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Trees, bunches, cauliflowers – A closer look at sulphurous corrosion on copper alloys and minerals (‘Black Spots’)

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Abstract

‘Black spots’, a sulphurous copper corrosion, is not only occurring on museum objects composed of copper or copper alloys, but also on pewter and copper minerals. Severe damage such as pitting of the surface may result.

The corrosion products are not exclusively sulphidic, as previously expected, but may also contain sulphates and amorphous phases which are not yet fully investigated.

New forms of ‘black spots’ were discovered, showing various colours and structures, such as dendritic tufts, or a cauliflower-like appearance.

The only successful long-term strategy to avoid the development of ‘black spots’ on museum objects is to take preventive measures.

Résumé

Une corrosion sulfureuse, appelée aussi ‚taches noires’, ne se trouve pas seulement sur des objets en cuivre ou alliage à base de cuivre, mais aussi sur des alliages à base d’étain qui contiennent des petites quantités de cuivre, et sur des minéraux. Le résultat, c’est une perte grave de la surface de l’objet. Les polluants responsables de ce processus sont le soufre élémentaire et des liaisons au sulfure gazeux. Les produits de corrosion ne sont pas exclusivement des liaisons au sulfure, comme on l’a présumé jusqu’ici, mais ils peuvent contenir aussi des phases oxydées. Ces phases ne sont pas encore étudiées entièrement.

La seule méthode couronnée de succès à prévenir la formation des ‘taches noires’ est l’emploi des mesures préventives.

Keywords: ‘black spots’ , identification guide, copper sulphides, minerals, pewter, preventive conservation, sulphur

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1. Introduction

It is some time ago that ‘black spots’ were first noticed on museum objects. Brinch-Madsen (1977) was the first to publish information of this phenomenon. Since then, ‘black spots’ have been referred to as copper sulphides. Severe damage may be caused by this kind of corrosion; pitting visible to the naked eye can occur on previously shiny metal surfaces.

Conservators are increasingly aware of ‘black spots’ in museum collections, though the reason for their development is often unclear. Since ‘black spots’ may develop unrecognised over many years, and museum objects may be moved from one location to another, important information on the development of corrosion may be lost, and so it is often impossible to track the pollutant source, i.e. materials emitting sulphur or other reduced sulphur compounds.

This paper discusses the specific growth patterns, microscopic appearance and chemical nature of ‘black spots’ and provides the reader with a guide for identifying them on museum objects. Collection surveys and laboratory experiments explain which circumstances can lead to the development of ‘black spots’, and which objects and materials are mainly affected. In conclusion, damage caused by ‘black spots’ is documented and

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practical advice is given on conservation treatment and preventive measures. The work was carried out for a dissertation in object conservation (Weichert, 2002).

2. Characterisation and analysis of 'black spots' - Influence of pollutants, environment and metal structure

To investigate the growth mechanisms of this extraordinary form of corrosion, 'black spots' were grown in laboratory experiments at the State Academy of Art and Design in Stuttgart and at the Netherlands Centre for Cultural Heritage (ICN) in Amsterdam. Plates of copper, copper alloys and tin alloys containing 1 to 10 % copper, were exposed to sulphur or aluminium sulphide at 100 % relative humidity (Table 1). Pollutant concentrations ranged from 1.4 ppb sulphur to approximately 4 ppm (Hjelm-Hansen 1984) hydrogen sulphide. The surfaces of the samples were prepared using sandpaper (240 and 600 grit) and glass bristle brushes. The plates were rinsed with deionised water and then cleaned with acetone in an ultrasonic bath. The samples were placed in desiccators with water filled containers.

Some of the test plates were worked using methods such as chasing, chiselling, engraving, and bending. These samples were exposed in a pollutant chamber at the ICN to 50 ppb H_2S at 65 % rh for 41 days, and to 200 ppb H_2S at 82.5 % rh for 17 days.

