EARLY PRODUCTION RECIPES FOR LEAD ANTIMONATE YELLOW IN ITALIAN ART*

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Lead antimonate yellow, or Naples Yellow, is one of the most common yellow pigments in Western European art. It was used mainly in the period from 1500 to 1850. During the 18th and 19th centuries, a whole range of production recipes was published. However, the early production history of the pigment is not well understood. In this paper, a study of two early production recipes is reported. Under the nomenclature of potters' *yellow, the recipes describe some production details of the pigment. Reconstructions of the historical lead antimonate yellow were made according to these sources. X-ray powder diffraction (XRPD) was used to examine the reaction products. Our findings show that various types of lead antimonate yellow can be formed, following the descriptions given in the recipes. Some of these types, notably lead–tin antimonate, have been found in earlier studies of authentic works of art. No evidence was found for a locally limited use of this pigment, as has previously been suggested. Documentary and analytical evidence indicates that the knowledge on lead antimonate yellows originates from Middle Eastern ceramic and glass industries. It is argued that the know-how on the production of lead antimonate yellows has been transferred via the migration of glass artists from the Eastern Mediterranean to Venice during the 15th century.*

KEYWORDS: ITALY, 16TH–17TH CENTURIES AD, PIGMENT, PIGMENT PRODUCTION, PAINT, PAINTING TECHNIQUE, LEAD ANTIMONATE, NAPLES YELLOW, X-RAY DIFFRACTION

INTRODUCTION

The history of lead antimonate goes back at least 3500 years. Lead antimonate has been identified frequently as an opacifying agent in Egyptian yellow coloured glass from the 18th Dynasty, *c*. 1450 BC (Wainwright *et al*. 1986). Lead antimonate was also known in the Mesopotamian, Babylonian and Assyrian cultures (Partington 1974; Hedges 1976). The use of lead antimonate in Western European art dates back to the early 16th century. In 1540, Biringuccio wrote about the use of antimony in making yellow glass enamels (Biringuccio 1966, 90–1). In the late 1550s, Picolpasso published a treatise on the potter's craft that contains a series of recipes for lead antimonate to obtain a yellow glaze on maiolica (Picolpasso 1976).

The circumstances under which lead antimonate emerged as a colouring agent in Italian Renaissance art are unclear. Was the pigment simply re-invented by Italian craftsmen? Or has lead antimonate been used continuously—but sporadically—from early antiquity to the 19th century?

Two early recipes shed some light on the early production history of Naples Yellow in Western European painting. We carried out a series of reconstruction experiments, in which lead antimonate yellow was synthesized according to the descriptions given in one of these recipes. The text of the manuals was studied in their historical context. The combination of textual interpretation, reconstruction experiments and scientific analyses is intended to gain insight into early modern lead antimonate production.

<div align="center">THE MARIANI MANUSCRIPT</div>

The first recipe to be discussed is taken from an early 17th century Italian treatise on miniature painting technique compiled by the miniaturist Valerio Mariani da Pesaro (1568–1625?). Mariani was a professional miniaturist who worked, during the larger part of his productive years, for the Duke of Urbino. Within the ducal palace in Pesaro, the duke founded a businesslike organization of craftsmen's and artists' workshops. One of the most detailed recipes discusses three methods for the preparation of so-called *giallo de' vasari*, or potters' yellow. Mariani's chapter on potters' yellow is as follows:

Potters' yellow
Potters' yellow is a very beautiful yellow made by the potters, which they make in two types, one which appears to be more subtle and works well for colouring drawings, and another which shows more body. The first they make like this: take five ounces of burnt lead in powder and sieved, and three ounces of antimony and two ounces of plain salt.

All this is crushed and sieved as is said and after the powders are well-united they are spread on several not glazed terra cotta plates half a finger thick to make them calcine better and then you put it in their [the potters'] furnaces to calcine one or two times in the same fire where they bake their pots.

The second way is the following: one takes 3 ounces of burnt lead, 2 ounces of antimony and one ounce of calcined wine residue. You place all this, arranged like the others mentioned above, on the furnace to calcine, but this mixture needs more fire than the first one.

[c. 16r]

You can also make this yellow of a fuller colour and more beautiful by taking 6 ounces of burnt lead and 4 ounces of antimony and one ounce of Alexandrine Tutty and 1 ounce of salt, and this all mixed together you grind it finely and put it on plates like the others, but you heat it outside the furnace at the ventilation pipes, and if by chance it will not get hot enough you will put it there again until it is done. But if it will come out too much cooked and if there is a fire, and it is melted, then you will grind it finely again, putting the material back on new plates, you will put it on a lower fire and if necessary one will repeat it several times and this way it will turn out beautifully.

