The influence of lead ions on the drying of oils

Charles S. Tumosa and Marion F. Mecklenburg

Abstract

Lead compounds or pigments alter the drying behavior and physical properties of oil paints and varnishes, enabling artists and craftsmen to tailor the properties most suited for their purposes. Investigations into the mechanism of these changes have, however, often been contradictory or misleading. Using modern theories of driers, the behavior of lead additives or pigments can be interpreted or classified.

Introduction

The systematic study of the drying of oils and paints was advanced by the publication in 1867 of *Chemistry of Drying Oils* [1], a monograph originally written in Dutch by G.J. Mulder. Among the then-current issues raised in the book, Mulder asks:

> Wherein consists the drying, the solidification [of oils]? Does it lie in the oil alone or also in the additives? What happens after drying?… I do not believe that anyone knows, because I have until now nowhere found an answer to these questions. One speaks of lead soaps in lead paints, but is this designation true? [1, p. 2]

Clearly the influence of the oils themselves, the additives (or impurities) within them and the reaction of pigments with the oils were questions that until that time had not been adequately answered. Since Mulder, chemists have established that certain metal ions affect the film formation of drying oils. The exact behavior of lead in the drying of paint films, however, continues to be obscured by the way that the lead is introduced into the oil, by the amount dissolved in the oil, and by its use in large amounts as the principal white pigment, basic lead carbonate.

Lead has been an intentional or unintentional component of artists' materials since antiquity [2] and throughout the twentieth century, the behavior of lead white (basic lead carbonate) in oils has been described from the different perspectives of artists and chemists. Chemists were trying to deal with making their products uniform for sale while artists were following tradition and novelty, arriving at their 'chemistry' by less-than-scientific means on highly variable starting materials. This made differences of opinion inevitable.

From the point of view of the artist, Wehlte writes: 'As a lead pigment it has a strong catalytic effect on oxidizable oils…. It is therefore a decidedly good drier…' [3, p. 70–71]. Gettens and Stout share the same opinion [4, p. 175] but commercial chemists have presented other findings. Sabin states, for instance, that 'white lead and oil do indeed dry more rapidly than oil alone, but so little is this increase that in practice it is not recognized' [5, p. 12].

Bennett comments on the effect of lead driers: 'By itself lead is not a powerful drying accelerator, at least for simple oil systems, and it does not appreciably alter the course of oxidation of the oil' [6, p. 54]. The opinions of artists and chemists need to be reconciled and there is useful information in the literature to resolve the issue. This paper will address the issues of lead ion influence on the oxidation of oils and the effects of lead pigment composition, impurities and solubility on the subsequent drying behavior of oils and oil paints.

Driers

Those metals that decrease the drying time (dry-to-the-touch or tack-free) and give better polymerized films are called driers. Stewart provides an inclusive definition of driers, clarifying that 'In current coatings terminology, a drier is a material that promotes or accelerates the drying, curing, or hardening of oxidizable coatings vehicles' [7, p. 211].

Meneghetti et al. further divide driers into two classes: those that affect the oxidation of oils and those that affect the polymerization process itself [8], building on the earlier distinction of Morley-Smith [9] between oxidative driers, which can be surface driers (cobalt, manganese, vanadium) or through driers (lead). Those driers affecting polymerization are called secondary or sometimes auxiliary driers and are often metals with only one possible oxidation state (zinc, calcium, potassium, lithium, sodium) although nothing precludes a multivalent metal from this category [10].

It is generally agreed that the ability of a metal compound to catalyze the oxidation of the oil and form a film depends upon both the solubility and the dissociation of the metal ion in the oil [6, 7, 11–13]. In order to get sufficient concentrations of metal ions to catalyze the oxidation of the oil, either the metal ions must be added separately (dissolved or reacted) or the metal ions must dissolve from the pigment itself. Dissociation into metal ions is quite important and a compound such as tetraethyl lead, which has covalent bonding and does not dissociate, exerts no influence on the drying of an oil [6].