Alloy	**Components**	**Material**	**Thickness / diameter**
Copper	E-Cu Purity 99.9 %; contains 0,005 to 0.04 % oxygen SF-Cu Purity 99.9 %; free of oxygen; contains 0.015 to 0.04 % phosphor	Sheet metal	0.6 mm
Bronze	Cu 94 % Sn 6 %	Sheet metal	0.5 to 0.79 mm
Bronze	Cu 92 % Sn 8 %	Sheet metal	1 mm
Lead bronze	Cu 77 % Pb 15 % Sn 8 %	Section of cast rod	Ca. 1 cm / 3 cm
Brass	Cu 85 % Zn 15 %	Sheet metal	1 mm
Brass	Cu 72 % Zn 28 %	Sheet metal	0.79 mm
Red brass	Cu 87.5 % Zn 5.5 % Sn 4.5 % Pb 2.5 %	Section of cast piece	Ca. 1 cm
Tin alloy	Sn 90 % Cu 10 %	Section of cast rod	Ca. 1 cm / 3 cm
Tin alloy	Sn 97 % Cu 3 %	Solder, drawn wire[1]	Diameter 3 mm
Tin alloy	Sn 99 % Cu 1%	Section of cast, triangular rod	Thickness ca. 1.5 cm
Tin alloy	Sn 95 % Sb 4 % Cu 1 %	Sheet metal	0.5 to 1.7 mm

Table 1:
Samples exposed in desiccators with elemental sulphur or hydrogen sulphide

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[1] Cu Rotin 3©, Felder Löttechnik GmbH, Oberhausen; DIN 1707 L-SnCu3/zh, without flux.

The comparison of test plates mainly shows a rough relationship between the copper content of an alloy and its tendency to develop ‘black spots’; copper had the highest tendency to develop ‘black spots’, whereas on alloys with relatively low copper contents (pewter, 1 to 10 % copper), either no ‘black spots’, or only small areas covered with rather flat, not very distinct species, were visible. However, the development of ‘black spots’ did not seem to be strictly proportional to the copper content of the alloy. Other alloy components such as lead, or trace elements, could have influenced the corrosion process.

Analysis of the corrosion product was carried out by x-ray diffraction and by the iodine-azide test (results see table 2). The corrosion products were either identified as copper sulphides, or both copper sulphides and copper sulphates were present, or they were amorphous and their composition could therefore not be determined by XRD (for further discussion see Eggert et al., this volume). The iodine-azide test detected sulphur or other reduced suphur compounds in every corrosion sample. Interestingly enough, the experiments showed that tenorite may develop on copper at temperatures as low as 50°C.

Alloy	Experimental method	Results of XRD analyses	Description of corrosion
Copper	Exposed to elemental sulphur, at 50°C, 100 % rh, for 14 weeks (equivalent to 64 ppb S)	Tenorite (CuO) and Cuprite (Cu_2O) identified; probably other phases present	Covered with tree-like, black, partially white corrosion; powdery, loosely adhering
Bronze (Cu 94%, Zn 6%)	Exposed to aluminium sulphide, at ca. 20°C, 100 % rh, for 14 weeks (equivalent to ca. 4 ppm H_2S)	Brochantite (Cu-sulphate) and covellite (CuS) identified	Covered with black, flaking corrosion; green, flaking corrosion underneath; no growth of characteristic ‘black spots’
Lead bronze (Cu 77%, Pb 15%, Zn 8%)	Exposed to aluminium sulphide, at ca. 20 °C, 100 % rh, for 14 weeks (equivalent to ca. 4 ppm H_2S)	Brochantite (Cu-sulphate), covellite (CuS) and quartz identified; presence of gerhardtite (Cu-nitrate) is possible	Covered with black, powdery or flaking corrosion; no growth of characteristic ‘black spots’
Brass (Cu 85%, Zn 15%)	Exposed to elemental sulphur, at 50°C, 100 % rh, for 14 weeks (equivalent to 64 ppb S)	Probably tenorite (CuO) present, or partially tenorite with other amorphous phases	Thinly covered with dark brown, powdery corrosion; no growth of characteristic ‘black spots’
Brass (Cu 72%, Zn 28%)	Exposed to elemental sulphur, at 50°C, 100 % rh, for 14 weeks (equivalent to 64 ppb S)	Mainly amorphous; probably partially covellite, with the same amount of schulenbergit (Cu-Zn-sulphate)	Thinly covered with light green corrosion; waxy to fluffy consistency; no growth of characteristic ‘black spots’
Red brass (Cu 87%, Zn 5,5%, Sn 4,5%, Pb 2,5%)	Exposed to elemental sulphur, at 50°C, 100 % rh, for 14 weeks (equivalent to 64 ppb S)	Tenorite (CuO) identified	Thinly covered with black-brown, powdery corrosion; no growth of characteristic ‘black spots’
Tin alloy (Sn 97%, Cu 3%)	Exposed to aluminium sulphide, at ca. 20 °C, 100 % rh, for 14 weeks (equivalent to ca. 4 ppm H_2S)	XRD (Debye Scherrer): covellite identified; at least one other crystalline phase present, could not be identified c) microchemical test: copper detected	Blue-black corrosion, growing in some areas; flat, not very distinct ‘black spots’
Tin alloy (Sn 95%, Sb 4%, Cu 1%).	Exposed to aluminium sulphide, at ca. 20 °C, 100 % rh, for 14 weeks (equivalent to ca. 4 ppm H_2S)	XRD: (Debye Scherrer): covellite identified; at least one other crystalline phase present, could not be identified c) Microchemical test: copper detected	Corrosion appeared to consist of different phases; black and whitish components were visible; corrosion partially growing as characteristic, tree-like spots

