Plastiline: Another Unsuspected Danger

in Display Causing Black Spots on Bronzes

Gerhard Eggert

Some brands of plastiline ('plasticine') contain elemental sulphur leading to an air pollution of some 1 ppb in equilibrium. This can cause severe damage to sensitive materials like copper or silver alloys in the course of time. A mediaeval bronze fibula developed 'black spots' of copper sulphide when mounted with plastiline for nine years in a display case. Therefore, recommendations are given for the use of plastiline in conservation.

Plastilin in der Vitrine: eine weitere unbekannte Gefahrenquelle und Ursache für „Schwarze Flecken" auf Bronzen

Einige Plastilinsorten enthalten elementaren Schwefel, wodurch unter Gleichgewichtsbedingungen eine Luftverunreinigung von ca. 1 ppb entsteht. Dies kann mit der Zeit zu schweren Schäden an empfindlichen Materialien wie Kupfer- oder Silberlegierungen führen. So entwickelte eine mittelalterliche Bronzefibel ‚Schwarze Flecken' aus Kupfersulfid, nachdem sie neun Jahre lang mit Plastilin in einer Vitrine montiert war. Daher werden Empfehlungen für den Umgang mit Plastilin in der Restaurierung gegeben.

Introduction

An Unsuspected Danger in Display is the title of a conservation classic where William A. Oddy[1] first described the application of what is now the ‚Oddy-Test'[2] to check display materials for emission of compounds corrosive to artifacts. Despite its usefulness and simplicity it is still not used everywhere and always in the mounting of exhibitions. Avoidable damages from unsuspected dangers are the consequences. This paper reports a case study where an unsuited display material caused the so called 'black spots on bronzes' which where first brought to the attention of the conservation community 30 years ago by Helge Brinch Madsen at the *11. Arbeitstagung der Arbeitsgemeinschaft des Technischen Museumspersonals* (ATM, later called AdR) in Münster 1976.[3]

Black Spots on Bronzes

Black Spots on Bronzes are a well-known phenomenon, which is described in detail elsewhere.[4] The term 'Black Spots' should not be taken literally: The spots can be also brown or of other colour and they are not flat. The three dimensional efflorescences resembling mould look like bushes or cauliflower or like shiny spherical pinheads under the microscope, see figs. 3–5 for an example discussed here.[5] They are formed by the chemical action of low amounts of some sulphur compounds in the atmosphere. In the laboratory they can be grown on copper containing materials by small amounts of hydrogen sulphide (H_2S), elemental sulphur (S_8), and most likely by carbonyl sulphide (COS). They occur on copper or copper alloys (including those with only minor copper content like pewter) or their corrosion products and copper minerals including sulphides.[6] Analyses by X-ray diffraction detected copper sulphides like covel-lite (CuS), digenite (Cu_9S_5), djurleite ($Cu_{31}S_{16}$), and chalco-cite (Cu_2S) as material of the spots. Recently, the copper sulphates chalcanthite ($CuSO_4 \cdot 5H_2O$)[7], antlerite ($Cu_3SO_4[OH]_4$), and brochantite ($Cu_4SO_4[OH]_6$) as possible oxidation products of sulphides have also been identified; sometimes no diffraction peaks can be found at all.[8] Here is clearly further research necessary to better characterize the X-ray amorphous material (e.g.: Is oxygen from partial oxidation present?).

Normal air pollution, e.g. SO_2, does not lead to black spots, otherwise they would be ubiquitious. In the literature only three cases could be found where the definite local source of the reduced sulphur species in the air could be identified:

