on the horses of San Marco.

Furthermore, we would like to point out that only the most important components are presented in Table 3 (hollow and filled boxes) for each of the given organic protective coatings. Minor ones, or those which were not considered in the analyses, are not presented. If the results from the investigations on the Tugendbrunnen, Nürnberg had already been completed, then Table 3 may possibly have looked quite different: the inclusion of

Fig. 3. X-ray diffractogram (section, impulse against angle 2θ) of sample 10, St. Georgsbrunnen in comparison with the identified corrosion products (see Table 1).

special components for the purposes of analysis by chromatography/mass spectrometry (filled boxes) greatly differs therefore from case to case.

As is clear from Table 3, the proportion of components with acidic functions, ie the fatty acids and dicarboxylic acids, is high. It is essential that these are free only for a short time after the application of the coating, and are then present as bound acids in the form of metal soaps (Table 3, highlighted area). This is especially valid for the dicarboxylic acids because of their greater acidity.

Discussion

The composition of the corrosion layers on the Cathedral doors differs from that of the St. Georgsbrunnen in one essential point: in the first case the corrosion products consist almost exclusively of antlerite and gypsum, in the other, they are dominated by brochantite among other products. We believe that this can be explained only by the local situation of the objects. Whereas the St. Georgsbrunnen is subject to all weathers, the Cathedral doors are protected from direct exposure by a Neo-Gothic portal (Figure 1), but are still subject to condensation, mist and frost. Recent investigations (Borgeest 1987) and also older ones (Weber *et al.* 1984) indicate that mist contains greater quantities of harmful substances than rain. In the present environmental conditions this leads to a sinking of the pH values to about pH 3: favourable conditions for the formation of antlerite (Pourbaix 1977). If, as is the case of the St. Georgsbrunnen, the bronze is subjected to all weathers, then part of the harmful substances can be washed out, thus favouring the formation of bronchantite (Pourbaix 1977).
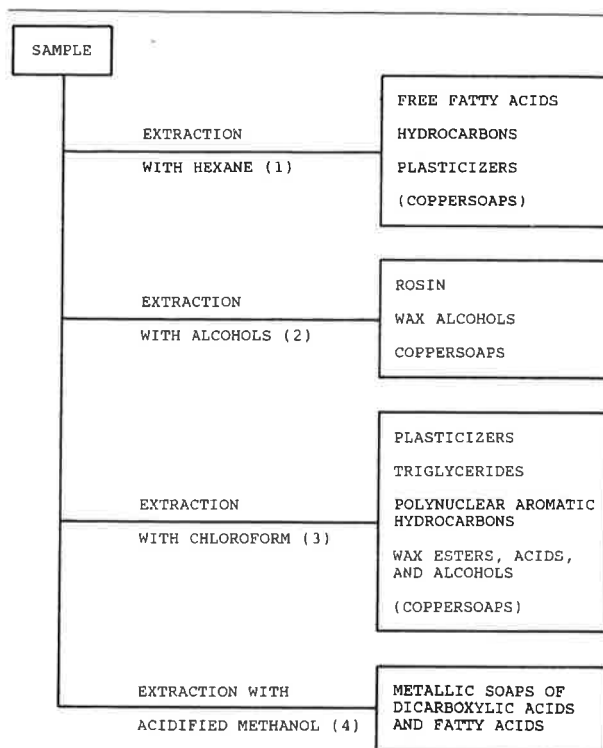

Fig. 4. Preparation scheme for the identification of organic components in the corrosion layer of bronzes. In the extraction steps (1)-(3) copper soaps are carried along which deviates from the given simplified plan.

In the same way, gypsum can be enriched as antlerite, but in protected positions. Although there is plenty of it all over the Cathedral doors, it could only be found in one sample from the St. Georgsbrunnen, and this came from under the visor of the helmet (Figure 2), which is not in a position subjected to all weathers. As has been only recently described (Cheng *et al.* 1987), gypsum can be formed easily from calcium carbonates under the catalytic influence of flying ashes. Therefore, carbonates act essentially as a buffer within the observed acidic environment. This supports our view that gypsum is a secondary formation. Connected to the formation of gypsum in and on the corrosion zone is a hydraulic expansion of the layers, causing flaking and the formation of sponge-like structures.
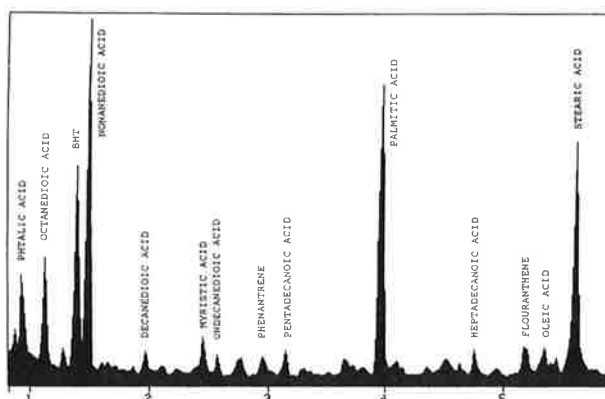