Table 2:
Analyses of exposed copper and tin alloys.

2.1 Trees, bunches, cauliflowers - Identifying black spots on museum objects

'Black spots' grown in the laboratory under accelerated conditions (see chapter 2) were mainly of a tree-like structure, with a stem and a more or less branched crown. Growth patterns of 'naturally' and more slowly grown corrosion identified on museum objects, were of a greater variety. Some were of the same tree-type, though many looked like cauliflowers, or appeared as hard and glassy mushrooms. A large proportion was finely branched and loosely adhering. The corrosion either grew in spots or sometimes covered wider areas of the object. The colours ranged from black to various shades of brown, to brass-like and metallic greenish or bluish, glittering spots. The SEM-structure of the 'black spots' varied significantly. Needle-like structures were observed, as well as platelet forms, tufts and 'black spots' that looked like algae (Figures 1-3). None of these varieties could be grown in the laboratory.

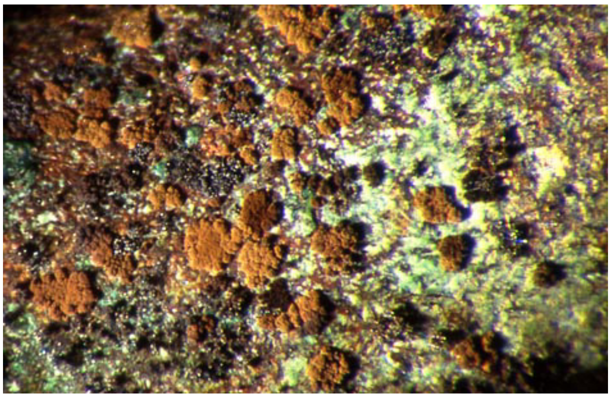

Figure 1: The 'cauliflower' type on a Roman bronze bracelet (622 a (1))[2].

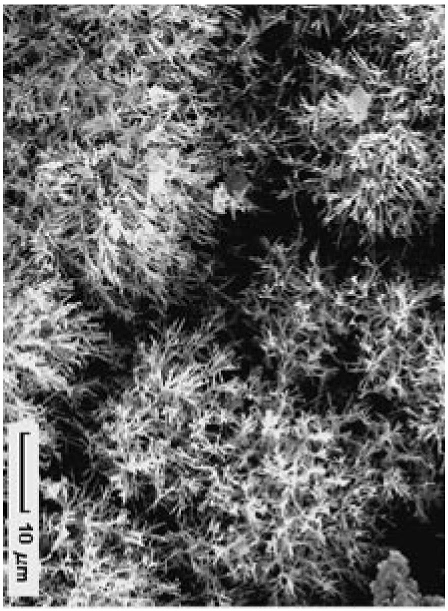

Figure 2: Needle structures on another bronze bracelet (A 626 d), probably Roman[3].