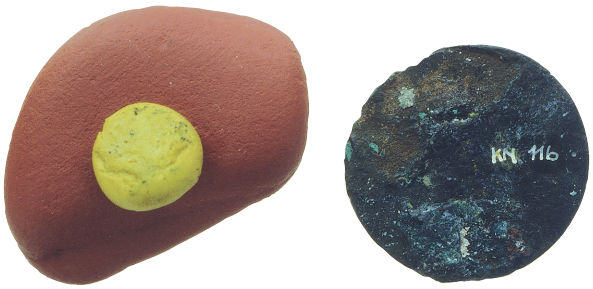
- wool, this material can emit COS from the decay of the amino acid cystine present in keratin, and rubber vulcanised with sulphur[9]
- hydrogen sulphide (?) emitted from a ceramic vessel excavated from an anaerobic site where sulphate reducing bacteria can exist (foul mud)[10]
- elemental sulphur (?) sublimed from wood of the Mahdia shipwreck which was sea-logged under reducing conditions.[11] (The wood of the Vasa shipwreck was shown to contain 0.2–4 % w/w elemental sulphur with an estimated total of 1,600 kg![12])

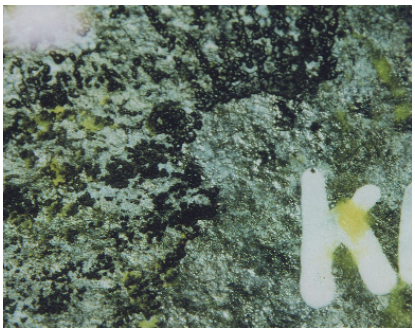
Compared with the number of observed occurrences of black spots, this is an astonishingly small number where the sulphur source necessary for their formation has definitely been identified.

In this case study, another unsuspected source is reported: A mediaeval bronze fibula (some 3 cm in diameter, fig. 1) excavated in a South German city was mounted for 9 years in a closed display case with yellow plastiline of an unknown brand (fig. 2). Black spots occurred on both sides, the backside where the metal was in direct contact with the mounting material (figs. 3, 4) and the obverse on view (fig. 5). X-ray diffraction of a black spot sample with a Debye-Scherrer camera identified covellite (CuS). The occurrence of these spots on surfaces, which obviously have been cleaned mechanically during previous conservation, proves that the crystal growth must have occurred later.

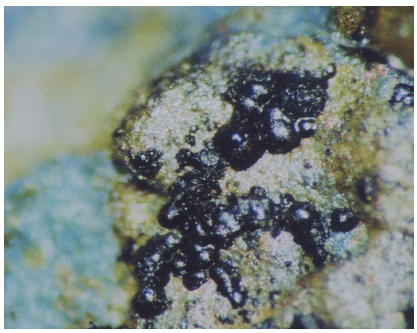
1
Obverse of the fibula, Ø 3 cm

2
Backside of the fibula, which was mounted with the yellow plastiline on a red stone

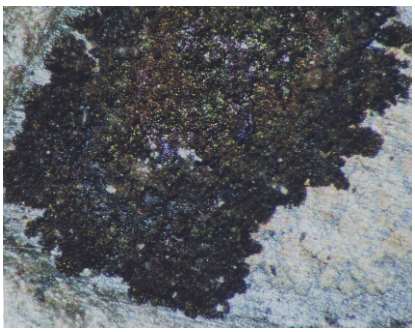




3
Microphotograph (6 x 9 mm) of black spots on the reverse and residues of the yellow plastiline. The area around the inventory letters has been protected by a lacquer.



4
Detail of black spots on the reverse (1.2 x 2.1 mm)



5
Microphotograph (1.3 x 2 mm) of black spot on the obverse

Plastiline

The term ‘plastiline’ (common in Italian and German) here is used as generic term to replace ‘plasticine’ which is common in the Anglo-Saxon world but trademarked and, therefore, could be misunderstood as relating to only one special product. It is a class of non-drying, non-hardening, untoxic (children’s toy!) modelling clays, whose required consistency can be adjusted by warmth (e.g. of hands) or variations in the composition.
Until today, some brands of plastiline contain a considerable amount of elemental sulphur. The German chemical encyclopaedias *Römpp*[13] and *Ullmann*[14] give based on analyses and experiments by *Giesel*[15] the following composition:

