Copper-Based Synthetic Medieval Blue Pigments

Mary Virginia Orna

College of New Rochelle, maryvirginiaorna@gmail.com

Follow this and additional works at: http://digitalcommons.cnr.edu/facpubs

Part of the Chemistry Commons

Recommended Citation
Chapter 9

Copper-Based Synthetic Medieval Blue Pigments

Mary Virginia Orna

Department of Chemistry, College of New Rochelle, New Rochelle, NY 10805

Blue pigments were in short supply in medieval times because only two naturally-occurring inorganic blue pigments, natural ultramarine and azurite, were known. Both pigments were difficult to obtain and consequently were very expensive. Medieval artists turned to the manufacture of copper-based blue pigments of surprising complexity in order to expand their palette. This paper outlines some of the methods used to obtain these complex pigments and elucidates their structures, when possible.

During the Middle Ages, the artist's interest in synthesizing blue pigments stemmed from the fact that blue, as a pigment, was in very short supply. An earlier study (1), which reviewed the availability of blue pigments from ancient times, showed that Egyptian blue, copper(II) sulfide, and azurite were the only inorganic blue pigments known in the ancient Roman empire. Indigo, an organic pigment and dye, was identified as the pigment used to decorate Roman parade shields, but its use in European painting and manuscript decoration was probably very limited until it began to be imported from India in the early 16th century (2). Egyptian blue was the first synthetic pigment: its earliest known occurrences can be dated to the Greek Bronze Age tombs in Knossos and Vergina (3-5) and to the third millennium B.C. in Egypt (6). Its subsequent use in tombs and in the manufacture of small objects has been amply documented (2). Egyptian blue was also the first pigment to be subjected to modern chemical analysis, beginning with the trial preparations by Sir Humphry Davy (7), and continued by Chase (8) and Tite, et al. (6), who showed through laboratory reproduction that the ancient Egyptian blue mineral (CaCuSi4O10) was formed as a result of the solid state reaction between silica, lime, and copper(II) oxide. On the other hand, copper(II) sulfide occurs naturally as the mineral covellite, although it too can be prepared synthetically (9). It was probably much used in antiquity, but it is not durable, decomposing slowly and spontaneously to black copper(II) oxide unless protected by varnish (10). The third ancient blue pigment, azurite, is a basic copper carbonate closely related to the green malachite and has the formula 2CuCO3·Cu(OH)2. It occurs naturally as a monoclinic crystalline material throughout Europe and the former Soviet Union. Although its use may date from the fourth dynasty in Egypt, it is known that it
Figure 1. Chronological chart of some important artists’ blue pigments. Solid areas signify periods of certain usage; striped areas signify periods of doubt. Usage.

Reproduced from reference 1 with permission.
was the most important and widely employed blue pigment throughout the Europe of the Middle Ages (11).

The use of a fourth blue pigment, natural ultramarine, derived from the semi-precious mineral lapis lazuli, can be traced to sixth and seventh century wall paintings in Afghanistan. It was introduced as a rare import to European artists in the thirteenth century, following the spectacular journeys of Marco Polo. During the subsequent three centuries, good quality ultramarine was as costly as gold, and patrons usually agreed to supply the pigment for a commissioned work or to pay for it separately at market price (12, 13).

Of these four inorganic blue pigments, only azurite and natural ultramarine seem to have survived into the Middle Ages. The secret of Egyptian blue manufacture was certainly lost by the ninth century, and the use of copper(II) sulfide fell into disuse in late Roman times.

Both azurite and ultramarine can be prepared synthetically. Azurite is made by precipitating a solution of copper(II) chloride with calcium hydroxide, and then heating the resulting precipitate with a mixture of potassium carbonate and calcium hydroxide. This procedure yields not only the basic copper(II) carbonate, but also a mixture of other products, notably the basic copper(II) chlorides (14, 15). Synthetic ultramarine was first observed as a byproduct in the soda furnaces at St. Gobain in 1814, and L. Gmelin was the first to synthesize it in 1822. Ultramarine blue, both natural and synthetic, is a clathrate complex consisting of a framework of [(Si,Al)O2] units enclosing a polysulfide, \( S_3^- \), which is responsible for the blue color (16). The trisulfide radical anion was identified as the chromophore only as recently as the mid-1970's (17). Of these synthetic materials, only synthetic azurite, under the name "blue verditer" was available to the medieval artist-craftsman. The modern blue pigments, among which are small (a potassium cobaltous silicate of varying composition), Prussian blue (ferroferricyanide salts with a variety of cations), and Thénard's blue (cobaltous aluminate) were not available until the mid- to late sixteenth century and later.