Italian original:

Giallo de Vasari
Il giallo de' vasari è un bellissimo giallo fatto da essi, il quale lo fanno di due sorte, una che riesce più sottile e riesce bene a colorire i disegni, et un'altro che riesce con piu corpo. Il primo fanno così: pigliano cinque oncie di piombo abrugiato in polvere et sedacciato, e oncie 3 d'antimonio e doi oncie di sal commune. Il tutto si pesta e sedaccia

come s'è detto e si distendono bene unite le polvere asieme sopra diversi piatti di terra non vetriata grosso un mezzo dito acciò si calcina meglio e si mette poi alla fornace loro a calcinare una o due volte al medesimo fuoco che si cuociono li loro vasi.

Il secondo modo è tale: si pigliano 3 oncie di piombo abrugiato, oncie 2 di antimonio e oncia una di feccia di vino calcinato. Il tutto, disposto come l'altro di sopra, si pone alla fornace e calcinare, ma mistura vuol più foco della prima.

[c.16r]

Si fa ancora tal giallo più carico di colore e più bello con prendere sei oncie di piombo abrugiato e quattro oncie di antimonio e oncie una di tutia allessandrina e oncie una di sale, meschiato il tutto insieme si pestano sottilmente e si pone sopra piatti come gli altri, ma si cuoce fuori della fornace alli sfiatatori, e se per caso non venisse cotta a bestanza si rimette di nuovo finch sia cotto. Ma se per caso riuscisse troppo cotto e che venisse fuoco, e colato si rimacina di nuovo et pesta sottilmente, rimettendo la materia sopra nuovi piatti, si ripone a fuoco piu lento et occorendo si farà più d'una volta e così verrà in tutta beltà.
(Mariani MS, c15.r; Hermens 1995, 30, 136)

Interestingly, Mariani mentions the production of three different types of lead antimonates. The recipes show ingredients similar to those used by Picolpasso: lead oxide and antimony combined with lees or salt. Mariani's third method includes Alexandrine tutty that, according to Picolpasso, is used by many: [. . .] *to make* zalulino *of the highest beauty* [. . .] (Picolpasso 1976, 122).

THE DARDUIN MANUSCRIPT

The second recipe that we would like to discuss is a note from the so-called *Darduin* manuscript. From the late 13th century onwards, the Venetian island of Murano developed a strong tradition in the art of making coloured glass. Murano glass was in demand all over Europe. Archival research has shown that glass objects were even exported to the Near East (Zecchin 1987, 397). The art of glass-making was usually a family business, as is exemplified by the workshop of the Darduin family, which was founded in the late 15th century. The family maintained a successful glass business for over a century. The so-called Darduin recipe book is a collection of technical recipes on glass colouring composed by several family members. The book not only contains recipes on the colouring of glass, but also a few references to the production of painting pigments:

Note on yellow enamel glass made by Mr Giacinto Manfreo; 20 january 1653: burnt lead 6 pounds; antimony 4 pounds; tuccia *2 pounds;* calcina *4 pounds, everything very well ground to a fine powder. Of all these well united powders I made a fry in a furnace in two* creppe di olla, *giving them three firings 24 hours each, and in 3 days I had my powder in a beautiful colour. Of this powder I took 13 pounds, 7 pounds of common minium;* quogli *2 pounds and 3 ounces, and therefore all together 22 pounds and 3 ounces.*

I poured the mentioned powder in a pan on high fire. After two hours I found an animo *of very beautiful yellow full of body and immediately I added 5 pounds of* crestallo cotto *better a bit more than less and I mixed it very well and I had a yellow glass enamel with body in a wonderful colour and this method I did in 6 hours and not more.*

Italian original (Archivio di Stato, Venice, fol. 95ᵛ. Rx. CCXCIII):

Nota del smalto zallo in corpo fatto nella fornasa del signor Giacinto Manfreo; 1653 Alli 20 Genaro: piombo brusado £6; antimonio £4; tuccia £2; calcina £4, tutto a peso sottil. Tutte queste polvere unite facci fritta in fornello in doi creppe di olla dandoli tre fuoghi di ore 24 l'uno et in tre giorni habbi la mia polvere in bellissimo color, ne pigliai di questa £13; Minio comun £7; quogli £2 onze 3, fu in tutto £22 onze 3.

Buttai la ditta polvere in paelato a tutto fuogo et doi hore doppo trovai un'anima di zallo molto bella et piena di corpo et subito li buttai crestallo cotto £5, piú tosto qualche cosa di piu et missiai benissimo et hebbi un smalto zallo in corpo in bellissimo color, et questa fattura la feci in hore sei et non piu.
(Darduin MS, fol. 95v. Rx. CCXCIII)

Apparently, this particular recipe was meant for the production of lead antimonate glass rather than a lead antimonate painting pigment. It is important to note that both recipes call for the use of similar ingredients, such as lead, antimony and *tutia*. In addition, the Darduin recipe mentions several glass-related materials, such as *quogli*, *calcina* and *cestallo cotto*. Coloured glass reconstruction experiments, also involving recipes from the Darduin manuscript, have already been carried out in an earlier study (Moretti and Hreglich 1984). It was therefore decided to focus our reconstruction experiments on the Mariani recipes, which are more directly related to the art of painting.