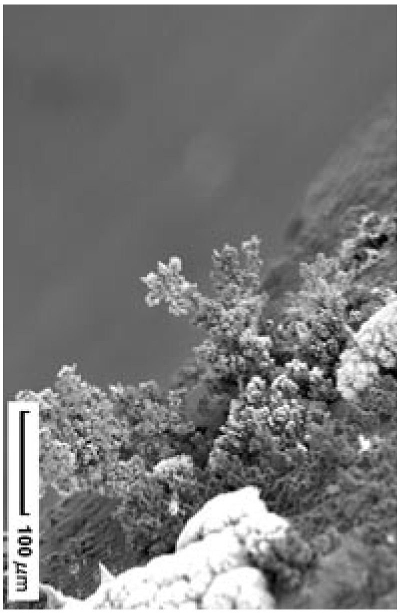

Figure 3: Dendritic growth forms on the same bracelet as in Figure 2 (A 626 d)[4].

The colour of the 'black spots' remained unchanged, regardless of whether they were still attached to the metal surface and illuminated by daylight, or removed from the object and viewed through the microscope. It is uncertain whether a certain colour or structural form of a 'black spot' can be attributed to a specific corrosion product composition. However, it is likely that there should be a connection between the colour and the dimension of the structure. On a bronze bracelet, black and brown efflorescence was visible to the naked eye. Viewed through the SEM, the single units of the structure of the black corrosion appeared smaller than those of the brown corrosion. X-ray diffraction analysis was carried out for both corrosion types; the black corrosion consisting of smaller units turned out to be covellite, the brown corrosion consisting of slightly larger units could be identified as chalcocite. This relationship between crystal size and colour was also reported by Lie and Scheifler (1982) for some whisker-like copper sulphides (chalcocite or a mixture of chalcocite and djurleite). Their crystals of a size below 0.7 µ were brown, whereas crystals of a size over 1 µ were black.

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[2] Museen der Stadt Landshut, Germany; width of photo relates to 0.35 cm of the original. The corrosion product was amorphous.

[3] Museen der Stadt Landshut, Germany; SEM photo by Ineke Joosten, ICN.

[4] SEM photo by Ineke Joosten, ICN.

An easy-to-use method for identifying ‘black spots’ on objects is the iodine-azide test (Lee and Thickett, 1996), combined with the use of analytical test strips for copper ions (Merckoquant by Merck). The first test indicates whether sulphur or other reduced sulphur compounds are present; with the test strips, the copper content of the corrosion product can be determined qualitatively. A small amount of the corrosion is placed on the test strip, which is then wetted using deionised water. If both tests are positive, the corrosion product in question contains copper ions and a reduced form of sulphur; the presence of some copper sulphide is likely. Care must be taken not to remove part of the metal or mineral when collecting the sample material, since this may falsify the result.

2.2 Dependence of growth on metal structure

A relationship between metal structure and the growth mechanism of ‘black spots’ seemed likely. An evaluation of the test plates from the experiments carried out at the Stuttgart Academy (see chapter 2) showed that in some cases, metal structure disrupted due to mechanical stress such as scratching, tearing or bending, clearly proved to be the starting point for the development of ‘black spots’.

Another theory is, that the growth of ‘black spots’ is influenced by the existence of an oxidation layer; and the formation of an oxidation layer is, in turn, influenced by the metal structure. Indeed, most of the test plates showed a relationship between a disruption of the metal structure, and the development of an oxidation layer.

To find more evidence, a survey on approximately one hundred objects made of copper alloys was carried out at the Museum of Landshut, Bavaria. Some artefacts showed a pronounced development of ‘black spots’ in areas of metal disruption (Figures 4 and 5). These disruptions were due to the production process of the object, such as chased decoration, or to later damage. Where forging structures were visible, the growth of ‘black spots’ followed them. Often a distinct grouping of ‘black spots’ could be observed, but without any obvious reason. In some cases, the influence of heat, heat in combination with metal distortion, or contact with other metals, was the starting point for the growing of ‘black spots’. Two bracelets showed growth of ‘black spots’ exclusively around a modern sample drill hole, forming a neat line along the rim of the hole (Figure 6). Another bracelet had developed ‘black spots’ in a narrow zone around a modern solder repair.

Figure 4: ‘Black spots’ forming along a tear in a Roman bronze fibula (A 584 a) [5].