From this review, one can see that European artists and craftsmen who were active between the ninth and sixteenth centuries had little choice in their use of blue pigments. Prohibitively costly, both natural ultramarine and azurite were hardly any choice at all. It is only natural, then, that much experimentation in the manufacture of synthetic inorganic blue pigments would have taken place throughout the Middle Ages. Figure 1 outlines the usage pattern of the major artists' blue pigments over the centuries.

**Synthetic Blue Pigments: Recipes**

Recipes for making artificial blue colors are very old. They are embedded in the literature of a technical tradition dating from the third century A.D. that managed to survive five centuries of "dark ages" to re-emerge in the late eighth or early ninth century in two Latin manuscripts, the so-called *Lucca Manuscript*, part of the *Liber Pontificalis* in the *Codex Lucensis 690* at Lucca, Italy, and the *Mappae Clavicula*, or a *Little Key to the World of Medieval Techniques*, that survives as a ninth century fragment and a more extended tenth century manuscript (18).

The recipes for synthetic blues contained in these and subsequent manuscripts that built upon the tradition of Lucca and the *Mappae* can be divided into three categories: (1) Pigments made from plant and animal materials; (2) Pigments based on synthesizing blue colors from silver, or the so-called "Silver Blue" recipes; and (3) Copper-based blue pigments.

Pigments made from plant materials are difficult to characterize. A recipe from the *Lucca Manuscript* tells us that an excellent azure-blue can be made from the petals of violet flowers ground with soap, and then heated with alum and urine. However, the identity of the plant from which the violet flowers came could be any one of several found in northern and southern Europe. Other plant recipes revolve around the
production of indigo, which is easier to characterize, but much more so as a dye than as a pigment (19). This paper will concentrate on the blue mineral pigments manufactured by medieval artists since they seem to have much more definite starting materials and characteristics.

The "Silver Blue" Recipes

"Silver blue" recipes from the Mappae Clavicula, the Strasbourg Manuscript (14th or 15th century) and the Bolognese Manuscript (15th century) call for subjecting sheets of the purest silver to must discarded from a wine press, to vinegar, and to vinegar in the presence of hot horse dung. In addition, the Bolognese Manuscript recommends alloying one part of copper with three parts of silver before carrying out the recipe. This latter recommendation would seem to suggest that by the 15th century, artists recognized the necessity of the presence of copper in order to obtain a reaction product, which one might assume was simply copper(II) acetate monohydrate. These recipes were carried out and reported on in a previous paper (20). The reaction products were analyzed by both the Debye-Scherrer X-ray powder diffraction method and by single-crystal X-ray crystallography and were found to be respectively copper(II) acetate monohydrate and tetra-µ-acetato-bisdiaqupcopper(II), a dinuclear crystal compound of copper(II) acetate (21-23).

Copper-Based Blue Pigments Made from Copper, Lime and Vinegar

The original Mappae Clavicula recipe (1) called for mixing copper with lime and vinegar. Many unpublished and unedited manuscripts from periods post-dating the Mappae contain this recipe since they are copies of the Mappae in whole or in part. One manuscript, Ms. Sloane 2584 (British Museum, London; 14th century) contains this recipe as the only remnant of the original Mappae recipes. Other compendia which contain it are the manuscript of Jehan LeBegue (24) and the Bolognese Manuscript. Another 14th century manuscript, Trinity College Ms. 1451, p. 7, contains the first mention of the addition of sal ammoniac (ammonium chloride) to the ingredients of the original Mappae recipe (1).

Synthesis of Blue Pigment Using the Original Mappae Clavicula Recipe.

The original Mappae Clavicula recipe (1) tells us: "...take a flask of the purest copper and put lime into it halfway up, and then fill it with very strong vinegar. Cover it and seal it. Then put the flask in the earth or some other warm place and leave it there for one month; later uncover the flask. This azure is not as good as the other (made from silver), yet it is serviceable for painting on wood and plaster wall."