Oxidation acceleration and induction time

Driers may act in different ways to alter the drying behavior of oils and they may either increase the oxygen uptake through catalytic action or they may reduce the time when oxygen uptake begins (the induction period) through precipitation or deactivation of antioxidants [14, 15]. Beginning in the 1950s, studies have revealed that in some cases the metal driers may form complexes that lower the activation energy for oxygen uptake [14, 16], while calcium, zinc and zirconium as well as transition metals can act as secondary or auxiliary catalysts and promote the decomposition of hydroperoxides into

free radicals [17, 18]. Bellettiere and Mahoney later established that driers that affect oxygen reactions are multivalent and can exist in two (or more) oxidation states [19]. This then excludes many metals as catalysts for the direct oxidation of oils but does not preclude their classification as auxiliary or secondary driers. Because a metal can function in more than one reaction category, lead compounds can be considered as both oxidizing driers and as polymerization-affecting driers.

In a series of drying tests using lead, manganese, cobalt, iron and copper resinates dissolved in oils, which was published in *Industrial and Engineering Chemistry* in 1924 [20], lead was found to be the least effective in drying linseed oil to a dry-to-the-touch criterion. More lead was needed to give equivalent drying times. In the free-radical autoxidation reactions that promote film formation, the ability of metals to increase the rate of hydroperoxide degradation leads to increased cross-linking. The reactivity with oxygen of organic polymers containing the metal salts of fatty acids follows the same order as the metal catalyzed autoxidation of oils.

This behavior puts lead in the rank listing of thermo-oxidative degradation as:

Co > Cr > Mn > Cu > Fe > V > Ni > Ti > Pb = Ca = Ag = Zn > Al > Mg

As Oswa notes, this also seems to correlate well with the ability of the metals to decompose the hydroperoxides formed on autoxidation [21].

By the late nineteenth century the chemistry of the drying process of oils was systematically approached and the efficiency of driers was studied. The synthesis of compounds that would dissolve easily in oils helped the study of driers. There is a certain amount of variability in the order of effectiveness, generally because of the compounds tested and the model system set up for study [20, 22–24]. The general conclusion is that the order of effectiveness for the three most commonly used driers is Co > Mn > Pb. The use of lead alone as a drier was abandoned by the end of the nineteenth century with the use of cobalt and manganese as the principal driers and with the continued use of lead only in combination with other metals [22, 25]. Because of color problems, physical considerations and effective interaction among different metals, combinations of metals became the usual practice for drier addition in the twentieth century [19]. The use of cobalt as the primary drier had relegated lead to the role of an auxiliary drier [8, 26]. Because both cobalt and manganese easily touch-dry the surface of a film but leave the subsurface soft, lead driers are added to help dry this subsurface, in the process known as through-drying [12].

The ability of lead to catalyze the absorption of oxygen using a methyl linoleate model system was investigated by Andersson and Nylen in the 1940s, and the results compared to cobalt and manganese [27]. The induction period of the three metals was found to be variable with cobalt reacting almost immediately but once the reaction started, the reaction velocity (absorption of oxygen per minute) was found to be the same for each metal. The reaction velocity depends upon the amount of metal concentration, as an earlier report had shown [25]. The ability of lead to catalyze the autoxidation of linseed oil

was less than that of the cobalt and manganese. Coffey, writing in the *Journal of the Chemical Society* in 1922, had shown that the main effect of cobalt, manganese and lead driers was to reduce the induction period while leaving the reaction rate of the main oxidation unaffected [28].

In the mid-twentieth century the toxic nature of lead compounds spurred interest in finding replacements for their function both as driers and as pigments. The U.S. limit for lead driers became 0.06% by the 1980s and they were completely eliminated by July 1987 in the U.K. [29]. Titanium dioxide and zinc oxide, generally in combination, replaced lead white as a pigment and other metals such as zirconium and calcium replaced lead in drier formulations primarily as auxiliary driers [26, 30].