Fig. 5. GC/MS ion chromatogram (section, total ion current against retention time in minutes) from sample 10, St. Georgsbrunnen, here the acidifed methanol extract (metal soaps).

Table 1

Corrosion products and phases determined by X-ray diffraction (dots) and confirmed by infra-red spectroscopy (hollow boxes) on Augsburg Cathedral doors (A), the St. Georgsbrunnen, Augsburg (B) and the Tugendbrunnen, Nürnberg (C). Components determined with both above procedures (filled boxes); possibly present components (?). Only those phases with positive identification are given which in the case of X-ray diffraction were identified using the JCPDS Powder Diffraction File (JCPDS No.): antlerite $CuSO_4$ x $2Cu(OH)_2$ JCPDS No. 7-407, brochantite $CuSO_4$ x $Cu(OH)_2$ JCPDS No. 13-398, brochantite hydrate $CuSO_4$ x $3Cu(OH)_2$ c $2H_2O$ JCPDS No. 20-364, anglesite $PbSO_4$ JCPDS No. 5-577, gypsum $CaSO_4$ x $2H_2O$ JCPDS No. 21-816, atacamite $Cu_2(OH)_3Cl$ JCPDS No. 25-269, paratacamite $Cu_2(OH)_3Cl$ JCPDS No. 25-1427, cuprite Cu_2O JCPDS No. 5-667, calcite $CaCO_3$ JCPDS No. 5-586 and 24-27, aragonite $CaCO_3$ JCPDS No. 24-25, calcite hydrate $CaCO_3$ x H_2O JCPDS No. 29-306, dolomite $CaMg(CO_3)_2$ JCPDS No. 11-78, basic lead carbonate $2PbCO_3$ x $Pb(OH)_2$ JCPDS No. 13-131, quartz SiO_2 JCPDS No. 5-490. Very high proportion (three dots), high proportion (two dots), low proportion (one dot) very low proportion [(one dot)]. In the case of the object in Augsburg the unidentified phases show a diffraction line of 42,82 2θ, which was also observed in samples from the Braunschweiger Burglöwen (Matteini *et al.* 1983). The Tugendbrunnen, Nürnberg shows two uncorrellatable peaks at 21.55 and 24.03 2θ.

		SULPHATES				CHLORIDES		OXIDES	CARBONATES					QUARTZ	UNIDENTIFIED PHASE(S)	COLOUR
	ANTLERITE	BROCHANTITE	BROCHANTITE HYDRATE	ANGLESITE	GYPSUM	ATACAMITE	PARATACAMITE	CUPRITE	CALCITE	ARAGONITE	CALCITE HYDRATE	DOLOMITE	BASIC LEAD CARBONATE			
A 20 SAMPLES	••	(•)		(•) ••	(•)	(•)	(•)				•			••	•	GREEN/LIGHT AND DARK
B SAMPLE 1	•	■■	■■			•										BLACK
2	■■ ••	■■		?		•								?		BLACK
3	■	■■	••	?	?	•										BLACK
4	■■ ••	■■		?												GREYISH
5	•	■■	■		?	••								••		BLACK
6	■■		••													BLACK
7	□	■■	■■		•											BLACK
8	■■	■■			•											REDDISH
9	■■	■		?		••								••		GREEN/RED
10	■■ ••	■			•									••		GREEN/BLACK SPOTS
11		□						□□		••				••		GREENDARK
12	■■ ••	•			•									•		GREEN
13	■■ ■■	■			•	••								••		GREEN/BLACK SPOTS
14	■■	□	?													GREEN/BROWN SPOTS
15	•	••				•										GREEN
C SAMPLE 1							••	(•)					(•)			REDDISH
2						••	(•)	••					(•)			GREY
3						••	••									GREY
4						(•)	••									GREY
5			?	?		••								(•)		GREY
6			?	?	••	•										BROWN
7			?	?		••	(•)									GREY
8						••	•					(•)				GREY
9			••			(•)								(•)		POISONOUS GREEN
10			?	?		(•)								••		GREY

In the Tungendbrunnen, Nürnberg it was observed that the various calcium carbonates made up the greatest proportion (Table 1). These arise on the one hand from the hard fountain water, and on the other from the growth of algae which form shells of calcite and aragonite. In agreement with the assumed function of the carbonates as a buffer, no antlerite or brochantite has been found in Nürnberg.