The synthesis carried out in our laboratory modified this recipe by using not a copper vessel, but copper plates, in a modern glass vessel. Since copper was the main reactant, this variation did not seem to be substantive. When the vessel was opened after a one-month incubation period, more than blue pigment was obtained. Since the mixture of the starting materials was not in stoichiometric amounts, large quantities of the starting materials remained unreacted, and many portions of the reaction vessel contained mixed crystals of green, blue and colorless hue. However, there was also a large amount of what looked like a pure blue crystalline compound. The blue color was unquestionably without traces of green, thus indicating that this compound was not either verdigris (copper(II) acetate) nor a form of azurite.

Elemental analysis of the product yielded 14.19% copper, 21.45% carbon, 5.40% hydrogen, 50.01% oxygen, and 8.95% calcium (obviously from the lime), by weight. The empirical formula from this elemental composition yielded a formula of \( \text{Cu(C}_2\text{H}_3\text{O}_2)_2\cdot\text{Ca(C}_2\text{H}_3\text{O}_2)_2\cdot6\text{H}_2\text{O} \) which was subsequently confirmed by X-ray crystallographic analysis. The d-values in Angstroms are given in Table I. Although the
crystals of this compound, calcium copper acetate hexahydrate, are a very pleasing deep blue, the crystals are soluble in water and the color fades to a pale blue when the material is ground to a fine powder. These factors call into question the value of this compound as a pigment. The original Mappeae recipe, we must recall, remarked that this pigment was not very good, but simply serviceable.

A literature search revealed that this compound can be prepared from solution by slow evaporation of an equimolar solution of calcium acetate and copper(II) acetate. After filtering off the pale green crystals that deposit initially, upon further evaporation, large, deep blue, tetragonal prisms crystallize out (25). The calcium copper acetate hexahydrate prepared in this manner in our laboratory exhibited the identical X-ray crystallographic characteristics as the compound prepared from the Mappeae recipe by an entirely different route, confirming the fact that the two preparations are chemically identical. Langs and Hare (26) were the first to determine its crystal structure. They showed that the acetate anion acts as a bidentate bridging ligand between the calcium and the copper ions in such a way as to produce polymeric chains of alternate metal ions. They also showed that the water molecules coordinate only to the calcium ions and bind the polymeric chains together by hydrogen bonding. Billing et al. (25) determined the preferred assignment of the electronic spectrum of the compound and also determined that the chromophore was the four-coordinate Cu-O₄ moiety. The coordination polyhedra about the Ca and Cu atoms are depicted in Figure 2.

**Synthesis of Blue Pigment Using the Recipe from Trinity College Ms. 1451.** The Trinity College Ms. 1451, a 14th century manuscript, contains the first mention of the addition of sal ammoniac (ammonium chloride) to the ingredients of the original Mappeae recipe: "...take of fyne vinegar half a pond, half a pond of lyme ontimeyn, iii pond of sal armonyak...and poudre alle these thre materials, take of them by himself alone first and thanne afterwardeis alle to gidres, and thanne take and medel al the poudre with gode strong vinegar distilled or eill with ather gode winyer vynegre that be strong in the manere of past and thanne put it al in a pot of bras or of copper and close hit from the eyre and thanne lette hit ondre hote hors donge ly on XV. dayes, and thanne take out and make hit up in to find the poudre as azure byzs..."

<table>
<thead>
<tr>
<th>d-Values (Å) for Calcium Copper Acetate Hexahydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.29-7.58 (1)a</td>
</tr>
<tr>
<td>7.04</td>
</tr>
<tr>
<td>6.31</td>
</tr>
<tr>
<td>6.04</td>
</tr>
<tr>
<td>5.84-5.55 (2)</td>
</tr>
<tr>
<td>4.76</td>
</tr>
<tr>
<td>3.73-3.48 (3)</td>
</tr>
</tbody>
</table>