Early workers found a range of 1.0% to 2.0% metal per weight of oil to be the most effective concentration for lead, although its effectiveness in decreasing drying time was reached at about 0.3% [11, 22, 31, 32]. The usual commercial concentrations for a lead drier as soluble salt are in the range from 0.5% to 1.0% metal per weight of oil and are often in combination with other metal driers [7]. The concentration of the lead drier is usually much higher than the other added driers.

Maintaining the solubility of the lead compounds once they are introduced into the oil is also an issue. Oil-soluble lead driers made by reacting lead compounds with linseed oil (called cooked driers) can precipitate over time, presumably by oxidation of the unsaturated fatty acid anions or reaction with other components of the oil [33]. Lead dissolved in oil frequently precipitates although considerable lead may be dissolved in oil, up to 45% [34, pp. 23–75]. The salts of the fully saturated fatty acids also separate on standing, although this problem was eventually eliminated by using the metal salts of naphthenic acid (introduced in 1924), 2-ethyl hexanoic (octoate) acid, and other acids [7, 15, 33, 34, p. 79].

Lead compounds introduced directly into raw oil may have another purpose as well. It was noted in 1934 by Knauss that the metal will precipitate some of the antioxidants present within the oil and, hence, reduce the induction time needed to initiate oxidation of the oil [15]. The proposition that lead salts will precipitate antioxidants is supported by the observation that the incorporation of zinc, calcium or aluminum linoleates into raw linseed oil can keep the oil from forming precipitates (i.e., complexes certain constituents of the oil) and yet keep the behavior of the raw oil [35].

Loss of drier activity on standing may be due to adsorption of the drier on the pigment [7, 19, 36] and can be significant in paint stored for a long time.

Lead compounds dissolved in non-drying oils can also accelerate oxidation; the drying of olive oil alone or in combination with linseed oil using lead and manganese salts has been studied [37, 38].

Small amounts of dissolved metal salts (less than 0.5%) can catalyze the photopolymerization of linseed oil in direct sunlight in the absence of air. Cobalt is by far the most effective metal in doing this with much smaller but significant effects caused by lead, zinc and manganese

[39]. Lead white pigment behaves differently, however, and has been shown to protect linseed oil from oxidation under UV radiation [40].

Boiled oils

From the 'earliest days' of oil painting lead has been introduced into oils to accelerate drying [2]. Starting in the early nineteenth century, however, more and more became known about the influence of metals on the drying behavior of oils and increasingly, other metals and combinations of metals were used. Lead and manganese resinates *in combination* were being described by the end of the nineteenth century and cobalt driers were introduced in the first decade of the twentieth century [2, 41].

The addition of driers to oils requires the introduction of the metal ions into the oil by either adding metal salts to the hot bulk oil (or a portion of the oil) or by preparing metal-salt solutions separately and then dissolving them in the oil [42]. In the case of the direct addition of lead compounds to an oil, commercial processes used litharge, red lead or basic lead acetate, sometimes in combination and in excess to compensate for any insoluble material formed [43, pp. 161–184; 44, pp. 8–16]. Litharge can discolor oils if allowed to burn at the bottom of the kettle while lead acetate can give a pale color because it rapidly decomposes on solution [44, pp. 8–9]. Litharge was not usually added to more than 0.1% to avoid darkening the oil [45, p. 177]. The mechanism of these salt additions generally involves first the hydrolysis of the glycerol ester and then reaction of the metal ion with the reaction products, fatty acids or even liberated glycerol [34, pp. 73–75; 46, 47]. This assumes that the initial concentrations of free fatty acids are small. The reaction occurs even in an inert atmosphere. Addition of the lead salts directly to the oil is usually done with heating, either at 'low' temperatures by steam, 100° C (212° F) for resonates, or at high temperatures, 204–260° C (400–500° F) for litharge and red lead [44, p. 10; 46]. Another effect of heating the bulk oils to dissolve lead salts is to prepolymerize the oil, producing a stand or blown oil, and this will influence the drying time as well. Care must be taken since linseed oil starts to decompose in the 230–236° C range and in practice the temperature for boiled oil is kept between 220° and 228° C for at least three to six hours and often longer [43, pp. 159–160].