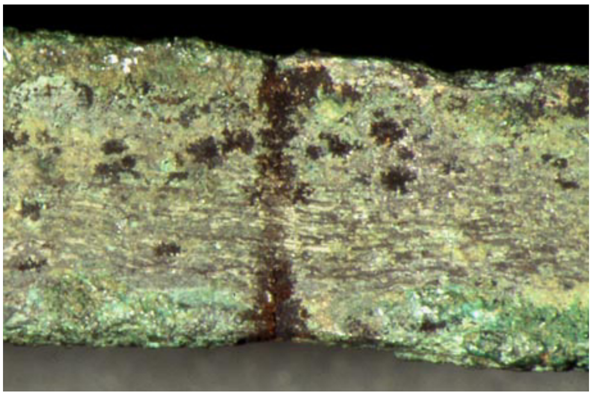

Figure 5: The development of ‘black spots’ on a Roman object (615 a-c) , following a disruption of the metal structure due to bending[6].

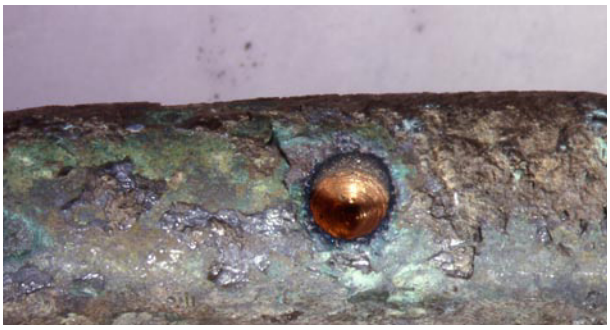

Figure 6: A modern drill hole in a Roman bronze bracelet (A 282 / 1)[7].

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[5] Museen der Stadt Landshut, Germany; width of photo relates to ca. 1.5 cm of the original

[6] Museen der Stadt Landshut, Germany; width of photo relates to 1.8 cm of the original.

[7] Museen der Stadt Landshut, Germany; width of photo relates to 3 cm of the original.

The survey also showed, that 'black spots' grow on both the metal surface and corrosion layers, but seem to prefer to grow directly on metal, or in areas where existing corrosion has become dislodged.

2.3 Why the spot is a spot

As an explanation for the characteristic appearance of 'black spots', Eggert and Sobottka-Braun (1999) suggested the local migration of copper ions from the metal into sulphide crystals which had formed on the metal surface; these crystals act as a nucleus for the development of a 'black spot'. Since copper sulphides are slightly conductive, copper ions can move within the sulphide crystal. At the surface of the crystal, copper ions may react with sulphur from the atmosphere; copper ions following up from the base will keep this mechanism going.

It is in any case characteristic for 'black spots' to spread from the point where their growth began. The question is, why certain areas of the object are more prone to the formation of nucleus crystals than others. One answer would be the microscopic disruption of the metal structure as discussed above. Another explanation could be the locally restricted attack of gas molecules, as observed in the form of pores in protective coatings (Weichert, 2002) or cable insulations (Kawawata and Ogura, 1971), or pores in corrosion layers.

3. What damage do 'black spots' cause, and which objects and alloys are in danger of being affected?

'Black spots' are a severe conservation problem. They disturb the appearance of the object before and after removal (Figure 7); underneath a black spot, the metal can be bright and shiny, in contrast to an otherwise dark and oxidised surface. Black spots cause pitting on metal surfaces (Figure 8); eventually, the surface of an object can partially be destroyed.

Figure 7: 'Black spots' covering large parts of a medieval bronze fibula (KN 116)[8]

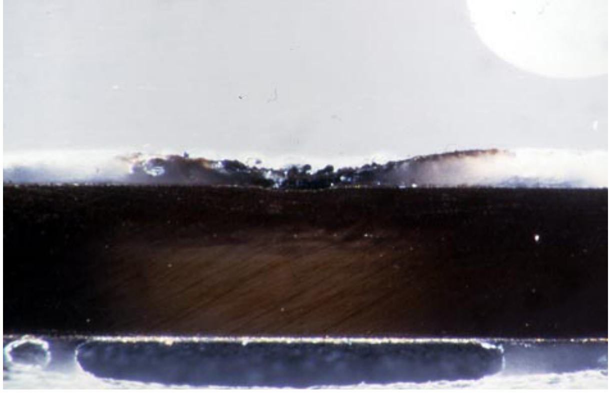

Figure 8: Copper test plate coated with microcrystalline wax COSMOLLOID H80©; a black, sulphurous corrosion had grown through a pore in the coating after exposure at ca. 4 ppm hydrogen sulphide for several weeks. A slight depression in the metal surface is visible[9].

