

Chapter 5

Putting on the Ritz: Lead in Pigments and Paints

*There nas quik-silver, litarge, ne brimstoon
Broas, ceruce, ne oilee of tarte noon,
Ne oynement that wolde clense and byte,
That him mighte helpen of his whelkes white
Nore of the knobbes sittinge on his chekes*

- Chaucer, *The Canterbury Tales* (1328-1400)

One of the very earliest uses of lead involved the manipulation of color. The desire to produce and control color has historically created many aspects of technology and society - for example, cosmetics, purple robes for emperors, fashion designs, and trade to India. The history of color chemistry shows that until the 1850s advent of organic chemistry utilizing petroleum tars, lead figured prominently in cosmetics, paints, and pigments. In most cases there was no suitable alternative to lead.

Because the early artists did not have a good source of green available their palettes consisted of white, black, red, yellow and blue. Four of these five colors could be made from lead-based pigments (Table 5.1).

White

Lead carbonate, cerruse, was the primary choice for white pigments for over 2,000 years. It is stable, it has good hiding power, and it is extremely easy to manufacture. The only competitive materials are antimony oxide, tin oxide, zinc oxide, and titanium oxide. Antimony was used as a hiding agent, opacifier, in glasses in

the Roman and pre-Roman period. It was replaced by tin in glass around 400 A.D. The disappearance of antimony is linked to the decline of antimony bearing litharge byproducts from silver mining (Figure 4.1). Tin oxide appears as the whitening material in glazes, forming the base of the Iznik and Majolica glazes. Zinc oxides were introduced as a competitor to lead carbonate in the mid to late 1800s. They did not acquire a large market share because of their poor ability to cover underlying layers of paint. Titanium oxide became commercially available in the 1920s but

Table 5.1

<u>Pigment</u>	<u>Compound</u>	<u>Name</u>
White	PbCO ₃	Cerruse
Black	PbS	Galena
Red	Pb ₃ O ₄ αPbO	Minium Litharge
Yellow	βPbO Pb ₂ Sb ₂ O ₇ Pb ₂ SnO _r PbSn _{x-1} Si _x O ₃ PbCrO ₄	Massicot Naples Yellow Lead Tin Yellow I Lead Tin Yellow II Yellow Chrome



Figure 5.1. Queen Elizabeth I of England had a receding hair line, possibly due to hair loss from whitening of her face.

did not fully replace lead carbonate until after World War II.

White lead, or cerusse, was used to white faces, a practice common in the classical Western world, China, Japan, and medieval Europe. The receding hairline associated with England's Queen Elizabeth I may have been caused by the death of hair follicles from lead-based white cosmetics (Figure 5.1). White lead was also used widely as a cosmetic in China and Japan. The Asiatic Society of Japan debated the toxicity of white lead cosmetics in 1878. It was noted that Dr. Taylor's report of numerous cases of cosmetic lead poisoning was disputed by M. Tanquerel who felt that the mix of white lead with starch minimized the toxicity. The report of Dr. Anderson was read into the minutes (Atkinson, 1878).

The effects are apparently limited to an alteration of the color of the skin to a dull dusky hue when the use of the substance is prolonged. Over many years, with, in some cases, and especially in the most inveterate painters, old prostitutes, for example, an indentation of the surface with very minute closely-set wrinkles, or rather linear depressions. A similar condition is sometimes seen in European actresses after 10 years or more stage experience. No symptoms of absorption appear even in the Yoshiwara. This is probably attributable to the fact that the process is always very slowly effected by habitually exposed surfaces, and

although there is little or no doubt that absorption may take place, it is so slow that elimination by the kidneys is able to keep pace with it and therefore no deposition in the tissue occurs.

Another product similar to face powder is that of pool chalk. A three year old child presented to her physician with poor appetite and an upper respiratory infection. She was found to be anemic and have elevated blood lead which was traced to pool chalk containing 72000 microgram lead per gram of chalk (ppm) (2000).

The use of cosmetics was not unnoticed by ancient male writers. In general, they perceived it as very bad form:

What have rouge and white lead to do on a Christian woman's face? The one simulates the natural red of cheeks and lips, the other the whiteness of the face and neck. They are fires that inflame young men, stimulants of lustful desire, plain evidence of an unchaste mind. How can a woman weep for her sins when tears lay her skin bare and make furrows on her face? Such adorning is not of the Lord, it is the mask of the Antichrist.

.... St Jerome (345-420 A.D.) Letter LIV

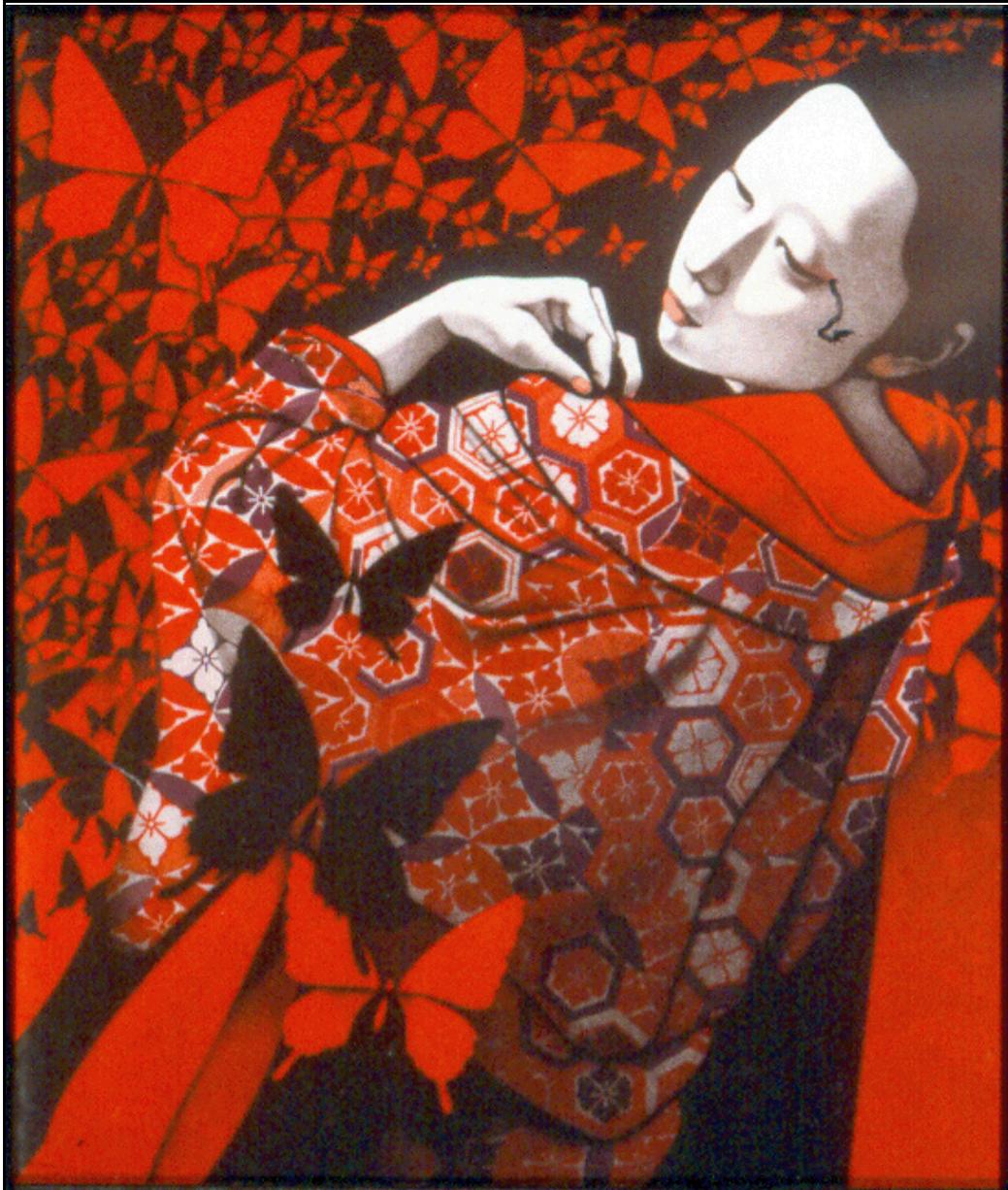


Figure 5.2 Saito's *Red Illusion*. The woman wears Oshiroi or white pigment as a cosmetic.

Now our married women are not like those described by Eubulus in The Wreath-Sellers: "They are not, Zeus knows, plastered over with layers of white lead, and they have not like you, their jowls smeared with mulberry juice. And if you go out on a summer's day the hairs blown about on your faces look grey, they are so full of white lead.

Athanaeous (Deipnosophistae 13.577.

The stylish use of white lead was not limited to women's faces. Men powdered their hair with white

lead. Figure 5.3 shows a 1770 cartoon by Collet, *The Englishman in Paris*, showing a gentleman getting his hair sprayed with white lead.

White lead paint was an indispensable component of the classical painters palette. The use of white lead in oil painting is nearly too numerous to mention. One example suffices. Edward Hopper's *The Night Hawks* obtained the luminescence of night lighting by underlying coats of white lead paint (NPR



Figure 5.3. Collet, 1770, *The Englishman in Paris* has his hair sprayed with white lead. Hulton Deutsch Collection, Ltd. in *Sweet Poison* by J. Eisinger, Nat. Hist. 7/96.

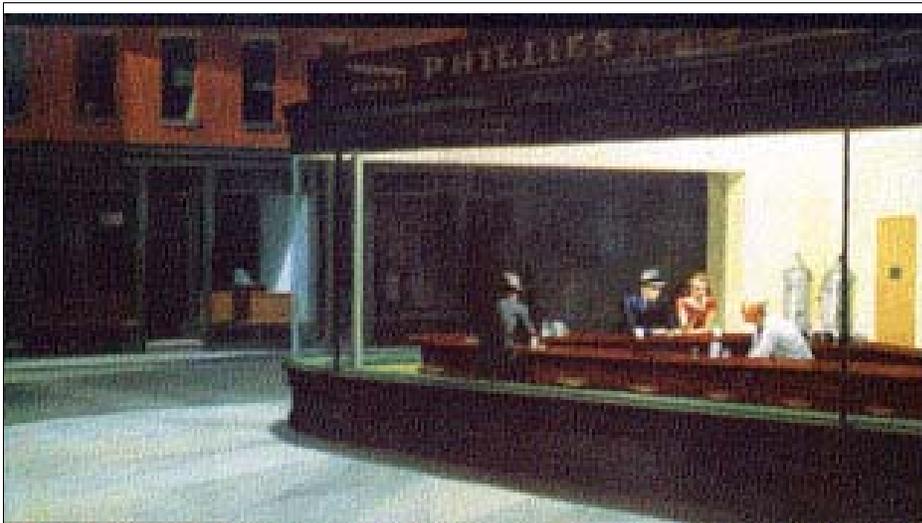


Figure 5.4. The effect of a fluorescent light is achieved by underlying coats of white lead. Edward Hopper *The Night Hawks*. Comments of Kim Pender, Art historian, Art Institute of Chicago, 2002.



Figure 5.5 .Cerusse (lead carbonate) on baryte (barium sulfate). (Author).

broadcast, Oct. 7, 2002) (Figure 5.4).

White lead ore, cerusse (Figure 5.5), was the white pigment of choice because it is easy to produce. From 1000 B.C. to the present, there have been numerous historical references to white lead, including both technical recipes and commentaries on its use. Table J.11 gives a few notable technical texts over human history, many of which refer to cerusse.

The Yellow Theocrat (Huang-ti), by refining, achieved gold and cinnabar-elixirs. The drugs left over from the refining were mercury, pinker than the red sunset-clouds, and lead, whiter than the pure-white snow. His Palatine women took the mercury to tint their lips, so that their lips were vermeil, and took the lead to spread on their faces, so that their faces were white. Thus when they washed them, these did not fall away.

I Shih-chen, (1260 A.D.)
(Yuan Dynasty)

White lead has been used as a kind of stucco, called *gesso* or *pastiglio* and described as follows in the *Bolognese Manuscript* (1400s):

220. *To make a paste with which can do both good and evil, and can seal and unseal any letter, and can model whatever you like, and which will become very*

hard after you have moulded it, if you suffer it do dry, and to which you may give whatever colour you please.

-Take gum-tragacanth and gumarabic, of each equal quantities, and steep them in sufficient water to cover them for 20 hours; then pound them very fine in a mortar. Next take 1 lb. of white lead to each ounce of the gums, and mix the whole together like dough; and, if you wish to have the paste white, do not add anything more to it. If you wish to have it of any other colour, mix with it whatever colour you like in a fine powder, and work the ingredients well together, in order that they may be thoroughly incorporated one with another. Then anoint your hands with castor oil, or linseed-oil, or oil of bitter almonds, and take this paste, and knead it very well in your hands; and when you have kneaded it well, you can impress whatever you choose upon it. If you wish the paste to remain soft, put it into a cabbage-leaf, and it will remain soft for as long a period as you like.

A similar recipe occurs in the *Marciana Manuscript* (Merrifield, 1967).

While the mineral cerusse (Figure 5.5 (Mottano et al., 1978)) is not as commonly found, it was easily synthesized by standard chemical refluxing lead over a heat source. Lead sheets were rolled into spirals, placed in earthenware pots over weak acetic acid (vinegar) and then covered with lead plate. The pots were set upon horse dung in a shed. The fermentative oxidation of the dung liberated heat and carbon dioxide. The heat volatilized the acetic acid whose reaction with the lead ore was followed by carbonation. This process probably originated in Europe and arrived in China by about the 5th century B.C.E. (Wai and Liu, 1991). One of the earliest Western recipes for white lead is given by Aristotle's pupil Theophrastus (372 B.C.) (Caley and Richards, 1956, p. 57):

Lead about the size of a brick is placed in jars over vinegar and when this acquires a thick mass, which it generally does in ten days then the jars are opened and a kind of mold is scraped off the lead and this is done again until it is all used up. The part that is scraped off is ground in a mortar and decanted frequently, and what is finally left at the bottom is white lead.

The Roman Pliny (23-79 A.D.) describes the manufacturing of white lead (Bailey, 1929-1932, p. 232):

Psimithium also, that is, cerussa, is produced at lead-works. The most highly spoken of is in Rhodes. It is made from very fine shavings of lead placed over a

vessel of very sour vinegar and so made to drip down. What falls from the lead into the actual vinegar is dried and then ground and sifted, and then again mixed with vinegar and divided into tablets and dried in the sun, in summer time. It's properties are the same as those of the substances mentioned above, only it is the mildest of them all, and beside that, it is useful for giving women a fair complexion; but like scum of silver, it is a deadly poison.

The Romans handed down this recipe through compilations, including the *Mappae Clavicula* (900 A.D.):

If you wish to make minium, either red or white, take a new pot and put lead sheets in it, fill the pot with very strong vinegar, cover it and seal it. Put the pot in a warm place and leave it there for one month. Later take the pot, uncover it, and shake out whatever surrounds the lead sheets into another earthenware pot and then set it on the fire. Stir the pigment continuously and when you see the pigment become white, like snow, take away as much as you like of it and that pigment is called ceruse. Then put the rest on the fire and stir continuously, until it becomes red, like other minium. Then take it away from the fire and leave it in the pot to cool it.

The recipe for cerusse also shows up in the work of the European metallurgist, Theophilus (1100s A.D.):

If you are going to make ceruse, thin out some lead plates and lay them together, dry, in a wooden chest the same way as the copper above. Then pour in hot vinegar or urine to cover them. After a month pry off the lid and remove whatever white there is and replace [the plates] as before. When you have enough ceruse and want to make minium out of it, grind it on a stone without using water, put it into two or three new pots and set them on blazing coals. You should also have a slender curved iron tool, one end of which is fitted into a wooden [handle] while the other end is board, and with it you can stir the ceruse and mix it from time to time. Keep on doing this until the minium becomes completely lead.

The Islamic bookmaker Badis (1025 A.D.) gives a note on testing white lead.

Some is Greek and some North African. Essentially it is the flower of the lead which deteriorates by means of vinegar. The best of it is strong in whiteness; it does

not tend toward blue (Levey, 1962).

Large-scale manufacturing of ceruse occurred in response to the wide spread custom of hair and face whitening in England. A Royal patent was issued in 1662. The patent described a manufacturing process similar to that described by Theophilus. Lead was cast into 3 by 6 foot plates thin enough to roll. The rolls were placed on supports above pots of vinegar which were set in rows on top of dung. A total of 1600 pots were handled at one time and cerusse was recovered after three weeks (Harley, 1967). Royal Society members worried about the workers involved in recovering and grinding of the pigments. These workers suffered from abdominal pains, contortions, shortness of breath, giddiness, and paralysis. In 1678, Vernatti described the symptoms to the Royal Society in his paper *A Relation on the Making of Ceruss* (Vernatti, 1678).

In 1783, the Royal Society offered a prize to whoever could invent a harmless method for making cerusse. In the 1790s, worker exposure was reduced by the invention of an automatic roller that replaced manual beating of the pigment to loosen it from the lead plates (1796). A French-manufactured kind of a fume hood for protecting men in the grinding process was described in the Royal Society of Arts Transactions for 1796 (1796).

The modern Dutch method for producing white lead does not significantly differ from the Roman process. What follows is a description of the Dutch process from a 1950 ink technology book.

In the Dutch process, white lead is formed by the action of weak acetic acid on soft, refined pig lead, cast into slabs in the presence of damp air and carbon dioxide. The floor of the brick corroding houses used for the process is covered with chestnut oak bark to a depth of one yard. A number of jars eight inches high by four inches diameter, filled with 3% acetic acid, are placed in an orderly array eighteen inches apart on the layer of bark; lead bars are laid horizontally on the shoulders of the pots. A temporary floor of rough boards is made above this stack on which a second stack is built up. The house normally contains eight stacks and is provided with a ventilating chimney; the house is left for four months. The bark ferments and provides heat and carbon dioxide. Water and acetic acid vapours rise by evaporation and the temperature settles down to 55°-65°C. The lead becomes corroded

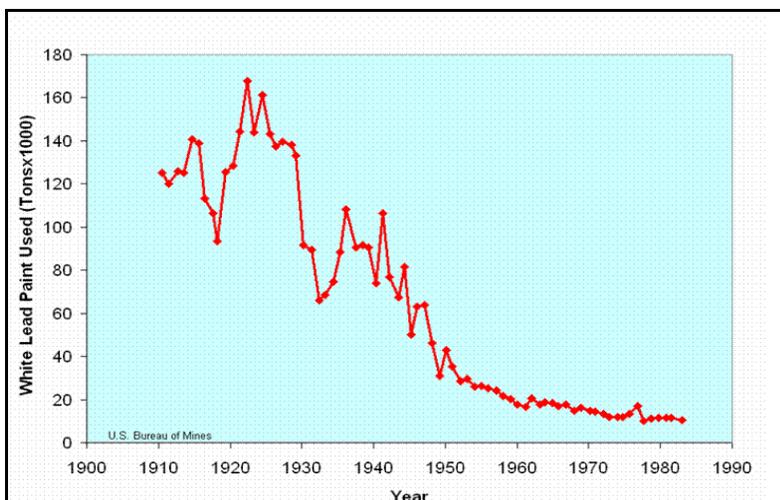


Figure 5.6 White lead paint consumption in the U.S. peaked in the 1920s. It was voluntarily banned from household interiors in 1955 and legislatively banned in 1978.

with basic lead carbonate which is crushed between grooved steel rollers and sieved, and this stage is repeated before the white lead is ground in water. (Apps, 1959, p. 118).