THE INTERPRETATION OF TEXTUAL SOURCES AND HISTORICAL TERMINOLOGY

As earlier research into technical sources has shown, the historical terminology in the source literature is not always clear (Goedings and Groen 1994). This also applies to the recipes of lead antimonate yellow studied. The authors of the manuscripts mention several ingredients for the production of the pigments that are readily translated, such as *Piombo abbrugiato* (burnt lead, or lead oxide, PbO), *Sal commune* (ordinary salt, NaCl) and *wine residue* (potassium tartrate, $KOCO(CHOH)_2COOK$). Other terms, however—notably *tuccia*, or *tutia allessandrina*, and *antimonio*—remain unclear. The reaction temperatures and reaction times are other unknown parameters.

The meaning of antimonio

In both manuscripts, *antimonio* is mentioned as the second ingredient for the production of lead antimonate yellow. According to the *Pirotechnia* by Biringuccio, *antimonio* was exported from Germany to Venice, and he comments that *antimonio* was used in the production of pigments. However, in which chemical form antimony was used as an ingredient in the pigment production remains unclear. The literature suggests three possible translations for *antimonio*: metallic antimony, antimony sulphide or antimony oxide (Meyer 1977, 18–19; Wainwright *et al.* 1986).

The meaning of tutia

In the second type of Mariani potters' yellow, as well as in the Darduin manuscript, a fourth ingredient is involved: *tuccia*, or *tutia allessandrina*. Recipe no. LVI of the Darduin manuscript

informs us that *tuzia d'Alessandria* could be acquired from chemists (*dalli droghieri*), as opposed to yellow or burnt lead, which was only available at the colour supplier (*da quelli dalli colori*; Zecchin 1987, 397). *Tutia*, or *tutty* in English, is usually translated as zinc oxide (Bosworth 1983, 970; Moretti and Hreglich 1984, n. 18; De Ruette 1985). However, we found evidence suggesting a possible second meaning of *tutia*. The term *tutia* is of Arabian origin and can be found in several Arabian historical sources. An interesting reference to *tutia* is made in the chemical section of the 10th-century Arab *Mafatih*, or the *Book of keys to the sciences* (Sezgin 1970, 315) According to this treatise, *tutia* must have had different meanings. The following remarks are made:

> *Al Tùtìjâ. Of these there is a green, a yellow and another type that is similar to the bark of trees; it has several types: the white kind, which is the Indian one, it is outstanding, and the yellow, which is the Chuzistanian* [= western Iran, J.D.] *kind, and the green kind, which is from Karmân and another type is known as* al muchawwa, *and there are several other kinds. The Indian kind is being used.*
> (Wiedemann 1970a, 93)

Another, more cryptic, remark concerning *tutia* is made elsewhere in the treatise:

> *Al Tùtìjâ is the smoke of copper and antimony.* (Wiedemann 1970a, 95)

Thus, the term *tutia* could have had several meanings. Adjectives such as *Indian* and *Chuzistanian* apparently indicate the geographical origin of different types of *tutia*. It is relevant to remark that the term *tutia* etymologically originates from Persian and Hindi languages (Lokotsch 1927, 165–6). Zinc ores are abundant in India, but tin deposits also occur on a large scale (Craddock 1990). In particular, the city of Kalah, on the Malaccan peninsula, seems to have had a tradition in the production of tin, as can be read in an Arab itinerary source. Furthermore, this source mentions that:

> *One finds yellow sulphur ores and copper ores and their fumes yield excellent types of tutiya. All kinds of tutiya are derived from the fume of copper, except for the Indian type, because this type—as mentioned earlier—is derived from the* qalacii *lead.* (De Schloezer 1845, 26)

Qalacii lead refers to lead from the city of Kalah, and therefore suggests a tin-containing product, which is likely to be tin oxide (Dozy 1881, 397a). Also, Wiedemann notes that the Indian tutty should be translated as tin oxide (Wiedemann 1970b, 16).

The first known use of *tutia* in the Arabian ceramics industry dates back to 1301. In the *Book on gems and parfums*, lead, antimony and *tutia* are mentioned together as a group of ingredients in the making of earthenware glazes (Ritter *et al*. 1935). However, in this manuscript no details are given on the exact production of lead antimonate. This source might be related to the finding of combined lead stannate and antimonate, which have been identified in a 14th-century Islamic glass, as was mentioned above. With regard to these findings, tin oxide would again be a more logical translation for tutty than zinc oxide.

In the course of the Middle Ages, *tutia* became an important item of merchandise. Alexandria seems to have been the market in which large quantities of *tutia* where traded (Labib 1965, 335). This is why Western merchants added the adjective *Alexandrian* tutty, as in the Mariani manuscript. Alexandrian tutty was not a local Egyptian product, but had been imported from Persia, India and China (Heydt 1936, II, 674).

During the 15th century and the early 16th century, the Republic of Venice was the leading economic power in the Mediterranean. Despite continuing military conflicts with the Islamic world, there was close economic contact between Venetian and Arabian merchants. The Venetians even maintained a trading outpost in Alexandria, from which all kinds of merchandise were imported to Italy. Alexandrian *tutia* might very well have been part of the imported merchant goods, especially since Venice seems to be the place where the Darduin manuscript was written in 1555.