Oils of the lightest color are produced by the introduction of lead acetate but its films may contain acetic acid or acetate and tend to be softer than films made with other lead salts such as litharge, lead borate or linoleate. Oils made from lead resinates seem to be clear and tough with little sediment [44, p. 16]. The use of metal acetates may leave residual acetic acid since the acid liberated can form complexes with the metal fatty acid compounds formed [48, pp. 97–98]. Lead oxides can also react with the non-lipid components to form sediments (43, pp. 157–158).

Driers may be added to oils at or near room temperatures (10–40° C) if the drier is soluble in the oil or previously dissolved in portions of oil or turpentine. This limits lead and manganese salts for driers to resinates or oleates [43, pp. 180–181].

When forming lead soaps for use as driers, the reaction products of litharge or red lead with linseed are unstable since the lead oleate, linoleate and linolenate are liable to oxidation in air and even more so under direct sunlight [48, pp. 197–205; 49]. These soaps may be prepared directly in situ by heating with oil or indirectly by treating hydrolyzed oil with aqueous metal salts followed by treatment with sodium hydroxide and slight heating (116° C) [50].

The industrial procedures for preparing driers in oils are covered in detail in several convenient English-language references [34, pp. 72–82; 43, pp. 1–35; 45, pp. 247–253; 51, pp. 94–105]. In addition, paint and varnish formulae with driers from nineteenth-century England have been investigated by Carlyle [52] while numerous ancient, mediaeval and renaissance recipes are available in Merrifield [53].

Lead paints

When pigments containing lead are added to oils, the most important short-term behavior is the reaction of the salts with the oil. In general the ability of the pigment to form metal salts (soaps) has been regarded as the prime factor in determining the suitability of lead-based paints, considering both drying behavior and mechanical properties.

The reactivity of pigments to oils depends upon their chemical composition and the drying behavior of paints varies with the composition of the pigments [7]. Since the pigments are not added with much heat to the oils, the reaction of the pigments with the oil must take place more slowly than the effects seen in the making of boiled oils.

Lead carbonates

The most important lead pigment is basic carbonate or lead white. Reviews of its history and use in painting have been published by, among others, Kühn and Pulsifer [54–56], and lead white is reviewed comprehensively with other pigments in volume two of *Artists' Pigments. A Handbook of Their History and Characteristics* [57].

The behavior of lead paints can be explained by variations in the composition of the pigment due to the method of preparation or to adulterants. In addition, to be an effective drier the metal ions must be soluble in the oil, i.e., dissolve into the oil from the pigment. The ability to do this also varies with chemical composition.

Methods of preparation: lead white

Numerous recipes for producing lead white, dating from antiquity to the nineteenth century, were catalogued by Merrifield and first published in 1849 [53]. According to traditional methods of preparation, lead metal is exposed to acetic acid fumes (vinegar) in the presence of decaying organic materials such as manure or wet tan-bark to provide heat and carbon dioxide. The modern (nineteenth- and twentieth-century) commercial practices for preparing lead white are more or less variations of these methods and are called either the Dutch or Stack process [58]. The resulting lead white is a mixed product containing the basic lead carbonate, neutral lead carbonate, possibly some lead oxide (litharge) and if the

product were improperly washed, the basic lead acetate and finely divided lead metal as well. The Dutch process does not promote sulfur-containing impurities unless left in place too long and then lead sulfide may darken the product. The composition of commercial white leads in the mid-eighteenth century were said to contain the basic, dibasic and neutral lead acetates [59]. U.S. Navy specifications state that acetate impurity was to be less than 0.15% [60], probably because lead acetate and the associated water contain less lead than the basic carbonate. The need for the assiduous removal of acetate was not universal and the presence of up to 5% basic lead acetate in lead white was even thought to be beneficial [61, pp. 24–25].