White lead pigment was used not only in artistic painting but also in structural painting. While white lead was phased out in 1921 in Europe it continued in use for some time in the U.S. Replacement pigments for white lead in the 1800s consisted primarily of ZnO which did not have the covering capacity of ceruse and thus required more coats of paint. Titanium dioxide was introduced onto the market in the very late 1910s early 1920s but did not take a large market share until after World War II. Figure 5.6 shows the total amount of white lead paint used in the U.S. in the 1900s. The composition

of the white lead varied somewhat from manufacturer to manufacturer. Typical components of white lead were: normal lead carbonate, $PbCO_3$ (ceruse); basic lead carbonates ($2PbCO_3 \cdot Pb(OH)_2$ and $4PbCO_3 \cdot 2Pb(OH)_2 \cdot PbO$); lead sulfate ($PbSO_4$); and lead silicate ($3PbO \cdot 2SiO_2 \cdot H_2O$).

Table 5.2
Life and Times of Goya

1746	Goya is born.
1759	Works as a copist of other paintings
1762	Goes to Rome to study
1774	Returns to Spain
1775	Begins work at Royal Tapestry Factory as a designer
1778	Makes etchings of Velazquez' paintings and is commissioned for frescos.
1780	Commissioned for portraits, Appointment to the San Fernando Academy
1792-3	Illness that leaves him deaf
1793	Begins "invented" works, filling albums with drawings; love affair with the Duchess of Alba
1799	The Caprichos are published
1808	Napoleon invades Spain, installs brother on throne
1811	Ferdinand VII re-installed on throne
1812	Wife Josefa dies
1819	Experiments with lithgraphy
1823	Constitution ended by Ferdinand
1824	Goya receives permission to leave Spain
1826	Permission to retire to Bordeaux
1828	Goya dies

Leaded Paints and the Painter: Goya

Francisco de Goya, the painter of the terrifying *Saturn Devouring His Child* was born in 1746 in the Aragonese village of Fuendetodos, Spain. He studied art by copying in the studio of the artist Luzan y Martinez. Goya made his way to Rome, studied there for a few months, married, and returned to Spain. Goya worked for the royal family as a tapestry designer. As was the custom, the designer painted the tapestry scenes close to life size. In the 17 years he did this work, Goya used a larger than normal amount of lead for the white backgrounds of the tapestry designs.

In 1792-1793, he suffered a devastating illness that deprived him of his hearing (Table 5.2). He had experienced earlier bouts of illness marked by lethargy. After the sickness that destroyed Goya's hearing the character of his paintings profoundly changed. Earlier Goy's paintings resembled those of Rubens. His later

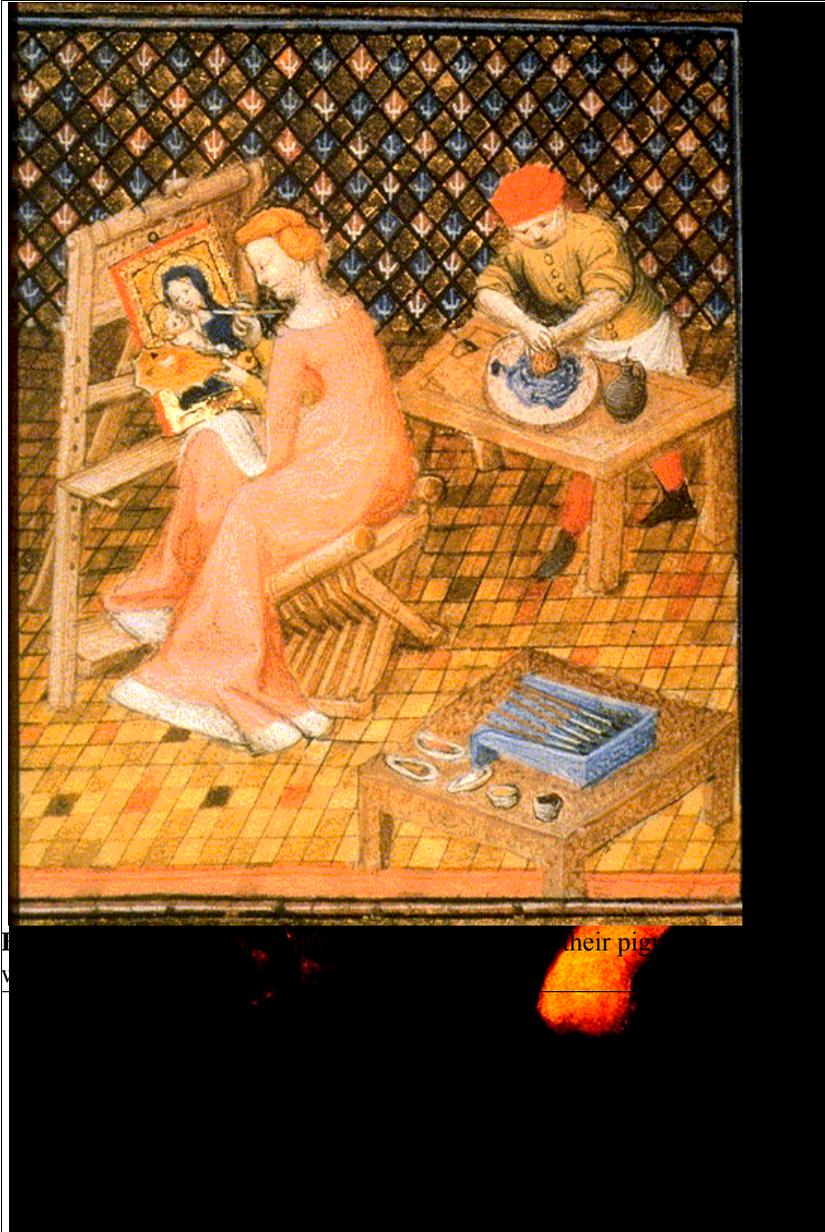


Figure 5.7. Francisco de Goya *Saturn Consumes His Child* in Goya: The Origin of Modern Temper in Art. Licht, University Books, 1979.

works were profoundly disturbing and hallucinogenic. Following his illness, he began the “invented” work and the *Caprichos* (Harris, 1969). His painting *Saturn Consumes His Child* also was accomplished during this time period (Figure 5.7). This was a tapestry-sized mural that confronted the visitor on entering Goya’s dining room. The work’s motif is the classical myth of Saturn (God of Lead) devouring his children, a myth Rubens had explored earlier. Unlike the traditional

Saturn, Goya’s devours a child who is not an infant, but who has a well-formed, more adult body. Nor does his Saturn have any features traditionally associated with the God: no scythe, no wings, nothing to denote the mythological meaning of chaos and order in the classical myth. It has been suggested that Goya was aware of his own exposure to lead and this picture indicates his experience of his own mortality. In the period preceding his illness Goya may have been aware of lead’s hazards and shifted his work from the cartoons of tapestries which required major use of white lead. In 1764, Vernatti published a treatise in London on the dangers of cerusse, white lead (Algarotti, 1764).

The painting may also be explained by the common belief at the time that witches’ sabbaths occurred on Saturday (day of Saturn) and that cannibalism was a part of the sorcery. A third interpretation relates to another common folk belief that Jews required the blood of an infant to make their Passover bread (Muller, 1984).

Art historians have debated the nature of Goya’s illness, particularly because it profoundly impacted his art. Among the proposed diseases are venereal disease, schizophrenia, or possibly lead encephalopathy caused by continuous contact with white lead (Glendinning, 1877; Nederland, 1972). In addition to hallucinations and lethargy, Goya’s

symptoms included impaired fertility, vertigo, paralysis of the right side, impairment of balance, loss of hearing, terminal deafness, speech disorders, temporary blindness, remittent palsy and tremors, convulsive and epileptoid-like manifestations, buzzing and other resounding “noises” in the head, facial pallor, mental confusion or delirium, apparent manifestations of paranoia, and severe ‘colics’ (Moffitt, 1988). Goya himself describes his symptoms in a letter to his friend, the businessman (Martín Zapater y Clavería):

I get in a bad humour - that is until, I put my hand to my belly [reference to masturbation]. So, you laugh? Well, try it yourself; then you'll see what a nice effect this works on you. You'll need this trick now since this is the time of evil thoughts, words and deeds. I owe this [remedy] to my Aunt Lorenza [an imaginary lover] who showed me how to do it. I'll confess to you that doing it bothered me at first, but now? Ha, now I don't fear even witches; fairies, fantasmas, bullying giants, rat-bastards, boogeymen, et cetera, nor any other kind of embodiments do I fear now - only human beings!

And in another letter:

I wouldn't have believed that even friendship could endure during this time I am now going through... when I am assaulted by my woes. Moreover I still haven't begun to work, nothing at all, having not the humour for it, due to my illnesses. Maybe next week I'll start, that is, if God wishes.... I haven't taken care of anything, unless it was something for you... Have pity on me, for there are still many troubles in this business. For my part, I must choose freedom, and even all the work needed to obtain it.

In 1793 he petitioned for a royal stipend so he could recuperate from his illness:

I must approach you for the favor of calling your attention to the fact that I have been bedridden for two months now due to acute stomach pains and that I am going to Seville and Cadiz on a leave. By your leave, I beg Your Excellency for your recommendation or permission that I be granted some money in Seville, a favor I would appreciate enormously.

On this trip, he collapsed in the home of Sebastián Martínez, who then wrote to Zapater:

Our Goya is a bit better but his progress is slow in indeed. I have faith now that the weather and the mineral baths at Trillo, which he shall take at the proper time, might eventually contribute to his recovery. The noises in his head and his deafness have not however abated previous mental agitation which made him lose his balance. Now he can go up and down stairs rather well and, in short, do other things he couldn't before.

Why was Goya one of the only artists to be impacted by lead? Most artists employed workers to



Figure 5.9. Lead sulfide (PbS) is a semiconductor which gives rise to its dark color. (Author)

grind pigments (see Figure 5.8). Goya, however, was apparently either too conscientious or too cheap to employ labor for grinding white. Other painters, ones who could not afford apprentices, may have been lead poisoned. Frederico Barocii (1530-1612) suffered a suspicious-sounding ailment. His biographer Giovanni Pietro Bellori described it (Moffitt, 1988):

It certainly seems incredible to hear of so many public as well as private works having been executed by this master, [all] with the utmost diligence and the greatest study combined with the liveliest observation and natural talent, [all executed during times] when his incurable illness allowed him only to work for an hour in the morning and another in the evening....All the rest of the day he spent in pain from stomach cramps, caused by continuous vomiting, which overcame him as soon as he had eaten. At night, he hardly slept, and, even during that short time, he was tormented by frightful dreams, and sometimes he moaned and made so much noise that one person would stay by him and wake him on purpose, in order to free him from this oppression. So it went on, ever since the day on which he believed he had been poisoned, until his death, that is, for fifty two years.

The painter Piero di Cosimo (1462-1521 A.D.) was similarly afflicted (Moffitt, 1988). He is described as follows by his contemporary Giorgio Vasari (Vasari, 1963):

The crying of babies irritated him, and so did the coughing of men, the sound of bells, the singing of friars....In his old age he became so strange and eccentric that he was unbearable. He would not allow his apprentices to be around him, so that he obtained less and less assistance by his uncouthness. He wanted to work, and not being able to on account of a paralysis, he became so enraged that he would try to force his helpless hands, while he doddered about and the brush and maul-stick fell from his grasp, a pitiful sight to behold.

The hazard of leaded white paint was known rather early, although not widely. A 1713 text by Bernardino Ramazzini (1633-1714), *De Morbis artificum diatriba* ("Diseases of Workers") lists details of illnesses attributed to lead's effects upon metalworkers, potters, and painters (Wright, 1964):

dysnopea, phthisis [asthma], apoplexy [sudden loss of musculature control], paralysis, cachexia [a general wasting of body due to chronic disease], swollen feet, loss of teeth, ulcerated gums, pains in the joints, and palsy.

The symptoms of potters were quite similar:

These then are the diseases that afflict men who handle lead [:] first their hands become palsied, then they become paralytic, splenetic, lethargic, cachetic.... toothless.... cadaverous and the color of lead.

Painters had similar difficulties:

Painters are attacked by various ailments, such as palsy of the limbs, cacheia, blackened teeth, unhealthy complexions, "melancholia", and loss of smell. It very seldom happens that painters look florid or healthy....[and the immediate cause is] the materials they handle and smell constantly, such as red lead, cinnebar [a sulfide of mercury], white lead....[in short, all] the numerous pigments made of various [toxic] mineral substances...Moreover, when at work painters wear dirty clothes smeared with [lead-based] paint, so that their mouths and noses inevitably breathe tainted air; this penetrates to the seat of the animal spirits, enters by the breathing passages the abode of the

blood, disturbs the economy of the natural functions, and excites the disorder mentioned above....In fact, the mineral world supplies the materials of almost every color in use, and this accounts for the really serious ailments that ensue. Painters, then, are inevitably attacked by the same disorders as others who work with metals, though [usually] in a milder form. This, then - and no other - is the explanation of the cachetic condition of painters, of their unhealthy coloring, and

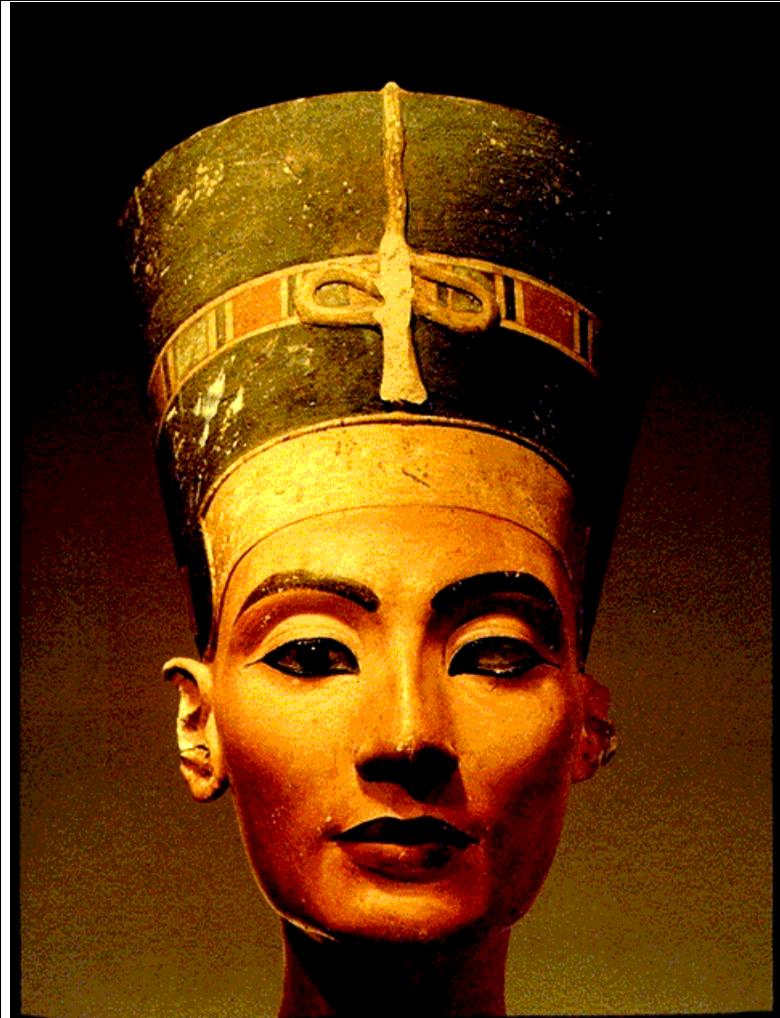


Figure 5.10. Queen Nefertiti, from *Life in Ancient Egypt* by Eugene Strouhal, Cambridge University Press, 1992. Berlin-Charlottenberg Agyptisches Museum.

[finally] of the melancholic fits, to which most of them are subject.

The “Color” Black

The mineral galena (Figure 5.9) was ground and used as a blackening agent, that is, as mascara, during the 18th Dynasty of Egypt. The example is the face of Queen Nefertiti (Figure 5.10) (Strouhal, 1992). Egyptian makeup contained a variety of lead compounds (Table E.20(Walter et al., 1999)). PbS was used as a darkening agent in shampoos as late as 1997 (Mielke et al., 1997), (Tribune, 1997).

Black is the opposite of white. With white, no

electronic transitions can take place. On the other hand, black requires the removal of light over the entire visible spectrum (400-700 nm). All light wavelengths must be able to move about electrons in the surface of the object. This can be accomplished by mixing pigments from all seven basic colors, so that one absorbs light across the entire spectrum. An alternative mechanism is to use the semi-conductor class of materials, of which PbS is one.

The semiconducting property of galena may explain its geologic marriage to silver (Chapter 1 and 2). It was recently postulated that Au^+ or Ag^+ ions adsorbed on galena can be reduced to the metal through the electron conducting properties of the semiconducting ore. Such reduction would result in the development of multiply phased minerals that might lead to the AgS/PbS marriage (Bakken et al., 1989; Boyle, 1968; Craig, 1967; Eggleston and Hochella, 1991; Starling et al., 1989; van Hook, 1960).

The Color Yellow

There are several lead based yellow pigments (Figure 5.11). Two types of lead tin yellow can be distinguished non-invasively on paintings because of their different structure types. The exact configurations of lead and oxygen bonds give rise to differing vibrational spectra (Table D.20). Each of the three yellow pigments has a slightly different position for the lattice Pb-O stretch mode (Clark et al., 1995; Virouroux et al., 1982). The different yellows also give different X-ray diffraction patterns (Table D.21).