3.1 Susceptibility of different copper alloys and tin alloys containing small amounts of copper (pewter)

'Black spots' on copper and copper alloys are now a known phenomenon. With laboratory experiments, described in chapter 2, the assumption was now verified, that copper sulphide corrosion can occur on alloys with a very low copper content of 1 to 3 %, when exposed to a very high concentration of hydrogen sulphide (4 ppm) over a period of several weeks. The identified crystalline phase was covellite, though other crystalline and possibly amorphous phases were present. Pewter with a significantly higher copper content (10 %) did not develop corrosion visible to the naked eye under the same experimental conditions. Presumably, a corrosion nucleus is necessary to initiate this kind of corrosion on pewter, as was observed in one experiment with corroded copper alloys and uncorroded pewter (copper content between 1 and 3 %), exposed to 4 ppm hydrogen

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[8] Museum der Stadt Konstanz; width of photo relates to 0.9 cm of the original.

[9] Width of photo relates to 0.9 cm of the original.

sulphide. The corrosion started to spread to the pewter, from a point where the two plates touched (Figure 9). The corrosion spread over a distance of approximately 3 cm.

One experiment, which needs verification, showed that copper alloys could be 'infected' by sprinkling on small amounts of powdered copper sulphide and leaving them in an atmosphere with sulphur at 50°C and 100% relative humidity for seven weeks; a black corrosion slowly spread from these spots.

Figure 9: 'Infected' pewter (3% copper content) after being in contact with heavily corroded copper alloys at ca. 4 ppm hydrogen sulphide for appr. 8 weeks[10].

3.2 Copper alloys and pewter from marine finds

Black, sulphurous corrosion can develop on copper alloy or pewter objects in contact with marine crusts and gunpowder containing elemental sulphur. This could be confirmed by an extensive survey of marine archaeological objects from the *Mary Rose* collection in Portsmouth, UK. The investigated objects belong to the inventory on board the *Mary Rose*, a war ship of King Henry VIII, which sank off the Portsmouth coast in 1545.

After the ship was raised and artefacts were being stored in the museum from the early 1980´s, some objects made from copper alloys and pewter, developed a black corrosion. On some copper alloys, the black corrosion product had a fuzzy appearance, even visible to the naked eye, which was only loosely attached to the metal, a characteristic feature of 'black spots'. Corrosion on some pewter objects, containing copper in amounts from only 0.7%, was described as 'a black brown sooty layer over a poor powdery surface', and also as 'a brown thick tarnish, initially localised in occurrence but eventually covering the entire surface. High in sulphur and unpleasant to look at' (personal correspondence between Mary MacQueen, formerly Mary Rose Trust, and Dr. Warwick, International Tin Research Institute, Greenford, England, February 1986).

XRF analysis of the pewter corrosion carried out in the 1980´s by Ernest H. Pitt and R. C. Hollyak, of Coventry Lancaster Polytechnic (internal reports), identified copper and sulphur, often as major components. Additionally, a positive iodine-azide test (Weichert 2002) proved the presence of sulphur or other reduced sulphur compounds. It is therefore likely, that the corrosion product consisted, at least partially, of copper sulphides. In one case, the corrosion of a pewter object (a fragmented jug, MR 78 A 118 1-3) was clearly identified by XRD; it mainly consisted of covellite. The object was covered with white, marine deposits.