By the early twentieth century other processes became important mainly in the commercial production of lead white. Quick-process pigments were made by treating molten lead with steam to produce a fine powder. The lead powder is placed in slowly rotating tubs and then carbon dioxide, generated from coke, and acetic acid are introduced. This process gives a pigment that is quite serviceable but often contains sulfur-derived impurities from the coke oxidation, e.g., lead sulfate, sulfite and sulfide. Metallic lead should not be in the product to more than 0.1% although it may exceed 1% in some cases [42, pp. 15–16, 35].

Another process of importance is the Kremnitz chamber process [42]. This process involved the treatment of a paste of litharge and acetic acid with carbon dioxide and steam at an elevated temperature. Again the product must be washed thoroughly to remove lead acetates but frequently the products were said to contain sodium carbonate or acetate as well [42, p. 21]. If the amount of carbon dioxide in the process is insufficient, the pigment will have unreacted litharge [62]. Wehlte considers this material inferior because it contains lead acetate, which must be removed [3, pp. 70–71]. Litharge reacts more readily than the carbonate and is preferred in the preparation of lead fatty acid salts [48, pp. 50–51].

There seems to have been a distinction between the commonplace lead white and the Kremnitz lead white. Mulder states that the Kremnitz white had more of a carbonate content than the usual lead white and originally had a whiter color but does not remain so [1, pp. 285–287].

The need for highly pure lead metal as a starting material has been stressed by Church [63] since impurities might add color or even different chemical properties to the pigment. Copper, nickel and iron have been described as impurities in lead and these can also accelerate the oxidation of oils if dissolved even at low concentrations [59, 63, pp. 127–128]. Copper metal in contact with linseed oil will dissolve readily and can reach concentrations of 4.1% by weight in dried thin films, although somewhat less than the 5.2% of lead dissolved in similar tests [64]. Copper can be introduced into oils by simple contact with storage or reaction vessels; it is especially efficient in catalyzing the autoxidation of oils and is active in the 10 to 100 ppm range [20, 65–67]. Antimony as an impurity is said to be responsible for the excessive amount of litharge found in some lead whites [42, p. 3].

Excessive dissolution of a pigment in a paint film to form metal soaps can result in the rapid deterioration of the film while a small amount of metal dissolved in the oil can act as a drier or even an anti-corrosive agent [68]. The C18 fatty acid soaps formed by the reaction of lead compounds with linseed oil can produce even smaller carboxylic acids on contact with water and air. Salts of azelaic, formic, acetic, propionic, butyric, suberic, pimelic and adipic acids have been isolated [69]. Interestingly, azaleic acid, the C9 diacid reaction product of the degradation of linseed oil fatty acids, is an efficient inhibitor of iron corrosion and helps explain the anti-corrosive nature of lead paints on iron [70].

Chemical composition

The chemical formulae for what is called basic lead carbonate have been variable over the past century. The crystallographic data for the carbonates have been evaluated and three major compounds seem to have emerged [71–74].

$PbCO_3$	normal carbonate
$2PbCO_3.Pb(OH)_2$	basic carbonate
$3PbCO_3.2Pb(OH)_2$	

Other compositions with varying amounts of carbonate or hydroxide have been considered to be impure mixtures of the above three compounds and may or may not contain litharge, PbO [45, p. 30; 54, 55, 75]. The lead white has been considered to be satisfactory if it contained between 20% and 33% lead hydroxide [60, p. 11]. There is evidence that the simple lead hydroxide, $Pb(OH)_2$, does not exist as a stable compound and a hydrated compound of the formula $(PbO).(0.4H_2O)$ seems to be commonly encountered [76].