Figure 5.12 shows Titian's painting *Death of Actaeon*. The yellow-leaves in the front are lead-tin type I (Clark et al., 1995). Similarly, the bright yellow of the man's cloak in Paulo Veronese's *Allegory of Love, IV*, is lead-tin type II (Clark et al., 1995) (Figure 5.13). Leonardo da Vinci also used Type I lead-tin yellow in the golden yellow of Mary's cloak in *Virgin of the Rocks* (Kuhn, 1968) (Figure 5.14). Our last example is that of Rubens, *The Dying Seneca*, which includes Type I lead-tin yellow (Kuhn, 1968) (Figure 5.15).

Spinello Aretino's *The Madonna and Child Enthroned with Angels* shows the use of both lead-tin yellow and red lead on a white lead background. The blue color is a mixture of deep blue with white lead (Gettens, 1947).

The use of the pigments varies systematically

with the historical period as shown in Figure 5.16 and Table J.13.

Why might the choice of yellow change with history? We have already seen part of the answer with respect to lead antimonate. We noted that the combination of red lead or leaded glass (where lead was used to lower the melting point of the glass) with an opaque white antimonial glass produces an intense yellow color such as that of the lovely Egyptian 18th dynasty core formed glasses (Figure 4.4). This compound is known as Naples yellow. The compound contains both lead and antimonate in two different eightfold polyhedra (Ivanov and Zavodnik, 1990; Natta and Baccaredda, 1933). The color in this compound arises from transfer of electrons from oxygen to lead (ligand to metal charge transfer). Antimony changes the unit cell dimensions of the lead dioxide, αPbO_2 (Hill, 1987) allowing the oxygen to get close enough to the lead to transfer electrons. This lead antimonate for yellow was lost from glassmaking about the 4th century A.D., the time of the fall of the Roman empire (Brill, 1968) (Figure 4.1). Chapter 4 suggests that the loss of antimony from glass and glazes resulted from decreased production of antimony-rich litharge, a product of silver cupellation.

The yellow lead antimonate was replaced by a lead tin compound for the next 1000 years (Table



Figure 5.11 Powders of pigments, Lead tin Yellow I, Lead Tin Yellow II, Lead Antimonate, and Lead Chromate. (Author)



Figure 5.12. Titian *The Death of Acteon*, Lead tin yellow Type I on foreground leaves. Clark, Dalton Trans. 1995.

A.10). Lead-tin yellow II, $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$, followed the yellow lead antimonate, $\text{Pb}_2\text{Sb}_2\text{O}_7$. Lead-tin II was first used in ancient glasses (>400 A.D.) accounting for its inclusion of Si. Lead-tin II pigments are observed in European medieval paints beginning in 1325 A.D. (Martin and Duval, 1990). The sequence suggests that recipes for lead-tin II were transmitted down the ages by glassworkers. With the weakening of the guild system, painters may have become aware of glass technology and appropriated lead-tin yellow from potters and glass workers. Piccolpasso records a recipe for lead yellow referring to a glass origin. In addition, the fact that giallorino was peculiar to Florence would also indicate an origin with glass (Bomgard et al., 1989).

Cennini (1437 A.D., Europe), however,

suggests that the Florentine yellow, giallorino, was derived from a mineral:

A colour known as giallorino is yellow and it is manufactured one. This colour is used in fresco and lasts forever, that is, on the wall, and on the panel with temperas....And as I understand it; this colour is actually a mineral originating in the neighborhood of great volcanos, so I tell you that it is a colour produced artificially, though not by alchemy.

Lead-tin II was used in pigments primarily from 1300 to 1450 A.D. (Figure 5.16). At one time it was thought to be completely of Sn with no Si and was given the formulation of $\text{Pb}_2\text{Sn}_2\text{O}_6$ [Morgenstern-Badarau, 1971 #664]. The structure of this system is thought to approximate that of PbSnO_3 if a small



Figure 5.13. Paolo Veronese *Allegory of Love*. The bright yellow on the man's cloak is Lead tin Type II yellow. From Clark, 1995.

amount of silica is incorporated (Rooksby, 1964). It has a cubic pyrochlore-type crystal structure with a space group of $Fd\bar{3}m$, $a = 10.719 \text{ \AA}$. The color becomes deeper yellow on incorporation of Si (Clark et al., 1995).

Lead-tin yellow I occurs when minium, Pb_3O_4 , is treated with tin. A recipe in the *Bolognese Manuscript* (1400s) calls for yellow to be roasted with minium and finely ground sand. This yellow compound was known and used between 1450 and 1750 A.D.. It is known as giallolino and sometimes,

confusingly, as massicot. It has a structure very similar to that of minium (Clark et al., 1995). Sn(IV) substitutes for Pb(IV) to create $Sn(IV)O_6$ octahedron with Pb(II) pyramids, and has the



Figure 5.14. Leonardo da Vinci *Madonna of the Rocks*

same mixed valence chemistry as minium (Clark et al., 1995). Charge transfer between Pb(II) and Sn(IV) gives rise to the intense yellow color.

Lead-tin I was replaced by lead antimonate, which was re-discovered and came into vogue around 1693 A.D. (Wainwright et al., 1986).

Lead oxides also produce color and were occasionally used in painting (Figure 5.17). While these oxides were not extensively used in paintings it is worth noting their color here. Colors varied from pink to yellow to red to black and we will make the claim in the next chapter that these color changes, along with t

Yellow: Massicot



Figure 5.17. Peter Paul Rubens *The Dying Seneca* uses Lead tin Type I. In Peter Paul Rubens *Man and Artist* by Christopher White, 1988.

he phase change from solid to liquid, formed key

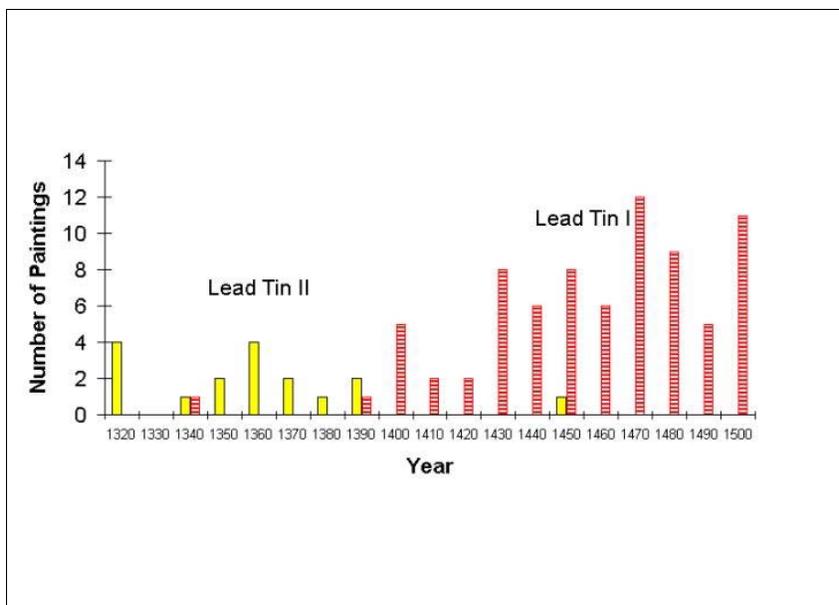


Figure 5.16. Analysis of museum paintings shows a transition between 1390 and 1400 oil paintings from Lead Tin II to Lead Tin I yellow. Data source: Hermann Kuhn, *Studies in conservation*, 13, 1968, 7-3; Elisabeth Martin and Alain R. Duval: *Les Deux Varietie de Jaune de Plomb et d'etain edude Chronologique*.

elements of alchemical theories.

One of the oxides is massicot, βPbO . There are three allotropic structures of lead monoxide: αPbO (litharge, red tetragonal), γPbO , and βPbO (massicot, yellow orthorhombic). In litharge and in massicot, lead forms a chain of Pb-O bonds (Figures 4.2, 4.52, and 4.53), which are side by side a second set of chains of O-Pb bonds. The chains lie above and below further chains. The distance between chains is controlled by the Pb^{2+} lone pair electrons, which are predominately s orbital in nature. Overall the structure of αPbO is open and porous (Adams and Stevens, 1977; Adams et al., 1992). X-ray crystallographic examination of litharge shows that lead has four

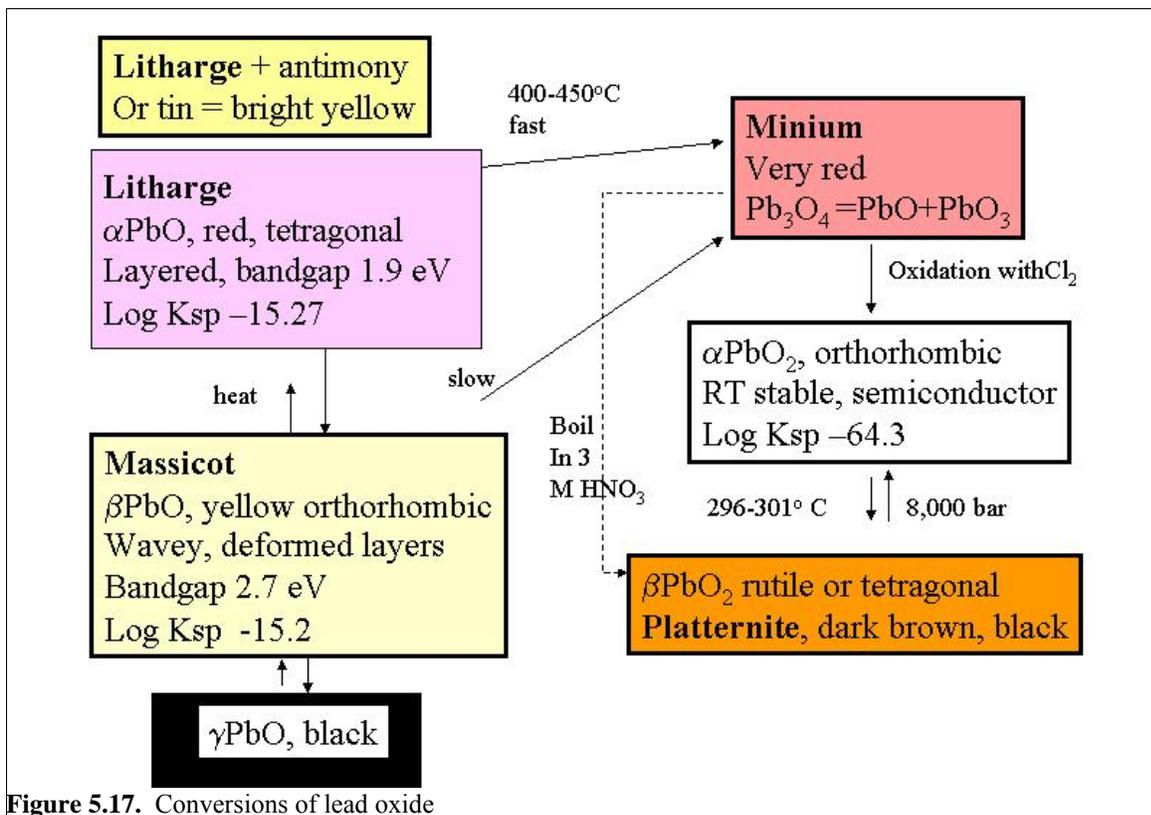


Figure 5.17. Conversions of lead oxide



Figure 5.18. Crocoite (Author)

nearly identical bonds with oxygen. The bond length is short enough to approach covalent binding. (The Pb-O bond is too small to involve the full van der Waals radii of Pb^{2+} (Hill, 1985)). Such not-quite covalent bonding in PbO results in semi-conducting behavior. Slight changes in the crystal lattice perturb the band structure. The transition from α PbO (litharge) to β PbO (massicot) involves shortening of two of the Pb-O bonds and is accompanied by a color change to yellow (Figures 4.2 and 5.22). The phase transition between these two forms of lead oxide can be achieved by heating to $489^{\circ}C$ (Trinq, 1984) (Figure 5.29). This temperature was easily accessible to our forebears. In the heating process, a third phase is sometimes observed (γ PbO). In this third phase the band gap is closed, resulting in a black color (Adams et al., 1992).

The use of massicot has not been well documented in part because of wide number of differently used terms. Daniel U. Thompson, commenting on medieval technology, indicates that potters referred to a yellow glaze from lead and antimony (Naples yellow) as giallulinum. Others referred to giallorino as massicot obtained by gentle roasting of white lead (Thompson, 1956). Massicot is not widely used due to its instability.

Yellow Chrome

The natural mineral crocoite, lead chromate (Figure 5.25) was found in Siberia in 1770. The chemist Vauquelin studied it in 1797 and discovered chromium, a previously unknown element. He reproduced the color of yellow chrome by precipitating lead acetate and nitrate with potassium chromate. This compound was made commercially available in large quantities in 1816 by Dr. Bollmann (1769-1821). This physician, who had arranged the escape of LaFayette from Austrian imprisonment, became a persona nongrata and immigrated to the United States. In 1814 after the Napoleonic Wars ended he returned to Europe and brought back a large quantity of chromium. He began producing 20 pounds of yellow chrome per day.

Chromium was discovered in the Shetland Islands in 1820. This discovery allowed English production to rely on local chrome sources (Harley, 1967).

Another producer of chrome yellow was Andreas Kurz. In 1830 he gushed

Kurz's chrome yellow is such a splendid success that the Princess Charlotte had her carriage painted with that dazzling pigment and the result is that carriages of the day are similarly coloured (Schofield, 1977).

As of May 1993, yellow chrome was still the preferred pigment for traffic paint due to its high reflectivity (night time visibility), cost, lightfastness, and hiding power (Humer, 1993). The organic substitutes cost \$6

to \$8 lb, compared to yellow chrome at \$1/lb. David Hockney's *Pearblossom Highway* shows the use of chrome yellow in highway pavement (Figure 5.27). Vanity Fair commissioned Hockney to produce a series of photo collages for an article on the final chapters of Vladimir Nabokov's 1955 novel *Lolita*. (This sequence is of Humbert Humbert's search for Lolita which should stop).

The photographs that represent yellow road markings have been carefully arranged to form a strong line perpendicular to the horizon. ... The road markings were photographed from above; the illusion of recession that would have resulted if he had photographed them conventionally was thereby prevented (Melia and Luckhardt, 1994).

The color of the chromate ion is yellow. The color arises from an electron transfer from oxygen to chromium (ligand to metal charge transfer) (Nassau, 1983, p. 143). The presence of lead in chrome yellow



Figure 5.19. David Hockney *Pearblossum Highway*. 1986. In Paul Melia and Ulrich Luckhardt “David Hockney” 1994.



Figure 5.20. Two forms of wulfenite, lead molybdate. One has very thin yellow sheets and the other blockier more orange cubes. The difference is due to the adjacent presence of crocoite, lead chromate. (Author).

is partially to create an insoluble compound and partially to tune the L6M an insoluble compound and partially to tune the L to M transfer. Tuning of the band gives a variety of chrome yellow pigments (Table E.14). Figure 5.20 shows how minor substituents can “tune” crystal shape and color. Wulfenite, lead molybdate, first described by the Jesuit mineralogist Franz Xaver van Wulfen in 1785, when pure gives sheet like yellow crystals. When it forms near crocoite, lead chromate, small amounts of chromate are incorporated into the crystal. The color deepens to red and the crystals become boxy.

The lead chrome pigments enjoyed an increasing market over the period 1962-1971 falling only with the limits placed on leaded pigments (Table I.6).

Toxicity of Yellow Paints

Lead chromate itself is apparently nontoxic. It seems to be toxic only when it is produced with zinc chromate, a carcinogen (Dalager et al., 1980). Cancer rates in paint plant workers manufacturing Zn chromate were elevated. Rates among Pb chromate workers were not (Davies, 1979; Davies, 1984). Lead chromate’s lower toxicity was attributed to better control of dust production (Handley, 1984; Hartogensis

and Szielhuis, 1962).

Lead pigments fed to dogs caused symptoms of toxicity at the levels shown in Table 5.4. These symptoms included lethargy, anorexia, dehydration, emaciation, followed by hyperirritability, disorientation, motor ataxia, and convulsions preceding death (Cristofano et al., 1976). The percent absorption of various lead compounds into rats varies from pigment to pigment as shown in Table 5.5. Clearly the most toxic material is lead carbonate (Bartrop and Meert, 1975).

Yellow chrome has been an adulterant in food materials. Yellow chrome (PbCrO₄) was used as a yellow food coloring for sweets and custards in the 1800s until it was banned following a rash of deaths (Mann, 1994). In 1949, 121 Gurkha soldiers stationed in Hong Kong reported sick with epigastric pain, nausea, constipation, and exquisite tenderness of the recti abdominis and other muscles. On hospital admission, all were found to be anemic. 19% of the patients had blue lines along their lip gums, and 60% had limited lateral gaze. The staple diet of these soldiers was a twice-daily meal of boiled rice, vegetables, and curried meat or fish. The curry was found to contain PrCrO₄. The soldiers were discovered to be ingesting 11,325 F g of lead a day (300 is typical) (Powers et al., 1969).

<u>Compound</u>	<u>ppm</u>
Ceruse (lead carbonate)	>2000
light chrome yellow	>5000
primrose chrome yellow	>5000
molybdate orange	>5000
medium chrome yellow	20,000

<u>Compound</u>	<u>%absorption compared to lead acetate</u>
Pb(OAc) ₂	0
control (no lead)	4
metallic lead (180-250 μm size)	14
PbCrO ₄	44
Lead octoate	62
Lead naphthenate	64
PbS	67
Lead tallate (drier)	121
PbCO ₃	164



Figure 5.21. Funeral effigy in Salisbury Cathedral. Much of the bright decorations of cathedral paintings were based on red lead. (Author).

Minium or Red Lead

Minium, Pb_2O_3 , has a structure consisting of octahedral chains of $Pb(IV)O_6$ joined by pyramidally co-ordinated $Pb(II)$ atoms (Chapter 4, Figure 4.54) (Clark et al., 1995). The color red observed in minium is due to an electron transfer between Pb^{2+} and Pb^{4+} .

Red lead's name derives from Pliny who called it *minium secundarium*. It was used extensively as a decorator's paint, but darkened on exposure to the air and formed sulfides. When used in a protective media such as egg tempura it is relatively stable. Egg tempura is made of egg yolk, an emulsion of fatty droplets suspended in egg protein and water. The water evaporates, the proteins denature, and the fats plasticize the paint. In this material, minium is stable. However Cennini, author of the earliest Western text on painting (1437), warns against the use of minimum because it darkens plastered surfaces (Thompson, 1933):

On the Character of a Red called Red Lead, Chap. XLI
A color known as red lead is red and it is manufactured by alchemy. The color is good only for working on

panel, for if you use it on the wall it soon turns black, on exposure to the air, and loses its color.