3.3 'Black spots' on minerals

It is known that copper minerals can, under certain circumstances, develop a black sulphurous efflorescence (Eggert, 2000). When different copper minerals are stored in the same closed display case, the interaction of single reactions can lead to the formation of reduced sulphur gases. Sulphur and reduced sulphur gases can also be directly emitted by adjacent minerals. Marcasite, for example, produces elemental sulphur during oxidation. Products resulting from the disintegration of pyrite can react with sulphide minerals, producing hydrogen sulphide (Waller et al., 2000). Discoloration of non-sulphidic copper minerals to a deep black is mainly due to the effect of sulphurous substances. Sulphurous, black corrosion products on copper sulphide minerals can also be the result of oxidation reactions which take place at an accelerated rate at a relative humidity from about 60%. The sulphur content of the sulphide is partially oxidised, i.e. a black efflorescence can develop without a pollution source (Howie, 1992).

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[10] width of photo relates to ca. 7 cm of the original

4. How can affected objects be treated? – Strategies for active treatment and preventive conservation

'Black spots' can in most cases easily be removed mechanically. Removing 'black spots' using chemicals (dithiolates) does not seem appropriate, because even more damage may be caused. But just removing the 'black spots' from the object will not solve the problem – if storage conditions are not adequate, they may reappear.

Therefore, the best way to solve the problem is to take preventive measures, i.e. environmental monitoring and control, suitable storage conditions, and the detection and removal of pollutant sources. To be able to find potentially harmful material, it is important to document all aspects concerning the collection, i.e., materials used for conservation, storage and display, loans, and movement of objects within the museum.

4.1 Storage

It is best practice to store susceptible material at low temperatures and relative humidity, and keep them clean of dust and dirt. Airtight display cases can, on the one hand protect the collection from external pollutants, but on the other hand may keep in harmful substances emitted by the objects themselves.

There are different pollutant absorbers available which absorb sulphurous components. Care should be taken when using pollutant absorbers in mineral collections (see chapter 4.3).

4.2 Detecting pollutant sources

Some materials which are used for conservation, storage and display, such as plasticine (Figure 10), certain fabrics (Werner, 1972; Weichert, 2002), paper (Rubin and Rubin, 1938), rubber and vulcanised glues (Howie, 1992; Oddy, 1973; Sease, 1994) and leather (Howie, 1992), could be harmful. Wool and felt (sometimes even when sold as 'synthetic') are typical examples of materials emitting reduced sulphur compounds (Sease, 1994; Brimblecombe et al., 1992).

Figure 10: Back of the fibula shown in Figure 7; 'black spots' spread from the area where plasticine was placed onto the surface for mounting[11].

Often it is not so obvious whether certain materials might be harmful. It is therefore absolutely necessary to test and re-test all materials used in connection with museum objects to see whether they might contain sulphur or sulphidic compounds; the available test methods are both inexpensive and easy to use. The Oddy Test (Lee and Thickett, 1996) can be employed to determine the general corrosiveness of a material. Disadvantages lie in the relatively long running time of the test and in the fact, that neither the corrosion product nor the pollutant can be characterized. With the iodine-azide test, quick and easy testing for elemental sulphur and other reduced sulphur compounds is possible. A microscopic sample of the material to be tested is sufficient.

If the pollutant source cannot be traced inside the museum, it is worthwhile to take a closer look outside – are there any paper mills, swamps or sewage plants (Sherwood, 1992, quoted from Strandberg, 1997) nearby?. Even mineral springs might emit reduced sulphur gases (Daubree, 1875; Lacroix, 1909, quoted from Scott, 2002).

It is difficult to predict a critical indoor pollution level; it has been proved that even the very low vapour pressure of sulphur at room temperature (app. 1 ppb at 20 °C) is sufficient to cause black spots on copper (Eggert and Sobottka-Braun, 1999). Also, the presence of one pollutant alone, often does not explain the damage; the interaction of different reduced sulphur compounds with organic acids or hydrochloric acid for example, may multiply the harmful effect (Watts, 1999).

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[11] Scale in mm.

4.3 Minerals, patinated objects and artefacts decorated with niello

Disintegration reactions of minerals caused by oxidative processes can only be prevented by storage at low relative humidity; 30% is recommended (Waller, 1992).

Some minerals themselves emit reduced sulphur compounds; it is therefore good advice to store potentially harmful minerals such as pyrite and marcasite in separate, airtight containers. Pollutant absorbents should only be used for such minerals that emit the pollutant as a result of a thermodynamic reaction, e.g. pyrite (Waller et al., 2000). They should not be employed for minerals that emit reduced sulphur gases through sublimation or evaporation, because this would accelerate their degradation. Minerals that emit a certain sulphurous gas should not be stored together with minerals that absorb the same substance; they will harm each other (Waller et al., 2000).

