The Colored Chemistry

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ABSTRACT

We discuss here materials used in the fabrication of works of art and handicrafts, among them pigments and dyes, gemstones and jewels. Attention is paid to their natural or synthetic origin and possible treatments. Methods of characterization are important not only for historical and restoration purposes and the reproduction of ancient processes, but also for the purposes of new productions. In particular, in the fields of the Effective Microorganisms and metal surfaces coloration, some goals have been reached in this direction due to convergence of different education and research experience of the authors.

KEYWORDS Chemistry, Restoration, Gemology, Colored metals, Synthetic materials, Treated materials, Effective Microorganisms

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1. Introduction

The cultural association SMATCH (Scientific Methodologies applied to Cultural Heritage) has been created with the purpose of understanding cultural heritage and critically study methods adopted to know and protect it. A science which was always engaged in the sector of "beautiful" is chemistry: in this field we do not make separations between synthetic and analytical chemistry, nor between organic and inorganic: distinction born from a prejudice denied since the indigo industrial synthesis (marketed by BASF, 1897). The material used for the "beautiful" (but the saffron is also used for the "good"…), such as gemstones or in general ornamental objects are made of natural raw materials, subjected, more often than people think, to chemical treatments. A special case is the diaspore (yellow gemological variety: zultanite) which shows (Haüy 1801) how a heat treatment (even at not very high temperature) could unpredictably produce a synthesis. But intentional synthetic processes and treatments are now very common. We will describe in the present paper some of our research activities presenting cultural and productive interest.

2. Pigments and dyes

We cite here only a few cases, some of them regarding materials used as pigments in wall painting and not only. The synthesis modalities of such materials are investigated, among the others, for restoration: the advantage for a chemist in fact consists in the possibility of having, obviously not in all cases, items available to compare with the materials of the artifact.

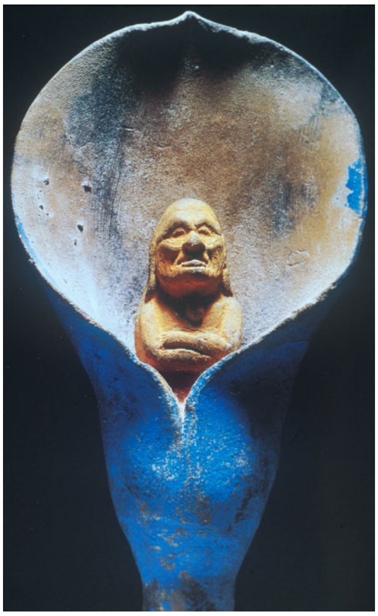

Fig. 1. Maya flower, Jaina (México). Photo courtesy of Giacomo Chiari.

In Europe, in the fabrics dyeing, both natural (in particular extracted from “indigofera tinctoria”) and synthetic indigo are employed. On the other hand, in the wall and other surfaces painting (Figure 1), in pre-Columbian times, but also later, we find the Maya blue, a composite material (indigo-palygorskite clay) of exceptional stability. The knowledge of nature and history of this material (Reyes-Valerio 1993, Chiari et al. 1999, Ajò et al. 2000, Berke 2007, Sánchez del Rio et al. 2011) is mostly due to the chemist (but also art historian and microbiologist!), Constantino Reyes-Valerio.

An ancient case of treatment is that of the odontolite, imitation of turquoise, obtained from fossil tusks of mastodon (Reiche et al. 2000) by modification of the oxidation state of manganese.

Fig. 2. Sumerian seal.

The lapis lazuli is very precious because (according to the gemological criteria) "beautiful, rare and durable". On the other hand, Sumerians produced seals (Figure 2) able of transferring with their own mark the magical properties of the stone (Ajò et al. 1996). Since then it was used in jewelry production and as precious pigment to paint the sky, the Madonna mantle and little else (Aula et al. 1997): as a matter of fact, since ancient times the use of beautiful materials, for personal or collective purposes, can have spiritual implications. The production of synthetic ultramarine (analogous of lapis lazuli) was known more than two centuries ago (Plester 1966, Berke 2007).