Minium was heavily used throughout the entire world in artwork. Figure 5.21 shows tomb effigies in Salisbury Cathedral. Much of the Cathedral paint was based on red lead. Lists of materials billed for painting in fourteenth-century Italy also show heavy use of minium (Bomgard et al., 1989). In 1371, artists billed the commission of San Pier Maggiore Altarpiece for 1 lb of lead white, 4 soldi, 2 oz of lead tin yellow, 2 solid, 1 lb of lead white, 4 soldi, 1 pound of lead white for making an ash-grey color for putting blue into the vaults, 4 soldi, and for orpiment (a pigment) with minium for the curtain, 6 soldi.

Red lead paints were used very early in history. It has been identified as the red paint on the clay army buried with the emperor who built the Great Wall of China (Ember, 1999) (Figure 5.23). This paint consists of Pb_3O_4 , $CaCO_3$, $Al_2O_3-SiO_2$ and Cu_2O . Red lead was used as a cosmetic as well. Early artwork using red lead is shown in Figure 5.22 *Lady under a*



Figure 5.22. *Lady Under a Tree*, 756 A.D., Japan. Face and cuffs are painted red. The lips are mercury sulfide, the cuffs are red lead. Kazuo Yamasaki. *Technical Studies on the Anceinte Art Objects of Japan*, 1965.

tree. It is from the Shosoin, a temple to the Great Buddha in Nara, Japan and dates back to the 700s A.D.(Yamasaki, 1965)

In the U.S., red lead historically is associated with printers and dyers, mostly concentrated in the Boston area during the 1700s. The recipe for red lead production was known as early as 1751. Lead was stirred over heat in an open vessel until a grey powder called "masticot" was obtained. This was heated to form minium, or red lead. By 1810 three red lead manufacturers existed in Boston (Holley, 1909). The

first paint patent was filed in 1865. (Industry, 1975). These early paints were a mixture of minerals (ZnO and Pb oxides) with KOH, resin, milk, and linseed oil. Litharge (αPbO) or sugar of lead (lead acetate) were added as drying agents. By 1902, the largest market for these heavy-duty paints (Patton's Sun Proof Paints!) were barns. It is tempting to speculate that the traditional American red barn originated in these paints. Figures 5.24 and 5.25 show variations on the American red barn motif by the painters by John Stuart Curry and Homer.



Figure 5.23 The Emperor Qin (259-210 B.C.) Was buried with an army of 8,000 warriors, servants, horses, and chariots at his necropolis of Shihuangdi. The necropolis took 36 years and 700,000 prisoners to build. This warrior's jacket is painted with minium. (Lois Ember, C&E News, Nov. 29, 1999).

Toxicity of Minium

Red lead has been used as a food adulterant. Accum, 1820, cites the following example (Accum, 1820, p. 290):

“A gentleman, who had occasion to reside for some time in a city in the West of England, was one night seized with a distressing but indscribable pain in the region of the abdomen and of the stomach, accompanied with a feeling of tension, which occasioned much restlessness, anxiety, and repugnance to food. He began to apprehend the access of an inflammatory disorder; but in twentyfour hours the symptoms entirely subsided. In four days afterwards he experienced an attack precisely similar; and he then recollected, that having, on both occasions, arrived from the country late in the evening, he had ordered a plate of toasted Gloucester cheese, of which he had partaken heartily.The circumstance was mentioned to the mistresss of the inn, who expressed great surprise, as the cheese in question was not purchased from a country dealer, but from a respectable shop in London.....A servant-maid mentioned that a kitten had been violently sick after having eaten the rind cut off from the cheese prepared for the gentleman's supper. The landlady, in consequence of this statement, ordered the cheese to be examined by a chemist in the vicinity, who returned for answer, that the cheese was contaminated with lead!....the cheese was colored with anotto, of inferior quality and recourse had been had to the expedient of colouring the commodity with vermilion.....The druggist (who sold the vermilion) adulterated with red lead to increase his profit, without any suspicion of the use to which it would be applied....”

Accum also reports that ripe cayenne pepper, is a bright orange-red color and is sometimes adulterated with red lead. This happened in fall 1994 when Hungarian paprika was diluted with red lead oxide (minium) (Figure 5. 26) (Kakosy

et al., 1996), (Nicoloff, 1924).



Figure 5.24. Homer *Snap the Whip* in *Three Hundred Years of American Painting* by Alexander Eliot.

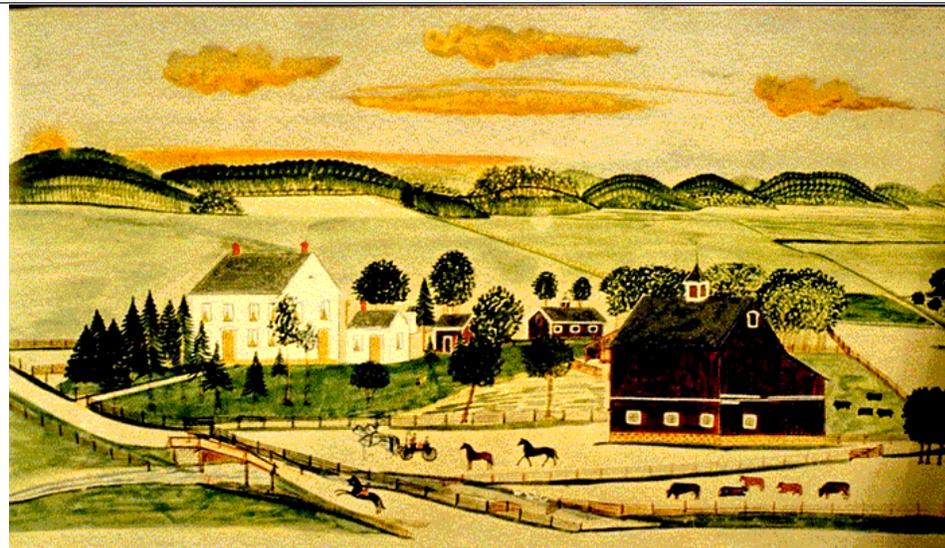


Figure 5.25. John Steuart Curry *Wisconsin Landscape*, in *300 Years of American Painting* by Alexander Eliot.



Figure 5.26. Minium (glass vial) has been used to adulterate paprika. (Author) The brand shown has no connection to lead adulteration.

INKS AND THE ILLUMINATED MANUSCRIPT

History of Paper

The use of lead-based pigments might be supposed important in the art of the illuminated manuscript. Actual chemical and physical characterization of ancient manuscripts is not common due to their fragility (Alexander, 1992, p. 39; Cains, 1990). However, the existing historical record suggests the importance of lead in this art form.

Illuminated manuscripts appear on papyri, parchment, and, more commonly, paper. Time line J.12 gives a time line for the development of writing materials. Early written technology was based on the rolled papyri, which was replaced in Eurasia by the sturdier vellum or parchment (calf/lambskin) by the end of the 1st century A.D. Illumination of vellum showed up in 4th or 5th centuries A.D. in the Book of Kings (Calkins, 1983) with narrative miniatures. Full-page miniatures first appeared in the Ashburnham Pentateuch (6th Century A. D., N. Africa.) The column-style illustration appears to derive from Mesopotamian tradition of scrolls.

Paper was invented by Ts'ai Lun of Sweiyang, Swei-chou. Ts'ai Lun entered the service of the Chinese Emperor Ho in 75 A.D. and was appointed director of the imperial arsenal in 89 A.D. The biography of Ts'ai Lun in the *Annals of the Han Dynasty* describes his invention:

From time of old, documents had been written on bamboo boards fastened together. There was also paper made of silk refuse. But silk was too expensive and the bamboo boards were too heavy, both were inconvenient. Therefore Ts'ai Lun conceived the idea of utilizing tree-bark or bast-fiber, hemp and also old rags and fishing nets for making paper. In A.D. 105 he submitted his invention to the emperor, who lauded his skill. From this moment there was no one who did not use his paper, and throughout the empire, all people called it the 'paper of the honorable Ts'ai'.

For this feat, he was made a marquess in 117 A.D. by the Dowager Empress. When she died, court intrigue turned against him, and he committed suicide by poison.

Papermaking remained a Chinese monopoly until 751 when the Arabs defeated the T'ang army and carried off papermakers to Samarkand. The papermaking industry was encouraged in Baghdad during 794 A.D. by the Caliph Harun ar-Rashid. By the 950s, paper had replaced papyrus in the Arab world. In 1150 A.D., a paper mill was established at Fabriano, Italy. Papermaking made its way to England only after the Edict of Nantes was revoked in 1685 and French exiles moved to England and America. (The Edict of Nantes was proclaimed in 1598 by Henry IV of France to promote religious tolerance. Henry IV was originally the leader of the Protestant Huguenots, but stated that "Paris is worth a Mass" and converted to Catholicism so that he could ascend the French throne in 1589.)

History of Pens

Writing not only consists of the material written on but also of the tool for writing. Early scribes used styli to make marks on wax or clay. When the surface worked on was wax the styli could be of nearly any durable media, such as metal. The use of a metal stylus for marking a surface continued in the production of illuminated manuscripts. The vellum surface was ruled first for page margins and line spacing. The ruling was accomplished by the use of a metal stylus, often lead. Figure 5.27 shows an image of a scribe ruling a surface prior to working it (de Hamel, 1992). Figure 5.28 shows tools used for marking, including a lead stylus marked with the name of the manufacturer Rogerus (De Hamel, p. 23). Figure 5.29 shows the types of marks that could be obtained using carbon, lead, and lead alloys (Petroski, 1990).

Once paper making arrived in Europe there

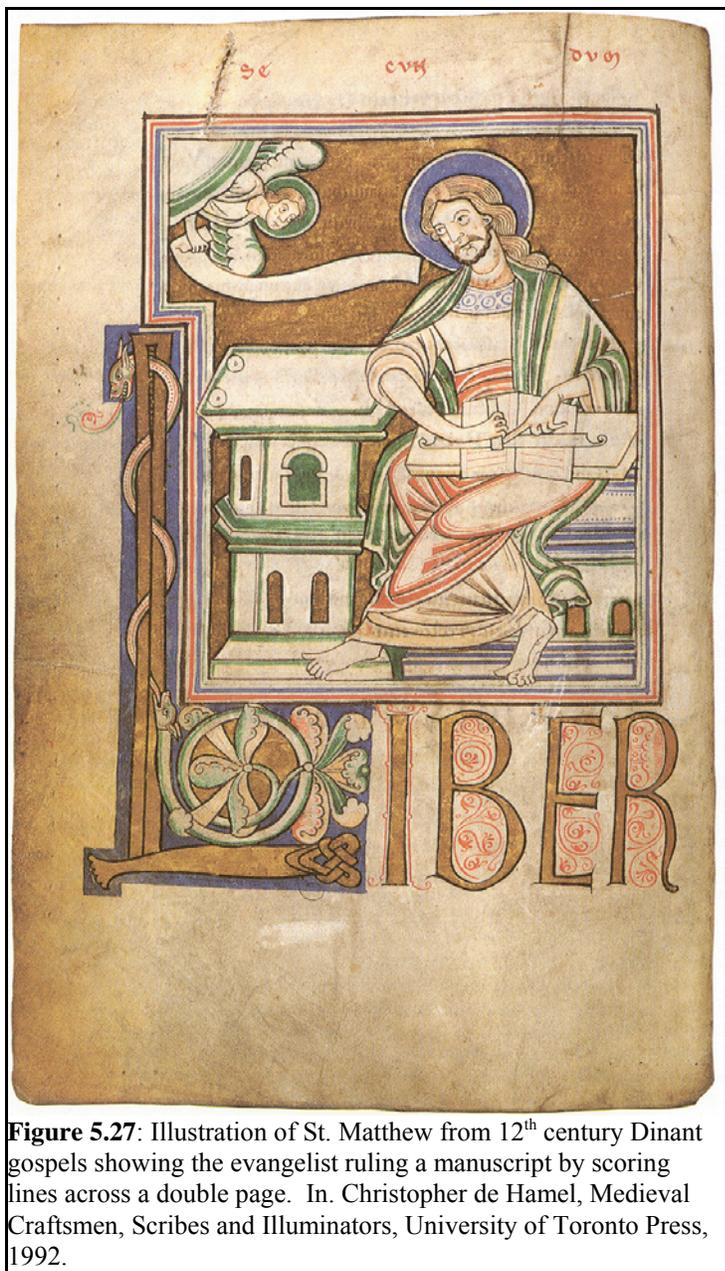


Figure 5.27: Illustration of St. Matthew from 12th century Dinant gospels showing the evangelist ruling a manuscript by scoring lines across a double page. In. Christopher de Hamel, *Medieval Craftsmen, Scribes and Illuminators*, University of Toronto Press, 1992.

was a period in which the art of metalpoint (or silverpoint or meticulous drawing) flourished. In this form of art a metal stylus was used to make marks on a specially prepared surface. The surface described by Cennino Cennini (1437) was dried chicken bones, burned until very white, then moistened with spittle.

Cennini wrote (Cennino d'Andrea Cennini, *The Craftsman's Handbook "Il Libro dell' Arte"* translated by Daniel V. Thompson, Jr. Dover Publications, N.Y., 1960)

You may also draw, without any bone, on this parchment with a style of lead; that is, a style made of two parts lead and one part tin, well beaten with a hammer.

On paper you may draw with the aforesaid lead without bone, and likewise with bone. And if you ever make a slip, so that you want to remove some stroke made by this little lead, take a bit of the crumb of some bread, and rub it over the paper, and you will remove whatever you wish.

For practicing Cennini recommends preparing a boxwood panel which has been well smoothed.

And when this little panel is thoroughly dry, take enough bone, ground diligently for two hours, to serve the purpose; and the finer it is, the better. Scrape it up afterward, take it and keep it wrapped up in a paper, dry. And when you need some for priming this little panel, take less than half a bean of this bone, or even less. And stir this bone up with saliva. Spread it all over the little panel with your fingers.

You must know what bone is good. Take bone from the second joints and wings of fowls, or of a capon; and the older they are the better. Just as you find them under the dining-table, put them into the fire; and when you see that they have turned whiter than ashes, draw them out, and grind them well on the porphyry.

This surface and that of paper could then be drawn with a lead stylus, termed a *plummet*, or a silver stylus. The technique was also used extensively by artists from the 1300s to the early 1600s. Metalpoint was superior to chalk in that it did not smudge and fade as compared to ink. It was portable. The artist Durer had a

“sketchbook” of prepared paper he used along with his stylus for journeys. The 1526 silverpoint sketch of Albrecht Durer *Sitting bishop and portrait of a man with a fur cap*, (Figure 5.30) was analyzed nondestructively in 2002 and found to have an underlying set of leadpoint strokes which indicate the

presence of a preliminary sketch prior to the silverpoint

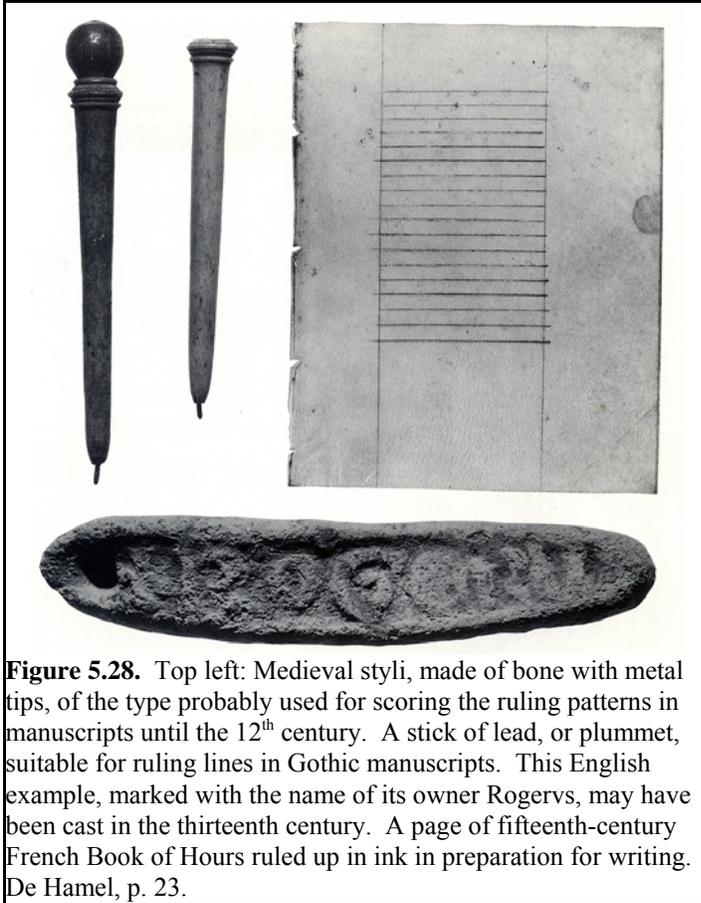


Figure 5.28. Top left: Medieval styli, made of bone with metal tips, of the type probably used for scoring the ruling patterns in manuscripts until the 12th century. A stick of lead, or plummet, suitable for ruling lines in Gothic manuscripts. This English example, marked with the name of its owner Rogervs, may have been cast in the thirteenth century. A page of fifteenth-century French Book of Hours ruled up in ink in preparation for writing. De Hamel, p. 23.



Figure 5.30: Durer's *Sitting Bishop and Man in Fur Cap*, 1526 in silverpoint is underlain by a prior sketch in leadpoint.

execution or extra strokes added to increase the contrast in the drawing (Reiche et al., 2002). The paper coating used by Durer was bone as evidenced by the presence of calcium and phosphate, unlike some media which includes small amounts of added white lead.

Metal point styli were replaced in the late 1500s by styli containing graphite, which was described by Konrad Gesner in his 1565 book *De Rerum Fossilium Lapidum et Gemmarum Maxime, Figuris et Similitudinibus Liber* as

a sort of lead (which I have heard some call English antimony), shaved to a point and inserted in a wooden handle

Graphite was mined from pits at Barrowdale, Cumberland where it was known as plumbago, black lead, *kellow*, *killow*, *wad*, or *wadt*.