Oxidation processes as mentioned above, can also lead to the disintegration of copper sulphides which are part of the object. Artificially patinated surfaces or niello decoration may oxidise and change colour when storage conditions are inappropriate.

4.4 Special precautions for marine artefacts and objects with adhering sulphurous substances

Marine crusts should be removed from the object as long as they are not important for the interpretation of the object. It is crucial to remove these deposits completely, since remaining sulphurous substances could be the starting point for further corrosion. Sulphur emitted by marine crusts can also harm adjacent objects; large pieces of these crusts or thickly covered artefacts should therefore not be stored in close contact (or in the same showcase) with sensitive material.

For objects from which sulphurous material cannot be removed, such as powder ladles and containers, weapons operated with gun powder, kettles used for boiling tar, or hollow objects filled with sulphurous cement (Eggert et al., 1999), storage at low temperature and a low relative humidity, is crucial.

4.5 Protective coatings on copper alloys and on pewter

The evaluation of test plates from laboratory experiments (test conditions as in chapter 2) and artefacts of the *Mary Rose* showed the protective effect of coatings on copper alloys generally to be of limited reliability. This can partially be due to the thoroughness of application (Figure 11) .

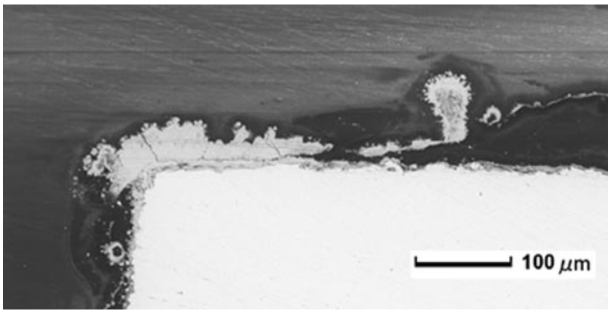

Figure 11: Copper test plate coated with microcrystalline wax (COSMOLLOID H80©, appearing black); 'black spots' grow along the edge, where the protective coating is thinned (application by immersion). The sample was exposed to hydrogen sulphide concentrations of ca. 4 ppm for three months[12].

However, the application of INCRALAC© in most cases prevented further corrosion on *Mary Rose* objects; the investigated coatings being fifteen to twenty years old. But due to the relatively small number of investigated objects, the results do not provide sufficient evidence.

A survey of 19 pewter objects from the *Mary Rose* collection, coated with silicone wax (12 objects, product name unknown), INCRALAC© (two objects), and FRIGILENE© (five objects) showed, that in most cases, further corrosion occurred, despite the protective coating. Four artefacts treated with microcrystalline wax remained stable.

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[12] SEM photo by Ineke Joosten, ICN.

5. Results and Discussion

‘Black spots’ do not only grow on copper and copper alloys, but also on alloys containing minimal percentages of copper, such as pewter, and even on copper minerals. It is possible, that copper sulphides which are part of the object, such as artificial patination or niello, can oxidise and change colour when storage conditions are inappropriate.

The exact composition of the corrosion product could not yet be determined in all cases. However, it is proved that ‘black spots’ are not exclusively copper sulphides, but can as well contain other phases, such as sulphates or amorphous components which could not yet be identified.

The growth mechanism of ‘black spots’ depends on many parameters, such as temperature, humidity, pollution concentration, and time, but also on alloy composition and metal structure. The pollutants in this process are known, but it is rarely possible to exactly determine the circumstances that lead to the formation of black spots on museum objects. It is therefore of great importance to record the collection history of an object properly (conservation treatment, materials used for display, loans, movement within the museum etc.).

Taking preventive measures is crucial for all collections, which means storage of metal objects at low temperatures and a low relative humidity, separation of sulphur-emitting exhibits, and testing of all materials in stores and exhibition rooms.

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Table of registered trade items

COSMOLLOID H80©
CU ROTIN 3©, tin solder
INCRALAC©,
FRIGILENE©,
MERCKOQUANT©

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