40 % Zinc oleate (i.e. oleic acid heated with ZnO)
18 % Japan wax and oil (natural or mineral)
23 % Flowers of sulphur
15 % China clay
4 % Mineral pigment

A recipe for homemade sulphur-free plastiline[16] mixes clay with microcrystalline wax (or beeswax), motor oil (or purified mineral oil to avoid unwanted smell), and automotive grease (or petroleum jelly). Some ingredients of plastiline found in recipes are listed in Tab. 1.[17]

Filler	Wax components	Oily components
clay, white or red	Japan wax	petroleum (jelly)
sulphur	microcrystalline wax	lanolin
talcum	beeswax	grease
magnesium oxide		glycerol
starch		olein
		castor oil
		palm oil

Tab. 1
Compounds (other than pigments or dyes) of plastiline mentioned in recipes

The product information for "Professional Plasteline" (Chavant, Inc., Red Bank, NJ) states: "The sulphur filler gives this clay a silky feel appreciated by many artists".[18] "Non-Sulphurated Plasteline", however, is "somewhat grabby".[19] The intention of its development "was to eliminate the sulphur filler in a professional grade sculpting clay, which often caused inhibition problems with various liquid rubber mold-making materials". Sculptors prefer sulphur-containing mixtures to clay because these have "no elasticity or rebound. When it [the plastiline, G.E.] is put in place, it stays there absolutely, whereas clay mixtures retract slightly", as John Twilley was told.[20]

There must have been some experience with corrosion among sculptors because another product is advertised: "It is SULPHUR FREE reducing odor and eliminating potential corrosion of susceptible metals".[21] At least some experienced metal conservators seem also to be aware of the risks of sulphur containing plastiline. It was even used in former decades to re-patinate stripped bronzes by applying warm plastiline overnight: "Only some brands of plasticine are effective, and these contain traces of sulphur compounds [sic, G.E.] which impart just the right degree of tarnish."[22] Nevertheless, the *Bibliographic Conservation Information Network* (BCIN)[23] and the *Art and Archaeology Technical Abstracts* (AATA)[24] have no relevant hits to literature on this problem. The German language conservation journal *Arbeitsblätter für Restauratoren*, whose 32 volumes from 1968 to 1999 appeared on CD-ROM (available from the VDR office), can be full-text searched electronically: 'Plastilin' was indeed brought in direct contact to metal objects during conservation or moulding without mentioning its composition or warning to use sulphur-free brands only.[25] In other countries practice might have been similar, but is – if reported at all – more hidden in the professional journals. Savage's *Art and antique restorers' handbook* recommended 'plasticine' as "admirable in cabinets for securing small objects" made of non-porous materials including explicitly metal.[26] The *Museum Workers Notebook* even gives "flower of sulfur" as ingredient in a recipe from the *Milwaukee Public Museum* for "preparing modeling clay" without any warning.[27] Public and private remarks of colleagues prior and after presenting this paper and own observations lead me to the assumption that knowledge of the dangers of plastiline is not widespread in the conservation profession today.

The author is aware of only three people warning against the use of plastiline with metals or its compounds in writing. David A. Scott clearly states hidden in a chapter on "Metallography and Ancient Metals":

> Missing parts [from sampling, G.E.] are sometimes filled with unsuitable materials such as Plasticine ..., which usually creates severe corrosion of exposed metal sufaces over a period of years in the museum collection. Sulfur containing fillers such as Plasticine should never be used for mounting, display, or gap-filling of metallic objects.[28]

In his recent book on *Copper and Bronze in Art* he continues after mentioning the repatination of stripped bronzes with plastiline:

> ... revealing a rich brown-black patina of copper sulfide. Such patinas also formed accidentally in old storage cabinets where Plasticine had been used previously as a mount or a temporary gap-filling material. – J. Twilley noted ... that the whiskerlike [!, G.E.] crystal growth on metallographic sections stored on Plasticine mounted glass slides was primarily chalcanthite.[31]

"...[T]he sulfur in the material causes immediate and serious oxide [sic] growth", is another warning posted by the silversmith and bronze sculptor Howard Newman to the email Conservation DistList.[30]