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Egyptian blue, a synthetic silicate of calcium and copper (Pozza et al. 2000, Berke 2007, Dyer and Sotiropoulou 2017) was used in ancient times in Egypt and later also in Italy (Colosi and Prestileo 2017, Bonifazi et al. 2017) in order to imitate copper minerals such as turquoise or azurite: the latter one, in particular, was subject to alterations in the wall paintings. Its production dates back to the I Dynasty (about 3100 B.C.) and originates from the pre-dynastic Egyptian and Asian culture. Initially the blue glassy material (frit) was used as a glaze, and subsequently it was used also as a pigment (Forbes 1955, Riederer 1997). The later use became frequent or exclusive since the V Dynasty (2494-2345 B.C.), for decoration of both organic and inorganic materials. In the Egyptian Middle Kingdom (2133-1786 B.C.) a further extension in its use is witnessed, mainly for decoration of tombs in which wall paintings of exceptional extension were made.

Marcus Vitruvius Pollio (Galiani, 1758) and Pliny the Elder (Plinii Secundi, 1873) inform us that the blue color (caeruleum), was introduced by Vestorius in Pozzuoli, in order to produce and sell it in Italy. The more detailed Roman sources is provided by Vitruvius (first century B.C.), while Pliny presents the diffusion of the Alexandrian blue manufactured in Pozzuoli: he makes indeed know that this color is labelled Vestorianum blue. The production in the Vestorius' factory and the spread of his blue pigment were such as to influence the III Pompeian painting style, originated in the Augustan period. In fact, from the year of Caesar's consulate (59 B.C.), the relationships with Egypt became more intense and frequent until the Age of Claudius (41-54 A.D.). The use of this pigment characterized the 3rd Pompeian style, in which an Egyptian (Vestorianum) blue produced in Pozzuoli was widely used for making blue skies.

Fig. 3. Powdered Egyptian blue functionalized with EM.

We think it appropriate to introduce here the case of white lead, in which a chromatic alteration is frequently observed towards brown, imputable to an oxidative process due to microorganisms which colonize the wall paintings, producing lead dioxide (plattnerite) (Petushkova and N.N.Lyalokova 1986). These microorganisms are able to oxidize other pigments containing bivalent lead such as massicot and minium. Furthermore, bacteria participate in the conversion of white lead to lead sulphide (black). These and several other evidences make it necessary the study and the experimentation, currently in progress, of antagonistic methods in order to restore and prevent the deterioration of wall paintings. Actually, the antioxidant power of Effective Microorganisms is now recognized and used on a large variety of substrates and in various conditions (Higa 1993, Higa 2018). Theirs reducing power is also exercised on metal ions. Trials are underway on altered pigments, using products based on Effective Microorganisms (EM): in particular, the Egyptian blue has been recently reproduced by EM-Biotech (Figure 3), not only for ornamental purposes but also as a material functionalized by the addition of beneficial microorganisms (EM), for the coating of tanks and swimming pools.

3. Precious materials for jewelry

In 1902 (the same times of the indigo BASF) Auguste Verneuil announced the synthesis of a ruby obtained by melting in the flame mixed oxide powders. In one of the laboratories of ICIS (CNR) in Padua, an instrument was designed and used (Figure 4) not very different from that of Verneuil (Maini et al. 2006).

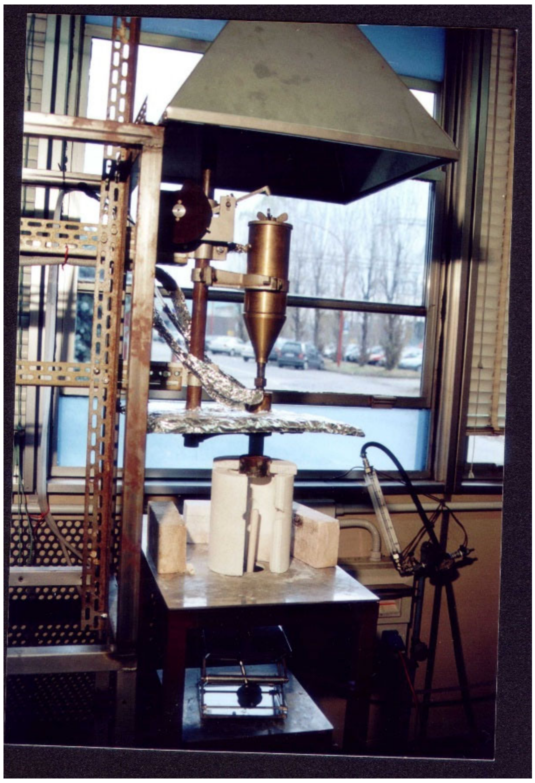

Fig. 4. The Verneuil apparatus of CNR in Padua.

Regardless of the commercial use (Figure 5) of the obtained crystals, not always practicable, a chemist likes to make reference samples, to be compared with an unknown material: "this at least I know how it was done".