In addition to different chemical combinations of lead carbonates or outright fraud by the use of adulterants, the chemical composition of 'lead whites' may have been quite variable and the term itself may refer to other materials. For example, Fielding in 1846 describes lead white as, 'White lead; an oxide of lead…under various names of Flake White, Nottingham White, sulphate of lead, &c.…Flake White is a superior kind of white lead …' [77, p. 178]. Other 'lead whites' included lead sulfate, basic lead sulfate and lead oxychloride [42, p. 2].

Commercial lead white pigments of the twentieth century may also contain litharge as part of their chemical composition, $4PbCO_3.2Pb(OH)_2.PbO$, which is a commercial patented pigment [62, 75].

Litharge may be found in some pigments where the corrosion process has not been controlled properly. The presence of litharge gives the lead white a yellow cast [42, p. 34]. The adverse nature of large amounts of litharge in contact with linseed oil was noted in the 1850s by Stas, who reported:

> … the introduction of a large amount of litharge gives a siccative pigment, very hard at first, but very liable to crack by the alterations of temperature, and even to crumble, as artists in oil sometimes notice on their canvas prepared with white lead to which litharge has been added [59, p. 376].

From a mechanical perspective, paints made from basic lead carbonate and cold-pressed linseed oil alone do not necessarily become brittle but maintain their flexibility for a considerable time [78]. This has long been a common shared experience [79, p. 121]. Brittleness in the lead white components of paintings may be the result of cleaning or varnish application and quantification of this behavior by tensile testing shows considerable sensitivity of paint films to even short-term solvent contact [80]. Thermomechanical data on the compression of lead white paint films treated with solvents can also be interpreted in this way [81].

Because of its reactivity even at ambient temperatures, the importance of litharge, PbO, as a component or as an impurity cannot be overstated. Problems in the paint industry with commercial pastes of red lead containing almost 15% litharge were determined to be due to the litharge that reacted with the oils to form fatty acid soaps. Red lead pastes hardened in a short time to an unworkable condition. The problem was eliminated when technological improvements reduced the litharge concentration to less than 3% [82].

Basic lead compounds (pigments) in contact with oil and air will react and dissolve at different rates, depending upon the chemical composition of the compounds. Litharge is the most rapidly reacting and in 80 days the lead concentration is almost 13% in the oil while highly dispersed red lead (Pb_3O_4) will only dissolve to 1.7% and lead white ($2PbCO_3.Pb(OH)_2$) to only 0.52% [82].

The question of whether or not basic lead carbonate will dissolve in linseed oil was amply reviewed by Boughton in 1916 [5]. Pure basic lead carbonate in linseed oil was tested over 25 months. From his experiments and from his critical reviews of previously published work, he determined that in *sealed* containers over the course of the 25 months, no lead was dissolved in the oil nor were there significant differences in the acid number of the pigmented oil in relation to the unpigmented oil. If, however, there was some partial amount of air available in the container, metal dissolved into the oil. In comparison with other published studies, Broughton concluded that these studies showed dissolution of metal ions because of the interaction of oil and pigment with air (and presumably moisture). That the lead soaps formed are important to the handling qualities of the paint is demonstrated by the fact that commercial painters valued the older mixed lead white paints or paste rather than more recently prepared paints [45, p. 173]. Reactive oils with high acid value are used to grind lead white pigments with excellent results [83]. Hydrolysis of linseed oil can be quite extensive in lead white paints even after drying. After ten years, one paint film stored under museum conditions was found to have its saturated fatty acid ester linkages reduced by almost 25% [84]. Commercial lead white outdoor paints in contact with light and moisture can reach this level in less than three years [75]. The study of a series of old oil paintings by Turner and Sargent showed hydrolysis levels of paints of up to 90% after two hundred years [85].