The Illuminated Manuscript

Once papermaking was well-established, bookmaking and decorative book pages began to flourish. In the Western world, bookmaking initially remained the province of monk copyists. Many of the copied books were illuminated as a way to signal the sacredness of the material (Figure 5.31) and to help in finding text while reading. The art of illumination expanded beyond emphasis or rubrication of chapter headings

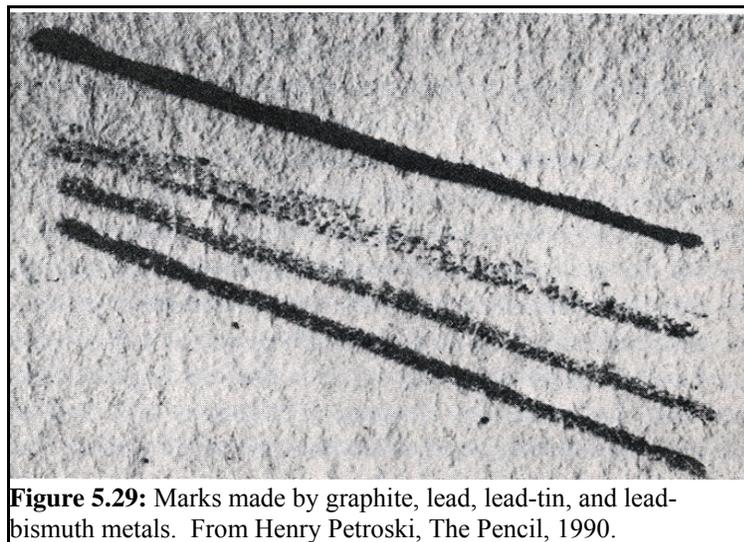


Figure 5.29: Marks made by graphite, lead, lead-tin, and lead-bismuth metals. From Henry Petroski, *The Pencil*, 1990.



Figure 5.31 An illuminated manuscript with rubrication.

into true miniaturized art. Miniaturized art especially flowered in Persia, with the creation of the Northern Indian Moghul Empire, and through the importation of Persian architecture and arts into India.

The first known Western (as opposed to Chinese) text on bookmaking was written in the Islamic world. Mu izz ibn Badis authored it around 1025 A.D.. Badis gives a recipe for rose-colored ink:

An ounce of lead (usrunj zarqun = castilian azarco = Persian adhargun “color of fire”. (Minium) is pulverized on a stone. On it are thrown a dirham of natron (an impure sodium carbonate) and two dirhams of gum arabic. It is rubbed with the hand until it is

good. Write with it (Levey, 1962, p. 23).

Another recipe is for rose-colored ink:

Two parts of white lead are taken and one part of red lead. They are put together with vinegar in a new pot which is then luted with clay and hair. The pot is put into a glass furnace in the upper part for three days. It is then taken out and the material pulverized. On it is poured water of white gallnut. A bit of gum arabic is put into it. Write with it. (Levey, 1962, p. 23).

The earliest Western European comments on



Figure 5.32. The small figure in the center of the manuscript face was originally white lead and minium which has darkened on exposure to modern air to lead sulfide.

Table 5.6 Metals in Comic Books in 1970 Spain/ ppm

<u>Lead</u>	<u>Chromium</u>
4280	420
2450	270
910	115
780	140
490	55
295	35
150	15
20	0

Table 5.7: 1992 survey of metals in inks, ppm

<u>Metal</u>	<u>Red</u>	<u>Blue</u>
As	<1.0	<1.0
Cd	15	10.5
Cr	<2	<3.3
Cu	2	25.4
Hg	<2.5	<3.1
Ni	2.4	1.6
Pb	<2.7	<3.5
Sb	<25	<34
Se	<0.9	<1.0

bookmaking appear in recipes for limning. Recipes for limning (illuminating manuscripts) followed the same basic recipes as the colorants for paints. Recipes for limning appear in *Mappae Clavicula: A Little Key to the World of Medieval Techniques* (Smith and Hawthorne, 1974), in Cennini, Theophilus, and in the works of anonymous art treatise of the 14th century (Thompson and Hamilton, 1933). Monastery purchasing records also indicate widespread use of minium. B. Guerard states that 10 pounds of minium and 3 pounds of dragonsblood and indigo were delivered to the abby of Saint-Germain during the regime of Charlemagne (Guerard, 1844).

Miniatures in illuminated manuscripts derive their name not from their size but from use of minium red-ink (Alexander, 1992; Calkins, 1983, p. 15). Du Cange says that the word miniature came from the phrase *minigraphia criptura cum minio ficta* where minio stands for minium (Du Cange, 1845). This liberal use of the red pigment minium also gave rise to the term “red-letter”. “Red-letter” is an adjective used to describe something that is memorably happy, especially a “red-letter day”. This usage derives from the *rubrication* of feasts in the church calendars.

Rubrication means to arrange, write, or print as a *rubric*. A rubric is a part of a manuscript or book, such as a title, heading, or initial letter, that appears in decorative red lettering or is otherwise distinguished from the rest of the text.

Figure 5.31 shows the uses of red pigment to set the letter off in an illuminated manuscript. The first example is a page from the Winchester Bible, (1100 A.D.) (Alexander and Braziller, 1978).

Scrolls from the *Diamond Sutra* (the world’s earliest completely printed book) were found among 60,000 paper manuscripts in a Buddhist library at Dunhuang, an oasis town in Gansu Province, China, along the Silk Road. The library was sealed before 1025 and rediscovered in the early 1900s. The *Diamond Sutra* documents have been analyzed by fast atom bombardment mass spectrometry (FAB-MS) and liquid secondary-ion mass spectrometry (L-SIMS) ((Gibbs and Seddon, 1995). In addition to identification of plant-based alkaloid yellow, non-destructive Raman spectroscopy was used to identify lead mineral pigments such as minium and lead carbonate (Gibbs et al., 1997). This method has identified the darkening of some of the Byzantine/Syriac Gospels (Figure 5.32) as the decomposition of cerusse to lead sulfide (Clark et al., 1997).

A similar study has been performed on 13th century Persian encyclopedia of Zakariya ibn Muhammad ibn Mahumud Abu Yahya (Qazwini) (Clark and Gibbs, 1998).

The use of mineral pigments in inks has continued unbroken from the time of the earliest illuminated manuscripts to the present. By the 1970s, U.S. inkmakers were warned to find alternative colors because of impending legislation (Stubbs and Manolakis, 1974). The legislation sought to reduce children’s contact with lead, cadmium, mercury, and chromium, through ingestion of colored printed material. Table 5.6 is based upon Fowles’ work demonstrating the large amount of metal in comic books (Fowles, 1976).

A more recent tabulation of red and blue polyamide inks shows that they have lower lead. However, cadmium has not been as reduced (Donvito et al., 1992) (Table 5.7).

In the *American Journal of Public Health* one physician estimated the amount of lead that could be ingested from spitballs from leaded inks, in an article titled “Spitballs may be Hazardous to your Health” (Joselow and Bogden, 1974). Assuming that “moderately effective” spitball contains 25 cm² of newsprint with 140 mg anhydrous pigments, each

spitball would contain 100 µg lead. This amount of lead would be significant if one consumed 2 or 3 spitballs a day.

In 2002, imported Tamarind candies from Mexico were identified as exceeding 21,000 ppm lead. The candies were contained in a printed orange-red wrapper which was the source of lead (Zuniga, 2002). Other imported ink and paints which contain lead include the McDonald's bobblehead Dolls of Chicago Bears Brian Urlacher and Anthony Thomas (Hananel, 2002).

Replacement Pigments

Replacement pigments for reds and yellows took some time in coming. Color chemistry was focused upon the textile industry. The textile industry in England expanded rapidly after 1840 when the mechanization of cotton production in Manchester made this cloth cheap. Another large locus of color chemistry (dyeing) was at the silk center of Lyons in France. The first major work on dyeing, *Lecons de chimie applique a la teinture*, was published by the chemist Michel Eugene Chevreul head of Gobelins dyeworks in Paris in 1829-30.

Color chemistry is intimately intertwined with modern German history as well. Germany had a long history of fragmented states despite its unification under Charlemagne (Karl the Great, 768-814 A.D.) and the associated naming of the Holy Roman Emperor from among the German states. The fragmented states assumed control of the Emperor's election by 1200 A.D. Following Luther's anti-church thesis against Catholic indulgences, some German states split off into the Protestant Schmalkadie League which opposed to the Emperor Charles V (1520-1558 A.D.). The schism of the states grew further under the alchemist Emperor Rudolf II (1576-1612). The tensions finally broke out fully in the Thirty Years' War (1618-1648) in which 3/4 of the population was lost. The states were reassociated following the Napoleonic Wars with English encouragement in the hope of counterbalancing French power. The German Confederation was "founded" with the Congress of Vienna of 1815.

The Napoleonic Wars also had a major impact on the system of education. The 42 medieval model universities of the German speaking world were impoverished, and fully half disappeared as a result of war. In 1810, Wilhelm von Humboldt proposed scrapping the medieval university system for one dedicated to experimental and pure investigations (Procter, 1991, p.71). One result of the new university system was an explosion of new intellectualism. Justus

Liebig put forth his 1840 text on the application of chemistry to agriculture. One of his students, August Wilhelm Hofmann (1818-1892) identified aniline, a purple dye, from coal tar in 1843 (Travis, 1993, p. 32). The year of 1845 was a time of great popular unrest that ultimately lead to Marxism. During that period Hofmann accepted the position of the first director of the London Royal College of Chemistry. The college was established with a mandate of usefulness to industry and agriculture. Because it did not make rapid progress in agriculture, the school became part of the Government School of Mines in 1853.

One of Hoffman's students was William Henry Perkin (1838-1907). Perkin entered the Royal College of Chemistry in 1853 at the age of 15 and worked on the aniline process. In his own home laboratory he studied how to obtain a low cost aniline derived from nitrated, then reduced, benzene. Nitration was the largest cost of aniline production because it required quantities of nitric acid (see Chapter 6). Perkin used iron in acetic acid as an electron source for the reduction. Perkin commercialized the process, but was unable to convince the industrial dyers of calico (cotton) to use his dye. It could not be "fixed" (bonded to the cloth), and it was still too expensive. (Cotton lacks nitrogen groups which can be used to covalently bind the dye to the surface.)

Napoleon III was first elected president of France in 1848, and then emperor in 1852. His court was keenly interested in the color purple, the supply of which could not be satisfied by the animal or mollusk dyes that were used in France. By August 1857 the *couleur mauve* was the rage of the world, particularly with the Empress Eugenie. The success of the purple color was referred to by an acquaintance of Perkin,

I am glad to hear that a rage for your colour has set in among that all-powerful class of the Community - The Ladies. If they once take a mania for it and you can supply the demand, your fame and fortune are secure.

French silk dyers broke the high prices of the animal-dye monopoly by joining forces with Perkins' firm in 1858. A patent was produced for his aniline process. French colorists devised a way of fixing the dye to cotton and then opened up a booming market in colored prints.

Lovely woman is just now afflicted with a malady which apparently is spreading to so serious an extent that it is high time to consider by what means it may be checked. As the complaint is quite a new one, doctors disagree of course as to its origin and nature. There

are many who regard it as of purely English growth and from the effect which it produces on the mind contend it must be treated as a form of mild insanity. Other learned men, however, including Dr. Punch, are disposed rather to view it as a kind of epidemic, and to ascribe its origin entirely to the French.... the mauve complaint is very catching with us.(Travis, 1993, quoting Punch 1859)

The dyers in Lyon began experimenting with other pigments. They were influenced by a paper Hoffman read at the *Academie des Sciences* in Paris. He indicated that coal tars could be extracted to give a red pigment. His findings ultimately led to *magenta*, or aniline red, as well as aniline blue, apparently discovered accidentally by a worker. The German firm of dye merchant Friedrich Bayer entered the aniline dye business in 1862 with one employee working on kitchen stoves. This business became so dominant that it displaced the American aniline dye industry that located at Albany, New York in the early 1860s. With the close of the American Civil War and the lifting of trade restrictions, the Germans made inroads into the American red pigment industry by 1870.

Another important early dyer was Heinrich Caro (1834-1920). Caro was trained as a dyer at the *Gewerbe Institut* in Berlin from 1852 to 1855. He traveled to England to purchase machinery in 1857. He was hired by the firm of Roberts, Dale, and Co. as an analytical chemist in 1859. This firm had been founded by John Dale, a former apprentice chemist and druggist and manager of a calico printing work. Caro also began experimenting on anilines, producing a patent for copper salts as oxidants in 1860.

Academic color chemistry continued to advance. Hoffman remained an academic chemist doing theoretical work on the benzene derivatives. He developed a rudimentary theory on the subject by 1863. In 1865 Hoffman left the Royal College of Chemistry in London and became a professor of the University of Berlin (founded by Humboldt).

The year 1866 was a momentous one for Germany. Prussian Chancellor Otto von Bismarck allied north and south German states to defeat Austria. A resurgence of German nationalism followed. Many German emigrants returned home. During the same year, Caro returned to Germany for an academic career in Heidelberg, as well as consulting work with *Badische Anilin und Soda Farbbik (BASF)*.

In 1870, Napoleon III attempted to oppose the growing power of the consolidated German States and was defeated and deposed. The next year William I of Prussia was declared Emperor of unified Germany.

Chemical industry began to flourish under the new state.

By 1874, Bayer's firm hired its first university-trained organic chemist. By the late 1800s, organic chemistry was well underway in Germany and organic dyes were found for the yellow hues. Yellow quinoline was introduced in 1882 by E. Jacobsen, yellow naphthol in 1879 by H. Caro, and Hanza yellow by the German manufacturers Meister, Lucius and Bruning just before World War I (Zollinger, 1987).

Although organic dyes were discovered and applied to the textile industry, they were not immediately used in the paint industry. The criteria for a good paint are color, drying ability, and reflectivity. The dyes did not polymerize (dry) well with the varnishes and oils of the times. They had little reflectivity when in the oil matrix. Nor could they scatter light as the particulate mineral pigments could. The full adoption of organic dyes in the paint industry did not occur until after these problems were resolved, and synthetic polymers such as the polyenes were developed (1938). Reflectivity remained an issue. It was solved through the addition of TiO_2 to the paint mix. Organic dyes bond to TiO_2 .

Other Uses of Lead in Paints

Lead as a Drying Agent

The replacement of yellow chrome by organic dyes was difficult. Organics are not crystalline and they lack an appropriate particle size to give good hiding power. A new technology for organic dyes is to coat TiO_2 particles with the pigment to achieve the necessary hiding power and refractive index (Cowley, 1986).

Mineral pigments not only provide color but opacity, reflectivity, anti-corrosion properties, and fast drying ability. Lead is a natural for all of these desirable properties. As an additive, lead is used, not surprisingly, as a mildewcide (Gooch, 1993), a corrosion inhibitor, a catalyst in the polymerization reactions, and an internal drier. (An internal drier allows drying to proceed internally as well as at the coating edge). Lead naphthate salts are used to assist in oxygen uptake. Given the partially covalent nature of lead bonding to oxygen, the ability of lead to enhance oxygen uptake within the paint and to facilitate O-O bond breaking to initiate radical polymerization should not be surprising. The polymer/organic dye-based industry had to wait until similar properties could be achieved without lead.

The same driers are used in inks. The

requirements of inks are similar to paint. Printing inks consist of pigment, varnish, solvent, and metallic drier. The varnish fixes the pigment to the paper so that it does not rub away and provides gloss for contrast with the paper. The drier catalyzes the drying process. Typical driers in the printing industry were lead naphthenate, litharge, and red lead. The role of the drier is to promote oxygen content throughout the entire varnish for even drying. Thus the drier acts as an oxygen carrier when dissolved in oil, requiring a variety of stable valence states.

Recipes for good drying oils are given in the medieval art texts compiled by Mrs. Merrifield.

According to Lebrun drying oil was prepared by suspending a piece of rag containing umber and minium in a vessel with nut-oil and boiling it. The mordants described in the Paduan MS and the Riposo of Borghini greatly resemble this drying oil. In the first, ochre is added to the other ingredients; in the second, giallorino, calcined bones, and burnt vitriol. Besides white-lead and minium, litharge, the semi-vitrified oxide of lead, was employed as a dryer for oil. The Jesuit, Father Lana, recommends, for this purpose, two ounces of litharge for each pound of oil (Merrifield, 1967).

Lead as an Anti-Corrosion Coating

Red lead Pb_3O_4 paints not only have a high refractive index but have a role as an anti-corrosion inhibitor. This is why they have been heavily used in primers for metallic structures. In 1987 it was estimated that 80% of all bridges nationwide had lead primer and that 23 to 40 states continued to use lead based primers (Garner et al., 1993). The most common paint choice for iron-based building structures has also been red lead.

Chapter 5 Part II: Chemistry of Paint and Color

Perception of Color

In the past, color was thought to reside in the object, not in the reflected light. Prism experiments by Sir Isaac Newton (1642-1727 A.D.) indicated that light contains all the colors. His finding was contrary to the received wisdom of the ancients. No less an authority than the Greek philosopher Plato declared in 388 B.C.:

There will be no difficulty in seeing how and by what mixtures the colors are made...He, however, who should attempt to verify all this by experiment would forget the difference of the human and the divine nature. For God only has the knowledge and also the power which are able to combine many things into one and again resolve the one into many. But no man either is or ever will be able to accomplish either the one or the other operation.

Aristotle, (350 B.C.), notwithstanding Plato's shrug of the shoulders, declared that light has no color:

Thus pure light, such as that from the sun has no color, but is made colored by its degradation when interacting with objects having specific properties which then produce color.

Newton's experiment was quite revolutionary. While his finding was readily accepted among scientists, the artistic community had prominent holdouts as late as the mid-1800s. Johann Wolfgang von Goethe (1749-1832) who not only was well known as poet and author, but was an artist and experimentalist, ridiculed Newton's theory of light in "moderate" language. The theory is:

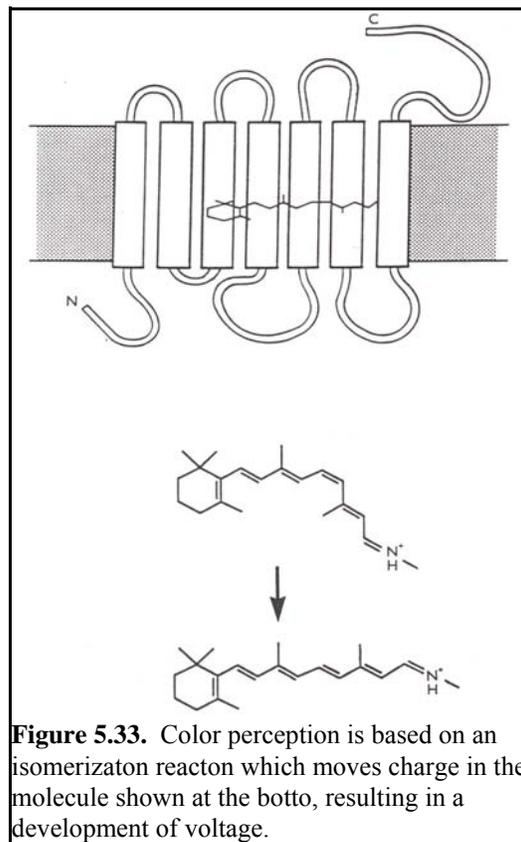
contra factual, a fairy tale, hocus-pocus, and word-rubbish. Newton himself uses *sophistry, is stubborn, shameless and uses self-deception bordering on dishonesty.* The followers of Newton are *captious and dishonest, utter thoughtless idiocies, and spend their time gluing, mending, patching, and embalming Newton's theory,* as well as are *incompetent, obscurantist, lazy, self-satisfied, merciless and persecutorial* (Sepper).