Fig. 5. Synthetic sapphire of commercial interest.

Many methods can help the identification and the characterization of a synthetic or treated material starting from elementary analysis not destructive such as X-ray fluorescence (XRF). Spectroscopic techniques, however, are always necessary. In any case, the study is more effective if the person performing the analyses (elementary, structural and spectroscopic) has also experience, at least in some case and to some extent, of syntheses and treatments. In this way it is possible to meet the needs of gemologists and jewelers (Giarola et al. 2012). In fact, in the manufacture of jewelry, for imitation purposes instead of sapphires blue spinels (mixed aluminum and magnesium oxides) are used. Practically, materials very often not existing in nature, are employed which share only a few properties with the imitated material, such as color and gloss, but differ for all remaining properties.

A material different from the more valuable one but showing a similar appearance not necessarily represents imitation on the moral and juridical level. The "Black Prince's Ruby"of the British Crown is actually a red spinel: it is not about an intentional imitation, but an innocent misunderstanding, due to the absence of proper instrumentation. In this regard, it should be stressed that such precious objects are not removable, so it is good to have portable instruments, as the FTIR interferometer used for study the marvelous diamond of Vallerano (Bedini et al. 2012), which could not leave 'Palazzo Massimo alle Terme" (Rome).

Some colors of gems, in particular of brownish diamonds, are considered "ugly" (of negligible commercial value). This reason stimulated the study of methods suitable to change the characteristics of the stones (in particular the color). Often a heat treatment is carried out in order to improve the color of a gem; but a heating procedure can be also effected for diagnostic purpose, producing desirably reversible phenomena; if instead we want to improve the color of a diamond for commercial purposes we desire irreversible changes.

It can also happen that a gem, for the production (not reversible !) of "little flaws, which are singly unperceived" (Shaw 1738) due to a thermal shock, loses apparently its color; but then it recovers it by means of an intentional treatment: in fact these cracks can favor the introduction of a dye, for example cochineal dissolved in alcohol (today we talk about "quench crackling"). We have to meditate on an interlacement of desired and non-desired phenomena.

One of the most important issues of current gemology is the HPHT (High Temperature, High Pressure) treatment of diamonds: high temperature (about 2000 °C), high pressure (about 60.000 atm), launched by General Electric in 1999, capable of transforming brownish diamonds into gems substantially colorless (up to color D).

In order to evaluate "a priori" the effectiveness of this kind of treatment, infrared spectroscopy is employed. In fact, the type I diamonds contain appreciable concentration of nitrogen which makes them less sensitive to physical treatment. On the contrary, this treatment is more effective for type IIa diamonds whose coloration is predominantly associated with dislocations in the crystal lattice: this means that the concentration of nitrogen is negligible. Therefore, IR spectroscopy helps to decide whether or not to apply the process, through an indirect reasoning that is worth reflecting on.

We have already mentioned that a chemist, if he can, creates his own materials: in the case of diamond, treatment for color change is too drastic for an ordinary laboratory; on the other hand in another laboratory of ICIS, some crystal of brownish zoisite (of no commercial interest) were "cooked in foil" at 300°C and atmospheric pressure, obtaining a "pseudo tanzanite" having a pleasant, not natural, blue-violet color.

An operation different from the HPHT treatment, but with some points of contact on the logical and operational level, is the synthesis of the diamond. In 1970 a crystal of potential gemological interest has been produced by General Electric, applying a HPHT technique, in conditions distinct from those of treatments. Catalysts or fluxes such as metals were used, this procedure suggesting a possible clue to spectroscopists as well as, in some cases, to microscopists. Diamonds produced by HPHT have definitively canceled the distinction between organic and inorganic chemistry, since they were synthesized from biologic compounds such as the peanut butter, then from the "the loved one" by an alternative procedure to burial or ordinary cremation. More recently, diamonds have been presented by the Apollo Diamond of Boston, exhibiting properties (including color and size) of gemological interest, obtained by the Chemical Vapor Deposition (CVD) technique. This method is also used for coatings with thin and hard films, also useful for the protection of some artifacts.

Fig. 6. Synthetic emerald "Malossi".

Some gemstones, such as emeralds (Figure 6), unlike corundums (rubies and sapphires) and diamonds, can grow (from a "seed") at high temperature in aqueous solution by a so-called hydrothermal synthesis (Adamo et al. 2005).