Numbers in parentheses signify relative intensity.
Figure 2. Coordination polyhedra about the Ca (●) and Cu (○) atoms in calcium copper acetate hexahydrate. Reproduced from reference 26 with permission.
This recipe was reproduced in our laboratory in two ways. The recipe calls for sealing the container (closing it from the air) and then placing it under hot horse dung for fifteen days. If the pot were truly sealed so that it was a closed system, the presence of the hot horse dung would not affect the results, but might simply act as a hot water bath since a great deal of heat is generated as the dung ferments. On the other hand, if the closure of the container were not complete, that is, if the closure were porous (unbeknownst to the medieval craftsman), then gaseous products from the fermenting hot horse dung, notably carbon dioxide and ammonia, could indeed influence the outcome of the synthesis. Therefore, this recipe was carried out by placing the starting materials in both closed and open systems. The closed system, startlingly enough, did not yield a blue pigment after the fifteen prescribed days. The open system gave striking results: a mass of blue birefringent rosettes of varying diameters. Although these rosettes visually resemble rosettes of cuprum carbonicum (a basic copper carbonate from the Forbes Collection of Pigments, Conservation Center, Institute of Fine Arts, New York University), they have no counterpart in the X-ray powder diffraction file and remain uncharacterized. One of the problems in characterizing them is the fact that the crystals are intimately mixed with unreacted starting material and other colorless reaction products. A color photomicrograph of these crystals can be seen in Reference 27.

Copper-Based Blue Pigments Made from Verdigris, Lime, Sal Ammoniac and Oil of Tartar (Potassium Carbonate)

Manuscripts calling for the ingredients named above are characteristic of the late 15th century and the 16th century. The following three manuscripts contain similar recipes: Ms. Additional 12461 (British Museum, London; 16th century), Ms. Ashmole 750 (Bodleian Library, Oxford; 15th century); Ms. 1243 (Biblioteca Riccardiana, Florence; 15th century). The following translation from the Latin was made from folio 48r of the latter manuscript: "To make the most durable azure. (Recipe): Mix well one part of sal ammoniac and three parts of verdigris with oil of tartar until it is soft and paste-like, or even softer. Then place it in a glass vessel under hot dung for a day; afterwards, you will find that the green has turned into the best blue. Another way of making the best blue. (Recipe): Mix together three parts of sal ammoniac and six parts of verdigris with oil of tartar until soft and paste-like, or even softer. Then place the paste into a glass ampule, and when it is well-stoppered and sealed, place it in a hot oven and let it stand for some days; afterwards, take it out and you will find it turned into the best azure."

According to Crosland, the "oil of tartar" referred to in the recipe given above is a saturated solution of potassium carbonate (28). Trial and error with respect to starting materials probably led to the selection of this reagent since it provided the carbonate necessary to produce a blue pigment similar to the "cuprum carbonicum" referred to in the previous section of this paper. Synthesis in our laboratory, using both alternatives given in the recipe, yielded a bright blue pigment which, on microscopic inspection, consisted of blue needles or cylinders mixed with colorless crystals of varying morphologies. Again, these crystals have no counterpart in the X-ray powder diffraction file and remain uncharacterized. Reference 27 contains a color photomicrograph of these needle-like crystals.

Conclusion

Copper-based blue materials manufactured from recipes found in medieval artists' manuals present a very complicated chemical profile. Although pure compounds such as the tetra-μ-acetato-bisdiaquocopper(II) and calcium copper acetate hexahydrate were produced, other compounds and mixtures of compounds at the moment defy characterization. H. Kühn (29) has identified several additional pure compounds.
formed when acetic acid vapor, water vapor and air act on copper and copper alloys, and some forms of azurite have been identified by Gettens and Stout (2), but none of these resemble the copper-based blue pigments obtained from the recipes utilized in this study. It is well-known that copper and copper-silver alloys yield a variety of complex compounds depending upon the materials that react with them, and future research may reveal some new exotic compounds. Some of these compounds are definitely green (30), but some involving reactions of copper with such reagents as sour milk and cream of tartar can form some blue copper compounds which include lactates and tartrates (31). These, in addition to the acetates and putative carbonates discussed in this study, indicate the degree of sophistication attained by medieval artists and craftsmen long before the advent of the modern chemical theory that would provide a theoretical basis for these syntheses.

Acknowledgments

Thanks are due to the staff of the Conservation Center, Institute of Fine Arts, New York University, for its generous assistance, use of its facilities, and for access to the Forbes Collection of Old Pigments.

Literature Cited


RECEIVED August 15, 1995