The mineralogist Paul Ramdohr has warned to mount chalcocite (Cu_2S) specimen with plastiline: "Since chalcocites react quickly with the sulphur contained in normal plasticine forming mould[-]like [!, G.E.] brown CuS, for mounting here bees' wax ('cera alba') should be used."[31]

Analysis of the plastiline

X-ray diffraction which allows to identify crystalline compounds in a mixture could only detect calcite (calcium carbonate) and the clay minerals kaolinite and illite in the plastiline used for mounting the mediaeval fibula. Therefore, the sulphur content must be lower than at least 5 %, higher values of crystalline sulphur would certainly have been detected.

An Oddy test (copper coupon hanging over 2 g of the plastiline for 28 days in a stoppered glass tube, 100 % rH, 60°C)[32] confirmed that the plastiline was the culprit: the copper sheet turned black and formed 3D spots rather rapidly. The presence of a reduced form of sulphur could also be shown by a modified Hepar test[33]: a silver coupon was wetted with a sodium carbonate solution and the plastiline pressed against it. When checked after 30 min a brown spot of silver sulphide has formed on the contact area.

Hydrogen bonded to carbon can react under heat with elemental sulphur to form hydrogen sulphide. In former times, mixtures of paraffin with sulphur have been used to generate this gas in the laboratory. Although there is at least one recipe for a mixture with only inorganic compounds[34], commercial brands of plastiline should always contain organic ingredients. Therefore this reaction can be used to check for the presence of sulphur; indeed the plastiline sample in question reacted heavily.

Quick test for possible sulphur content in plastiline

Place a tiny amount of substance in a small test tube and gently heat it in a flame. When elemental sulphur is present hydrogen sulphide is set free, easily detected by its smell of rotten eggs (if no other smells occur) or by a wet lead acetate paper[35] placed over the tube which turns brown to black when the test is positive.

Conclusion

Solid sulphur has the low but measurable equilibrium vapour pressure of some 1 ppb at room temperature. Wherever and as long solid sulphur is present it tries to maintain this equilibrium vapour pressure by sublimation of S_8 molecules into the gas phase. Model experiments have shown that black spots are easily formed on copper under these conditions.[36] It is, therefore, no wonder that black spots did not only form where the pastiline was in direct contact to the fibula but also on the other side which could be reached by sulphur species only via the gas phase. The amount of sulphur in plastiline is large compared with that lost by sublimation. Therefore, 9 years as in this case could not exhaust this source.

The possible ingredients of plastiline lead to the following recommendations for conservators:

- To be sure to have only sulphur free brands in your laboratory, check them with the quick test described above.
- To be sure that no other harmful gases (e.g. aldehydes and organic acids) are emitted from the organic ingredients check all those sulphur free brands additionally by the Oddy test.
- Be aware that the Oddy test gives only an answer whether harmful volatile compounds are emitted. In direct contact non-volatile substances (e.g. long chain carboxylic acids from vegetable oil or beeswax) could enhance corrosion as well. Therefore, avoid direct contact of objects and plastiline whenever possible (e.g. use a plastic foil or a lacquer as barrier). This will also prevent liquid ingredients from migrating into porous objects; note for instance that plastiline placed on paper for some time will cause a 'fatty' spot!
- If under exceptionable circumstances the direct contact between endangered objects like silver or copper alloys and plastiline cannot be avoided then only self-formulated products from safe materials should be used. Clay and purified products from petroleum like microcrystalline wax, paraffin wax, and paraffin oil are considered as safe.[37] Afterwards, the objects must be cleaned with petroleum ether.
- Sometimes plastiline has also been used for creating artifacts, which are collected.[38] If these are displayed in closed cases no sensitive metals or pigments should be around. Instead, polished silver and copper test coupons can be placed in the same cases to monitor the risks.[39]

Suspect dangers everywhere and test your materials – then there will be no longer unsuspected dangers!