The chlorides must be mentioned as a further electrolyte alongside SO_X, however this is not connected to the previous arguments. The chloride content on the Cathedral doors is only negligibly greater than that of the exposed St. Georgsbrunnen. In the latter it was obsrved that the chloride content is greater in the lower zone of the corrosion layer, i.e. the zone next to the bronze. Unexpectedly, but in agreement with X-ray diffraction, a sample from the Tugendbrunnen, Nürnberg, on which large amounts of atacamite are found, contained a chloride content increased by a factor of 15-20. An explanation of this observation is left to current investigations (winter salt, fountain water with a high chloride content) however, the evaluation follows the usual arguments (Organ 1963; Ullrich 1985).

We believe that brochantite hydrate has been detected for the first time on outdoor bronzes; it has only been found on the stone pedestal of the St. Georgsbrunnen within the green-blue drainage zone. The genesis of this unusual sulphate is unknown.

From the plan of the sampling areas of the St. Georgsbrunnen (Fig. 2) it is evident that high proportions of lead sulphate (anglesite) are found in the upper part of the figure. It is not clear whether the high lead content is due to the alloy, to pigments containing lead from earlier paint layers, or to additives in protective coatings.

Table 2

Results of optical emission spectral anlysis of the investigated powder samples from the corrosion layers of the Augsburg Cathedral doors (A), of the St. Georgsbrunnen (B) and of the Tugendbrunnen, Nürnberg (C). The sequence of the detected elements corresponds to a semi-quantitative estimation of the content of each element (content decreases to the right).

		DETECTED ELEMENTS
A	20 SAMPLES	Cu Mg Ca Si Al Ag Fe Pb Sn Mn Zn Ti Na Au
B	15 SAMPLES	Cu Mg Ag Si Sn Al Pb Fe Zn Sb As Ca Bi Mn P Ba Sn Ti
C	8 SAMPLES	Ca Cu Mg Si Pb Al Sn Fe Zn Ag Ni Mn As Sr Bi

Table 3

List of the most important components in the usual organic protective coatings for bronzes (hollow and filled boxes). See text. The components used for identification are marked with filled boxes. In the case of nitrocellulose, solubility tests as well as the diphenlyamine test were used for identification (hollow box with cross).

	NITROCELLULOSE LACQUER	LINSEED OIL	BEESWAX	ASPHALT	PARAFFINS	
		■				FATTY ACIDS (AS GLYCERYL ESTERS)
AS METALLIC SOAPS		■	□			FATTY ACIDS (C_6-C_{23})
			■			WAX ACIDS (FATTY ACIDS, C_{24}-C_{30})
		■	■			DICARBOXYLIC ACIDS
		□	□			UNSATURATED FATTY ACIDS
			■		■	HYDROCARBONS
			□			WAX ESTERS (MONOESTERS)
			■			WAX ALCOHOLS ($>C_{16}$)
				■		POLYNUCLEAR AROMATIC HYDROCARBONS
	■					PLASTICIZERS
	⊠					NITROCELLULOSE

Table 4

Summary of the identified remains of organic coatings on the Augsburg Cathedral doors (A) and the St. Georgsbrunnen (C); very high proportion (three dots), high proportion (two dots), low proportion (one dot) and very low proportion [(one dot)], pentachlorophenol from insecticides (a) and rubber dust (b).