The use of *tutia* in the 16th-century Venetian glass and ceramics industry might be explained by two large waves of immigration of Eastern Mediterranean glassworkers to Venice during the 15th century. As has been shown above, the first evidence of large-scale glass production on the Venetian island of Murano dates back to the late 13th century. The peak of Venetian glass art in the 16th century, however, was preceded by two other main production centres elsewhere (Phillipe 1982, 21–36).

In the Islamic world, glass manufacturing started in around the eighth century AD and reached its peak in Syria at the end of the Abbasid period (in the 13th century) and in Egypt in the Mamluk epoch (in the 14th century). Islamic glassworkers understood the production of clear glass and enamelled and stained glasses. The Syrio-Egyptian tradition is particularly known for its coloured glass mosaics, fixed in wood or stucco. However, the importance of Islamic art diminished rapidly around AD 1400, when the great Mogul leader Tamarlane conquered Syria. Some of the Damascus glassworkers were transferred to Samarkand, Tamarlane's capital. With its excellent trade contacts in the Eastern Mediterranean, however, Venice must have been an attractive alternative for many other Syrian glass artists.

The Eastern Roman Empire of Byzantium was the second main producer of artistic glass. The Byzantine tradition of glass manufacturing goes back to classical Roman times. Although the art of glass-making fell almost into oblivion after the collapse of the Western Roman Empire, Byzantine glassworkers continued the production of glass. In the centuries that followed, Byzantine glass absorbed various influences, notably from Slavonian and Oriental art, resulting in a great diversity of Byzantine glass art. In the 15th century, the political, cultural and artistic influence of the Eastern Roman Empire began to decline, because of continuing military clashes with the Islamic world. Finally, in 1453, the Turks conquered Byzantium. As a result, Venice received a second wave of experienced glassworkers. Soon after this wave of immigration, Venice monopolized artistic glass manufacture and built itself a notable reputation, exporting large amounts of fine glass. Venetian glassworkers are known for their ingenious techniques, combining the technical knowledge of Islamic and Byzantine glass manufacturing. Thus, it seems very likely that foreign, mostly Arab, artists introduced the knowledge on the production of lead antimonate to the Venetian glass workshops. In addition, these foreign workers seem to have adhered to Middle Eastern production materials such as *tutia*.

In conclusion, *tutia* seems to refer to a number of materials, zinc oxide and tin oxide being the most likely compounds. In spite of this, other important parameters in the recipes, such as the exact chemical form of the ingredients, the reaction temperatures and the reaction times, remain unclear. In order to clarify these and other questions, reconstruction experiments were carried out. In addition, several pieces of historical yellow-glazed ceramics were subjected to scientific analyses.

THE MATERIALS AND TECHNIQUES OF RECONSTRUCTION EXPERIMENTS AND DIFFRACTION STUDIES

For the reconstruction experiments, use was made of PbO [PDF 38-1477], Sb_2O_3 [PDF 5-534], Sb [PDF 35-732], Sb_2S_3 [PDF 6-474], SnO_2 [PDF 41-1445], NaCl [PDF 78-0751], ZnO

[PDF 36-1451] and KOCO(CHOH)$_2$COOK (potassium tartrate) [PDF 1-205] from various suppliers. X-ray powder diffraction (XRPD) was used to ascertain the identification of these materials. Several mixtures of the ingredients were made, on the basis of the recipes and interpretations discussed above. The ingredients were mixed in a mortar and ground to a fine powder. The mixtures were put into high-temperature crucibles (crucible type 131-01, Haldenwänger, Berlin, Germany). The powder mixtures were then heated in an oven (type LF1, Vectstar, Chesterfield, UK) at various temperatures.

In order to clarify the exact meaning of *antimonio* and *tutia*, the first type of potters' yellow, described by Mariani, was reconstructed in various ways. Mariani's recipe suggests a mixture of burnt lead (PbO), an antimony component (either Sb, Sb$_2$O$_3$ or Sb$_2$S$_3$) and sea salt (NaCl) in a weight ratio of 5:3:1. Therefore, three groups of reconstruction experiments were carried out with Sb, Sb$_2$O$_3$ and Sb$_2$S$_3$ as possible translations of *antimonio*. The mixtures were calcinated for 24 h at various temperatures. Potters' yellow type II was made in a similar way, by heating a mixture of PbO, Sb$_2$O$_3$ and K-tartrate, in the weight ratio mentioned in the recipe. The third type of Naples Yellow was also reconstructed in this way, with zinc oxide and tin oxide as possible translations of *tutia*.