The "real" explanation is that light is composed of a variety of wavelengths. When it

interacts with matter some of the wavelengths are removed. The remaining wavelengths of light are observed by the eye and interpreted as color.

A beam of sunlight (white light) can be passed through a prism and separated into a series of *monochromatic* bands of light. Monochromatic light can also come from a laser source that emits a light of a narrow wavelength regime (<2nm). The light so formed can be perceived by the human eye as color.

The eye's measurement of those colors is a complex phenomena that originates in a photo-induced conformational change of a molecule. The pigment 11-cis retinal consists of a fixed dipole at the end of a diene chain (Figure 5.33) (Baylor, 1995). Under the action of light the diene chain undergoes a *cis/trans* conformation that lengthens the compound. The result is a displacement of the permanent dipole, or a



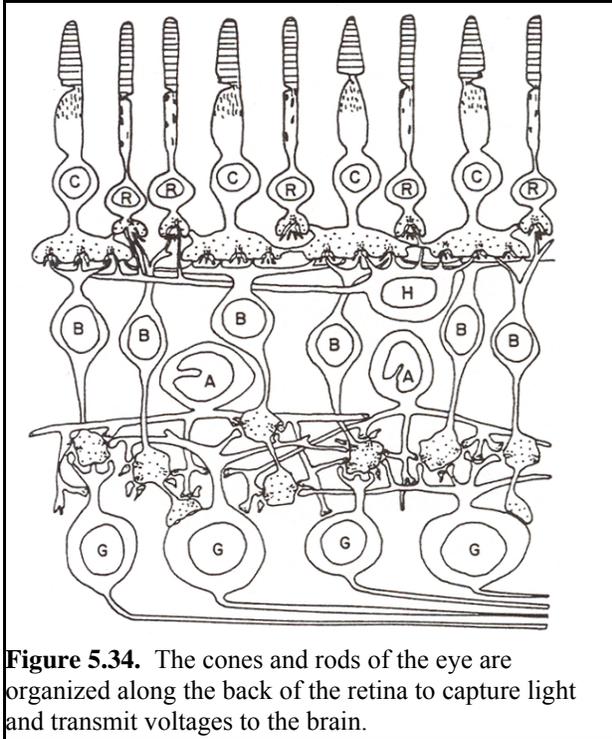


Figure 5.34. The cones and rods of the eye are organized along the back of the retina to capture light and transmit voltages to the brain.

separation of charge in space. This is sensed as a voltage change that transmits as a signal to the brain.

The primate retina contains three sets of *cones* and one set of *rods* (Figure 5.34) (2). The three cones create voltage signals over different wavelength regions with variable sensitivity (Figures 5.35 and 5.36) (Nassau, 1983). Their response is relatively weak as compared to that of rods. The rods pick up minute numbers of photons over the whole wavelength region and give sensations of intensity, or dark and light. The perception of color derives from the processing of voltages from all three cones and from the rods:

$$[5.1] \quad \text{Color} = V_{\text{blue}} + V_{\text{green}} + V_{\text{red}} + V_{\text{total photons}}$$

When the signal from each cone and rod is intense, the eye perceives “white” light. The perception of white light involves all wavelengths of light simultaneously.

Because color perception is the sum of four separate signals, each originating across a broad range of wavelengths, the same color perception can be obtained by several different combinations. For example, a monochromatic yellow beam at 580 nm creates a higher voltage signal from the green cones than from red, with little input from the blue cones. The color yellow can also be obtained by combining light at 510 nm with light at 650 nm. The combination of these two beams excites both the green and red cones as does light at 580 nm. In the same fashion there are several ways to arouse the perception of pink.

Thus far we have assumed that the light stimulating the eye is composed of laser-like light beams. When the light is obtained by reflection off an absorbing surface the beams of light are not “monochromatic” and the perception of color is shaded by this lack of “purity” known as saturation. For example, when the color magenta is obtained by “pure” light between 480 and 600 nm a purplish tinge is obtained. Magenta obtained by light that is not pure (unsaturated) results in a pinkish tinged magenta.

WHITE Absence of Color

White paint does not absorb any light between 400-700 nm. In Chapter 4, it was shown that color for glasses arose from the transition metal d orbital interaction with light.

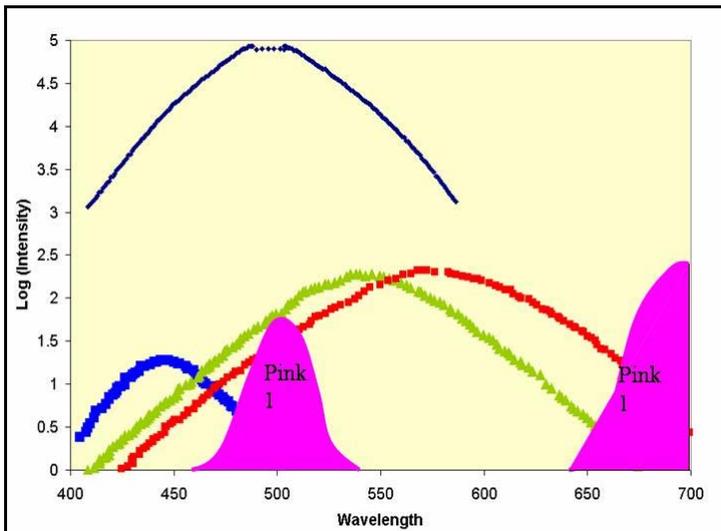


Figure 5.35: The relative intensity of stimulation of the three cones (blue, green, and red) and the rods. When light centered around 500 and 675 nm is present the stimulation of the blue cone is proportional to the area of pink under the blue line, while the green cone stimulation is the sum of the areas under the green line corresponding to stimulation at ~500 and ~675 nm. Similarly, stimulation of the red cone consists of two areas. The total stimulation of each cone and the total summed stimulation are interpreted by the eye as the color pink (Compare to Figure 5.36 and 5.37).

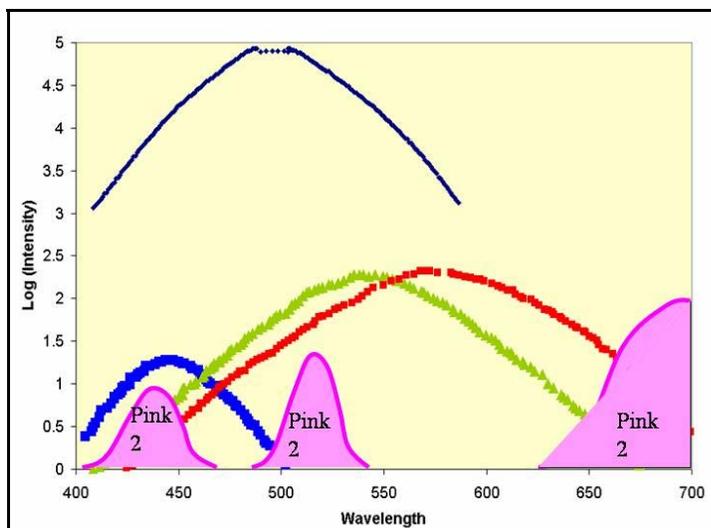


Figure 5.36. The stimulation of the three cones by an alternative set of wavelengths results in the same proportional intensity of blue, green, and red as in Figure 5.35 (see Figure 5.37).. Data and concept adapted from Nassau (1983).

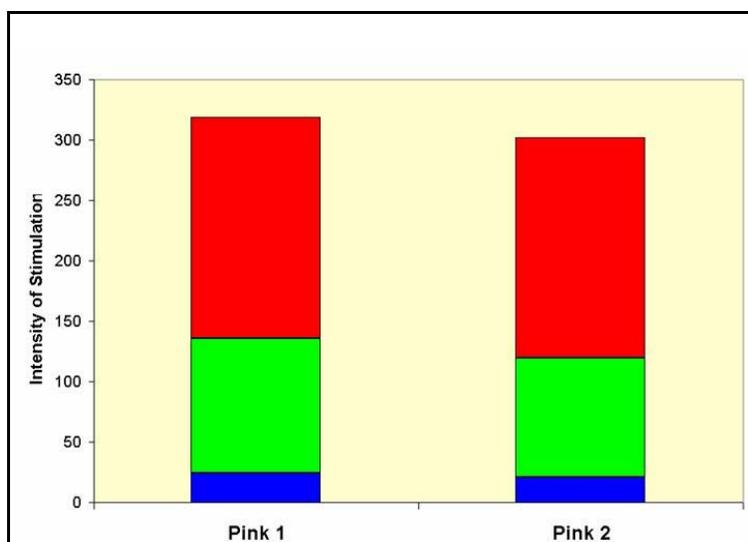


Figure 5.37: The total summed stimulation of the three cones and the proportional stimulation of each cone is similar for two different combinations of wavelengths shown in Figures 5.35 and 5.36. Each result in a perception of the color pink.

The electron configuration of Sc^+ is s^2d^0 and that of Ti^{2+} is s^2d^0 . Zn takes the opposite tack. It conserves a filled d orbital and removes s electrons so that Zn^{2+} is s^0d^{10} . With all d orbitals filled, Zn^{2+} does not have any vacancies into which it can promote electrons. Other possibly colorless atoms are the cations formed from outside the d block - Ca^{2+} , Mg^{2+} , Pb^{2+} , Al^{3+} , Sn^{2+} , and Sb^{3+} , or Bi^{3+} . Notice that this list does not include any monovalent cations.

Why? A good white pigment must also have low solubility when the cation is combined with an anion. Solubility rules are based upon charge density and radii of combining species (Table D.1). Most monovalent cations form soluble salts due to their high charge density. For the same reason, many anions must be ruled out. The remaining candidates are only among the more insoluble oxides of the above cations.

The paint must be able to coat a surface and “hide” it, that is, to reflect all the light from the upper surface. Reflection is controlled by the index of refraction and the particle size of the pigment. Most binders, for example, egg tempura, have an index of refraction of 1.35. Decent pigments have refractive indices ranging from 1.5 to 2.8. $\text{Al}(\text{OH})_3$ is good in glazes because it has a refractive index of 1.54. TiO_2 with a refractive index of 2.72 has true hiding power as a white paint.

Potential white pigment candidates, based on their solubility and lack of d electron activity are PbCO_3 , TiO_2 , ZnO , ZnCO_3 , SnO_2 , and antimonyl oxides (Table D.18). Because they lack d electron activity, whiteness is expected for all of them, although some of them do give color anyway. This effect arises from a charge transfer band described below.

Suitable candidates for a white pigment lack d orbital electrons capable of making a transition from a low lying d-orbital to a vacant high-lying one (Table D.18).

This means that no first row transition metals but Sc, Ti, and Zn are useful as white pigments. Sc and Ti are candidates because, when ionized, they remove electrons from the s orbital and not the filled d orbital.

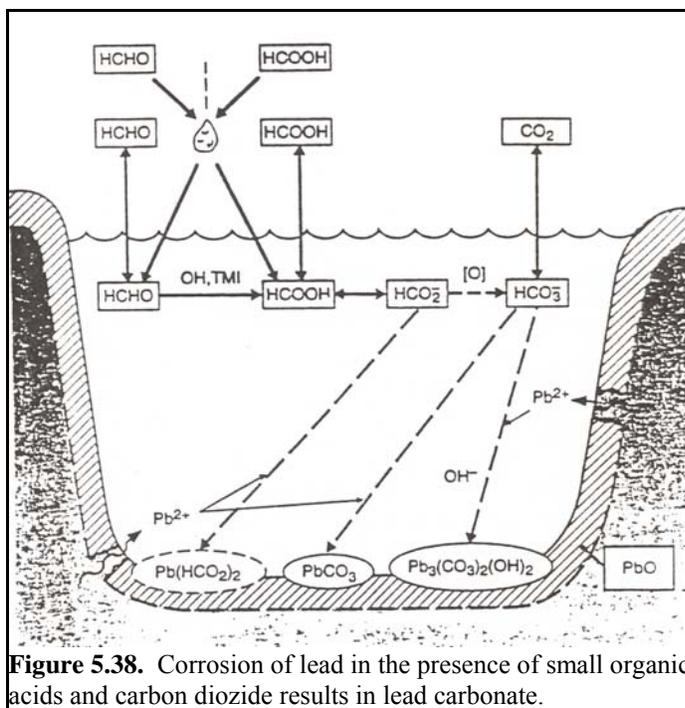
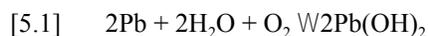


Figure 5.38. Corrosion of lead in the presence of small organic acids and carbon dioxide results in lead carbonate.

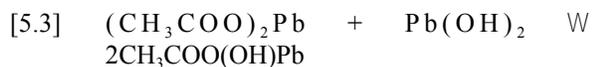
Making Cerruse

Recipes for cerruse production involve placing lead sheets in a pot of wine or vinegar and the pot in a pile of horse dung. The pot is loosely sealed. Lead carbonate is harvested after several months.

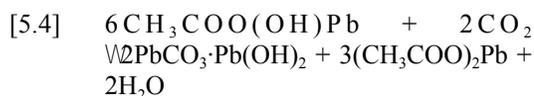
The chemistry of cerruse production (Figure 5.38) can be discerned from modern studies on lead metal corrosion due to atmospheric gases (Graedel, 1994). Lead exposed to air has a 3-6 nm PbO surface layer. The porosity of this layer is due to the lone 2s pair of electrons on lead oxide. Over this layer, perhaps ten layers of water exist at 100% relative humidity.



The volatilized acetic acid dissolves in the water layer, loses a proton, and produces an acidic surface which conducts charge well. The resultant acetate anion precipitates with lead ion moving through the porous PbO underlayer. This reaction is termed "aggressive" (Donovan and Stringer, 1972).



Once the acetate layer is formed, the CO_2 liberated during fermentation dissolves into the acidic surface water to form carbonate. The pH eventually rises high enough to precipitate a mixed layer of PbCO_3 and hydroxides, or cerrusite.



No viable alternatives to lead based white pigments were available until the manufacture of titanium was perfected. Titanium was not discovered until the 1700s, and its bulk manufacture required the ability to routinely handle high melting points (1660 °C).

After rutile, TiO_2 , was successfully manufactured, lead was slowly replaced in white pigments in the U.S. (Replacement was faster in Europe based on a ban of lead enacted in the early 1920s). Titanium can be used as a white pigment because Ti^{4+} in TiO_2 exists as a d^0 species with no excitable electrons. Therefore it cannot undergo

a crystal field-based electron excitation in the visible region (Henrich and Cox, 1994). In addition, TiO_2 solid is mostly ionic in character. Its bandgap is thus in the colorless region. It absorbs no visible light and consequently is observed as white. TiO_2 is also as insoluble as PbCO_3 . TiO_2 has a very good molar refractive index due to the number and efficacy of packing of oxygens in the crystal lattice.

Color of Metals

In Chapter 3 it was seen that a particular composition of Cu/Sn gave a bright mirror finish. The chemical explanation for the silver color of the mirror bronze is due to the action of the electrons in the electron "sea" of the metal.

In a covalently bound solid, electrons are localized within the bond created from the atomic orbitals of the two combining atoms. This bond is separated energetically from other spatially close bonds. Close by, the electron sees its own the anti-bonding orbital, which at visible light and ambient temperature is inaccessible. In a metallic solid atoms are completely delocalized. Because of the close energy levels between spatially close bonds (a band of bonds) the electron is free to explore space and move

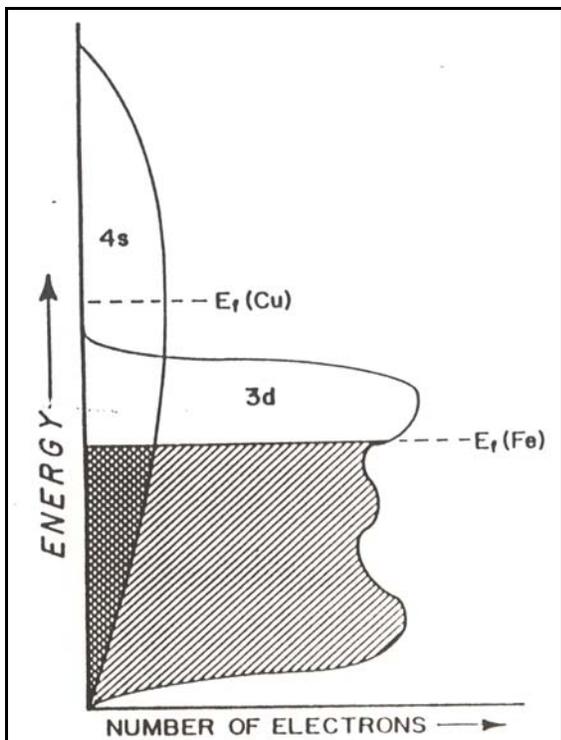


Figure 5.39 Plot of the number of electrons (x axis) of a given energy (y axis). Cu has primarily 4s electrons of low energy while iron has a larger number of 3d electrons of low energy. Original source: J. Slater, Quantum Theory of Matter, 1951, McGraw-Hill

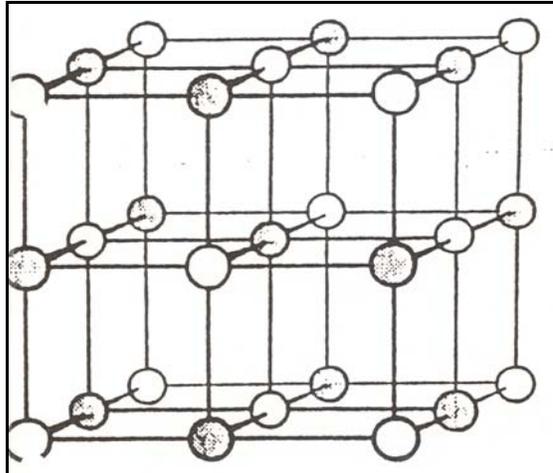


Figure 5.42: Structure of lead.

freely. Electrons fill all the lower half of the energy states (Figure 5.39).