Acknowledgement

This paper is the updated version of a lecture at Jack Ogden's "Exposure 2001" conference in Hildesheim whose postprints unfortunately never made it to the printer's.

I gratefully acknowledge the various helpful contributions of Nina Frankenhauser, Heiner Grieb, Heide Härlin, Maja Weichert (at that time all in Stuttgart), Bruno Barbier (Bonn), Helmut Preuß (Konstanz), Dorothee Schroth (Bensheim), David A. Scott (Los Angeles), and John Twilley (Hawthorne, NY) to this project. Thank you all!

Prof. Dr. Gerhard Eggert
Studiengang „Konservierung und Restaurierung von archäologischen, ethnologischen und kunsthandwerklichen Objekten"
Staatliche Akademie der Bildenden Künste
Am Weißenhof 1
D-70191 Stuttgart

Annotations

1 Oddy 1973
2 Lee/Thickett 1996
3 Brinch Madsen 1978
4 Eggert et al. 2004; Weichert et al. 2004
5 Weichert et al. 2004
6 Eggert 2000; Eggert et al. 2004; Weichert et al. 2004
7 Eggert et al. 1999
8 Eggert et al. 2004
9 Sease 1994
10 Green 1992
11 Eggert/Sobottka-Braun 1999
12 Sandström et al. 2002
13 Römpp-Lexikon Chemie, 8th ed., Stuttgart 1987, s.v. Knetmassen
14 Ullmanns Encyklopädie der technischen Chemie, 2nd ed., München 1931, s.v. Modellierwachs
15 Giesel 1878

16 http://users.lmi.net/~drewid/plastilene_recipe.html (accessed May 27th, 2006)
17 Sources: ref. mentioned in text; Bennett 1934, p. 249; Ziolkowsky 1982, pp. 7–9
18 http://www.chavant.com/index_main.shtml, _ Tech section _ Clay Bodies _ Professional Plasteline (accessed May 27th, 2006)
19 http://www.chavant.com/index_main.shtml, _ Tech section _Clay Bodies _ NSP Plasteline (accessed May 27th, 2006)
20 JohnTwilley, email to the author, January 5th, 2005
21 http://www.chavant.com/index_main.shtml, _ Tech section _Clay Bodies _ Y2 Klay (accessed May 27th, 2006)
22 Plenderleith / Werner 1971, pp. 261, 265 (note 9c)
23 http://www.bcin.ca (accessed May 27th, 2006)
24 http://aata.getty.edu/NPS/ (accessed May 27th, 2006)
25 Arbeitsgemeinschaft der Restauratoren (Ed.), Arbeitsblätter für Restauratoren [Elektronische Ressource]: Beiträge der Ausgaben 1/32.1968/99,2 (2001), Stegen 2001, see here: Silver (Gr. 3), p. 23 f. [1977], p. 121 [1993]; (Gr. 18), p. 26 [1971]. Bronze (Gr. 2), p. 20 [1970]
26 Savage 1954, s.v. plasticine (unchanged also in the 2nd rev. ed. of 1967, reprinted 1980)
27 Long 1961, p. 04-01-2
28 Scott 1991, p. 58
29 Scott 2002, p. 396, note 2
30 http://palimpsest.stanford.edu/byform/mailing-lists/cdl/1997/1574.html (accessed May 27th, 2006), message Id: cdl-11-54-003, distributed 17 December 1997
31 Ramdohr 1980, p. 444
32 Lee/Thickett 1996
33 No thermal reduction needed; see any textbook of qualitative inorganic analysis.
34 DRP 188219: sand, clay, magnesum chloride and carbonate, and borax mixed with water.
35 Merck no. 1.09511.0001; or soak a filter paper in a lead acetate solution (approx. 8 g in 100 ml H_2O).
36 Eggert/Sobottka-Braun 1999
37 See note 16 for a recipe.
38 Demandewitz 2005
39 Waller et al. 2000; Martius/Raquet 2005

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Fig. 1–5: Maja Weichert