The diffraction data of the reconstruction samples were collected using a Phillips X'Pert Pro diffractometer (Philips, Eindhoven, The Netherlands). This instrument was also used for sample-free analysis of several art objects, as it allows XRPD to be carried out directly on the work of art, which is placed on a modified sample stage. If not stated otherwise, data collection took place with a step size of 0.01° and a holding time of 6 s, at 50 mA and 40 kV. Special software was used for peak analysis as well as multiple-phase identification, including Profit version 1.0b, X'Pert Plus version 1.0 (Philips, Eindhoven, The Netherlands) and PCPDFWIN version 2.1 (© JCPDS-ICDD, June 2000). As most samples proved to have a multiple-phase composition, the relative amount of phases was sometimes estimated visually. Some multiphase diffractograms proved to consist of up to eight phases. In such cases, the presence of some compounds, notably trace amount phases, could not be established with absolute certainty.

X-ray fluorescence spectrometry (XRF) was carried out directly on objects at the Netherlands Institute for Cultural Heritage in Amsterdam. This technique allows for the identification of most elements with an atomic number $Z > 13$ (Al). Use was made of a Tracor Spectrace 6000 series spectrometer with a rhodium target. Excitation of the samples was at a tube voltage of 35 kV and a current of 0.25 mA for 300 s.

<div align="center">RESULTS</div>

Not all experiments on the type I potters' yellow led to the formation of high concentrations of lead antimonate. In several cases, the product contained multiple phases, some of which could not be matched with PDF entries. Our observations are summarized in Tables 1 and 2.

Potters' yellow type I

Using different translations for *antimonio*, Sb$_2$O$_3$ led to the purest form of antimonate yellow. Unlike using metallic antimony, the use of antimony oxide resulted in several shades of yellow. This relation between the reaction temperature and colour of the reaction product has also been described by Zerr and Rübencamp (1922, 374). Mariani, however, makes no reference to such a temperature dependency of potters' yellow. Higher temperatures, up to 1100°C, led to a slightly more yellow colour of the reaction product, while at lower temperatures the product

Table 1 *Reconstructions of three types of Mariani potters' yellows with different ingredients and at different temperatures*

	Components	Temperature (℃)						
		650	700	750	800	900	1000	1100
Type I	Sb_2S_3	Black material; no ID		Brownish material; minor amounts of $Pb_2Sb_2O_7$ plus other unidentified phase(s)				
	Sb	Brownish material containing minor amounts of $Pb_2Sb_2O_7$ plus other unidentified phase(s)						
	Sb_2O_3	See Table 2		$Pb_2Sb_2O_7$ (>95%)				
Type II	Sb_2O_3 + K (tartrate)	$Pb_2Sb_2O_7$ (<75%) $K_3Sb_3O_9$				$Pb_2Sb_2O_7$ (>95%) $NaSbCl_6$ type		
Type III	Sb_2O_3 + SnO_2	$Pb_2Sb_{2-x}Sn_xO_{6.5}$ (<50%) $PbSb_2O_6$ Sb_6O_{13} SnO_2 NaCl		$Pb_2Sb_{2-x}Sn_xO_{6.5}$ (>90%) SnO_2 NaCl				

Table 2 *The qualitative phase composition of Mariani type I using Sb_2O_3 as antimony compound fired at 650℃*

PDF number	Compound
74-1354	$Pb_2Sb_2O_7$
78-0751	NaCl
34-1149	$Pb_{3+x}Sb_2O_{8+x}$
22-0381	$Pb_5Sb_2O_8$
84-1423	$PbSb_2O_6$
78-2066	Sb_2O_4
23-0331	Pb_2O_3
76-1799	Pb_3O_4

Note: PDF 34-1149 merely contains a list of *d*-spacings and does not provide any further crystallographic information, such as the unit-cell dimensions, crystal system or space group. The reliability of the reflection list as well as the phase stoichiometry could not be verified. The presence of this particular phase is therefore questionable. See also Bush and Venevtsev (1978).

had a more reddish tone. Although not possible within the framework of the present study, it seems worthwhile to carry out reflectance spectroscopy in order to study the colour shift in more detail.

The product that was formed at temperatures up to 1000°C had a highly porous structure and could easily be removed from the crucible. In 1797, de Massoul wrote that Naples Yellow *resembles a sandy, porous stone; its grains are from a fine yellow* (De Massoul 1797, 137). Mariani explicitly stated that *un*varnished crucibles should be used. It seems probable that the use of varnished crucibles would have caused the reaction product to stick to the crucible. According to a late 18th century recipe for Naples Yellow, the adhesion of the reaction product should be prevented in the following manner: *in order to prevent attachment through heat, the*

plates are first covered with ash (Paape 1794, 60–1). Apparently, the removal of the reaction product has remained problematic over the years. At $T > 1000°C$, all experiments resulted in a very hard, shiny reaction product that could not easily be removed from the crucible. Thus, temperatures between 700°C and 1000°C seem to have been the correct conditions for historical lead antimonate production.

The diffraction maxima of $Pb_2Sb_2O_7$ in the lower temperature range are somewhat broadened, indicating a still small average pigment crystallite size. Interestingly, at 650°C all diffraction maxima of cubic $Pb_2Sb_2O_7$ seem to have split up into two distinctly separate maxima. This suggests the presence of two phases of $Pb_2Sb_2O_7$ with slightly different unit cells. The splitting up of the $Pb_2Sb_2O_7$ peaks cannot be explained by lowering the symmetry to the tetragonal or orthorhombic system, as this would not affect the strongest of the diffraction maximum, the (222) reflection.