Because there is no energy gap between electrons in occupied orbitals and electrons in unoccupied orbitals it can be predicted that the metal absorbs any wave length of light. It can then also be predicted that all metals should be black. Metals, however, adsorb so much light, that light does not have the ability to penetrate the material much further than a few hundred atoms. The absorption of light causes an electron to move from an occupied orbital to an unoccupied orbital with a concurrent change in the electric field. This energy is re-radiated from the 100 atom thick layer. The re-radiated light is observed as high reflectivity. Metallic luster is the result of very strong absorption.

The color perceived (gold is gold) is based on the total number of electrons capable of making high or low energy transitions. This, in turn, is based on the electronic structure of the metal. Copper, for example, is $3d^{10}4s^1$, with 11 electrons, but only 1 in the s orbital (Figure 5.39), so the density of states making an s to d transition is lower. These s to d transitions are of high energy and occur in the blue region. Blue light is not absorbed and therefore not re-radiated or reflected. On the other hand lower energy transitions in the red are absorbed and re-radiated and so we observe copper to be reddish in color (Figure 5.40).

Iron has an electron configuration of

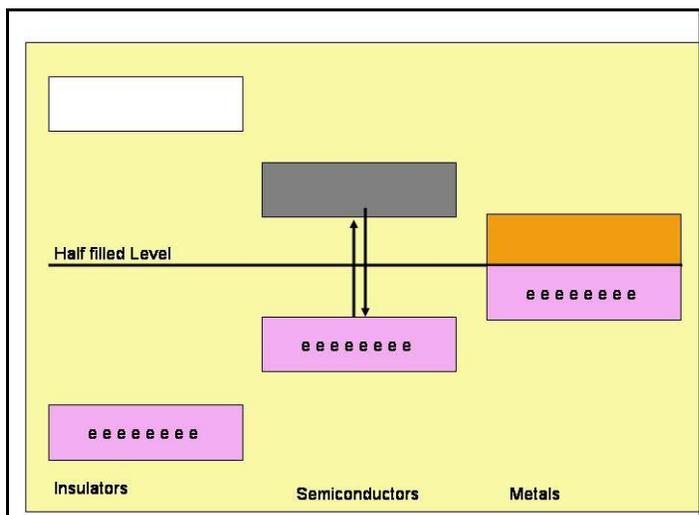
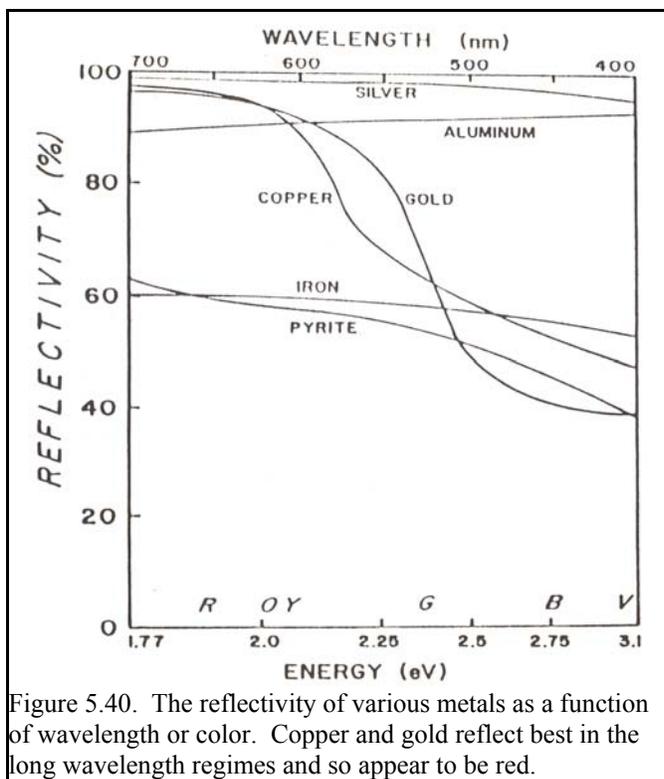


Figure 5.41: The energy difference between orbitals occupied by electrons and those that are empty vary between insulators, semiconductors, and metals. The lack of energy gap for metals means that electrons can move freely.



d^6s^2 with a full s band so that transitions take place between d electrons. In addition, there is a higher density of d band states. The wide range of transitions possible in the d electrons means that iron absorbs and reflects nearly all wavelengths (Figure 5.40). Under thermal motion there can be a slight band gap between the filled and unfilled orbitals, the breadth of the gap depending upon the s or d configuration of the electrons. Based on the mix of metals in the alloy there may be a highly intense absorption of all types of electrons and re-radiation of all light (white, mirror) from the δ phase of the Cu/Sn alloy.

Semi-Conductor Colors: PbS's black

Semiconducting materials occupy the middle ground between metallic and covalent solids. In a semiconducting material (Figure 5.41), the electron is not as tightly held as it is in a covalently bonded material (an insulator), nor as loosely held as in a metal. A band of bonding, or filled, orbitals - the valence band- is separated from a band of (empty) antibonding orbitals (conduction band) by an energy accessible thermally ($\Delta E - kT$) or via visible or infrared light.

The region between atoms which have

metallic (delocalized electrons) behavior and those atoms which engage in covalent bonding is occupied by the elements in the lower portions of the boron, carbon, nitrogen, and oxygen families. (Figure 4.46). Carbon family members Si and Ge are elemental semiconductors. Atom members from groups on either side combine to form isoelectronic semiconducting compounds (GaAs, ZnSe, and CuBr). Lead, as the bottom member of the carbon family, fits in this category of quasi-metallic, quasi-covalent binding. Lead is a component of the semiconducting material PbS (structure is shown in Figure 5.42). PbS is extensively used as an IR detector (Table F.18) due to its low energy band gap. For the same reason, PbS was used until 1980s as a darkening agent (light absorption) in shampoo.

Several common semiconducting materials are the binary compounds PbS, PbSe, and PbTe (Table F.18). PbSe and PbTe, like PbS, have a symmetrical cubic crystal structure that uses the 2 p electrons and leaving the 2 s electrons intact as a lone pair.

As we might expect, the crystal lattice of the undoped (1:1) compound such as GaAs or PbS increases when using larger atoms as one moves down the periodic table. An example is the series S to Se to Te (crystal lattice of 5.93 to 6.12 to 6.13 Å). This change in the crystal lattice affects the degree of overlap in the bonds with PbTe having the least overlap and therefore the least strongly held electrons. These electrons can be excited with lower energy wavelengths. The cutoff ranges for PbS, PbSe, and PbTe at 77°K vary as predicted. Lead sulfide (PbS) has a slightly higher bandgap, as evidenced by its inability to absorb far into the infrared region (it stops absorbing at 4 μm). PbSe and PbTe absorb out to 6 μm (Figure 5.43) (Greninger et al., 1973-). These materials are used in a variety of infrared sensors, such as those in tv remote controls. The low bandgap of PbS (Figure 5.43) makes it respond well to long wavelength light (IR). It can also be used to make TiO_2 respond to long wavelength light (Figure 5.44).

A similar size effect occurs when altering the unit cell structure of GaPAs (Figure 5.45 and Table F.18) (Ellis et al., 1993).

The black color of galena ore is due to the low bandgap energy in which all wavelength shorter than 3 μm are absorbed. The very low bandgap energy of PbS can be attributed to the position of lead at the bottom of the carbon family (Ellis et al., 1993). The splitting of the valence and conduction bands (HOMO

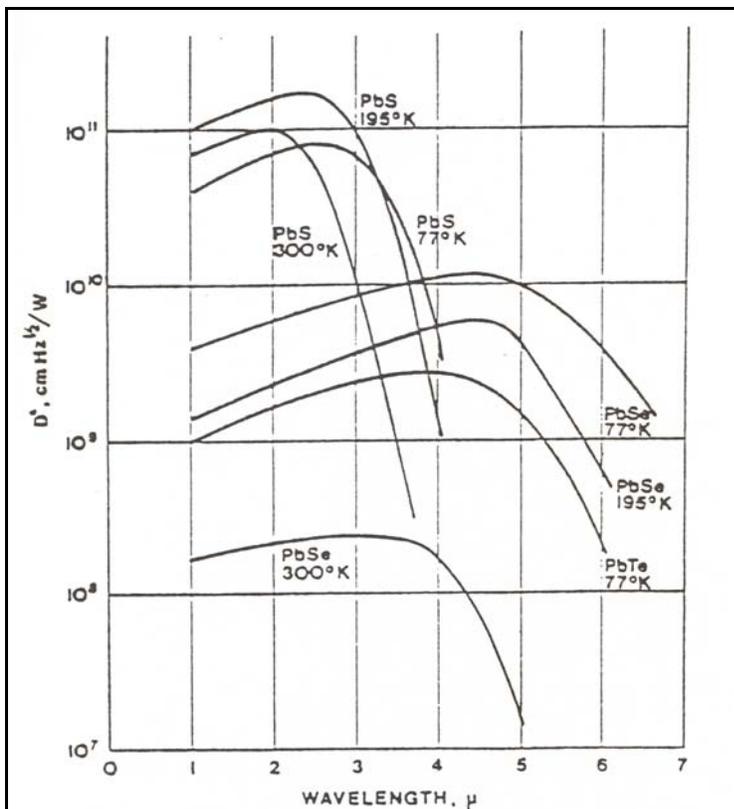


Figure 5.43. Different lead semiconducting compounds absorb light over different wavelength ranges. Those who absorb to longer wavelengths have lower bandgap energies.

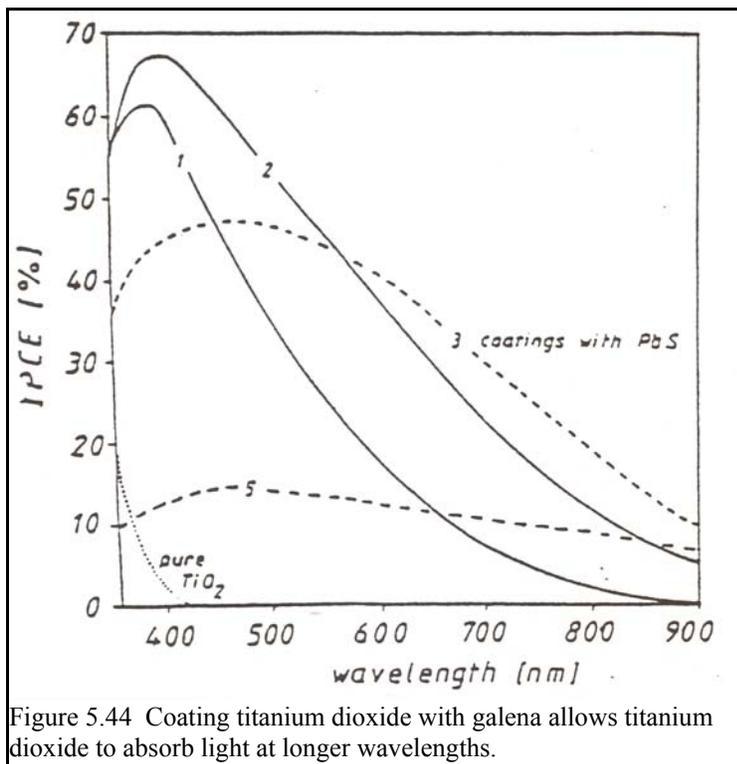


Figure 5.44 Coating titanium dioxide with galena allows titanium dioxide to absorb light at longer wavelengths.

and LUMO) is caused by orbital overlap. As the atoms become larger, the crystal lattice becomes larger also and the orbital overlap decreases. The result is less orbital splitting (a smaller bandgap). This trend is well illustrated with the isoelectric family of GaAs, ZnSe, and CuBr (Table F.18). Within a single composition crystal, in which doping changes the unit cell dimension, a direct correlation between bulk structure and bandgap can be observed.

The visible - i.e. color - forming aspect of the lead semiconductors is related to the size of the macroscopic crystal. When a photon (light packet) is absorbed by a semiconductor with promotion of an electron into the conduction band, an "electron-hole" pair (an "exciton") is formed. The "exciton" is delocalized over a given distance. When that distance approaches the same magnitude as the diameter of the semiconductor crystal, "quantum effects" become important (Figure 5.46). These quantum effects can increase the bandgap to that of visible light (Nedeljkovic et al., 1993; Torimoto et al., 1993; Vogel et al., 1994; Wang and Herron, 1991a; Wang and Herron, 1991b). This size effect imparts color small crystals, causing yellow-brown PbS instead of black-colored bulk PbS (Wang and Herron, 1991a). The requirement is that the bulk electron delocalization length (1-10 nm) be less than the size of the particle (Motte et al., 1995). Chemically deposited PbSe films of sizes of 3 nm to 1 μm have been studied (Gorer et al., 1995). The effective bandgap of these species change with size becoming larger (moving from IR to UV absorption) with smaller size. Oriented films of these particles have been obtained by templating their construction in host materials such as PbI₂ (Lifshitz et al., 1996; Lifshitz et al., 1995) and aluminum oxides (Routkevitch et al., 1996).

Other semiconducting lead compounds have been discovered. One of them is Pb₂CrO₅. This crystal is isomorphic with Pb₂SO₅ and Pb₂SeO₅ (Morita and Toda, 1984; Ruckman et al., 1972). In this crystal, planes containing Cr and Pb atoms with some Os are separated by a plane

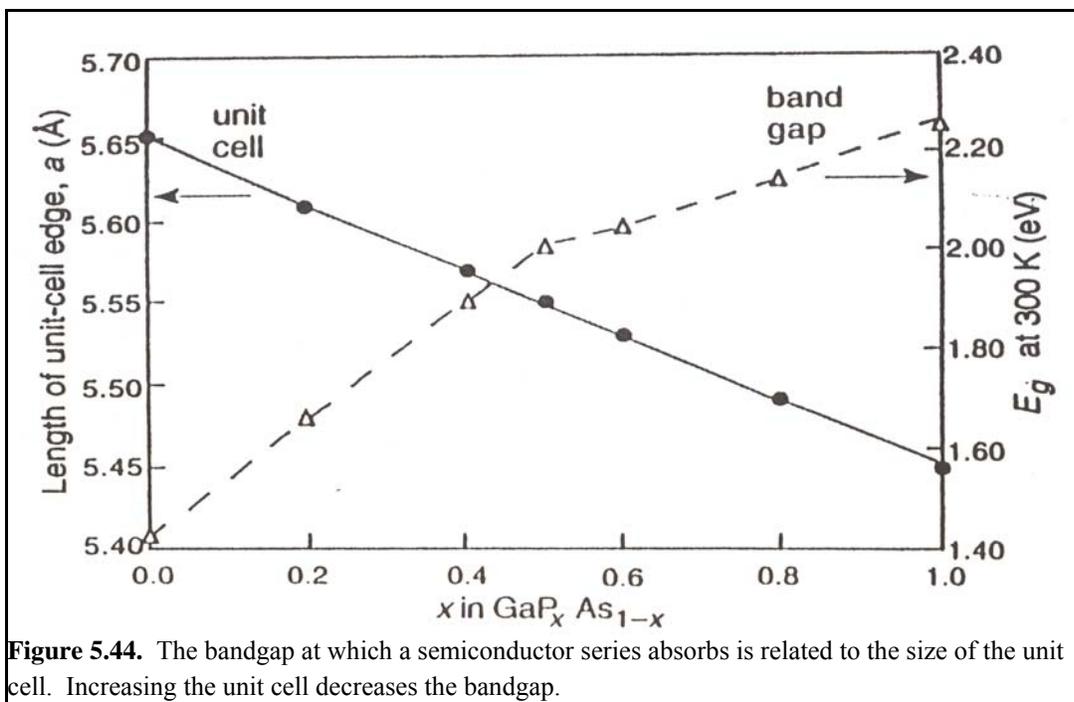


Figure 5.44. The bandgap at which a semiconductor series absorbs is related to the size of the unit cell. Increasing the unit cell decreases the bandgap.

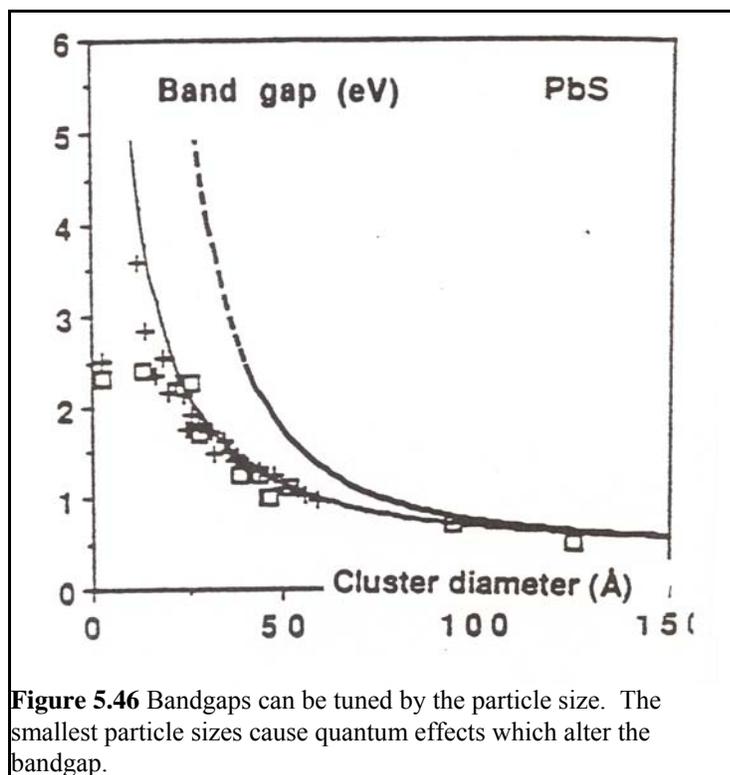
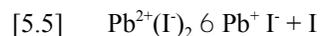


Figure 5.46 Bandgaps can be tuned by the particle size. The smallest particle sizes cause quantum effects which alter the bandgap.

containing O atoms. This structure is consistent with the formation of a valence band composed primarily of oxygen p electrons and a conduction band of Pb d electron-accepting orbitals. Semiconductor behavior is noted at estimated bandgaps of 2.3-2.4 eV within the visible region (Toda and Morita, 1987) or 2.1 eV (590 nm) (Toda and Yoshida, 1988). This semiconducting behavior is being investigated as a high speed imaging array (Toda et al., 1993; Yoshida and Toda, 1990).