The drying behavior of a basic lead carbonate was described in 1923 by Rhodes and Van Wirt [86], who found that the total amount of oxygen absorbed in a pigmented oil was greater than a control oil without pigment. This effect occurs later in the oxidation stage rather than in the beginning. Interestingly more volatiles were reported to form with the pigmented oil than the non-pigmented oil.

Considerable information concerning the composition of basic lead compounds and their varying composition has been compiled. The weathering behavior of paints made from some of these materials has been reviewed and with the exception of basic lead sulfate, considerable reaction of the pigment with the oil to form soaps has been noted [75]. By 1950 exterior paints contained zinc white or titanium dioxide in addition to lead white with manganese or cobalt driers as well [87].

Lead sulfate

The lead sulfate of the paint industry refers to the basic lead sulfate, $2Pb(SO_4).PbO$, which, like the basic lead carbonate, may be of variable composition [88]. Precipitated lead sulfate was considered inferior to the neutral lead sulfate that could make a good paint but by 1916 lead sulfate pigment was becoming less common [45, pp. 34–35].

Sublimed white lead is an amorphous white pigment made from lead and zinc ores with an approximate composition of 75% lead sulfate, 20% lead oxide and 5% zinc oxide. U.S. Government specifications for the basic sulfate white lead [sic] showed a range of 11% to 18% lead oxide and a maximum of 9% zinc oxide [89, p. 1]. The properties were different than those of simple mixtures of the components and must represent a complex chemical compound. It dries much slower than the simple mixture of its components [45, pp. 35–37].

The drying behavior of paints pigmented with basic lead sulfate has been described, also by Rhodes and Van Wirt [86]. The pigment is less strongly basic than basic lead carbonate and does not react as readily with the linseed oil to form lead salts, giving a longer induction period and a smaller accelerating effect than the carbonate pigment.

Lead acetates

The lead acetates form a series of compounds as neutral lead acetate, basic lead acetates, lead tetraacetate as well as various hydrates of these. While used as a drier and not as a pigment, the lead acetates share the same problems as outlined above. The purity of both the starting materials and of the final product influences the behavior of the material [90, pp. 32–34]. The use of lead acetate as a drier among nineteenth-century British artists has been ably reviewed by Carlyle [52] but the paints suffer from the decomposition of the salt to give acetic acid, the reactive nature of which is well known. The problem of using 'excess' lead acetate results in efflorescences that mar varnishes or obscure paintings [52, 63, p. 109].

Lead oxides: litharge

Litharge can exist in a range of pale colors but Wehlte is of the opinion that it was never used as an artists' pigment [3, p. 82] although clearly it must have been part of pigment mixtures. When lead metal is heated in air, the first oxide formed is PbO or litharge. Litharge when

mixed with oils reacts quickly with free fatty acids and causes 'livering' upon drying. The lead soap formed is soft and does not interfere with the working qualities of the paint [91]. In commercial paints litharge was traditionally mixed with lampblack or carbon black to give paints that dry quickly and a similar technique has been recommended in the fine arts as well. These paints had to be used soon after mixing [1, p. 282; 45, pp. 53–54].

Lead oxides: red lead

The history, use and properties of red lead have been recently reviewed by FitzHugh [92]. Red lead, Pb_3O_4, may be formed when litharge is heated to temperatures over 316° C (600° F). It generally contains some litharge (from 2% to 15%) and reacts quite readily with drying oils. Red lead pigmented oils must be used quickly or they will dry, becoming unfit for use [45, pp. 54–61; 92]. Films formed from red lead and oil become even more brittle over time than those formed from litharge [45, p. 162].

Other lead compounds

The comments made about the preparation of basic lead carbonate are also applicable to other minor lead-based pigments. The purity of the starting materials and completeness of reaction will also influence the drying abilities of the oxide-based pigments.