Cubic lead antimonate belongs to the mineral group of pyrochlores, phases with the approximate stoichiometry $A_xB_yO_z$ ($x \approx 2$, $y \approx 2$, $z \approx 7$). Various lead-containing pyrochlores of this type are known, mostly cubic phases crystallized in space group 227. These highly symmetrical phases exhibit a wide range of unit-cell dimensions (10.20–10.63 Å). The size of the unit cell seems to depend on the ratio of the lead and the secondary metal, and sometimes even a tertiary metal, as well as on the differences in ion radii between both elements. Both lead and the secondary metal may occur in different electronic states, apparently allowing for a broad range of constituencies. Consequently, lead-containing pyrochlores occur with a wide range of unit-cell dimensions. In all of our samples, including type II and type III potters' yellow, slightly different unit-cell parameters were observed, ranging from 10.40 Å to 10.50 Å, suggesting different ratios of Pb and Sb. However, no obvious relation could be established between the unit-cell size and the temperature at which the sample was heated.

In conclusion, *antimonio* seems to refer to Sb_2O_3. This ingredient yielded cubic $Pb_2Sb_2O_7$ in its purest form, with a fairly porous structure. Due to its porosity, the reaction product could easily be removed from the crucible.

Potters' yellow type II

Mariani makes the remark that type II requires a higher firing temperature than type I. This comment seems to be in line with our experimental observations. The formation of a dominant lead antimonate phase starts at a substantially higher temperature (1000°C), compared to 650°C in the type I series. Up to 900°C, lead antimonate is formed, but not in high concentrations. In addition to lead antimonate, the diffractogram suggests the presence of a phase similar to Na_3SbO_3 [PDF 73-0904] and $K_2NaSb_3O_9$ [PDF 83-1899] (Table 3). The latter of the two phases, in which K has partly replaced Na, gave an even closer match with our diffractogram. This strongly indicates the presence of an isostructural phase with stoichiometry $K_3Sb_3O_9$ (no PDF entry). At 1000°C, lead antimonate was formed at a high yield. One or more crystalline by-products, with diffraction maxima matching those of $NaSbCl_6$ [PDF 76-2019], were present in minor amounts. Since none of the ingredients contained any Cl, the unidentified minor phase must have a different elemental composition. The presence of $K_3Sb_3O_9$, as observed in samples heated at lower temperatures, could not be detected.

Similar to the type I series, the lead antimonate product had a highly porous structure, which again allowed for easy removal of the pigment from the crucible. Another characteristic similar to type I is the variation in tonal hue as a function of the reaction temperature. In general, however, type II had a slightly paler tone.

Table 3   *The peak list of Mariani potters' yellow type II, 1000°C: PDF 76-2019 peaks with $I/I_0 \leq 100$ are not listed, unless when matching with an observed reflection*

Mar II, 1000°C		$Pb_2Sb_2O_7$ (PDF 74-1354)		$NaSbCl_6$ (PDF 76-2019)	
I/I_0	d-value	I/I_0	d-value	I/I_0	d-value
21	6.49			9	6.939
12	5.99	52	6.004		
31	5.80				
81	5.54			999	5.4903
				148	5.3585
10	5.081				
				156	4.5205
38	4.208				
21	4.1117				
18	3.9165				
16	3.4731			194	3.4552
36	3.4107				
78	3.1042	25	3.1357	31	3.1184
999	3.0030	999	3.0022		
60	2.8044			183	2.8028
70	2.7950				
73	2.7697			169	2.7624
66	2.7630				
22	2.6524			18	2.6792
305	2.6008	352	2.6000		
21	2.5408			29	2.5224
19	2.3887	49	2.3859		
19	2.2422			148	2.2321
25	2.1957				
8	2.1684				
22	2.1241	2	2.1228		
22	2.0182	20	2.0014		
452	1.8393	362	1.8384		
7	1.7885				
15	1.7780				
16	1.7745				
36	1.7350	14	1.7579		
10	1.7144				
19	1.6246				
22	1.6181				
41	1.5726	3	1.5859		
372	1.5685	323	1.5678		
16	1.5610				
118	1.5014	80	1.5011		
15	1.4777	6	1.4562		
11	1.4021	5	1.3539		
49	1.3009	41	1.3000		

Table 4 *The pieces of pottery analysed with XRPD for lead antimonite*

No.	Description of pottery	Geographical origin	Date
1	Northern Dutch Maiolica	Province of Holland	*c.* 1600–25
2	Maiolica	Province of Holland	*c.* 1680–1700
3	Maiolica	Italy (Montelupo?–Faënza?)	*c.* 1560

Note: pottery fragments were dated by Mr J. D. van Dam, Conservator of Ceramics at the Rijksmuseum (pers. comm., 28 September 2000).