Charge Transfer Color

At its most extreme, the charge transfer process resembles an electron transfer process. Lead iodide, a yellow species, exemplifies charge transfer color:



In this reaction, divalent lead accepts an electron from one monovalent, ligand, or anion I⁻. This is called a ligand to metal charge transfer. This process occurs with an energy achievable by 450 nm light which leads to a yellow color. This type of charge transfer is responsible for the intense colors of inorganic

compounds, particularly when no transition metals are present with ligand field splitting of d electrons. Possible charge transfer systems involve $L(t_1) \rightarrow M(e)$; $L(t_1) \rightarrow M(t_2^*)$; $L(t_1) \rightarrow M(e)$; and $L(t_2) \rightarrow M(t_2^*)$ transfers.

Cation-anion bonding helps to determine whether there will be a charge transfer band. The metal's ionization energy must be high enough for the remaining empty orbitals to be low in energy. That is, the metal orbitals must lie low enough to stabilize an incoming electron. The cations that fit this criteria are transition and post-transition metal ions in a high oxidation state: Cr(VI), Fe(III), Mo(VI), Mn(VII), Pb(IV, II). The ligand must be a nonmetal with a low electron affinity, so that its filled orbitals can be easily oxidized (Huheey, 1978). Many iodides, such as HgI_2 (red), are examples of this process.

Many pigments are based on charge transfer processes (Table F.20) (Brill, 1980; Nassau, 1983). Sources disagree about the proper placement of CdS and HgS. Nassau refers to these two compounds as true semiconductors. If they are, they can be classified with galena, PbS, described above under black pigments (Huheey, 1978, p. 457).

In lead chrome yellow, the color arises from a charge transfer from the ligand (O) to the metal (Cr). A similar process occurs in lead antimonate (Naples Yellow) where the charge transfer is between oxygen and lead (Figure 4.54). In minium and lead tin I, which has a structure similar to minium, the charge transfer is between mixed valent metals (Gavarri et al., 1981). In minium the charge transfer is between Pb(II) and Pb(IV) and in lead tin yellow I the charge transfer is between Pb(II) and Sn(IV).

The use of the two different lead tin yellow compounds can be tracked by Raman spectroscopy. Figure 5.47 shows both the structural similarity of PbSn I and lead antimonate, as well as the difference between the two lead tin yellows.

Crystal Lattice Tuning of Color

Following the first manufacture of chrome yellow, experimentation showed that the incorporating of small amounts of alternative metals can tune the pigment to scarlet. Lederle in Germany added a small amount of molybdenum to lead sulphate-lead chromate mixture and obtained scarlet. Schultze observed that the mineral wulfenite is deep red when it occurs next to crocoite (Schultze, 1863). The mixture of molybdate and chromate lead crystals at high temperature resulted in an easily made scarlet chrome (Jaeger and Germs, 1921) (Figure 5.20). A patent was placed on scarlet

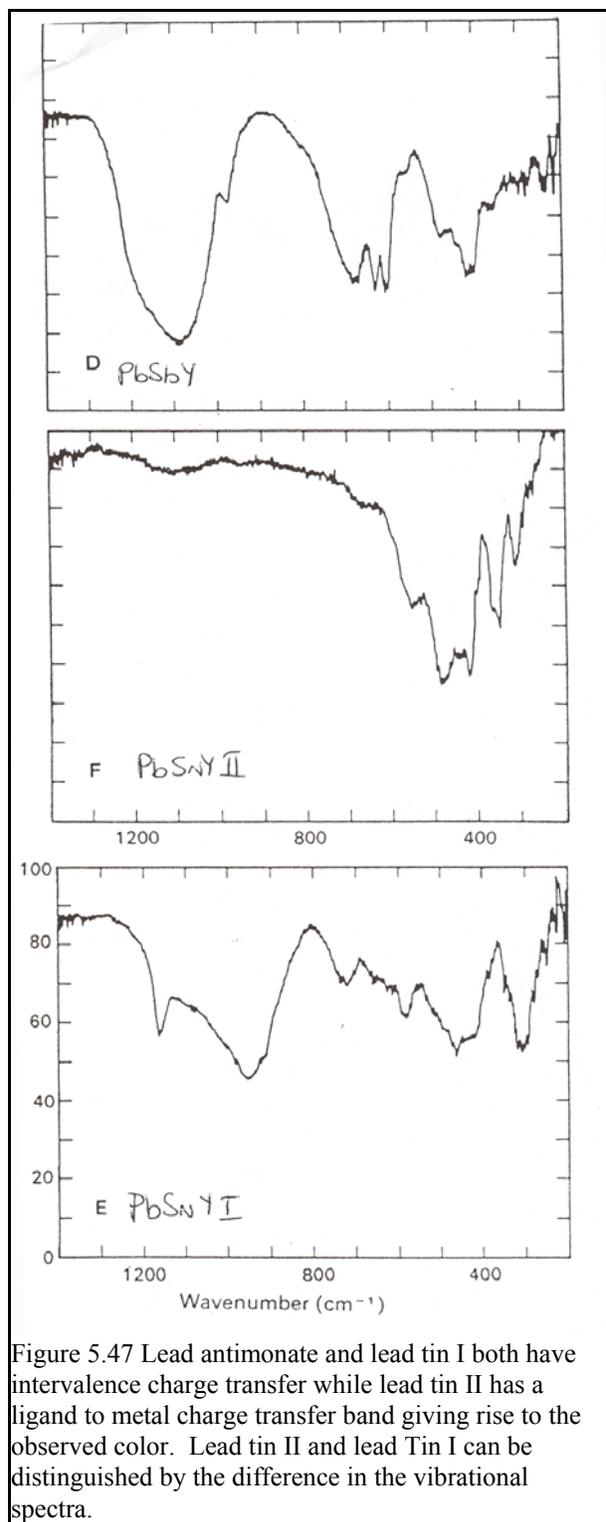
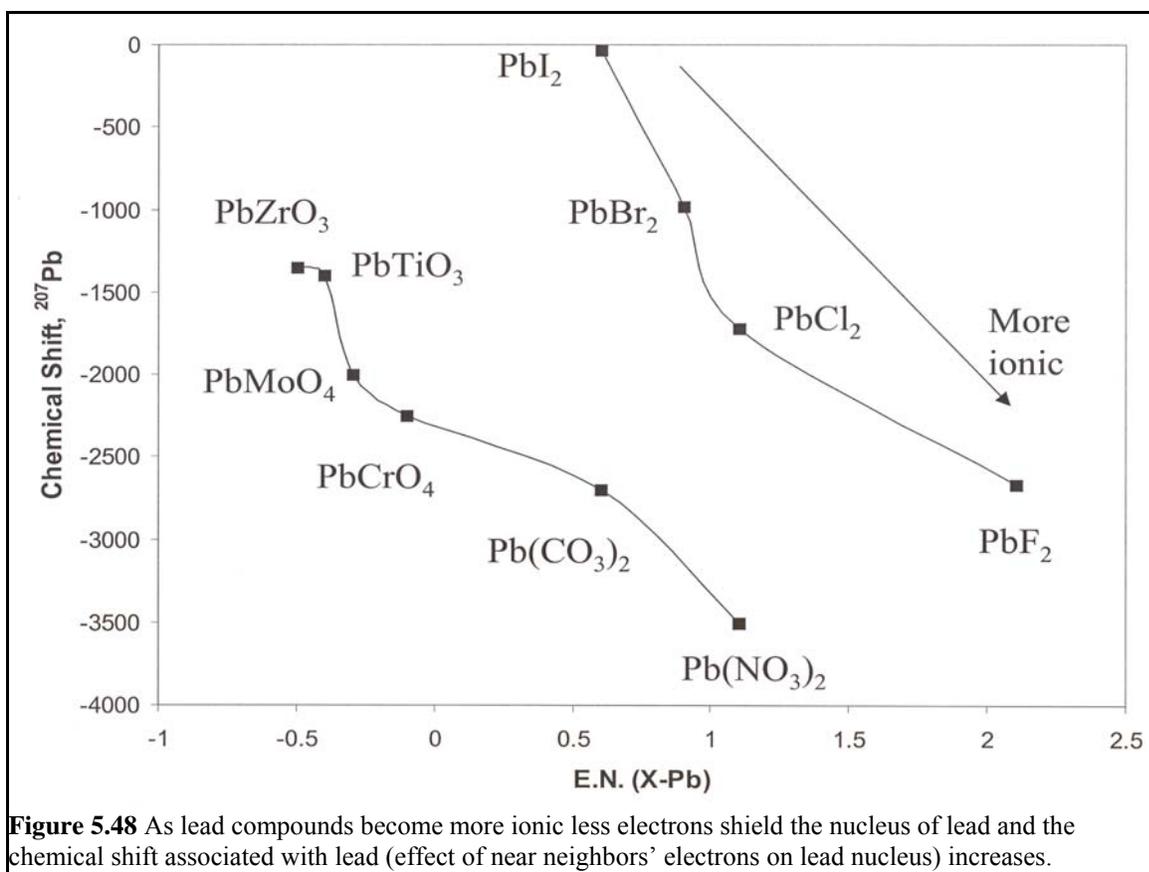


Figure 5.47 Lead antimonate and lead tin I both have intervalence charge transfer while lead tin II has a ligand to metal charge transfer band giving rise to the observed color. Lead tin II and lead Tin I can be distinguished by the difference in the vibrational spectra.

chrome in 1933, and in 1943 scarlet chrome was improved with respect to its light fastness.



The effect of “playing” with the sulfate and molybdate proportions in the mineral tunes the charge transfer band in the oxide by tuning the structure. Chrome yellow has a variety of shades from light greenish yellow to dark reddish yellow, depending upon the amount of additives such as lead sulfates or molybdates in the crystal lattice (Table E.14 (Coffer and McCoy, 1947)). An increase in the sulfur content (usually as SO_4^{2-}) decreases the crystal lattice of PbCrO_4 in all three dimensions consistent with a smaller ionic radius of sulfur to chromium (40 pm to 26 pm). The decrease in the crystal lattice favors the rhombic form (Figure 1.26) of the lead chromate, and stabilizes it in the light yellow color. Addition of molybdate, such as that in the mineral wulfenite, stabilizes the chromate structure in the tetragonal structure, favoring an orange to red color.

The tuning of the crystal lattice affects the way that electrons are shared between the complex anion and the lead cation. In turn, this electron sharing affects the electron transfer energy between the oxygen and the cation in the complex anion. The type of electron configuration around lead can be observed through ^{207}Pb nuclear magnetic resonance (NMR)

experiments. In this type of experiment, the spin of the lead nucleus is perturbed by an applied external magnetic field. The magnitude of the external field is shielded by the number of electrons about the lead atom and by the manner in which they are shared. If $\text{Pb}(\text{CH}_3)_4$ is taken as a standard, lead has a large share of the electrons from the covalent bond with carbon. These electrons shield the nuclei of the lead atom well. When lead has less electron shielding, the lead nucleus will be more greatly perturbed as occurs when lead loses electrons to become a cation. This perturbation is measured as a “chemical shift” or frequency which must be applied to perturb the nucleus. Figure 5.48 plots of the chemical shift parameter vs the difference in electronegativity between lead and a second metal down a series of lead/metal/oxides (Neue et al., In press). When the difference in electronegativity is negative, lead has a higher affinity for electrons than the second metal. The lead pulls electrons toward its nucleus and causes greater shielding of the nucleus. Note the significant difference between PbMoO_4 and PbCrO_4 . The lead has less electron density in the chromate than in the molybdate, suggesting that oxygen in a charge transfer event, donates electrons more

readily to chromium than to molybdenum. This variation in energy results in the color difference between the crocoite and molybdate species.

Some interesting periodic chemistry is associated with lead chromates. Lead chromate can be successively dissolved and re-precipitated to create concentric rings of its salt. The mechanism for this periodic solubility of lead chromate is thought to be due to the absorption of light by chromate at 400-550 nm. The excited state chromate ion moves more rapidly than through gels than the ground state and precipitates even more readily. It forms a nucleation site for further precipitation. The region around the site is thus depleted and the probability of further nucleating sites is reduced (Das et al., 1987a; Das et al., 1987b; Das et al., 1987c).

Organic Replacement pigments

Organic dye structures are shown in Figure 5.49. Their colors correlate with the gap between the highest energy molecular orbital occupied by an electron and the lowest energy molecular orbital unoccupied by an electron. The gap is largest for single bonds. It decreases as the number of double bonds increases, allowing for electron delocalization. Dye molecules contain either C=C groups, polyene groups, arylmethine dyes (ring-C-ring), or C=N or

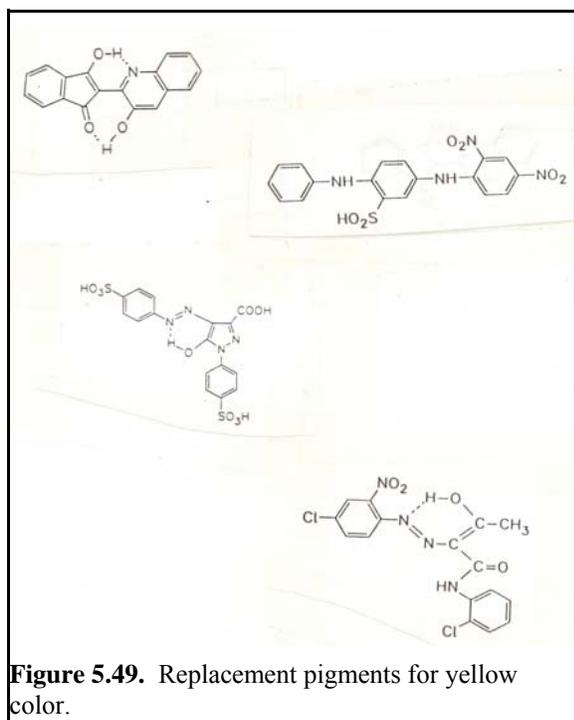


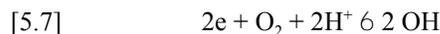
Figure 5.49. Replacement pigments for yellow color.

N=N linkages (Figure 5.49). Gap color can be tuned by adding functional groups to the compound that withdraw electrons and thus stabilize and narrow the gap, shifting absorbance of light to red. Functional groups that insert electrons can be added to destabilize and broaden the gap, shifting absorbance of light to blue.

Anticorrosion

Four mechanisms for anti-corrosive action in paints have been identified.

- 1) The paint must adhere to the surface so that no water permeates from the sides or through dimples.
- 2) The paint can inhibit oxygen transport to the metallic surface. Oxygen is the main electron acceptor involved in corrosion:



In order these two reactions to proceed, charge neutrality must be maintained. Ions must be moved from the reacting site to make up for the introduction of the divalent cation, Fe^{2+} .

- 3) The third anti-corrosive mechanism is based upon limiting the transport of either water or ions that carry charge within the paint film. This mechanism occurs within polyamide paints whose cationic nitrogen functionality (RNH^+R) imparts a net positive charge to the paint film. The positive charge retards the movement of Na^+ through the paint film by charge exclusion (Ruvolo-Filho and da Costa, 1993).

- 4) Alternative metal ions are added to the paint. These compete with the electrochemical reaction, either by displacing the iron electrons or donating electrons to oxygen. The Zn phosphate and Zn aminosalicylate paints are based on this last mechanism (Kalenda, 1993).

The most effective anti-corrosive paints are those in which access to the corroding site is blocked. In lead-based paints, the lead initiates polymerization reactions that create denser barrier near the surface. The anti-corrosive ability of other paints derives from the ionic dissolution of minerals within the paint. For example, Zn chromate produces mobile CrO_4^{2-} ions that move to the corroding site, then deposit to reform a dense film that prevents further charge flow through the paint. Since lead is being phased out as a primer, research is underway to find substitutes is as anti-corrosive as red lead (Adrian and Bittner, 1986; Funke, 1986). Paints are compared and ranked by their

densities and anti-corrosive ability, measured by the amount of corrosion surrounding a scratch mark (Table F.21) (Fragata and Dopico, 1991). As the density decreases, the efficacy of the paint increases. This finding is consistent with increased solubility and transit of materials to the reacting site. Lead is an outlier with a large density and yet good anti-corrosive action, consistent with its alternative mode of action.

Chapter 5: Problems

1. What are the three “primary” colors?
2. What are the chemical requirements for a white paint?
3. Which compounds fulfill these requirements?
4. Did St. Jerome appreciate a well made-up woman?
5. Approximately when does white lead appear in human history?
6. Who was Vernotti, and why is he important to the history of lead?
7. What are the reasons to suggest that Francisco de Goya was extensively lead poisoned?
8. What is the “Dutch” process?
9. Who is Ramazzini, and why is he important to the history of lead?
10. PbS is used in remote sensors. T or F.
11. What is the charge transfer process in minium? What color is minium?
12. How can humans temperatures accessible in h pre-industrial technologies produce minium?
13. What common food products are often adulterated with minium?
14. Give an approximate timeline for yellow pigments.
15. How was the technology for yellow transferred from the 18th dynasty of Egypt to the painter Rubens?
16. How are the various lead yellows distinguished from each other?
17. Chromium was discovered from what natural mineral?
18. How is the color of the chrome pigments tuned?
19. Rank the various lead pigments according to their toxicity.
20. What appear to be good substitutes for minium ?
25. What is the bandgap of a metal?
26. Calculate the bandgap of TiO_2 in terms of the wavelength of light that it can absorb.
27. Which metal is more likely to have good electron conductivity and low melting point: Cu or Fe or Au? Why?
28. A bandgap of 8.5 eV is observed for NaCl. Can we observe absorption of visble light for this bandgap?
29. The trend in unit cell volume is $\text{PbTe} > \text{PbSe} > \text{PbS}$. Is this trend consistent with the periodic chart?
30. The larger the unit cell volume, the shorter the wavelength of light absorbed. True or False.
31. PbS has a black color because its bandgap is large. True or False.
32. What is meant by a quantum-sized particle?
33. Write the chemical reaction describing a charge transfer process.
34. On a periodic table, indicate which elements are most likely to be found in charge transfer compounds.
35. Why are β and α PbO differently colored?
36. Relate the toxicity of each pigment , its solubility constants, and its relative anion/cation charge densities.
37. Explain the chemistry that makes for a good corrosion inhibitor in a coating.

Problems Related to Part 2 of Chapter 5

21. Which of the three “cones” in the eye has the greater sensitivity, B or G?
22. If a light emitting diode (LED) gives off light at 435 and at 550 nm, what color will the human eye “see”?
23. What value of refractive index is necessary for a good white pigment?
24. Diagram the series of chemical reactions involved in the production of lead carbonate.

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