Lead-tin yellow is a yellow pigment made by heating a mixture of lead and tin oxides. The drying time and behavior of this pigment in linseed oil was found by the authors to be the same in both cold-pressed linseed oil and the same oil with lead added as a drier. Since the lead in the pigment (and presumably any lead impurities) is cationic, the lead may dissolve in the oil with the formation of fatty acid salts and help decrease the drying time [93]. Lead-tin yellow in dried paints will give lead soaps over time [94].

Naples yellow is a pigment created by heating a mixture of lead and antimony oxides (or salts). It is also called lead-antimonate yellow. The pigment is described as having a strong drying effect on drying oils. A description and history of the pigment has been published in volume one of *Artists' Pigments. A Handbook of Their History and Characteristics* [95]. A lead-tin-antimony yellow has also been described as being a product associated with Italian glass manufacture [96].

The formation of lead salts from red lead, lead white and Naples yellow has been studied by Fourier transform infrared spectroscopy (FTIR) showing hydrolysis of the oil as well as salt formation [97]. A similar study, but using heating at 125° C to accelerate the reaction, showed lead salts forming from pigmented oils with red lead, litharge, lead white and Naples yellow but, interestingly enough, not with white lead sulfate, which may explain the poor performance of the pure sulfate as a drier [98].

The formation of lead salts (soaps) from pigments can influence the behavior of the paints. Oil soluble salts can alter the uptake of oxygen during the drying process and insoluble soaps can aid in the suspension of pigments and improve the storage quality of the paint [6, p. 56]. Lead soaps may be added to pigments to facilitate milling [33]. A water insoluble lead naphthenate can be combined with a water-soluble sodium naphthenate to make a mixture soluble in mineral spirits. The solution is effective for wetting and dispersal for use with pigments and paints [99].

The prior reaction of basic lead carbonate with a saturated fatty acid salt (e.g., sodium stearate) to form a complex pigment, which is then mulled with linseed oil is the basis for a French patent for a leaded paint [100].

The ability of lead compounds to form fatty acid salts by reaction with the oil medium may explain the appearance of dry-to-the-touch behavior more than the catalysis of oxidation or shortening of induction time. In searching for substitutes for lead in cobalt-lead drier combinations, zirconium and calcium were found to be suitable replacements, although neither is capable of changing oxidation state in the oil [8, 10, 101]. This is consistent with earlier findings that show lead to be less efficient a drier than, for example, potassium or zirconium naphthenates in air-dried alkyd paints [24]. Klebsattel summarizes a considerable literature, stating that 'Lead as an oxidation assistant is not particularly powerful, but, as an aid to polymerization, it is excellent' [102].

Conclusions

The effects of lead on the film formation of varnishes and paints may be described as threefold:

- First, lead ions have an accelerating effect on the uptake of oxygen and autoxidation but are not as effective as cobalt, manganese or other metals. This effect is seen only if the lead dissolves into the oil and dissociates, but not all lead compounds will dissolve and dissociate.

- Second, the drying behavior is obscured because lead is effective in promoting through-drying, which affects the subsequent organization of the polymer, behaving similarly to non-catalytic driers such as zirconium and calcium.

- Third, there is the formation of lead soaps in the presence of moisture and air even before the paint is applied. These influence the wetting of pigments and also form gels in addition to promoting oxidation.

The differences in chemical behavior of lead-based paints are the result of variation in the quality and purity of the pigments and the oils used in making them. As industrial standards made for more uniform starting materials, paints have taken on a more predictable behavior. At present there are highly formulated and characterized artists' oil paints.

Acknowledgements

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Authors

Charles S. Tumosa is a senior research chemist at the Smithsonian Center for Materials Research and Education in Suitland, Maryland. He received his PhD in Chemistry from Virginia Polytechnic Institute and State University in 1972.

Marion F. Mecklenburg is a senior physical scientist at the Smithsonian Center for Materials Research and Education. He has worked as a conservator for 20 years and holds a PhD in Structural Engineering from the University of Maryland.