Interestingly, Mariani makes a clear distinction between the optical properties of type I and type II lead antimonates. According to his recipe, type I is *more subtle and works well for colouring*, while type II *shows more body*. Mariani seems to suggest a difference in hiding power between the two types. Type I, which is especially suitable for drawing according to Mariani, might have a lower hiding power than type II, which has *more body*, most likely alluding to a higher degree of opacity. Therefore, a logical step would be to study possible differences in optical refractive properties between types I and II. Given the similarity in crystallographic composition, cubic $Pb_2Sb_2O_7$ being the dominant phase in both cases, a significant difference in refractive properties does not seem to be very likely. On the other hand, the possibility that the by-product(s) formed in type II influence the optical appearance of the paint, as described by Mariani, cannot be excluded. In this respect, it is remarked that $K_3Sb_3O_9$ has been found in rather large amounts (up to 25% at $T < 1000°C$). It should also be noted that earlier studies of maiolica have shown the presence of potash in lead antimonate yellows (Tite 1991).

Potters' yellow type III

The recipe for the third type of potters' yellow calls for burnt lead, antimony oxide and *tutia*, which most likely should be translated as zinc oxide or tin oxide. Two series of reconstruction experiments were carried out with both SnO_2 and ZnO. Both translations of *tutia* resulted in a bright yellow product, a lead antimonate phase being the dominant compound in both cases. Nonetheless, a number of characteristic by-products clearly distinguish the two types at temperatures higher than 700°C. The ZnO version of *tutia* led to the formation of various phases, including red-coloured Pb_3O_4. A thin red top layer that had formed after heating already suggested the presence of Pb_3O_4. This may also explain the slightly reddish hue of yellow in the ZnO version after grinding of the product. It seems possible that Zn has been incorporated in the lead antimonate structure. Besides pure lead antimonate, also other isostructural compounds of the pyrochlore type are known; for example, $Pb(HfSb)O_{6.5}$, $Pb(SnSb)O_{6.5}$, $Pb(ZrSb)O_{6.5}$ and $Pb(TiSb)O_{6.5}$ [PDF 78-1547 to PDF 78-1550]. Also, a yellow-coloured lead and zinc-containing compound exists ($Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}$) [PDF 34-0395], with an approximately pyrochlore stoichiometry and a cell parameter (10.60 Å) that is comparable to that of our samples. It is therefore likely that a similar pyrochlore-type crystal with an approximate stoichiometry $Pb_2Sb_{2-x}Zn_xO_{6.5}$ has been formed in our sample.

The second experimental series of potters' yellow type III, using SnO_2 as a possible translation for *tutia*, probably resulted in a similar lead–tin antimonate pyrochlore-type structure,

$Pb_2Sb_{2-x}Sn_xO_{6.5}$. Similar to the Zn series, the lead antimonate structure contains small amounts of initial ingredients, in this case SnO_2. This suggests that Sn has been partially incorporated in the lead antimony phase, but to a larger extent than Zn in the Zn type III pigment, because the reconstruction of the latter yielded a higher amount of (Zn) by-products. Again, the exact elemental composition could not be revealed from XRPD data and would require additional research.

SCIENTIFIC ANALYSIS OF LEAD ANTIMONATE YELLOWS ON WORKS OF ART

In addition to the literary studies and reconstruction experiments described above, we carried out scientific analyses of yellow paint on historical objects. Several elemental measurements were performed on yellow paint as present in the illustrations of the Mariani manuscript itself. XRF analysis of the yellow drapery of the scene *The Martyrdom of Saint Marc* showed peaks for Pb, Sn and Sb, suggesting the use of type III potters' yellow. This also supports the interpretation of *tutia* as tin oxide, rather than zinc oxide.

Lead antimonate was also identified as yellow pigments on several pieces of European pottery of various origins from the collection of the Rijksmuseum. Analysis was carried out non-destructively with XRPD, using the Phillips X'Pert 1 program. The yellow layer on all pieces of maiolica proved to be particularly rich in a lead antimonate phase. Except for lead antimonate, the diffractogram showed the presence of SnO_2, notably reflections at 26.61° 2θ/3.351 Å ($I/I_0 = 13$), 33.89° 2θ/2.644 Å ($I/I_0 = 17$) and 51.79° 2θ/1.765 Å ($I/I_0 = 8$). Initially, it was thought that tin-containing type III lead antimonate had been discovered, as suggested by the presence of SnO_2, which was also observed in the reconstruction experiments. However, it was soon found that SnO_2 had been used as a ground on the ceramics, as has been shown in other technical examinations of maiolica (Tite 1991). Lead antimonate was applied on top of this layer, which explains the presence of SnO_2 reflections in the measurement of the yellow parts on our ceramics.

DISCUSSION

The reconstruction experiments on the yellow pigment can be related directly to scientific analyses of lead and antimony containing yellows on works of art. Potters' yellow has been identified on Italian maiolica, as described by Wainwright *et al.* (1986, 223) and as shown above. In these cases, the type of lead antimonate used proved to be of high purity. No by-products could be identified, suggesting the use of a potters' yellow type I recipe.