What has been written up to now implies the knowledge of the structure of the materials, in particular of their defects and their impurities; for this purpose it has often been used, among the other techniques, photoluminescence spectroscopy not only for identification purposes but even more for the determination of the oxidation state and coordination of the chromophoric centers.

A very instructive case, in which the distinction between synthetic and natural (same crystalline matrix, same chemical impurities) required the use of different spectroscopies, is that of blue sapphires. The guiding idea consists in the relatively easiness of reproducing in a laboratory the chemical composition of a sapphire (Al203 with a small concentration of iron and titanium); a bit more difficult is the control of the oxidation state of iron: mainly bivalent in natural corundum (presumably born in oxygen deficiency), trivalent in some synthetics, probably grown up in the air. In general: two materials of the same composition, but born in different natural or laboratory contexts, may have some in common properties, in particular the color, and also density, hardness and refractive index. But they can have different properties as, in this case, the photoluminescence. The fact that, in cases like these, emission and absorption do not go hand in hand can be a problem for imitators but an advantage for gemologists and jewelers (and their customers).

Fig. 7. Strongly oxidized glass.

Even in a sector at first sight "less noble", like that of industrial glass, a tight control of the oxidation state of the iron is fundamental: almost totally oxidized in the glass of Figure 7. This was a subject, together with many others, of the collaboration between ICIS and the Experimental Glass Station (Murano, Venice) (Ajò et al. 1999).

Finally, it may be considered that gems are often set in jewels (whose color effect depends on the combination of stones and metals, or of different gems): the prevalent use of yellow gold, in particular for diamonds, has been gradually overcome by the employment of platinum and white gold, not to mention rhodium-plated metals: yellow gold (or colored) remains the preferred in commerce especially for diamonds that show shades of yellow (for example with a relevant concentration of nitrogen). The combination of the color of the metal with the embedded gemstones is so important that in recent decades new techniques are used to obtain color variations of gold, no longer only due to the different alloys used, but also to the special rhodium treatment (galvanic process).

The rhodium is not only used to make white gold bright and shiny but also to color it (in blue, in black, but the latter not very stable to physical stress). Our present project is to use new metals which after particular treatments produce, by interference, effects till now unthinkable except if obtained through enamelling techniques. The best results so far were obtained with titanium. The study of new surface colors aims to the realization of elegant contrasts between metal and gems, or shades of tone on tone. Besides, some metal colors can today be obtained with PVD (Physical Vapor Deposition) but we are studying also techniques such as DLC (Diamond-like carbon) coatings.

4. Funding

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5. Conflict of Interest

This research holds no conflicts of interest.

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7. Short biography of the author(s)

David Ajò - Graduated in Chemistry (University of Rome) and Graduate Gemologist (Gemological Institute of America), worked on synthesis and spectroscopic investigations of materials used in works of art and handicraft, as Research Director of CNR (National Research Council, Padua). Fellow of “Fondazione di Storia” ONLUS (Vicenza). Contract professor at the Università Cattolica del S. Cuore, seat of Brescia, 2002-2011.

Stella Nunziante Cesaro - Graduated in Physics and Chemistry (University of Rome), worked on high temperature systems at the research center ISMN of CNR in Rome. President of the Cultural Association “Scientific Methods Applied to Cultural Heritage” (SMATCH), Rome. Collaborates with the Department of Classics at ‘Sapienza’ (University of Rome).

Giuseppe Elettivo - Graduated in Geology at the University of Calabria (Arcavacata di Rende, CS), specialized in the mineral-petrographic field. Independent gemologist, collaborated with ICIS of CNR (Padua) within a project of the Province of Padua, and taught in the gemology school IRIGEM (Rosà, VI). Expert in estimate and evaluation in jewelry and in the use of precious and non-precious metals.

Federica Fenzi - Graduated in Chemistry (University of Padua) she carried out research at CNR (Padua, 2001-2014), with archaeometric studies on glass, ceramics, bronze, pigments, hydraulic binders, and developing syntheses of eco-sustainable materials for industry and restoration. Since 2013 contract professor of chemistry at the Academy of Fine Arts (Verona) and Santa Paola Institute (Mantua).

Sabrina Tegani - Graduate Gemologist (Gemological Institute of America), she learned gemstones cutting at IRIGEM (Rosà, VI), She worked in the Gemological Education Certification Institute (Milan) as analyst gemologist and gemology educator. Activity in antique and modern jewelry, among the others as rough diamonds analyst and consultant, recently started her business with her sole proprietorship "Rialto".

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