		PARAFFINS	ASPHALT	BEESWAX	LINSEED OIL	NITROCELLULOSE LACQUER	ADDITIONAL COMPOUNDS
A	20 SAMPLES	•••		•	•		(a)
B	SAMPLE 1	(•)			(•)		(b)
	2	••	••		••		
	3	•			•	••	(b)
	4				(•)		(b)
	5				(•)		
	6	•			(•)		
	7						
	8						
	9						
	10	••	••		•••		
	11	•••	•••		•••	•••	
	12	•		•••		•	
	13						
	14						
	15	(•)		(•)	(•)	(•)	(b)

This leads to a closer appraisal of the role and value of organic protective coatings on the bronzes: paraffins, beeswax, and linseed oil as used on the Cathedral doors, or in addition to all these, asphalt and nitrocellulose lacquer on the St. Georgsbrunnen.

If these films contain or can set free fatty acids or dicarboxylic acids, then they can produce chemical compounds, so-called metal soaps, with metal ions such as lead or copper. Lead soaps are chemically stable, whilst copper soaps have many negative properties; from our point of view they are extremely mobile within fatty and oily phases and increase the rate of their oxidation (Pokorny *et al.* 1964). Copper soaps are themselves chemically unstable and surface active. Therefore, among other things, they can be washed out.

Some of these properties require a closer inspection. The mobility of the copper soap works against the intrinsic hydrophobic character of the usual organic protective coatings. Although harmful substances can no longer reach the surface of the bronze directly, the copper soaps act as a transport medium for copper cations within the films. The readiness of the copper soaps to react is high because of their surface activity and their instability in an acidic environment. This is especially valid in our present environmental conditions and allows the possibility of a rapid copper transfer through the protective film, and subsequent reaction to the known copper corrosion products, nowadays mostly sulphates.

In our opinion, based on these observations and supported by extensive experimental results, protective coatings on bronzes containing or setting free fatty acids do not deserve to be called "protective" and cannot fulfil this function.

A further property of copper ions in organic matrixes should be mentioned: the influence of copper ions, oxygen, humidity, light and heat causes oxidation of double bonds in unsaturated fatty acids, as well as alkenes, esters, alcohols and ketones. This can result in low molecular weight fatty acids and dicarboxylic acids. These in turn are far more aggressive than the original products present and attack not only metallic copper and its alloys, but also dissolve oxide- and carbonate-containing layers.

The damaging influence of fatty acids on metals has been described long ago (Stather 1935); however, this is only vaguely mentioned, underestimated or even ignored in the relevant literature on the conservation and restoration of bronzes (e.g. Townsend 1984). This paper experimentally supports the theory of damage to bronzes by the "protective" coating for the first time, and underlines our demand to abandon the use of certain coatings in future, in particular acid-containing waxes, e.g. beeswax or lanolin, along with coatings containing oil. In this connection it must be borne in mind that coatings containing synthetic resins may contain fatty acids as secondary plasticisers, and coatings containing asphalt are usually mixed with oils. Generally, such conservation materials should be exactly specified and, if possible, be checked by a scientist.

Lastly, it must be mentioned that although the frequently recommended industrially manufactured paraffins do not generally contain any acidic components, it has however been observed that there is a noticeable brittleness due to the loss of low molecular weight components (Burmester and Koller 1985).

Summary

In summary, this contribution shows the necessity of expanding the spectrum of corrosion products to be identified. In addition to the purely inorganic compounds, which we believe should be more extensively determined, metal soaps along with purely organic components should be considered in future.

In view of the reactivity, as well as the known catalytic functions of copper ions within the total corrosion, the composition of protective coatings should be critically checked. Also the non-specified components (additives such as fillers, plasticisers and emulsifiers) must be taken into account.

In particular we would like to warn against the application of beeswax or lanolin, waxes and oils which are not acid-free as a conservatory measure on archaeological bronzes, on outdoor bronzes and other copper alloys, as well as copper itself.

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It must be pointed out that the authors know only of the results being given in the above reference, and there they are only summarised. Riederer gives the proportions of copper of 70-88%, tin of 2.0-6.3%, lead of 2.0-28%, zinc of 0.004-2.8%, iron of 0.02-0.16%, nickel of 0-0.05%, silver of 0.06-0.09%, antimony of 0.03-0.14% and arsenic of 0.05-0.10%. The proportion of copper given by Riederer has clearly been calculated as the difference of the sum of the other elements from 100%, ie not an experimental result.

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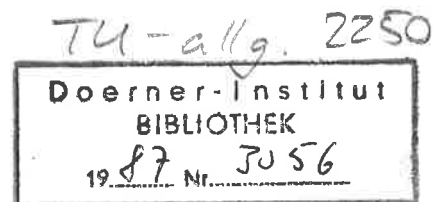Doerner Institute
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