As mentioned above, lead antimonates were formed in different shades, showing a brighter yellow at higher temperatures. Therefore, it seems worthwhile to investigate further possible relations between the unit-cell dimensions, the ratio of Pb and Sb and their electronic state, as well the exact colour of the product formed. These more fundamental aspects, however, could not be studied within the framework of the present research.

Potters' yellow type II has not been identified on historical samples so far. Findings of potassium in lead antimonates, as shown by Tite (1991), may however indicate the actual use of lead antimonate yellow type II on authentic works of art. It should be noted that the identification of minor by-products characteristic of type II requires high-resolution diffraction equipment, such as a Guinier-type camera or a high-resolution diffractometer. Therefore, the possibility exists that lead antimonate type II may have gone unnoticed in past examinations. In future studies on lead antimonate yellow, adequate analytical techniques will have to be

employed. In particular, TEM, which allows for single-crystal electron diffraction as well as EDS analysis, is likely to be the most suitable technique.

Potters' yellow type III can be related to the identification of lead–tin antimonates on paintings of various origins. Roy and Berrie have observed the use of a lead–tin antimonate phase on mid-17th-century Roman paintings by Poussin, Gentileschi, Sassoferato and others (Roy and Berrie 1996, 160–5). The authors suggested that the use of this pigment might have been restricted to the period around 1650 and to the area of Rome. However, given the origin of the manuscripts in which the production of this pigment has been described, this idea must be rejected. In addition, a number of other occurrences of a lead–tin antimonate yellow have been reported. Dik and Wallert have found a tin-containing phase of lead antimonate in an early 18th-century painting by Jan van Huysum (Dik and Wallert 1999). Also, there is some evidence that this pigment may have been present in earlier studies, but was not recognized as such. First of all, lead–tin antimonate seems to have been used on Titian's *Girl with Fruit Bowl* from Berlin, dated 1555 (Fischer 1999). In this case, X-ray diffraction of a yellow sample from the paint gave a match with the PDF file for a cubic pyrochlore structure with an axis of around 10.48 Å. In addition, X-ray fluorescence showed a substantial presence of antimony, tin and lead at the sample location. On the basis of the elemental and structural analyses, it was concluded that lead antimonate with an admixture of lead–tin yellow had been used. With hindsight, it seems more logical that Titian had made use of lead–tin antimonate, which must have been in use before 1580, according to the Mariani manuscript.

Secondly, Groen and De Keijzer have examined the yellow paint of a picture by the Dutch painter Jan Huchtenberg, dated between 1718 and 1733. Similar to the Titian examination, tin and antimony were found when performing EDS analysis of a yellow layer in paint cross-section. From the elemental constitution, it was concluded that a physical mixture of lead–tin yellow and lead antimonate yellow had been used (Groen and De Keijzer 1996). Again, a more intricate mixture of tin and antimony within the crystal structure may be a likely second possibility (Karin Groen 2002, pers. comm.).

Given the outcome of the type III experiments, zinc may also have been a possible ingredient in lead antimonate production. To the authors' knowledge, a zinc-containing version of lead antimonate has not yet been found on authentic pigment samples. In the light of our study, however, such a finding may well be possible.

CONCLUSIONS

The present study suggests that Eastern Mediterranean artists introduced lead antimonate, or *potters' yellow*, to Venetian glass-making at the end of the 15th century. During that century, Venice absorbed two waves of immigration of glass and ceramic artists, notably after the fall of two main glass production centres, Damascus in the early 1410s and Constantinople (Byzantium) in 1452. Both recipes studied in this paper call for the use of *tutia allessandrina*, tin or zinc oxide, in the production of lead antimonate. Thus, long after the pigment had been introduced to the Italian arts, a main ingredient for its production was still imported from the Middle East. This shows how closely the manufacturing of lead–tin yellow is linked to the Eastern Mediterranean.

In addition, our reconstruction experiments have shown that various kinds of lead–tin yellow can be formed using the production recipes in the Mariani manuscript. We have observed at least three—possibly four—types of potters' yellow: a highly pure lead antimonate (type I), a lead antimonate with an as yet unidentified potassium antimonate salt (type II) and a lead

antimonate that contains either tin or zinc (type III). Two of our reconstructed types of lead antimonate, namely pure lead antimonate type I and the tin-containing type III, can be associated with earlier analyses of lead antimonate of historical objects. Our findings seem to contradict an earlier study, which suggested a limited occurrence of lead–tin antimonate yellow, restricted to mid-17th-century paintings only. Although type II and the Zn version of type III do not seem to have been found on works of art as yet, their presence in historical paint may be established in future studies.

Given the analytical difficulties in identifying the various forms of lead antimonates, we advise the use of adequate analytical instrumentation in future studies on lead antimonate. Detailed elemental as well structural information is required to identify the various forms. This presents a major complexity in the analysis of small and highly heterogeneous samples from original works of art.

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